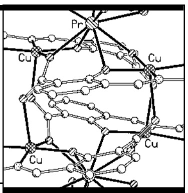
The structures and magnetic properties of complexes containing 3d- and 4f-metals



CHEMICAL SOCIETY REVIEWS

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Heterometallic complexes containing 3d-/4f-metals have been made with a variety of ligands including Schiff-bases, pyridonates and amino-alcohols. The majority of species with Schiff-base ligands are trinuclear with Cu_2Ln cores, and with other ligands larger oligomers are found, ranging as large as $Cu_{12}La_8$ and $Cu_{12}Ln_6$ clusters (Ln = Y, Nd, Sm or Gd). The magnetic properties displayed by these polynuclear species are discussed, and the magnetic coupling between Cu^{II} and Gd^{III} is always found to be ferromagnetic.

1 Introduction

Whenever two magnetic ions are brought into close proximity our natural inclination is to assume that, like bar magnets, they will arrange themselves so that they couple anti-ferromagnetically, and thus reduce the overall magnetism of the dimer. This prejudice is probably reinforced by studies of dimeric copper complexes such as copper acetate, or by the magnetic behaviour of the active sites of any metalloprotein which contains more than one magnetic metal centre. When the prejudice is confronted by contrary fact, the observation gains a good deal of piquancy, and the divergence from cliché is in itself an important scientific reminder that the magnetic behaviour of atoms and ions is not as simple as that of bar magnets.

In 1985 Italian scientists, led by Gatteschi,[1] observed that when copper(II) and gadolinium(III) were brought into close proximity the coupling between the ions was ferromagnetic. This was surprising as gadolinium(III) has unpaired electrons in all seven 4f-orbitals, and it might be expected that at least one of these orbitals would overlap with the semi-occupied orbital on copper(II). Such an interaction between two half-occupied orbitals would be anti-ferromagnetic, as it would create a molecular orbital which could contain both electrons. Such an interaction is observed between Cu^{II} and the d^5-centre Mn^{II} where the coupling is always anti-ferromagnetic.[2] The explanation cannot lie in the interaction between ground state configurations.

The 4f-orbitals of the lanthanoids are small, internal orbitals and this leads to the interaction between the Cu^{II} 3d- and Gd^{III} 4f-orbitals being minimal, and hence the overlap which would lead to anti-ferromagnetic coupling is of little importance. The important interaction is between the semi-occupied orbital, say $d_{x^2-y^2}$, on Cu^{II} and an empty orbital on the Gd^{III} centre.[3,4] In such a charge transfer configuration there are two possible orientations for the electron transferred from Cu^{II} to Gd^{III}. If it aligns antiparallel to the seven electrons in the 4f-orbitals this would lead to an $S = 3$ spin state, and would be equivalent to anti-ferromagnetic exchange. If the additional electron aligns parallel to the seven 4f-electrons, this would give an $S = 4$ spin state, and is equivalent to ferromagnetic exchange. Due to Hund's rule the latter will be lower in energy than the former, and hence this excited state of the system favours ferromagnetic exchange. Initially there was some debate about which gadolinium orbital was the electron acceptor, but it now seems clear that the 5d-orbitals are best suited to this role.[4] It is the interaction of this charge transfer configuration with the ground state which leads to the ferromagnetic coupling that is always observed.

The interaction reported was weak[1]—with a ferromagnetic J value of around 5 cm^{-1}, and was found in a trinuclear Gd_2Cu complex. The initial report posed two questions: could the interaction ever be sufficiently strong to be of more than purely academic interest, and if it were found in larger or even polymeric complexes, could it be a way of producing high spin molecules or even molecular ferromagnets. At about the same time as this chemistry appeared, the high T_c superconductors containing copper–lanthanoid mixtures were also reported, and a second potential use of these heterometallic cages became apparent—perhaps they could be used as precursors for producing new mixed-metal perovskite phases. Therefore, in addition to Cu–Gd complexes, Cu–Ln complexes in general became the subject for study.

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2 Complexes using Schiff-base ligands

The initial work in the area used polydentate Schiff-base ligands to bridge between metal centres; later others have used oxamido ligands, and our own work has been based on pyridonates. All these ligands have in common a mixed-donor set, where it was intended that hard O-donors would favour binding to the oxophilic lanthanoid centres, while the softer N-donor would bind to the copper centres. More recent work has shown that this differentiation is unnecessary, and ligands with exclusively O-donors will work equally well.

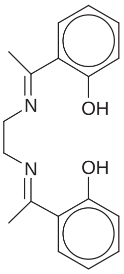
Several Schiff-base ligands have been used (**L1**–**L10**).[1,3–6] In all cases the procedure used to make mixed-metal complexes was first to complex a Cu^{II} centre into a cavity of the Schiff-base, normally consisting of an N_2O_2 donor set. Having isolated a copper complex this was then used as a ligand for the lanthanoid metal, with the hydroxy-oxygen atoms acting as μ_2-bridges. The high coordination number favoured by 4f-metal centres normally led to coordination of two copper–Schiff-base complexes to each centre, and hence trinuclear Cu_2Gd complexes (Fig. 1). In one such synthesis incorporation of hydroxide, combined with hydrolysis of the Schiff-base, gave a tetranuclear Cu_2Gd_2 cage.[3] Use of the ligand **L7** gave dimerisation of the trinuclear Cu_2Ln units through the carboxylate function (Fig. 2).[4]

This oligomerisation presents problems for studying the magnetic properties of such cages, as allowance needs to be made for anti-ferromagnetic exchange between like metals, in addition to ferromagnetic exchange between Cu–Gd, however, results supported the initial observation that the Cu–Gd exchange was always ferromagnetic. The problem of oligomerisation was recognised by Sakamoto *et al.* and the Schiff-base ligands **L5**, **L8** and **L9** were used to attempt to restrict the cages to discrete dinuclear species.[6] Unfortunately no crystallographic studies were reported for these molecules, however this paper has been influential in later work.

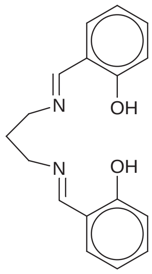
3 Complexes using non-Schiff-base ligands

Work with pyridonate ligands led immediately to structures with higher nuclearity, and with largely unpredictable structures. The first complexes reported used 2-pyridone in a reaction with copper hydroxide and an hydrated lanthanoid nitrate to give Cu_4Ln_2 cages (where Ln = Gd or Dy),[7] where the six metal centres are found at the vertices of a distorted octahedron, with the Ln metals *trans* to one another (Fig. 3). A very similar reaction, but starting with copper methoxide, led to still larger Cu_8Ln_2 cages (Ln = Nd or Y).[8] The ten metals at the core of the structure lie in two mutually-perpendicular intersecting planes (Fig. 4). The six metals, two Ln and four Cu, in the first plane lie on the vertices of two squares with the two Ln sites common to both. The second plane of four Cu atoms passes through the centre of the larger plane, and again the Cu atoms are arranged at the vertices of a square.

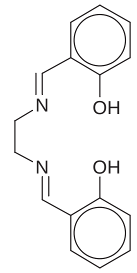
These reactions used a copper salt, either hydroxide or methoxide, to deprotonate the 2-pyridone *in situ*. Deprotonation of the ligand, prior to reaction with metal salts, resulted in a Cu_4La_4 cage, where a central La_4O_2 'butterfly' separates two dinuclear copper units.[9] At this stage it became apparent that isolation of the homometallic copper complexes of the pyridonate ligands, prior to reaction with a lanthanoid salt, might lead to cleaner, and higher yielding reactions. Pursuing this strategy, and using analogues of 2-pyridone substituted in the 6-position, we produced a series of predominantly tetranuclear



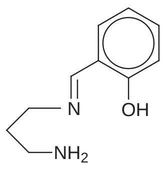
L1



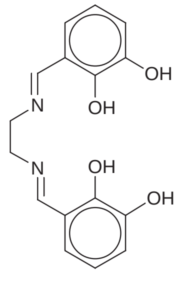
L2



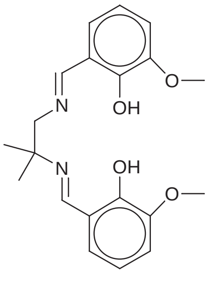
L3



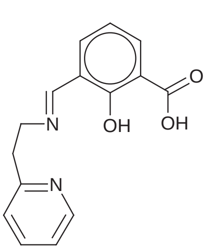
L4



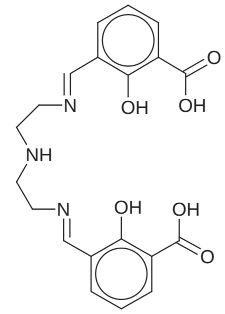
L5



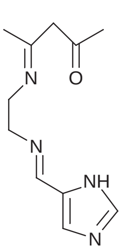
L6



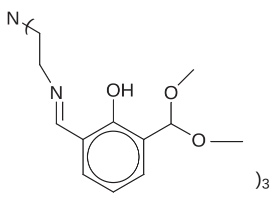
L7



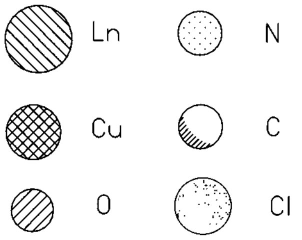
L8



L9



L10



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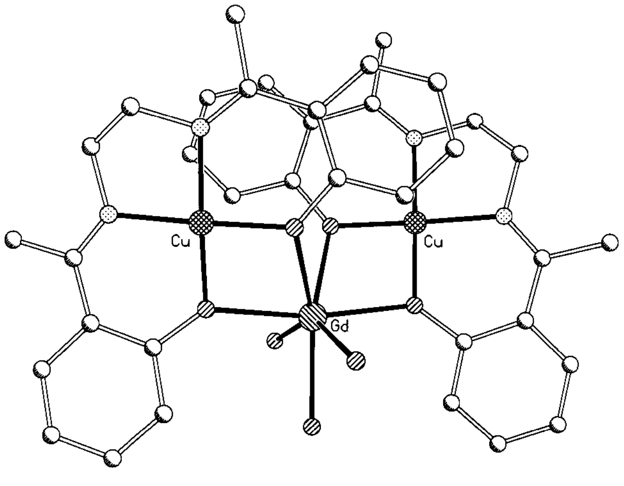

Fig. 1 The structure of $[Cu_2Gd(L1)_2(H_2O)_3]^{3+}$[1]

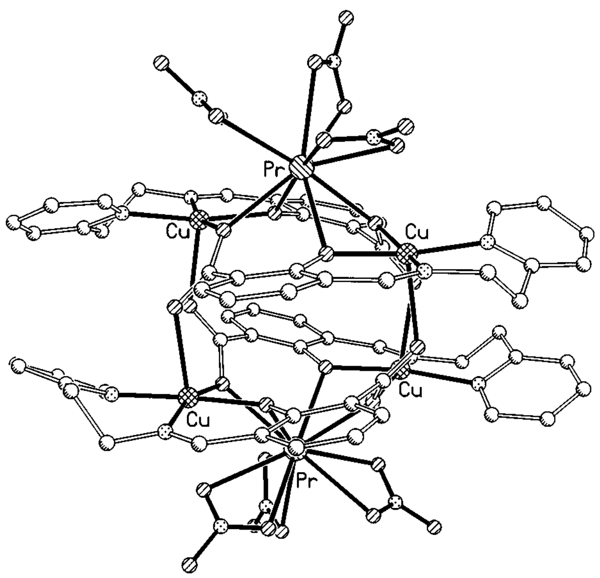

Fig. 2 The structure of $[Cu_4Pr_2(L7)_4(NO_3)_6]$[4]

cages, where the exact product depends on the lanthanoid, solvent and pyridonate derivative involved.[10–15] It is noticeable that the work with the substituted pyridonates leads, in general, to lower nuclearities than cages which feature the parent ligand.

The majority of structures fall into two broad types. In Type I structures,[13] there is a central Cu_2O_2 ring, with pyridonate ligands attached to the copper centres through the ring N-donor, and which bridge on to peripheral Ln atoms through the O-donor (Fig. 5). The oxygen atoms of the central Cu_2O_2 ring are derived from either methoxide, if methanol is used as a solvent, or hydroxide if other solvents are used. This structure is favoured by the 6-methyl-2-pyridonate ligand (mhp),[13,14] and is also found for complexes of the heavier 4f-elements with 6-chloro- and 6-bromo-2-pyridonate. Type II structures feature either Cu_3Ln or Cu_2Ln_2 held together by eight pyridonate ligands (Fig. 6).[14,15] These structures are found for the 6-halo-derivatives of these ligands. For the Cu_3Ln cores, a central $CuLnO_2$ ring is present, with the oxygen atoms provided by two pyridonate ligands, with the N-donors of these pyridonates attached to the remaining Cu centres. Two further pyridonates are attached to the Cu of the central ring through N-donors with the oxygen attached to the remaining Cu centres. The final four pyridonates bridge between the Ln and the external copper atoms. For the Cu_2Ln_2 cores a very similar arrangement of pyridonates is found, but here the central core is an Ln_2O_2 ring.

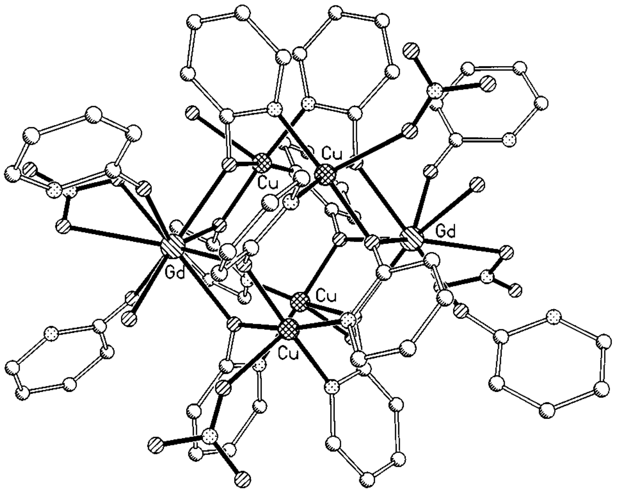

Fig. 3 The structure of $[Cu_4Gd_2(hp)_8(Hhp)_4(OH)_2(NO_3)_4(H_2O)_2]$ (where Hhp = 2-pyridone)[7]

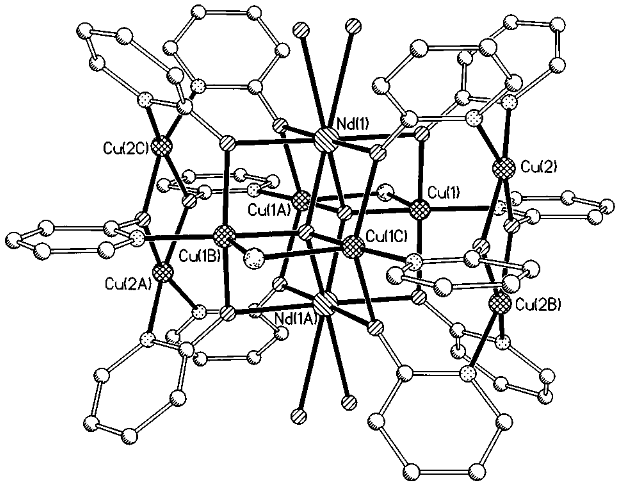

Fig. 4 The structure of $[Cu_8Nd_2(O)_2(hp)_{12}(Cl)_2(OMe)_4(H_2O)_4]$ (where Hhp = 2-pyridone)[8]

Initially we thought that Type I structures were favoured by use of MeOH as a solvent, however it has become apparent that the controlling influences are more subtle. For the mhp ligand Type I structures are found even in the absence of MeOH, with bridging hydroxides incorporated instead.[14] With 6-fluoro-2-pyridonate Type II structures are found even in the presence of MeOH.[15] One control is probably the basicity of the deprotonated pyridonate ligand. For mhp the electron donating methyl group leads to a reasonable basicity for the ligand, which allows deprotonation of either the solvent or any waters of crystallisation present, and hence leads to bridging methoxide or hydroxide ligands and Type I cages. For 6-fluoro-2-pyridonate the strongly electronegative fluorine reduces the basicity and deprotonation of solvent is never seen, and hence coordination of solvent has little structural importance. For the 6-chloro- and 6-bromo-2-pyridonates, which have intermediate basicity, early 4f-elements give Type I, and late lanthanoids Type II cages. This observation is more difficult to rationalise.

We also find that lanthanum itself has a quite different coordination chemistry with these ligands than the smaller 4f-elements, probably because the larger radius of the La centre

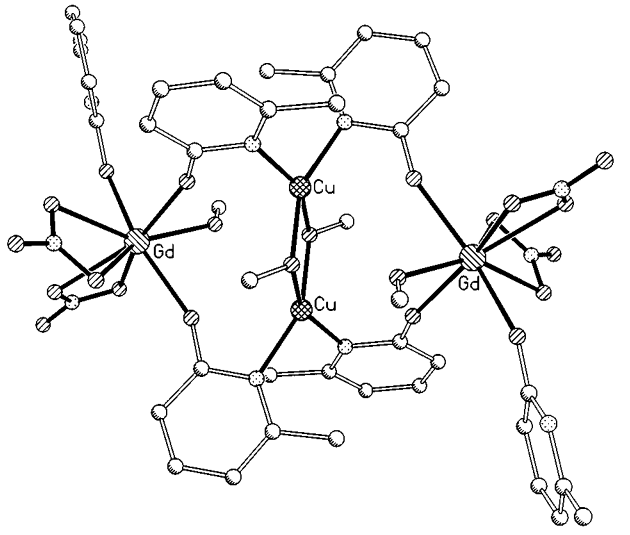

Fig. 5 The 'Type I' structure of $[Cu_2Gd_2(OMe)_2(mhp)_4(NO_3)_4(Hmhp)_2(MeOH)_2]$ (where Hmhp = 6-methyl-2-pyridone)[13]

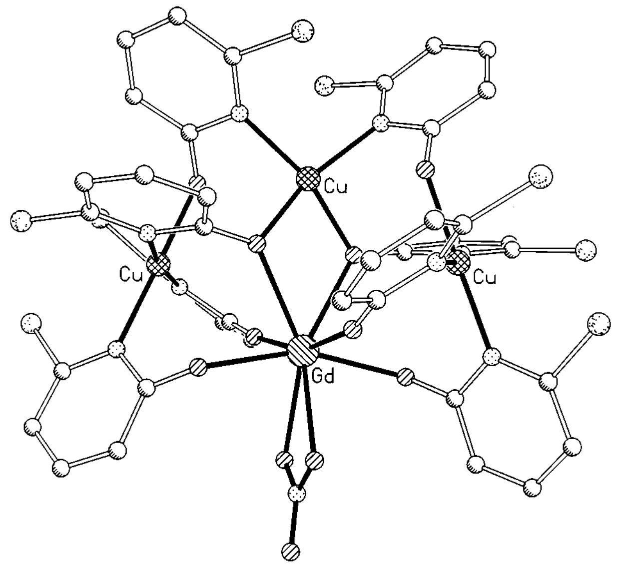

Fig. 6 The 'Type II' structure of $[Cu_3Gd(chp)_8(NO_3)]$ (where Hchp = 6-chloro-2-pyridone)[15]

leads to a higher coordination number. Both the Cu_4La_4 cage mentioned above,[9] and an extremely asymmetric Cu_3La cage seem unique to this metal,[11] however the most unusual result involves the reaction of $[Cu_6Na(mhp)_{12}][NO_3]$ with hydrated lanthanum nitrate in dichloromethane.[15] With later lanthanoids this reaction generates Type I Cu_2Ln_2 complexes, but here a cage with a $Cu_{12}La_8(\mu_3\text{-}OH)_{24}$ core results (Fig. 7). The structure has non-crystallographic O_h symmetry, with eight La atoms at the corners of a cube, and the twelve Cu centres at the mid-points of the edges of the cube (thus forming a cuboctahedron). The cage is stabilised by a shell of disordered pyridonate, nitrate and water molecules attached to the lanthanum sites which are nine or ten coordinate. None of these peripheral molecules bridge between metal sites, and the cage is exclusively held together by hydroxy bridges. There is also a central disordered nitrate anion captured within the cage.

This last, very high nuclearity cage appears to be an attractive by-way in the pyridonate chemistry. We have been unable to scale-up the reaction, or make the cage with any lanthanoid except lanthanum. However, work from China using betaine ligands—either pyridinioacetate[16] or pyridiniopropionate[17]—has generated cages containing a $Cu_{12}Ln_6(\mu_3\text{-}OH)_{24}$ core (Ln = Y, Nd, Sm or Gd) (Fig. 8). The curiosity here is that the cuboctahedron of copper centres is largely unchanged from the core in the $Cu_{12}La_8(\mu_3\text{-}OH)_{24}$ cage, but now, rather than being contained in a cube of 4f-metals, it is contained in an octahedron. The non-crystallographic O_h symmetry is also retained, however the 24 μ_3-hydroxides which hold together the cage are supplemented by bridging betaine ligands which span $Gd\cdots Cu$ vectors. The structure includes a central, disordered perchlorate anion which may be involved in templating the structure. These later reactions are moderately high-yielding, and seem applicable to many of the 4f-metals. Unfortunately the magnetic properties of these cages are dominated by the antiferromagnetic exchange between Cu^{II} ions, and hence only low spin species result.[16]

Two further classes of mixed-donor ligands have been investigated. Ligands based on oxamido ligands have been used to make both trinuclear[18] and polymeric Cu–Gd cages.[19,20] In both cases the Cu–Gd coupling is found to be ferromagnetic. The latter complexes contain 2D-sheets linked by oxamido and oxalate ligands,[19,20] and in the initial reports there was no evidence, such as phase transitions, of long-range magnetic ordering even down to 1.3 K. Later studies suggest that two-dimensional ordering is found at lower temperatures.[21]

The final class of mixed-donor ligands investigated are amino-alcohols. Wang and co-workers have reported the use of both 1,3-bis(dimethylamino)propan-2-ol[22] and 2,6-bis-(dimethylamino)-4-methylphenol in this chemistry.[23] The former ligand generates triangular Cu_2Ln cages in good yield (Ln = La or Nd), and a dimeric Cu–Pr cage in very low yield.[24] The latter amino-alcohol gave good yields of dimeric Cu–Pr cages by reaction of copper methoxide and praesodymium tris(hexafluoroacetylacetonate) with the ligand in THF.[23]

Two of these series of cages—Cu_2Ln_2 cages with 6-methyl-2-pyridonate[13] and Cu_2Ln cages with 1,3-bis(dimethylamino)-propan-2-ol[22]—have been studied as potential precursors for synthesis of mixed-metal oxides. The observations appear to be similar; initial decomposition is to oxide or oxide-carbonate phases of the individual metals, followed by reaction of these phases to give mixed-metal oxides at moderate temperatures, *e.g.* X-ray powder diffraction analysis indicates that La_2CuO_4 begins to form at around 670 °C and $Yb_2Cu_2O_5$ at around 520 °C.[13] Unfortunately diffraction peaks due to CuO are found in all these samples at low temperatures, and prolonged annealing is required to produce even moderately pure mixed-metal oxides. Preparation of thin films of superconducting oxides has been reported by Wang using salts of copper, barium and lanthanoids mixed in the presence of amino-alcohols but without isolating molecular precursors.[25]

4 Magnetic studies and possible magneto-structural correlations

Magnetic studies of these complexes have shown that in all cases the interaction between Cu^{II} and Gd^{III} appears to be ferromagnetic, confirming initial observations. The range of cages reported has allowed exploration of possible correlations between the structures of these heterometallic cages and the magnitude of the magnetic exchange interaction, *J*, between Cu^{II} and Gd^{III} centres. However a difficulty is that the absolute range covered by these measurements is rather small, with the largest *J*-value reported being some 7.4 cm^{-1} (found for $\{Cu(\mathbf{L3})_2Gd(H_2O)\}$) and the smallest around 0.1 cm^{-1}.

There is some correlation between J and the $Cu\cdots Gd$ distance, and this can be fitted to an exponential function such that $-J = A\exp[Bd_{Gd\cdots Cu}]$ (where $A = 6.5 \times 10^4$ and $B = -2.833$, with J in cm^{-1} and $d_{Gd\cdots Cu}$ in Å).[14] This correlation was made on purely empirical grounds, and remains to be proven, but

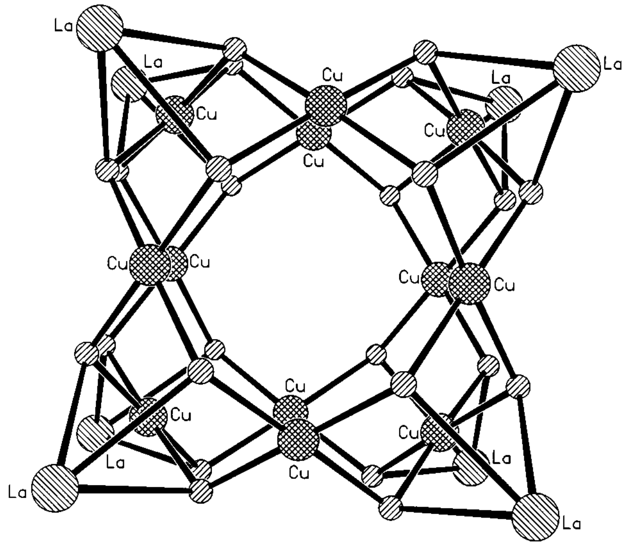

Fig. 7 The $[Cu_{12}La_8(OH)_{24}]$ core of the polynuclear complex $[Cu_{12}La_8(OH)_{24}(NO_3)_{21.2}(Hmhp)_{13}(H_2O)_{5.5}][NO_3]_{2.8}$ (where Hmhp = 6-methyl-2-pyridone).[15] The view taken is perpendicular to one square face of the Cu_{12} cuboctahedron and the equivalent view is also used for Fig. 8

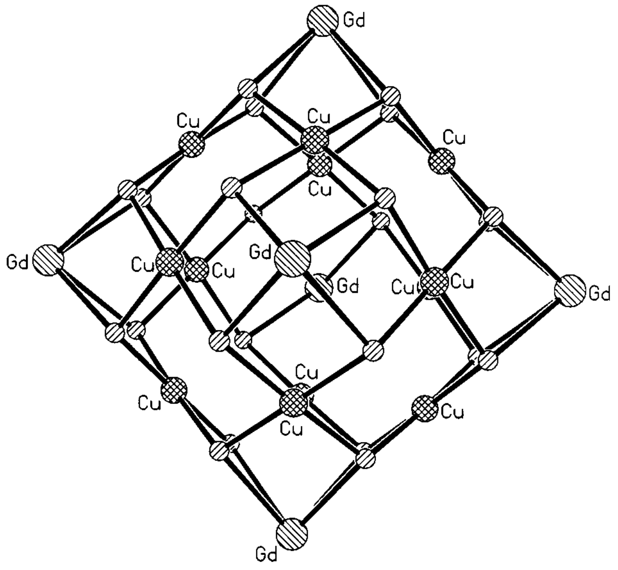

Fig. 8 The $[Cu_{12}Gd_8(OH)_{24}]$ core of the polynuclear complex $[Cu_{12}Gd_8(OH)_{24}(O_2CCH_2CH_2NC_5H_5)_{12}(H_2O)_{16}(ClO_4)][ClO_4]_{17}$[17]

indicates that the nearer the Cu and Gd approach each other, the larger the exchange. This might be expected given that the accepted mechanism for this ferromagnetic interaction involves an excited state in which an electron has been transferred from Cu to Gd. Perhaps more importantly it also sets an upper limit for this exchange interaction of around 10 cm^{-1}, as the Gd···Cu separation is never likely to be less than 3.1 Å.

The best means of testing such a correlation is to synthesise discrete dinuclear CuGd complexes, where no anti-ferromagnetic exchange between like metals is present to confuse the interpretation of the Gd···Cu exchange. This was recognised several years ago by Sakamoto *et al.*[6] The Wang group managed to make a discrete Cu–Pr complex using 2,6-bis(dimethylamino)-4-methylphenol,[23] but did not make the Gd analogue where the magnetic properties would have been amenable to modelling. Oligomerisation is prevented in this cage by using three hexafluoroacetylacetonate ligands to block coordination sites on the praesodymium. Similar approaches have since been reported by Costes *et al.*,[26] using Schiff-base **L6** and blocking six sites on Gd using nitrate, Kahn's group using Schiff-base **L3** and blocking six sites using hexafluoroacetylacetonate,[27] and a Polish group using 1,3-bis(dimethylamino)propan-2-ol as a bridging ligand, and blocking six sites using triflate.[28]

These results suggest that a correlation between distance and the exchange integral is oversimplified, and Kahn has suggested[27] that because the magnitude of the exchange coupling is dependent on the exchange transfer integral between the Gd 5d-orbitals, and the Cu 3d-orbitals, then in systems with a $GdCuO_2$ ring, the exchange integral will be correlated with the angle between the GdO_2 and CuO_2 planes,[27] with the maximum value found when the two planes are co-planar. The argument also supports the view that the Cu···Gd distance is important, as the transfer integral is certainly dependent on the inter-nuclear distance. Results from Costes *et al.* feature a planar $GdCuO_2$ ring,[26] and the coupling in question is only 7.0 cm^{-1}, which again support the view that the ferromagnetic coupling between Cu and Gd is never likely to be greater than 10 cm^{-1}. A problem with this latter correlation is that it has limited immediate applicability—essentially it is only of use for compounds which contain the two metals bridged by two μ-oxygen donors. Many Cu–Gd complexes are known which do not contain this structural feature.

A different approach to synthesising discrete units is to design a ligand which provides all the donor groups necessary to encapsulate both Cu and Gd centres. The tripodal Schiff-base ligand **L10** provides three N-donors, three hydroxy O-donors and six acetal oxygen donors, and therefore seemed suitable for such a role.[29] Unfortunately, while a Ni–La complex could be made with such a ligand, copper could not be readily incorporated into the cavity 'designed' for a 3d-metal centre and there is a considerable problem of hydrolysis of the acetal groups.[29] More robust versions of this tripodal ligand can be envisaged.

In none of these complexes have particularly high spin ground states been observed. In trinuclear Cu_2Gd species an $S = 9/2$ ground state is expected and found, but for all higher oligomers (as opposed to oxamido-bridged polymers), anti-ferromagnetic exchange between copper centres predominates and leads to molecules with low spin or even diamagnetic ground states. The problem is in the topology of the larger cages, where short Cu···Cu contacts are normally found. Other than the work with oxamido-ligands no means of segregating the metals into alternating Cu and Gd sites have yet been reported.

5 Conclusions

The future of magnetic studies of heterometallic 3d–4f complexes is in the study of more complicated ions than Cu^{II} and Gd^{III}. All other paramagnetic 4f-ions are anisotropic, and this will introduce anisotropy into the magnetic ground state of any cage. As anisotropy appears vital in forming 'single-molecule magnets', then studies of such cages are potentially exciting. The work to isolate discrete dinuclear Cu–Gd cages will be particularly useful as this will allow study of isostructural Cu–Ln complexes. Kahn has already studied a series of oxamido-bridged polymers of formula $Ln_2[Cu(opba)]_3$,[30] where Ln = any 4f-element from Tb to Yb and opba = *ortho*-phenylenebis(oxamato). For Tb and Dy there is a divergence in $\chi_M T$ at low temperature (χ_M is the molar magnetic susceptibility), indicating magnetic ordering and possibly the presence of one-dimensional ferro- or ferri-magnets. For Ln = Ho, Er, Tm or Yb no significant Cu···Ln interaction could be measured. These results are probably the first concrete indication of the likely diversity of magnetic properties that can be expected when orbitally-degenerate 4f-metals are involved in mixed-metal complexes.

Equally, moving to other 3d-metals will be challenging and may lead to novel properties. We have shown that pyridonate ligands can be used to make Co–Ln, Ni–Ln[31] and Mn–Ln cages[32] using similar procedures to those adopted for Cu–Ln cages.

Perhaps most excitingly a very beautiful Ni_6Sm cage has been reported using L-prolinate as a ligand (Fig. 9).[33] This last result is particularly intriguing because the procedure used should be general to many 3d-metals, and it should be possible to replace the central Sm ion with a range of other 4f-metals. The structure contains a central icosahedrally coordinated Sm ion surrounded by an octahedron of Ni centres. The Ni···Ni contacts are much longer (5.23 Å) than the Sm···Ni vectors (3.70 Å), and this may lead, for the correct combination of 3d- and 4f-metals, to ferromagnetic exchange between dissimilar metals dominating over anti-ferromagnetic exchange between like. No magnetic properties of this cage or related cages have yet been reported.

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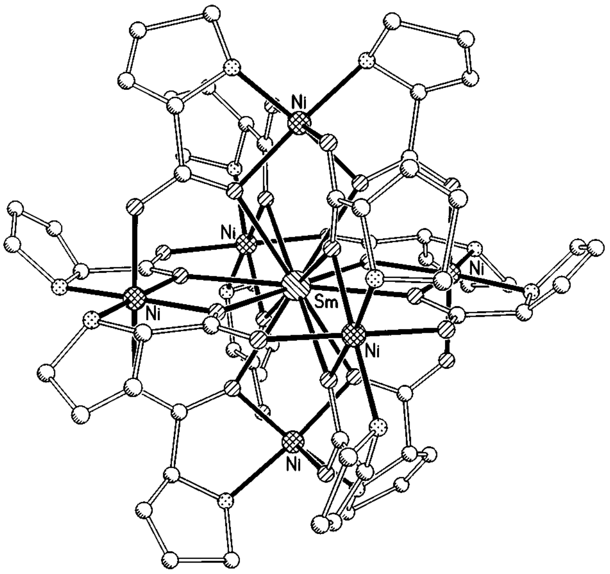

Fig. 9 The structure of the heptanuclear cage $[Sm\{Ni(pro)_2\}_6]^{3+}$ (where pro = L-proline)[33]

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