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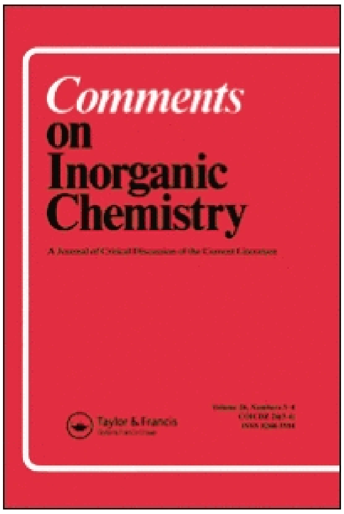

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Publication details, including instructions for authors and subscription information:
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To cite this Article Winpenny, Richard E. P.(1999) 'Families of High Nuclearity Cages', Comments on Inorganic Chemistry, 20: 4, 233 — 262
To link to this Article: DOI: 10.1080/02603599908021445
URL: http://dx.doi.org/10.1080/02603599908021445

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Families of High Nuclearity Cages

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The structural diversity displayed by polymetallic cages is discussed, concentrating on the chemistry of cobalt and nickel stabilised by carboxylate and pyridonate ligands. The structures can be broken down into "families of cages", five of which are identified. Adamantine-cages have been made with hepta- and nona-nuclear cores. Tricapped trigonal prisms with deca-, undeca- and dodeca-nuclear metal arrays have been made for Co and Ni, and related cages for Cr and Fe have also been synthesised. Perhaps the most aesthetically pleasing family are the metal wheels, which vary in nuclearity from eight to eighteen, and which have been found for the metals from Ti to Ni - excluding Mn. Cages based on oligomers of cubanes form the fourth family, and the fifth group is related to simple mineral archetypes such as the rock-salt or cadmium iodide structure.

Keywords: *cages, molecular magnets, cobalt, nickel, X-ray structures*

INTRODUCTION

The number of polynuclear cage complexes of the 3d-metals has increased enormously in the last several years. This is partly due to

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Comments Inorg. Chem.
1999, Vol. 20, No. 4-6, pp. 233-262
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Science Publishers imprint.
Printed in Malaysia

improvements in characterisation techniques – more intense X-ray sources and better software has led to many more crystallographic determinations being possible - but mainly because the discovery of novel properties for these cages has stimulated the examination of new means of making and controlling structures.

Probably the most exciting new properties discovered have been in the field of magnetism. In 1988 a cyclic hexanuclear manganese complex bridged by nitronyl nitroxide ligands was reported, which had a spin ground state of S = 12.[1] This compares with the highest spin achievable for a single metal centre of 7/2 for Gd(III), and remains higher than that achieved using organic radicals.[2] This observation spurred other scientists to look for high spin ground states, with around another dozen or so now known which have ground states of S = 9 or higher. What was less expected was that some of these molecular species would show behaviour typical of "single molecule magnets" in addition to high spin states.

The first, and most fully-studied, single molecule magnets are dodecanuclear manganese cages of formula $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$, which can be made with R = Me,[3,4] Ph[5] or Et,[5] and which have ground states of S = 9 or 10. These molecules show very slow relaxation of their magnetisation below 10 K, due to a large anisotropy barrier caused by zero-field splitting of the S = 9 or 10 ground state.[6] This leads to a picture where the M = ±10 components are the lowest in energy, with only these levels populated at low temperature in zero-field. If the sample is magnetised then one of these two components – say the M = +10 level – is lowered in energy, and this level is then preferentially populated. If the external magnetic field is then switched off, there is now a marked energy barrier for loss of the magnetisation because the system has to pass from M = + 10 → M = +9, and +9 → +8 etc... over the M = 0 level and then down again to occupy the M =-10 level. The presence of this energy barrier explains the long relaxation times observed.

This observation poses the question, "why these compounds and not the other high spin cages"? The answer appears to be that the high spin state is here combined with a high anisotropy of the spin caused by the presence of Jahn-Teller distorted Mn(III) ions in the structure. The size of the energy barrier is DS^2, where D is the zero-field splitting parameter of the S ground state of the molecule. The vital issue is the sign of D – it must be negative for an energy barrier to reorientation to exist. If D were positive then M = 0 would be at the bottom of a well, and no significant barrier to reorientation of magnetisation exists. More recent studies indicate that these Mn_{12} cages are not unique, as at least three other distinct systems have shown similar behaviour – an Fe_8 cage with an S = 10 ground state,[7] Mn_4 cages with an S = 9/2 ground state,[8] and recently a V_4 cage with an S = 3 ground state.[9] A Co_{24} cage may also be a "single molecule magnet", but at present is much less well-characterised magnetically.[10]

These properties are more exciting than the simple high-spin molecules because these features are those of a single molecule magnetic memory – albeit one functioning at less than 10 K. The cages have also allowed studies of quantum-tunnelling to be performed as the particle size and energy barrier seem ideal for seeing quantum effects within these macroscopic systems.[11,12] Hysteresis loops for these cages show distinct "steps", where the external magnetic field brings energy levels within one well into alignment with energy levels in the other well. Therefore for physicists these molecules present a wonderful opportunity to examine behaviour at the quantum-classical interface.

For a synthetic chemist many questions remain. It is difficult enough to make by design molecules which will have high spin ground states; it is currently impossible to predict the sign and magnitude of the anisotropy of those ground states. To demonstrate the difficulty, it is easy to see that if you bring together two S = 1 centres – say Ni(II) ions – the spin ground state will be S = 0 if anti-ferromagnetic exchange predominates or S = 2 if ferromagnetic coupling is present. In some cases correlations between structure and magnetism will allow a prediction of the ground state for the dinuclear compound.[13] The relationship between the anisotropy of this ground state and the anisotropy of the Ni(II) centres which are interacting is much more unpredictable.

To begin to address this problem we need to study many more cages thoroughly, using susceptibility measurements but also spectroscopic techniques which may give exchange couplings and zero-field splittings directly. To carry out such studies the primary requirement is to have a body of cages to examine, preferably cages where there is a systematic variation in properties. Our aim therefore, and the subject of this review, has been to create families of high nuclearity cages where such systematic analysis of properties may become possible.

The families discussed below are mainly based on our own work using simple bridging ligands such as carboxylates and pyridonates, however where a "family resemblance" exists to compounds reported by other groups, such molecules have also been included in the discussion. There has been no attempt to be exhaustive. Both carboxylates and pyridonates are well-known bridging ligands, with a considerable history of being used to make dimeric species of the 4d- and 5d-metals.[14] In such chemistry the ligands are very similar, normally displaying a 1,3-bridging mode spanning the metal-metal vector. In the cage chemistry described below carboxylates and pyridonates show much more distinctive coordination chemistry.

Carboxylate ligands generally adopt one of the three bonding modes shown in Figure 1. The 1,3-bridging mode (**B**) remains the most commonly seen in the cages. For the pyridonate ligands nine coordination modes are adopted, six of which have no analogue in the carboxylate chemistry (Figure 2). Presumably the presence of dissimilar donor atoms within the pyridonate ligands leads to this greater coordinative flexibility, however the versatility of the ligands was unexpected. What is also interesting is that the coordination mode observed depends on the nature of the substituent in the 6-position of the ring (X in Figure 2). For example, the 1,1-bridging mode through the exocyclic oxygen (**E**) is only observed for pyridonates where X is electron-withdrawing such as Cl or Br; where X = Me, the ring nitrogen is always found bound to a metal-site.

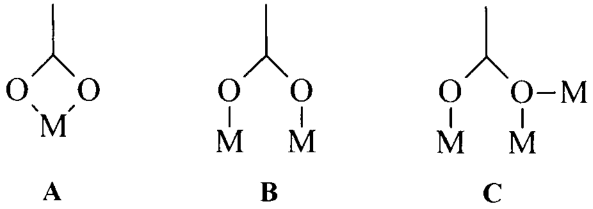

FIGURE 1 The bonding modes shown by carboxylate ligands in the cages discussed below

Much of the chemistry described below involves heteroleptic ligand sets – often carboxylate and pyridonate, plus hydroxide or solvate molecules. In many ways the large number of cages structurally-characterised is due to the diversity of ligands present – each ligand has a specific role to play in stabilising the structure as it crystallises. The mixture of

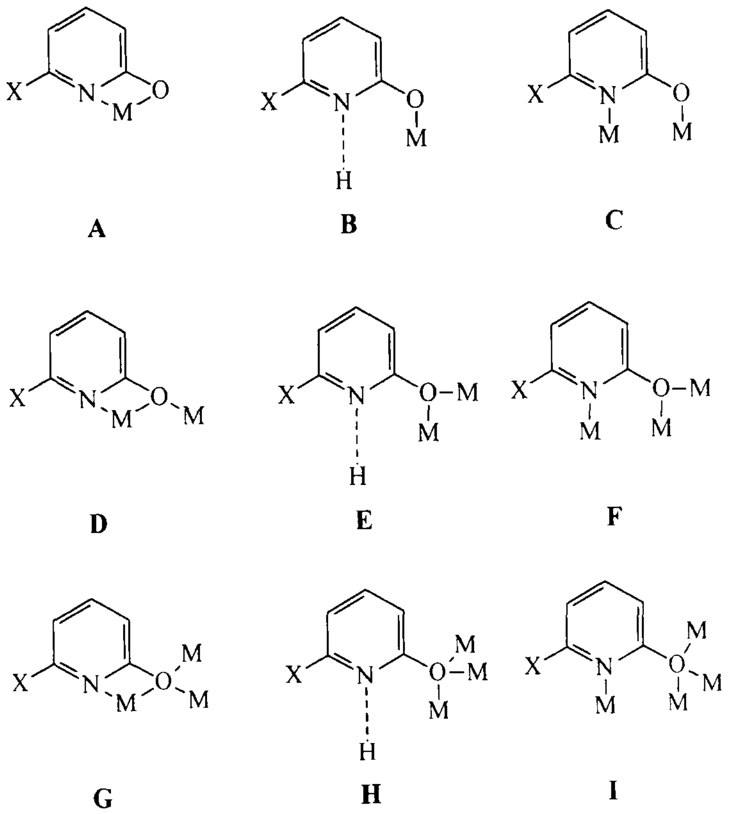

FIGURE 2 The bonding modes shown by pyridonate ligands in the cages discussed below

ligands are introduced in one of two steps of each reaction sequence. Firstly, there is a "mixing" step, in which the components – metal and any ligands are combined. We have explored two such mixing steps in some depth. The more conventional approach is to dissolve, then mix, metal chloride or nitrate salts and deprotonated carboxylates and pyridonates in a polar solvent – frequently methanol. This reaction solution is stirred, and then evaporated to dryness to achieve mixing. The second approach is to use metal carboxylates, hydroxides or methoxides as reagents, and react them with pyridones in the molten state. The pyridones melt at around 130°C, which is ideal for such chemistry, and a paste containing an intimate mixture of metal, carboxylate and pyridonate is produced. For both approaches the second step is to extract the crude material with a suitable solvent – and a wide-range can be used - followed by filtration and crystallisation by evaporation or diffusion of a non-polar solvent such as diethyl ether into the solution.

ADAMANTANES[15]

Reaction of cobalt(II) methoxide with molten 6-chloro-2-pyridone results in a purple paste which can be crystallised from ethyl acetate to give $[Co_9(chp)_{18}]$ **1** (chp = 6-chloro-2-pyridonate) (Figure 3). This seems a good place to start as this is the only homoleptic cage we have made. Examining the literature indicates that while for carbonyl clusters homoleptic cages are common, and work from Lehn,[16] and others[17,18] have now produced many high nuclearity cages using complex organic ligands, for simple ligands such as carboxylates or alkoxides the presence of only one ligand type is the exception rather than the rule – normally oxide, hydroxide or solvate are also found in the structures.

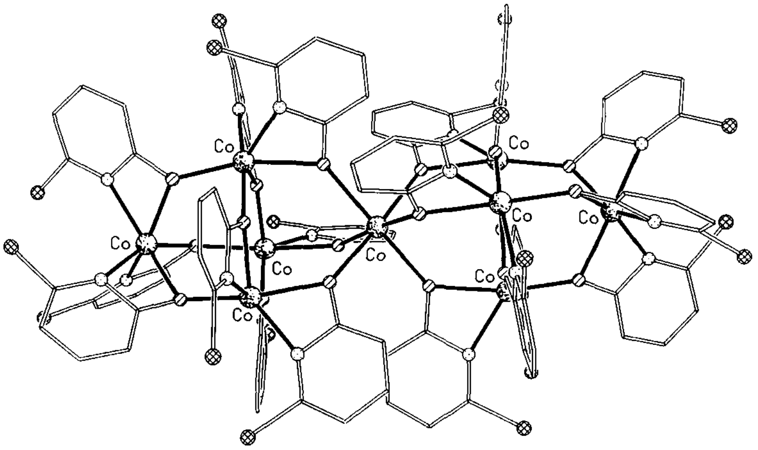

FIGURE 3 The structure of $[Co_9(chp)_{18}]$ **1**

The core of **1** consists of four Co_4 tetrahedra sharing two faces and one vertex, with each edge of these tetrahedra occupied by O-donors from pyridonate ligands which all use bonding mode **D** (Figure 2). This contrasts with dinuclear homoleptic complexes of pyridonates ligands, e.g. with copper or chromium,[19] which all show bonding mode **C.** Probably the dislike cobalt has for forming metal-metal bonds accounts for the unusual topology of the cage, and the surprising binding of the ligand.

The presence of O-atoms on each Co... Co edge means that the structure consists of M_4O_6 adamantanes. While isolated M_4O_6 adamantanes are well-known – with examples reported for the metals from titanium to iron[20–28] – it had never previously been found for later 3d-metals, and linked adamantanes were restricted to an edge-sharing Fe_6 cage reported by Nair and Hagen.[29] **1** is in fact a member of a family of adamantanes, with three nickel analogues easily synthesised by similar means.[15] These are all heteroleptic however, incorporating some solvate or hydroxide moieties into the final structure. For example, the heptanuclear cage $[Ni_7(chp)_{12}(MeOH)_6Cl_2]$ **2** contains the central pair of vertex-sharing adamantanes of **1**, but six MeOH ligands occupy the sites on the six unshared nickel sites. The bonding of MeOH to the "basal" nickel centres of the adamantanes creates cavities which are ideal for H-bonding to two chloride anions. In $[Ni_7(chp)_{12}(OH)_2(MeOH)_6]$ **3,** two μ_3-hydroxides bridge the basal nickel sites, distorting the ideal adamantine geometry, and in $[Ni_9(chp)_{16}(OH)_2(MeCN)_2]$ **4** the sites occupied by MeOH in **2** and **3** are occupied by two $[Ni(chp)_3]^-$ "complex anions" and acetonitrile solvate. The chief difference between the synthesis of **4** and **2** and **3,** is that MeCN was used for the crystallisation step for **4,** rather than MeOH. The less coordinating solvent leads to a slightly higher nuclearity.

Although four members of this family are known – and presumably exact cobalt analogues of **2** – **4,** and an exact Ni analogue of **1** could also be made – the family is quite limited. We have previously found that 6-bromo-2-pyridonate can adopt similar coordination modes to the 6-chloro-derivative and this might help extend the family a little. The magnetic properties are dominated by anti-ferromagnetic exchange between neighbouring centres, and in each case the ground state appears to be quite low (S = 1 for the three Ni cages, and 3/2 for the Co cage).

In the adamantane structures reported by other workers, in general, the oxygen atoms on the edges of the metal polyhedra have been either oxide or hydroxide,[20–28] with terminal ligands such as cyclopentadienyl, 1,4,7-triazacyclononane or 1,3,5-triaminocyclohexane completing the metal coordination sphere. The only other example where the oxygen-bridge is derived from a polyatomic ligand is in an iron cage where a phenolic oxygen derived from a complex pentadentate ligand bridges an Fe...Fe edge.[27]

TRICAPPED TRIGONAL PRISMS

This is a much more extensive group of compounds than the adamantanes. The earliest member made was $[Co_{12}(OH)_6(mhp)_{12}(O_2CMe)_6]$ **5**,[30] (mhp = 6-methyl-2-pyridonate) which was reported by the Garner group in 1983. We have concentrated on making further cobalt and nickel congeners, but other groups have made iron and chromium relations (see below).

The components of these cages can be brought together in two ways. Initially we prepared the cobalt or nickel carboxylate and reacted this with molten Hmhp followed by crystallisation from solvents such as CH_2Cl_2 or MeCN. However, later we have discovered that mixing the hydrated metal chloride with the sodium carboxylate and sodium pyridonate in MeOH, followed by filtration then evaporation to dryness, also created a paste which, on extraction, gave crystals of polynuclear cages with tricapped trigonal prismatic cores.

These cages crystallise in a variety of space groups. A regular centred-tricapped-trigonal prism (ttp) could have symmetry as high as D_{3h}, and although we never observe a Co or Ni cage with such high symmetry several of the cages are disposed about a crystallographic three-fold axis. In each case the cage contains a core based on a decanuclear centred-ttp bridged in a similar manner by hydroxide, carboxylate and pyridonate ligands. A variation in the nuclearity of the cages occurs due to the presence or absence of further metals on the trigonal faces of the prism; where the ligands vary it is only in the way in which these upper and lower trigonal faces are ligated.

The structure of $[Co_{12}(OH)_6(mhp)_{12}(O_2CMe)_6]$ **5**[30] is shown in Figure 4 and the metal polyhedron in Figure 5. The central cobalt [Co(1)] is bound to six μ_3-hydroxides which bridge to the nine further metals forming the ttp. The metal atoms at the vertices of the prism [Co(5), Co(6), Co(5A), Co(6A), Co(5B) and Co(6B)] share one μ_3-OH with Co(1), while the metal atoms capping the rectangular faces of the prism [Co(4), Co(4A) and Co(4B) share two μ_3-hydroxides with Co(1), forming three M_2O_2 rings.

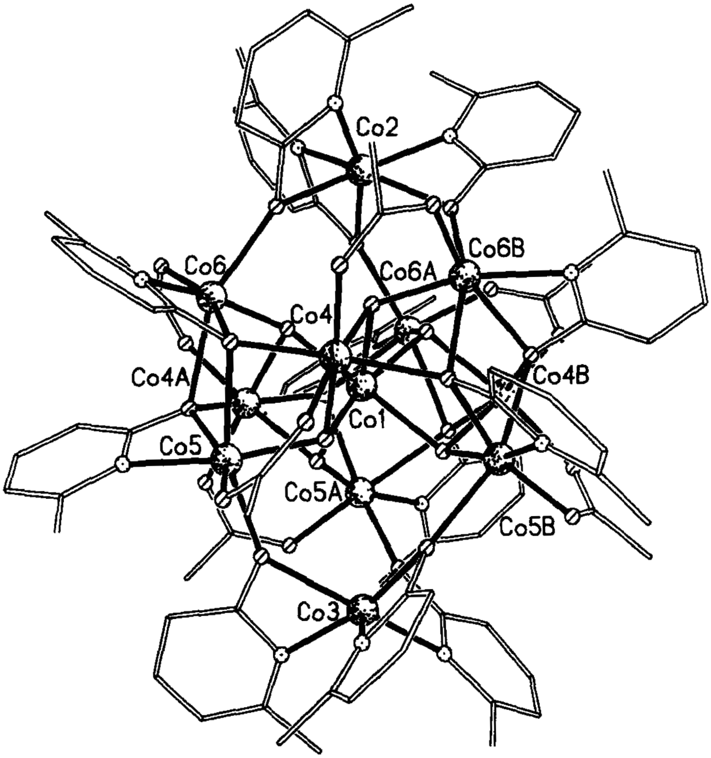

FIGURE 4 The structure of $[Co_{12}(OH)_6(mhp)_{12}(O_2CMe)_6]$ **5**

The exterior of this central ttp is bridged by six mhp and six acetate ligands. Each mhp ligand adopts bonding mode **G**, chelating to one of the cobalt atoms at the vertices of the prism and bridging to two further Co sites through the exocyclic O-atom. The three metal sites attached to the O-atom are: the metal vertex to which the N-atom is bound [e.g. Co(6B)], the other vertex forming a side of the trigonal prism [e.g. Co(5B)] and a metal site capping a square face of the trigonal prism

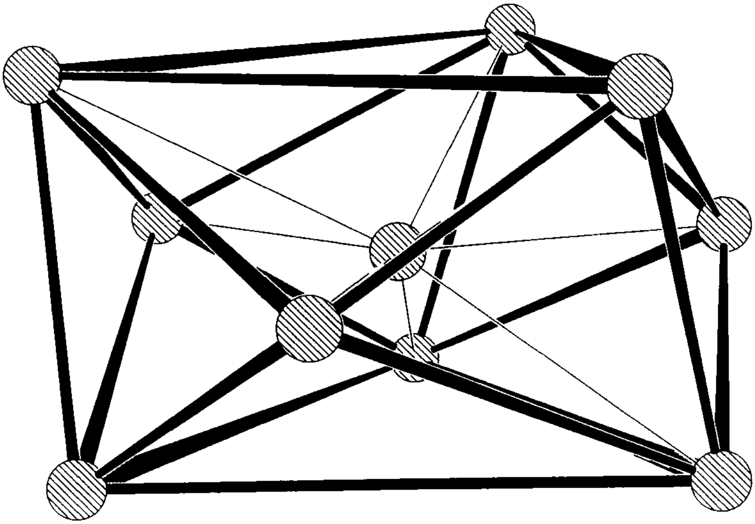

FIGURE 5 The metal core of a centred-tricapped-trigonal prism

[e.g. Co(4B)]. The six μ_3-O-donors from the pyridonates therefore occupy the six triangular faces around the "waist" of the ttp, i.e. they centre the faces bounded by one-cap- and two vertex-metal sites.

The carboxylates bridge in a 1,3-fashion between cap- and vertex-sites, with each cap attached to two acetate ligands. For example, carboxylates bridge between Co(4) and Co(6B), and Co(4) and Co(5). The result of these various bridges is to create a central $[M_{10}(\mu_3\text{-}OH)_6(\eta^2,\mu_3\text{-xhp})_6(\eta^2,\ \mu_2\text{-}O_2CR)_6]^{2+}$ fragment, and this fragment recurs in the other cobalt and nickel trigonal prisms made, differing only in the carboxylates present.

The metal sites are each six-coordinate, with the central metal bonded exclusively to μ_3-hydroxides. The capping sites are bonded to two μ_3-hydroxides, two μ_3-O-atoms from mhp, and two oxygens derived from carboxylates. The vertex-sites are bound to only five donors from within this central fragment: one μ_3-hydroxide, two μ_3-O-atoms from mhp, one oxygen from a carboxylate and one N-donor from an mhp ligand. The final coordination site for these vertex-metals is where the structural variation in these cages takes place. In **5** six μ_2-O-atoms from mhp ligands each occupy one of these sites, with these ligands part of two $[Co(mhp)_3]^-$ fragments which occupy both the upper and lower triangular faces of the trigonal prism. Thus the $[Co(mhp)_3]^-$ fragments could be regarded as trinucleating ligands, containing mhp ligands which have adopted coordination mode **D.**

We have been unable to make the exact nickel analogue of **5,** however using chloroacetate we have crystallised $[Ni_{12}(OH)_6(mhp)_{12}(O_2CCH_2Cl)_6]$ **6,**[31] which has the same dodecanuclear metal core. Using acetate we have thus far only managed to make undecanuclear cages with nickel[32] - $[Ni_{11}(OH)_6(mhp)_9(O_2CMe)_6(H_2O)_3]_2[CO_3]$ **7** and $[Ni_{11}(OH)_6(mhp)_9(O_2CMe)_7(Hmhp)_2]$ **8** – which have lost one of the capping atoms on the triangular faces of the prism, and the differ from each other in the ligation on this uncapped triangular face. In **8,** the three coordination sites on this face are occupied by one acetate and two Hmhp ligands which supply the three O-donors required to make the three Ni atoms in this face six-coordinate. In **7** the three sites are occupied by three water molecules. This creates a very hydrophilic face for the cage and in the crystal two molecules of **4** interact *via* six hydrogen bonds to produce a dimer of undecanuclear cages, as shown in Figure 6. The six H-bonds have O...O distances of between 2.57 and 2.90 Å. There are no significant intermolecular interactions in **8.**

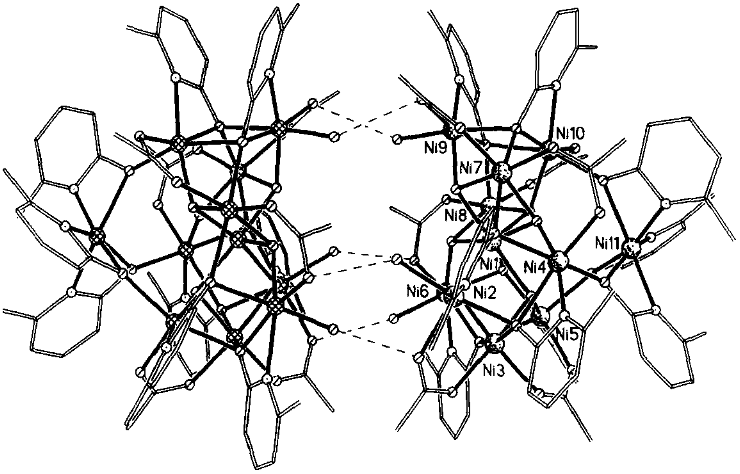

FIGURE 6 A dimer of $[Ni_{11}(OH)_6(mhp)_9(O_2CMe)_6(H_2O)_3]_2[CO_3]$ 7

This change from a dodecanuclear to an undecanuclear cage was unexpected. Yet more unexpected was the chance crystallisation of a species intermediate between these two cages. $[Ni_{11}(OH)_6(chp)_9(O_2CPh)_6(EtOH)_3][Ni(chp)_3]$ **9** is shown in Figure 7,[33] and was formed unexpectedly and in 15 % yield. It crystallises with a C_3 axis coincident with the trigonal axis of the cage. Many of the features described for **5** can be recognised, including the central $[M_{10}(\mu_3\text{-}OH)_6(\eta^2,\mu_3\text{-}xhp)_6(\eta^2,\mu_2\text{-}O_2CR)_6]^{2+}$ fragment.

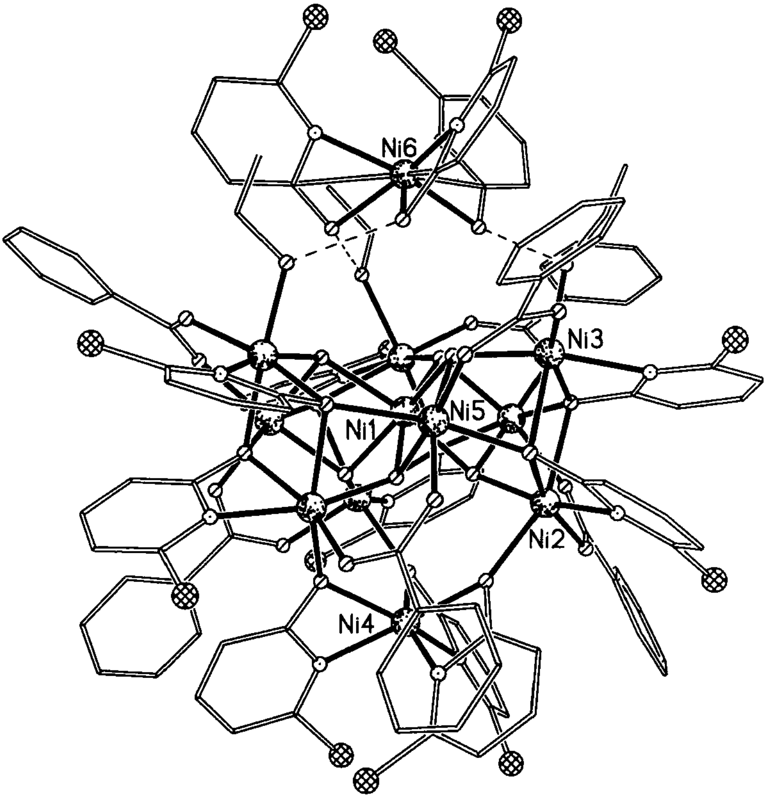

FIGURE 7 The structure of $[Ni_{11}(OH)_6(chp)_9(O_2CPh)_6(EtOH)_3][Ni(chp)_3]$ **9**

The significant change between **5** and **9** is again the ligation of one of the triangular faces. In **9** three molecules of EtOH – carried forward from the first step of the synthesis – are bound to Ni(3) and its symmetry equivalents, thus displacing the cap. A $[Ni(chp)_3]^-$ fragment is hydrogen-bonded to these EtOH molecules. The O...O distance for these H-bonds is 2.60 Å. The other triangular face of the prism has retained a $[Ni(chp)_3]^-$ cap, attached through three μ_2-O-atoms from chp to Ni(2) and its symmetry equivalents.

In **9** the pyridonate present is 6-chloro-2-pyridonate, which is one of only two examples we have of this pyridonate featuring in a cage based on a ttp, while the carboxylate present is benzoate. This indicated a range of carboxylates, and perhaps pyridonates could be used to stabilise these structures. For nickel this is undoubtedly the case, and we have made further cages where the carboxylate can be *iso*-butyrate and diphenylacetate.[31] These cages lack both additional caps on the trigonal axis of the prism. For cobalt we have made decanuclear cages with benzoate[33] and trimethylacetate (pivalate) ligands.[31] The range of such cages is summarised in Table I. The family therefore contains eight Co and Ni members.

TABLE I Co and Ni Cages with TTP Cores

	Metal	*Carboxylate*	*Pyridonate*
M_{12}	Co	O_2CMe	mhp
	Ni	O_2CCH_2Cl	mhp
M_{11}	Ni	O_2CMe	mhp
	Ni	O_2CPh	chp
M_{10}	Co	O_2CPh	mhp
	Co	O_2CCMe_3	mhp
	Ni	O_2CCHMe_2	mhp
	Ni	O_2CCHPh_2	chp

Surprisingly we have been unable to crystallise many of the direct analogues, and some of these results are themselves intriguing. Thus while we can make a decanuclear ttp of cobalt, stabilised by mhp and O_2CCMe_3 ligands, with nickel the structure found distorts towards a new polyhedron.[34] Two cages, $[Ni_{10}(OH)_4(mhp)_{10}(O_2CCMe_3)_6(MeOH)_2]$ **10**, and $[Ni_{10}(OH)_4(mhp)_{10}(O_2CCMe_3)_6(H_2O)_2]$ **11** have been crystallised. The structure of **10** is shown in Figure 8 and **11** differs chemically only in the presence of two terminal water ligands, rather than two terminal methanols.

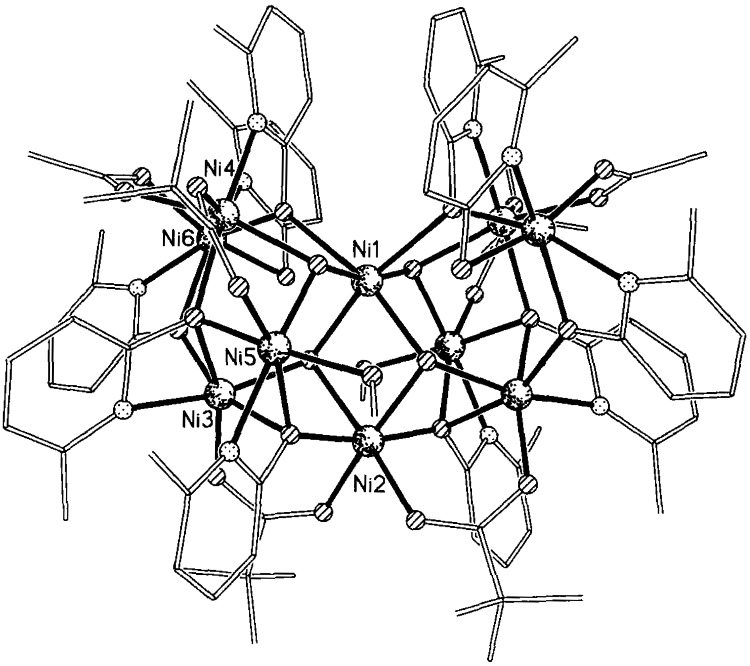

FIGURE 8 The structure of $[Ni_{10}(OH)_4(mhp)_{10}(O_2CCMe_3)_6(MeOH)_2]$ **10**

10 crystallises with a two-fold axis passing through Ni(1) and Ni(2) and is held together by four μ_3-OH ligands, six 1,3-bridging carboxylates and ten pyridonate ligands. The metal array does not describe a complete polyhedron, however addition of further vertices using molecular graphics, reveals a centred 14-vertex deltahedron as shown in Figure 9. The five missing vertices delineate an equatorial fissure, as if the deltahedron had been cut through the centre with the two sides falling apart slightly. Given the absence of so many vertices the overall geometry is surprisingly regular with Ni(1) at the centre, Ni(3), Ni(3a), Ni(5) and Ni(5a) occupying four of the vertices of one hexagon and Ni(4), Ni(4a), Ni(6) and Ni(6a) four of the vertices of the second hexagon. Ni(2) caps the former hexagon.

The mhp ligands present adopt four different coordination modes: **A, D, F** and **G,** and therefore shows a much more diverse coordination

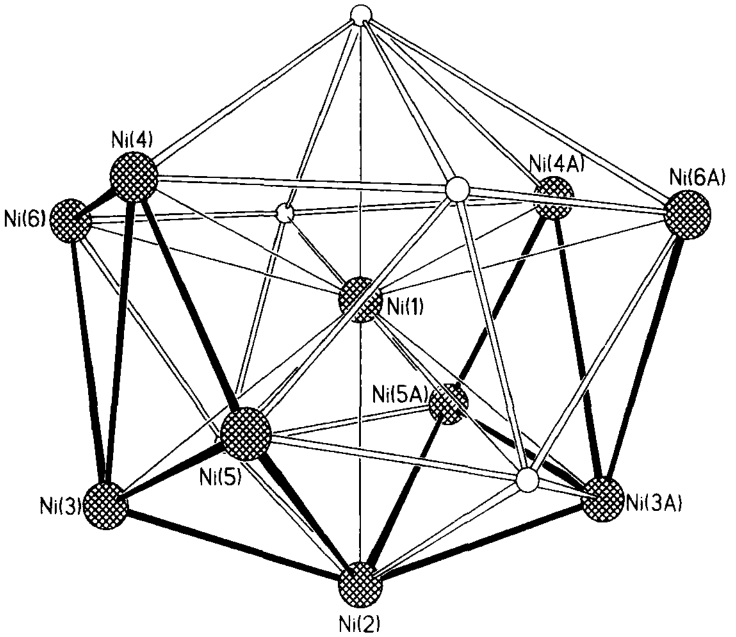

FIGURE 9 The metal core of a tetraicosahedron. The shaded circles are the Ni sites in **10**, and the open circles the additional vertices required to complete the polyhedron

chemistry in **10** and **11** than in the structures based on ttps. The carboxylates all act as 1,3-bridges. The metal coordination sites are also more diverse than in the ttps, with the six independent sites chemically non-equivalent. Ni(1) is bound to four μ_3-hydroxides, and two μ_2-oxygens from mhp ligands. Ni(2) lies at the base of the tetraicosahedron and is bound to two μ_3-hydroxides, two μ_3-O-atoms from mhp, and two carboxylate oxygens. Ni(3) is bound two chelating mhp ligands, one μ_3-hydroxide and one carboxylate oxygen; Ni(4) is only five-coordinate, bound to one N-donor from an mhp, one μ_3-hydroxide, one μ_3-oxygen from an mhp, and two oxygens from carboxylates; Ni(5) is bound to two μ_3-hydroxides, one chelating mhp, one carboxylate oxygen and the terminal MeOH; Ni(6) is bound to two chelating mhps, one further mhp oxygen and one carboxylate oxygen.

Given two examples and moderate yields of this new polyhedron it is difficult to dismiss **10** and **11** as irrelevant exceptions, and it could be the case that the larger trimethylacetate ligand is imposing sufficient strain on the structure for a reorganisation to be favourable. However whatever factors are involved must be very finely balanced as the same ligands with cobalt lead to a cage which crystallises as a ttp.

A further curiosity is that while nickel can form ttps with either mhp or chp ligands, with cobalt presence of chp in these reactions lead to heptanuclear cages of formula $[Co_7(OH)_2(chp)_8(O_2CR)_4(MeCN)]$ (R = Ph, **12** or CMe_3 **13**).[35] The structure of **12** is shown in Figure 10, and contains an irregular metal polyhedron which is symmetric about a mirror-plane passing through Co(2), Co(3) and Co(5). The polyhedron can be described as a square-based pyramid, consisting of Co(1), Co(1a), Co(4), Co(4a) and Co(2), capped on a triangular face by Co(3), and on a neighbouring edge by Co(5). Two μ_3-hydroxides feature in the cage, bridging Co(1), Co(la) and Co(2), and Co(4), Co(4a) and Co(5) respectively. The carboxylates within the structure are all 1,3-bridging, while the chp ligands adopt bonding modes **C, D, F** and **G** – i.e. each of the four crystallographically independent pyridonates adopts a different binding mode.

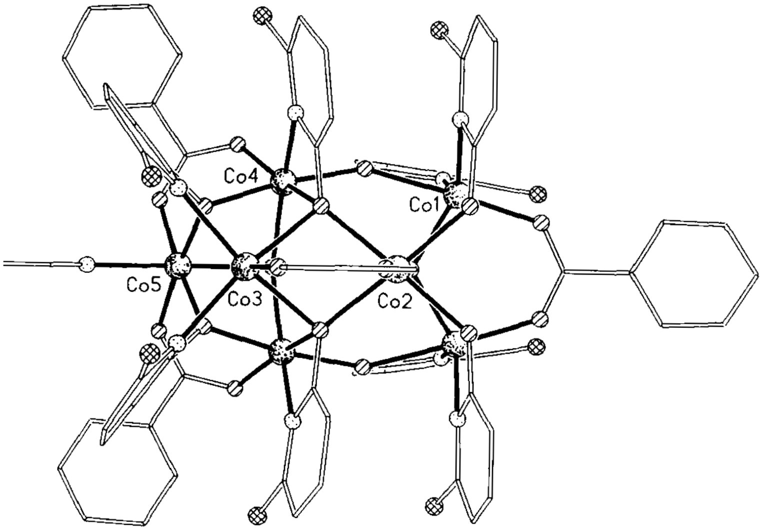

FIGURE 10 The structure of $[Co_7(OH)_2(chp)_8(O_2CPh)_4(MeCN)]$ **12**

The synthetic process therefore appears to give a variety of structures and two plausible explanations can be given. The first is that something about the combination of metal, carboxylate and pyridonate lead to exceptions such as **10** – **13.** For **10** and **11** we can argue that the trimethylacetate ligand is causing reorganisation due to steric crowding, and that as bond lengths to Ni(II) are shorter than to Co(II) then any intra-ligand repulsions will be more important for nickel cages than for their cobalt congeners. Explaining the change to **12** and **13** is much more difficult.

The second explanation allows for the fact that the only possible characterisation tool for all these cages is X-ray crystallography, and the differences resulting from similar syntheses may be due to fractional crystallisation rather than due to the relative stabilities of cages. Or in other words, the thermodynamically important properties are not associated with intra-molecular forces but with solubility products. These are impossible to predict or rationalise. If this explanation is correct then each reaction sequence contains a matrix of possible products, and which is found is determined exclusively by which forms the best single crystals. Characterisation of the reaction solutions would then be necessary to understand reactivity however this has proved impossible until now. Discovering spectroscopic techniques for analysing, and chromatographic techniques for separating, all intermediates and products of such reactions are a major challenge in the field.

The ttps extend beyond nickel and cobalt. Both iron(III) and chromium(III) form similar structures with exclusively carboxylate ligands. For iron a compound of formula $[Fe_{11}O_6(OH)_6(O_2CPh)_{15}]$ **14** has been reported by Lippard and co-workers.[36] Compared with **5** it lacks the central metal site. The chromium complex, reported as $[Cr_{12}O_{12}(O_2CCMe_3)_{15}]$ **15** by Batsanov *et al*,[37] is virtually identical to the Fe cage, but has the central metal site.

The range of cages belonging to this family is therefore extensive. The lack of a manganese ttp is also intriguing, given that so many polynuclear Mn cages have been reported which contain the correct mixture of carboxylate and oxide/hydroxide ligands. This absence may be connected with the preferred structure of the M_2O_3 oxides. For chromium and iron the mineral has the corundum structure, and the ttp core found in Cr_{12} and Fe_{11} cages can be related to corundum. For Mn_2O_3 the mineral has a structure related to fluorite, from which the ttp core can not be abstracted. This relationship between mineral and preferred cage structure is clearly unproven, but it suggests that the other metals and metalloids which adopt the corundum structure (Ti, V, Al and Ga) should also give ttp cages under the correct conditions.

The magnetic properties of these cages are interesting, and extremely varied. **14** has been studied in some detail by the Lippard group, and these studies show that anti-ferromagnetic exchange is dominant in the cage, leading to a spin ground state of $S = 1/2$.[36] We have examined the nickel cages and found that the ground state can vary between $S = 8$, 4 and 2, depending on the carboxylate and pyridonate present.[31] It is very difficult to rationalise this variation in ground state by structural considerations. We have recently examined the magnetism of **15**, and found an $S = 6$ ground state, which can be confirmed by Q- and K-band epr spectra which show the expected twelve-line pattern centred at $g = 1.98$.[38]

WHEELS

The synthesis which results in ttps can be re-routed by using THF as the solvent for the crystallisation step. With both nickel and cobalt isomorphic compounds of formula $[M_{12}(xhp)_{12}(O_2CMe)_{12}(H_2O)_6(THF)_6]$ can be made (xhp = chp or 6-bromo-2-pyridonate).[39,40] The structures are cyclic dodecanuclear wheels (Figure 11), where the metal sites are bridged by pyridonates, which adopt bridging mode **E,** and by acetate ligands which adopt two distinct structural roles. Six of the acetates lie outside the metal wheel, and bridge in a 1,3-fashion ; the remaining six acetates lie within the ring, and bridge in a 1,1,3-fashion (**C** in Figure 1). Although the conventional ball-and-stick representation of the crystal structure implies that there is some space within the cavity of the molecule, in fact the methyl groups of the acetate fill this volume extremely efficiently.

The close relations within this family are quite limited in number, for three reasons. Firstly, acetate is the only carboxylate which has the correct size to pack together within the dodecanuclear wheel, if the carboxylate is any bigger then the structure is unfeasible. Secondly, the bonding mode adopted by the pyridonate, binding to the metals exclusively through the exocyclic oxygen donor, is only ever found for pyridonates with the substituent in the six-position is electron-withdrawing. This limits us to 6-chloro- and 6-bromo-2-pyridonate as readily available ligands. Thirdly, the involvement of THF in binding to six of the

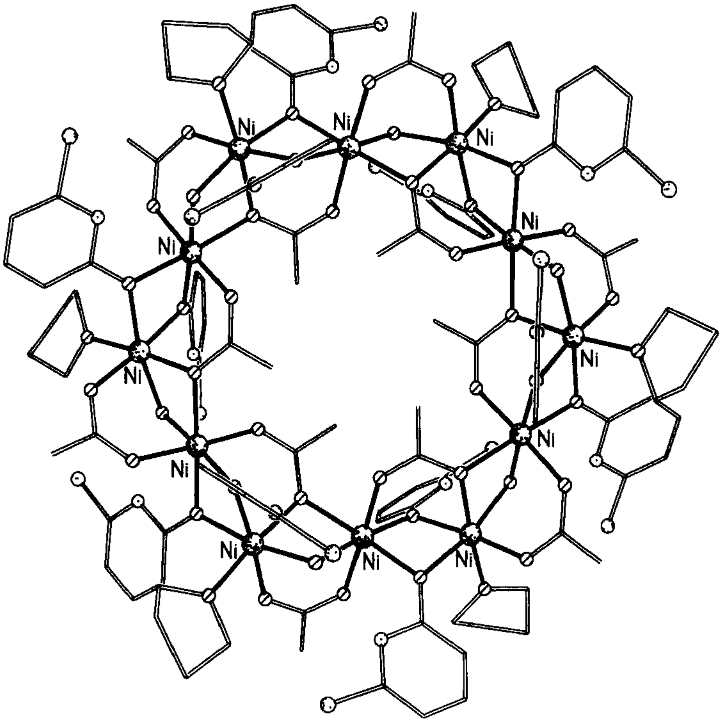

FIGURE 11 The structure of $[Ni_{12}(chp)_{12}(O_2CMe)_{12}(H_2O)_6(THF)_6]$

metal sites seems important in forming the structure, and we have thus far been unable to crystallise other wheels featuring different solvents bound to these sites.

The magnetochemistry of these wheels is fascinating for the nickel congeners, but less exciting for their cobalt relations. For nickel, ferromagnetic exchange is found between the neighbouring $S = 1$ metal sites, resulting in an $S = 12$ ground state.[39] This is among the highest found for a molecular species, and these are the first very high spin molecules where the exchange coupling is exclusively ferromagnetic. In earlier examples where $S \geq 8$, the high ground state results from a balance of anti-ferromagnetic exchanges. The Co_{12} wheels are disappointing, with anti-ferromagnetic exchange leading to almost diamagnetic molecules at low temperature.[40] While the close relations of these wheels are limited, wheels of earlier transition metals are becoming increasingly well-established. Octanuclear wheels are known for titanium $[Ti(O)(O_2CC_6F_5)_2]_8$,[41] vanadium $[V_8(OH)_4(OEt)_8(O_2CMe)_{12}]$,[42] chromium $[CrF(O_2CCMe_3)_2]_8$.[43] iron $[FeF(O_2CCMe_3)_2]_8$,[44] and cobalt $[Co(OMe)_2(O_2CMe)]_8$;[45] decanuclear wheels for iron $[Fe(OMe)_2(O_2CR)]_{10}$ (R = CH_2Cl or CH_3),[46,47] and recently an octadecanuclear iron wheel has been reported.[48] In addition to these there are also a family of "metallocrowns", where such wheels are centred by an additional metal. It is intriguing that these wheels should form with different nuclearities for different metals.

Manganese is presently absent from the family of wheels (although centred cyclic structures with Mn exist). Our attempts to make an Mn wheel similar to the cobalt and nickel wheels led to a one-dimensional polymer $[Mn_2(chp)_2(O_2CMe)_2(MeOH)_2]_n$.[49] There is in this structure curvature between each binuclear unit, however on this occasion it leads to a zigzag polymer rather than a wheel. There must be a fine balance between these two alternative structures, and possibly other wheels could be discovered by subtle modifications of syntheses which are reported to give nonlinear one-dimensional polymers.

CUBANES AND OLIGOMERS OF CUBANES

Perhaps the simplest polynuclear cages to make are heterocubanes, where four metal centres occupy alternate corners of a cube with μ_3-bridging atoms at the other corners. In our studies we have made both nickel and cobalt cubanes of formula $[M_4(OMe)_4(chp)_4(MeOH)_7]$ (M = Co, **16**; Ni, **17**),[32,35] where methoxide groups are integral to the formation of the cube. Similar cubanes exist with a wide range of ligands in the terminal sites, complimenting the bridging methoxides.

The structures of these cubes, where the growth of the polynuclear cages is terminated by the presence of seven molecules of MeOH solvate, suggested to us that these tetranuclear cages could be used as building blocks for higher nuclearity species. This appears to be the case, and we have found two tactics can be used to transform simple cubanes into oligomers of cubanes.

The first tactic is to drive off the coordinated solvate by prolonged heating. The loss of the coordinated MeOH creates vacancies on the metals, and this causes terminal chp ligands to adopt bridging modes. The result is the formation of a dodecanuclear species $[Co_{12}(chp)_{18}(OH)_4Cl_2(Hchp)_2(MeOH)2]$ **16**,[35] which involves two cubanes bridged by a central eight-membered ring which contains two further cobalt atoms (Figure 12). The structure is not a straight oligomerisation of **17** as the cubanes in **16** are $[Co_4O_3Cl]$, and the cobalts within the eight-membered ring must be derived from "cannibalisation" of other cubanes. The change in coordination of the ligands is quite profound. In the original tetranuclear species chp is found in bonding modes **A** and **B**, while in **18** the deprotonated pyridonates adopt modes **B, C, D** and **G.** Again, the immense flexibility of these ligands is of vital importance in stabilising the larger cage.

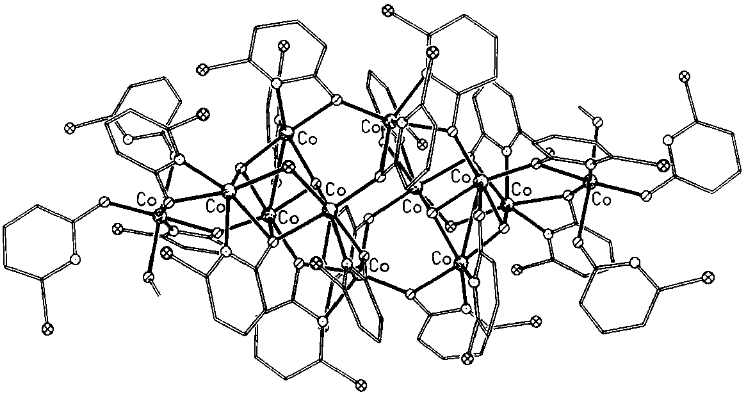

FIGURE 12 The structure of $[Co_{12}(chp)_{18}(OH)_4Cl_2(Hchp)_2(MeOH)_2]$ **16**

A second means of oligomerising cubanes is to add a linking group. Addition of sodium phthalate (phth) to the reaction which produces the Ni cubane **17**, creates a much larger assembly of cages of formula $[Ni_{16}Na_6(OMe)_{10}(OH)_2(chp)_4(phth)_{10}(Hphth)_2(MeOH)_{20}]$ **19** (Figure 13).[50] The first surprise is that the phthalate has displaced chp from **17**, and not MeOH. The second, and major surprise, is that in addition to linking together nickel cubanes, the phthalate ligands have also stabilised a central sodium octahedron – which in itself is unusual, although related lithium octahedra have been reported.

This central Na_6 is the point of attachment for the remainder of the structure. There are eight phthalate groups bound to this cage – one to

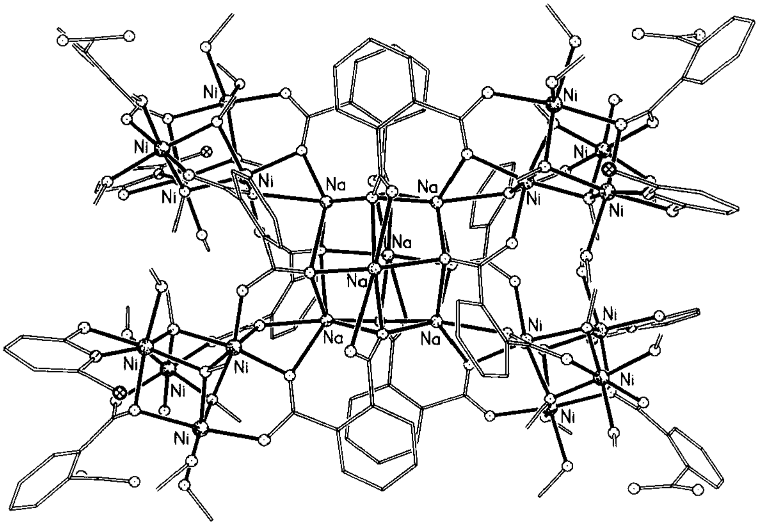

FIGURE 13 The structure of $[Ni_{16}Na_6(OMe)_{10}(OH)_2(chp)_4(phth)_{10}(Hphth)_2(MeOH)_{20}]$ **19**

each of the eight faces of the octahedra. These dicarboxylates then bind in pairs to four Ni_4 cubanes at the periphery of the "supra-cage". These cubanes are distorted in that OMe only occupies three of the four vertices, with the final vertex occupied by a μ_2-O atom from a phthalate. The exterior of these cubanes is coated with MeOH, and each has a chelating chp ligand attached to one of the nickel sites. Therefore in some ways the reaction which produces **19** has proceeded as planned – the phthalate ligands do serve as bridges between cubanes – but in most other ways the result is unpredictable. It appears that the synthesis of high nuclearity cages will continue to rely on a mixture of design and serendipity.

The complexity of the structure mitigates against attempting to model the magnetic behaviour of **19** in any meaningful way, but we can derive the order of the spin states from the shape of the $\chi_M T$ against T plot (where χ_M is the molar susceptibility). $\chi_M T$ rises as the temperature falls, reaching a maximum at 15 K, before falling again. The values indicate that the $S = 0$ states of each cubane are depopulated first – hence the rise in $\chi_M T$ – then the $S = 4$ states are depopulated in favour of a ground state for each Ni cubane of S = 2. It seems probably that even at 2 K inter-cubane interactions are of little importance.

Phthalate has also been used in other high nuclearity cages. We have managed to crystallise a complex of formula $[Co_{13}(chp)_{20}(phth)_2(OH)_2]$,[35] in which an irregular array of cobalt centres is coated with chp ligands, and contains two phthalate ligands at the centre of the cage. The Christou group has reported an Mn_{18} cage,[51] where again phthalate is an important part of the structure.

CAGES BASED ON MINERAL ARCHETYPES

In an earlier section the relationship between tricapped-trigonal-prisms and the corundum structure was remarked upon, however considerable effort is required to visualise this relationship. In other cages the relationship is extremely obvious.

In our work the largest such example is a tetraicosanuclear cobalt cage, $[Co_{24}(OH)_{18}(OMe)_2Cl_6(mhp)_{22}]$ **20**,[10] where a planar array of cobalt centres is bridged by μ_3-hydroxides in a structure related to the cadmium iodide structure (Figure 14). It is also related to heptadeca- and nonadeca-nuclear iron(III) cages reported by Powell and co-workers.[52] **20** is produced from reaction of anhydrous cobalt chloride with Na(mhp) in MeOH, followed by evaporation to dryness then extraction and crystallisation for EtOAc. The hydroxides in the cage come from water within the EtOAc during crystallisation.

The majority of the cobalt sites in **20** are octahedral, and at the centre of the cage the geometries are fairly regular as the metals are bound exclusively to hydroxides, methoxides or chlorides, and therefore have no chelating ligands attached to them. At the edge of the cage much more distorted geometries are found, and several of the cobalt sites are tetrahedral and trigonal bipyramidal. The twenty-two mhp ligands coating the circumference of the cobalt hydroxide disc adopt three bonding modes: **C**, **D** and **F**.

The magnetic propertis of **20** look extremely exciting.[10] Below 4.5 K field-cooled and zero-field-cooled susceptibility measurements diverge, which is an indication of spin-freezing. These initial measurements have not yet been extended to prove that **20** is the first example of a cobalt-containing single molecule magnet.

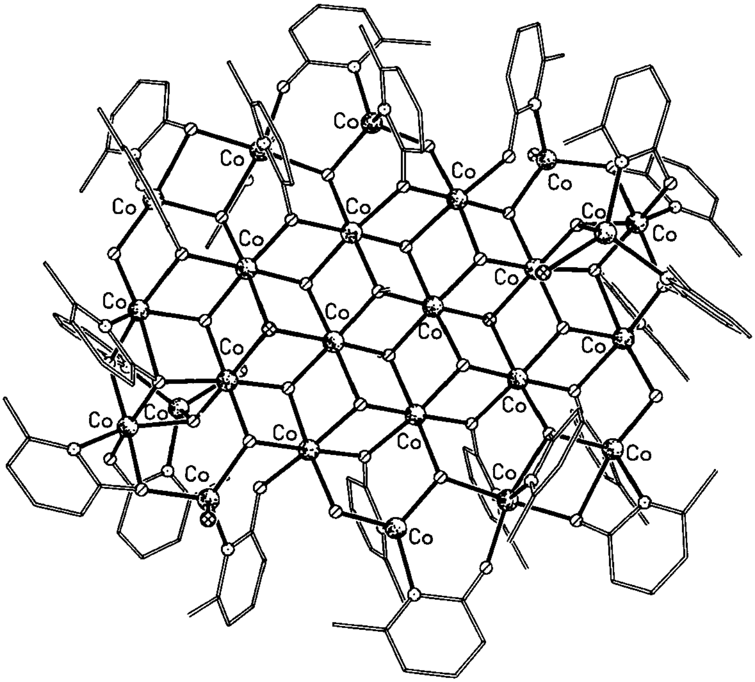

FIGURE 14 The structure of $[Co_{24}(OH)_{18}(OMe)_2Cl_6(mhp)_{22}]$ **20**

The reaction which gives **20** is similar, although not identical to those which gave adamantane-based structures (see above), differing chiefly in the use of mhp in place of chp. Reacting nickel hydroxide with Hmhp in an exactly analogous reaction, produces a green paste which can be crystallised from MeCN. The compound crystallised has a formula $[Ni_6(OH)_6\{Ni(mhp)_3\}_5(Hmhp)(Cl)(H_2O)_2]$ **21**,[53] and the structure contains a face-sharing $Ni_6(OH)_6$ double-cubane core which is closely related to the NiO structure (Figure 15).

The double-cubane is bound to five $\{Ni(mhp)_3\}$ "complex ligands", within which the mhp ligands chelate to the Ni atom with a *fac*-geometry. This produces a potentially tridentate oxygen donor complex-ligand. Two of these units use all three O-atoms to bind to Ni-sites of the double-cubane, while the remaining three units use two O-atoms to bind to Ni-atoms, and the final oxygen to form a hydrogen bond to an hydrox-

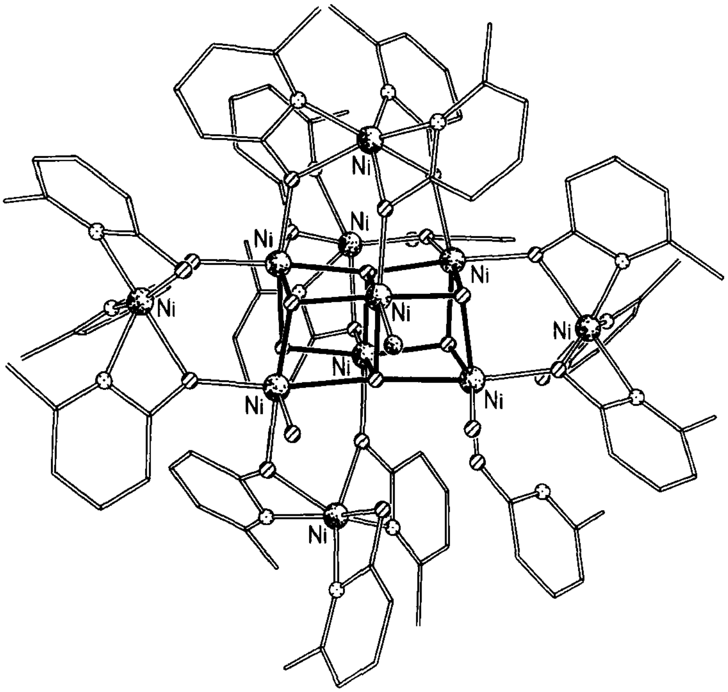

FIGURE 15 The structure of $[Ni_6(OH)_6\{Ni(mhp)_3\}_5Cl(Hmhp)(H_2O)_2]$ **21**

ide of the central core. Four terminal ligands complete the coordination spheres of the Ni-centers of the double-cubane.

The synthesis of **20** and **21**, when compared with the synthesis of the adamantane cages, illustrates another potential difference between the various pyridonate derivatives. The electron-withdrawing chloro-substituent in chp not only leads to some bonding modes (e.g. **E**), which are never seen for mhp, but also lowers the basicity of the ligand. Hence reactions which remain homoleptic with chp, can lead to incorporation of hydroxide when mhp is used, simply because the more basic pyridonate deprotonates any water present much more readily.

A further structure related to a mineral is made in a quite different way. $[Mn_{18}O_{14}(MeO)_{14}(O_2CCMe_3)_8(MeOH)_6]$ **22** can be made,[53] in very low yield, from reaction of manganous chloride with sodium trimethylacetate and sodium methoxide in MeOH (Figure 16). The structure of **2** is best visualised as a central, distorted Mn_4O_4 cubane, with each face of this cubane shared with a further cubane, leading to a face-sharing hepta-cubane $Mn_{16}(O)_{14}(OMe)_2$. Of the fourteen oxides, four act as μ_6-, two as μ_4- and eight as μ_3-bridges. The two methoxides are both μ_3-bridging. The sixteen manganese centers within the hepta-cubane are mixed-valent, with fourteen Mn(III) and two Mn(II). Two additional Mn centres, which are both Mn(II), are attached to the two μ_4-oxides and carboxylates also bridge between these sites and the central core.

The structure is clearly related to rock-salt, which is the structure of MnO, however in **22** the mean oxidation state of the manganese is more akin to that in Mn_3O_4, which contains mixed-valent Mn(II)/Mn(III) and which has a spinel structure. Therefore, although **22** can be related to a mineral archetype, it is not the mineral which contains the same combination of metal and oxidation state. Other polynuclear structures have been reported which involve face-sharing cubanes. For example, Christou and co-workers have reported an octanuclear triple-cubane structure involving cobalt,[54] and Hendrickson *et al* a tridecanuclear manganese "super-cubane" which involves eight-cubanes each sharing three faces with their neighbours, leading to a cube of cubanes.[55] The cubane array in **22** is a distorted extension of these previous structures. The magnetic properties of **21** and **22** are disappointing as both appear to have very low spin ground states.

CONCLUSIONS

The rules invented by Wade to describe the structures of boranes in terms of their electron count remain a paradigm which all structural chemists wish to emulate. In the area of polynuclear cages (as opposed to clusters), no such underpinning principle has yet been discovered. It sometimes appears that whenever we believe we have identified a clear trend, the next structure determined will inevitably prove to be an exception!

Probably it is too early to be looking for a single principle in any case. The immense diversity of structures found, which differ in the ligands present and the metals used, makes the problem wholly different in magnitude to boranes, or even carbonyl clusters. The metals present can

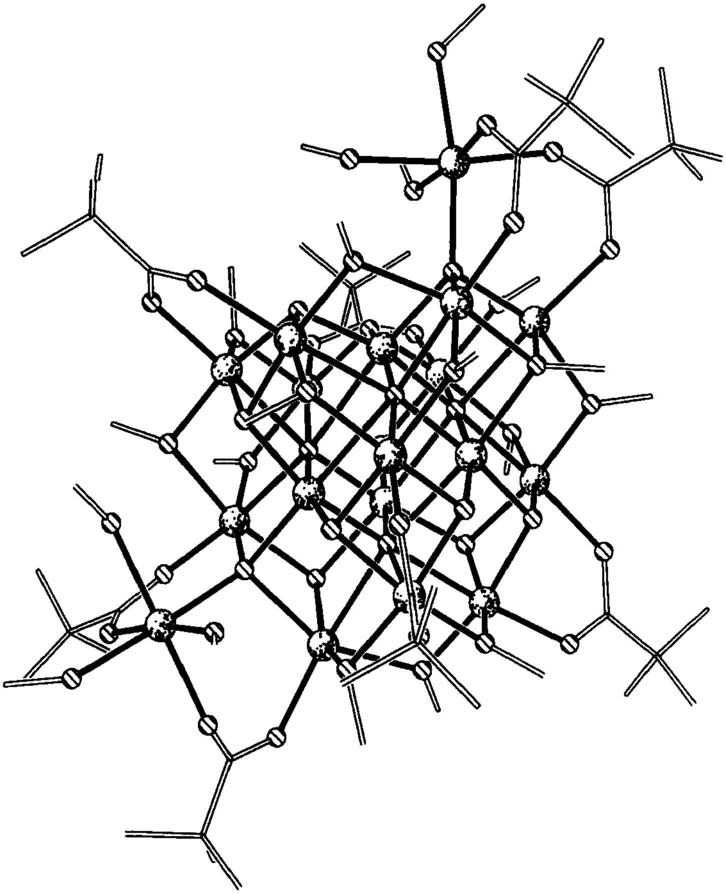

FIGURE 16 The structure of $[Mn_{18}O_{14}(MeO)_{14}(O_2CCMe_3)_8(MeOH)_6]$ 22

sometimes vary oxidation state, often show variations in coordination number and invariably show a range of distorted coordination geometries. Similarly ligands such as carboxylates, alkoxides and pyridonates have utility precisely because they are flexible. Therefore, at present, no control of structure is known in either a theoretical or practical sense.

The loss of control has been more than compensated for by the vast diversity of structures discovered, by ourselves and other groups, using simple bridging ligands. The asymmetry and complexity of some of these arrays are such that they would not have been targetted in a designed synthesis. Nature can be a more imaginative architect than many supramolecular chemists. The initial explorations outlined above – and it should be clear that thus far only the surface of polymetallic chemistry has been revealed – suggest many new paths to be explored. Each of the families of cages is capable of growth. Some 3d-metals (especially vanadium and chromium) are vastly under-represented considering how interesting their magnetic properties could be. Perhaps most importantly, the most paramagnetic metal centres found in a cage remains only twenty-four,[10] compared with diamagnetic cages which now contain up to one hundred and seventy-six metals.[56] It is probably when several paramagnetic cages of these dimensions have been characterised and fully-analysed that the technological potential of this area of chemistry will become clear.

Acknowledgments

The synthetic work on which this review is based was carried out by Euan Brechin, Alasdair Graham, Craig Grant, Mark Murrie and Greg Solan, with structural studies by Steve Harris and Simon Parsons. The magnetochemistry was performed by Andrew Harrison, Jeremy Rawson and Gavin Whittaker in Edinburgh, and in collaboration with Cristiano Benelli from Florence. The work was supported by EPSRC(UK), The Leverhulme Trust and NATO.

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