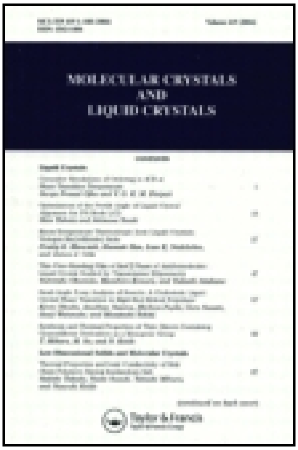

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Structural Variations and Magnetic Studies of Polymetallic Cages

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Structural Variations and Magnetic Studies of Polymetallic Cages

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Families of cages, where similar structures can be made with different 3d-metals are discussed. A variety of synthetic strategies have been developed, and magnetic and spectroscopic measurements on some of these cages are described. The majority of the structures described are based on tricapped-trigonal prisms, but variations in structure caused by steric requirements of the ligands are seen. Spin ground states of S = 8, 4 and 2 are observed for a series of nickel cages, and an EPR active spin state of S = 6 for a chromium cage.

Keywords: polynuclear cages; X-ray crystallography; magnetic susceptibility; EPR spectroscopy

INTRODUCTION

The observation[1] that some polymetallic cages show behaviour typical of "single molecule magnets" was unexpected, and has given great impetus to the study of high spin molecules. 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, Ph or Et, and which have ground states of S = 9 or 10. 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[2], Mn_4 cages with an S = 9/2 ground state[3], and recently a V_4 cage with an S = 3 ground state[4].

These observations pose the question, "why these compounds and not other high spin cages"? The answer appears to be that in these molecules a high spin state is combined with a high anisotropy of the spin, and this creates an energy barrier to reorientation of the spin of 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 potential energy well, and no significant barrier to reorientation of magnetisation would exist.

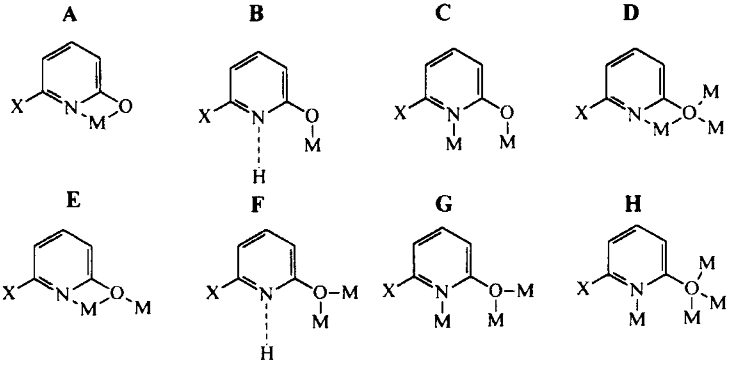
These properties are more exciting than other high-spin molecules because the retention of magnetisation in the absence of an external field are those of a single molecule magnetic memory - albeit one functioning at less than 10 K. The cages have also allowed studies of quantum-tunnelling to be performed as the particle size and energy barrier seem ideal for seeing quantum effects within these macroscopic systems[5,6]. 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 to make, by design, molecules which will have high spin ground states, but it is currently impossible to predict the sign and magnitude of the anisotropy of these ground states. 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, has been to create families of high nuclearity cages where such systematic analysis of properties may become possible.

FAMILIES OF HIGH NUCLEARITY CAGES

The ligands we have been using, such as carboxylates and pyridonates, have a considerable history in coordination chemistry, and with 4d- and 5d-metals the preferred bonding mode is 1,3-bridging, creating dinuclear metal compounds which often contain metal-metal bonds. We find with the 3d-metals the coordinative flexibility of these ligands, in particular of the pyridonate ligands, is vast[7]. At least eight different binding modes can be identified for these ligands (Scheme 1).

Scheme 1



This means that when we use these ligands we lose a good deal of control over structure as it is difficult to predict which bonding mode the ligand will adopt. The gain is a great structural diversity which will be reflected, although not exhaustively discussed, in the following text.

Dodecanuclear Metal Wheels

The reaction of nickel acetate with 6-chloro-2-pyridone (Hchp) at 130°C produces a green paste, which can be extracted with THF and crystallised to give $[Ni_{12}(chp)_{12}(O_2CMe)_{12}(H_2O)_6(THF)_6]$ **1** (Figure 1)[8]. The molecule lies on a crystallographic -3 axis, therefore there are only two independent nickel sites in the compound. Both are six-coordinate, bound to oxygen-donors which are derived from a mixture of chp, acetate, THF and water. The chp ligands all bridge in a 1,1-fashion through the exocyclic oxygen atom while the acetate ligands bridge in two ways; within the metallocycle are six 1,1,3-bridging carboxylates, and outside the ring six 1,3-bridges. THF acts as a terminal ligand while H_2O acts as a μ_2-bridge.

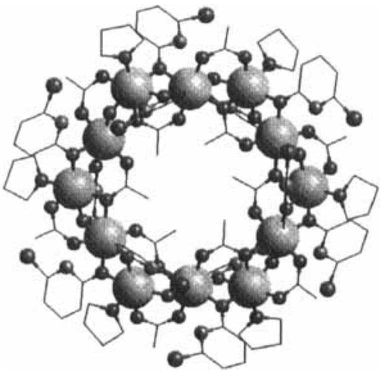


Figure 1. The structure of **1**

The twelve Ni centres are coupled ferromagnetically, as can be shown by a χ_mT against T plot. The coupling is weak, of the order of 4 cm^{-1}, and leads to an S = 12 spin ground state. Even at very low temperature there is no sign of a maxima in the χ_mT against T plot, indicating that both zero-field splitting within the ground state, and any inter-molecular interactions are weak in this cage. Perhaps surprisingly this is the first cage with a very high spin ground state where the coupling is ferromagnetic. Very recently a Mn_6 cage with an S = 12 ground state has been reported where the coupling is also ferromagnetic[9], but in all other high spin cages the strongest interactions are anti-ferromagnetic.

The beautiful structure and attractive magnetic properties of **1** made us look for other members of this family. The chp ligand can be replaced by 6-bromo-2-pyridonate, creating another Ni_{12} wheel. We can make the cobalt analogue of **1**, starting from cobalt acetate[10]. $[Co_{12}(chp)_{12}(O_2CMe)_{12}(H_2O)_6(THF)_6]$ **2** is isostructural with **1**, but unfortunately magnetic studies indicate that in **2** the coupling is anti-ferromagnetic, and the ground state for **2** is diamagnetic. We have been unable to make any other "close relations" of these cages. The reasons are: the only carboxylate which fits into the centre of the cage is acetate - for larger carboxylates the wheel is not feasible; the bonding mode of the chp ligand - using only the O-donor - is only stable when the six-substituent of the pyridonate is electron-withdrawing; the solvent has to be THF, as it coordinates to six of the metal sites - more coordinating solvents lead to smaller cages. Therefore we have looked for cages with a potential to create larger families.

Tricapped Trigonal Prisms

There are now ten members of this family, found for all the elements from chromium to nickel, with the exception of manganese. It is not obvious why manganese should be an exception - the single molecule magnets [$Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4$] have a very similar stoichiometry to the tricapped trigonal prisms formed by chromium and iron, but a very different shape. The known structures are listed in Table 1.

TABLE 1 Metal cages with Tricapped Trigonal Prismatic Cores

	Metal	Carboxylate	Pyridonate	Spin Ground State	References
M_{12}	Cr	O_2CCMe_3	-	6	11
	Co	O_2CMe	mhp	n.k.	12
	Ni	O_2CCH_2Cl	mhp	8	13
M_{11}	Fe	O_2CPh	-	½	14
	Ni	O_2CMe	mhp	4	13,15
	Ni	O_2CPh	chp	n. k.	16
M_{10}	Co	O_2CPh	mhp	n. k.	16
	Co	O_2CCMe_3	mhp	n. k.	13
	Ni	O_2CCHMe_2	mhp	n. k.	13
	Ni	O_2CCHPh_2	chp	2	13

n.k. = not known; mhp = 6-methyl-2-pyridonate

Our work has concentrated on cobalt and nickel. The cages formed are stabilised by both carboxylate and pyridonate. The largest are dodecanuclear and have the stoichiometry [$M_{12}(OH)_6(mhp)_{12}(O_2CR)_6$] (M = Co, R = Me **3**; M = Ni, R = CH_2Cl **4**], the structure of **4** is shown in Figure 2. These cages contain a central metal surrounded by six μ_3-hydroxides which bridge to six metal sites at the vertices of a trigonal prism, and to three further metal centres which cap the rectangular faces of the prism. In **3** and **4** two further metal centres are attached to the upper and lower trigonal faces of the prism through bridging pyridonates.

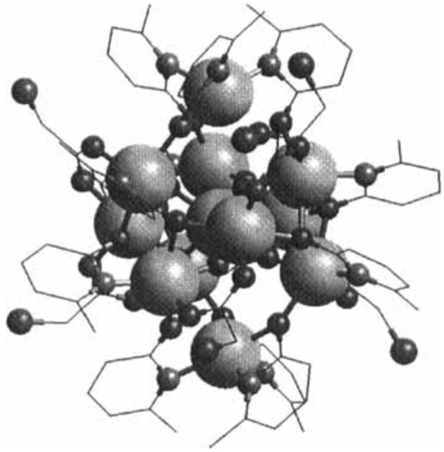


Figure 2 The structure of **4**

In the lower nuclearity structures one or both of the final two metal sites on the trigonal axis of the prism are absent. In the undecanuclear cage $[Ni_{11}(OH)_6(mhp)_9(O_2CMe)_6(H_2O)_3]_2[CO_3]$ **5**, the absence of one such metal leads to dimerisation of the cages via six H-bonds (Figure 3). In the decanuclear cages these faces are occupied by weakly bound solvate molecules, pyridonate ligands and counter-ions. The central metal core, which is bridged by external pyridonates and carboxylates in addition to the internal μ_3-OH groups, is identical between these various structures.

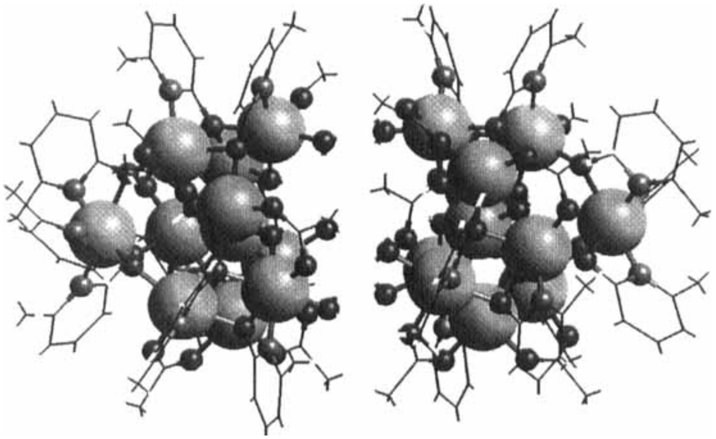
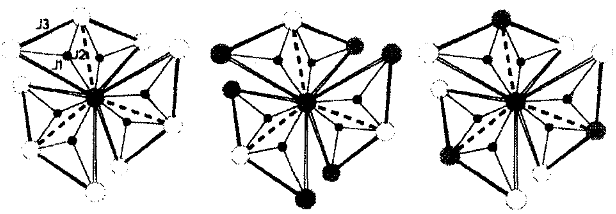


Figure 3 The structure of **5**

The existence of this series of cages has allowed us to carry out magnetic studies on related structures[13]. The behaviour of the magnetic susceptibility of compounds **4**, **5** and a decanuclear cage $[Ni_{10}(OH)_6(chp)_6(O_2CCHPh_2)_6(Cl)_2(Hchp)(H_2O)_2(MeOH)]$ **6** were studied over the 1.8 - 250 K temperature range. In each case the magnetic behaviour down to around 10 K is typically "ferrimagnetic", i.e. anti-ferromagnetic exchange stabilising non-diamagnetic ground states, however the multiplicity of these ground states varies dramatically between the three cages. For **4** χ_MT goes through a maximum at 12 K, where the value is around 42 cm^3 K mol^{-1}. Such a value, allowing for two additional $S = 1$ centres in the molecule, is consistent with an $S = 8$ ground state for the centred-tricapped-trigonal prismatic core. For **5** the maximum in χ_MT is much less dramatic, and the value of 11 cm^3 K mol^{-1} suggests an

S = 4 ground state. For **6**, the maximum is almost unnoticeable, and this leads us to believe we have an S = 2 ground state.

Unfortunately none of the nickel cages has the ideal D_{3h} symmetry of a tricapped-trigonal prism, therefore we have had to make some assumptions to reduce the complexity of the problem when attempting to model this data. The major assumption is that only interactions mediated by the μ_3-hydroxides are of importance in determining the magnetic properties of the cage. Three exchange parameters were used in the model: J_1 represents the exchange between the central Ni atom and the six Ni sites at the vertices of the trigonal prisms; J_2 is the exchange between the central Ni site and the Ni atoms capping the rectangular faces; J_3 is the exchange between the vertex and capping nickel atoms. The scheme, and the results obtained by fitting the data, are shown in Figure 4 (negative



Ni12 cage
S = 8
J1 = 11.8 cm-1
J2 = -3.8 cm-1
J3 = -6.6 cm-1

Ni11 cage
S = 4
J1 = -19.5 cm-1
J2 = 53.1 cm-1
J3 = -1.7 cm-1

Ni10 cage
S = 2
J1 = 6.5 cm-1
J2 = 2.5 cm-1
J3 = 6.0 cm-1

Figure 4 A schematic representation of the spin ground states in **4**, **5** and **6**

values represent ferromagnetic exchange).

Figure 4 also attempts to show how such diverse spin ground states can arise from structurally similar cages. The filled circles represent Ni sites where the spins are aligned in one direction, the open circles sites where the spin is aligned in the reverse direction. In addition to the exchange integrals the model also requires zero-field splitting of the spin ground states to reproduce the data. For each compound this is between 4 and 8 cm^{-1}.

It is difficult to find a structural parameter which correlates with the different exchange parameters found for these cages. This is perhaps best illustrated by considering the bond angles about the bridging hydroxides.

TABLE 2 Bond angles[a] at bridging hydroxides in Ni cages

	Ni12	Ni11	Ni10
Ni_{cent}-OH-Ni_{cap} angle range (Influences J2)	99.2 - 100.0	95.7 - 99.5	96.5 - 98.0
Ni_{cent}-OH-Ni_{cap} aver. angle (Influences J2)	99.65	97.5	97.5
Ni_{cent}-OH-Ni_{vert} angle range (Influences J1)	118.3 - 119.6	121.2 - 122.8	120.6 - 122.2
Ni_{cent}-OH-Ni_{vert} aver. angle (Influences J1)	119.1	121.95	121.3
Ni_{vert}-OH-Ni_{cap} angle range (Influences J3)	101.5 - 103.0	97.5 - 104.8	99.4 - 103.6
Ni_{vert}-OH-Ni_{cap} aver. angle (Influences J3)	102.5	101.1	101.4
Average of sum of angles at each OH	321.1	320.6	320.2

a. Average standard deviation 0.2°

The difficulty is that the variation of bond angles within an individual structure is as great as the variation between structures, and that if previously published correlations of exchange integral with bond angle are correct then our simplified exchange scheme is not valid. The alternative - including a different exchange integral for each bond angle - is vastly over-parameterised. The measured values of $\chi_M T$ for the three cages supports the assignment of the ground states whether the model is valid or not. Spectroscopy might clarify these assignments in the future.

For the nickel cages there appears to be some correlation of the nuclearity of the cage and the degree of substitution of the carboxylate. For acetate and chloroacetate dodecanuclear and undecanuclear cages result. Where there are two substituents on the α-carbon (benzoate or diphenylacetate) decanuclear cages are formed. It therefore seemed worthwhile to examine whether more sterically demanding carboxylates would also support similar metal polyhedra.

Reactions using pivalate (trimethylacetate) give markedly different structures[17]. Two cages, $[Ni_{10}(OH)_4(mhp)_{10}(O_2CCMe_3)_6(MeOH)_2]$ **7**, and $[Ni_{10}(OH)_4(mhp)_{10}(O_2CCMe_3)_6(H_2O)_2]$ **8** have been crystallised from reactions involving nickel chloride, Na(mhp) and $Na(O_2CCMe_3)$. The structure of **7** is shown in Figure 5 and **8** differs chemically only in the presence of two terminal water ligands, rather than two terminal methanols. The cages are 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 "virtual" addition of further vertices reveals a centred 14-vertex deltahedron as shown in Figure 6: the complete 1:6:1:6:1 polyhedron has been found in some inter-metallic phases. The five missing vertices (darker spheres in Fig. 6) 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.

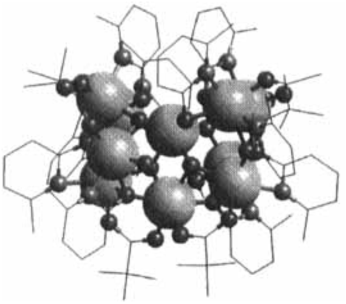


Figure 5 The structure of **7**

Given two examples and moderate yields of this new polyhedron it is difficult to dismiss **7** and **8** as irrelevant exceptions, and it could be the case that the larger trimethylacetate ligand is imposing sufficient strain on the

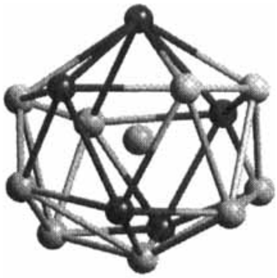


Figure 6 The metal core of **7**

structure for reorganisation to be favourable. However whatever factors are involved must be finely balanced as a decanuclear cobalt complex with trimethylacetate crystallises as a tricapped-trigonal prism[15].

This disruption of the tricapped trigonal prismatic structure can be taken a step further by using inter-ligand Coulombic repulsion. The zwitterionic ligand betaine ($O_2CCH_2NMe_3$) is ideal for this purpose. A similar reaction here leads to a nonanuclear nickel cage $[Ni_9(CO_3)(OH)_6(chp)_3(O_2CCH_2NMe_3)_9(Hchp)_3(Cl)]^{6+}$ **9**[18]. The structure (Figure 7) shows a planar hexagon of Ni centres "templated" on a central carbonate ion. The final three Ni sites in the cage are attached to the hexagon through bridging hydroxides, pyridonates and betaine ligands.

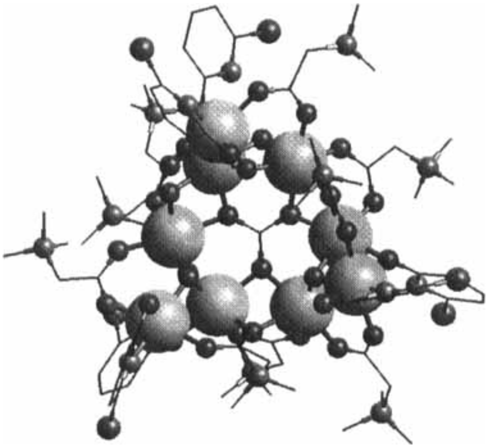


Figure 7 The structure of **9**

These results using "over-crowding" ligands suggests a new route to cages. The involvement of carbonate, which arises from atmospheric CO_2, which acts as a template for the cage is reminiscent of similar reactions in polyoxometallate chemistry and again suggests a future strand worth exploring as a means of directing structure of high nuclearity cages.

Our investigations of tricapped trigonal prisms, and use of pivalate as a ligand led us to a paper from Gérbéléu and co-workers[11]. This is the report of a dodecanuclear chromium cage, and is probably the only successful synthesis of a high nuclearity cage of this metal. The reaction is unusual. Chromium nitrate is mixed with sodium pivalate in water, and the resulting pale blue precipitate is heated to 400°C in a stream of nitrogen. This produces a green solid which can be crystallised from a range of solvents. The formula given by Gérbéléu is $[Cr_{12}O_{12}(O_2CCMe_3)_{15}]$, which would involve mixed-valent Cr(III)/(IV). Such a mixed-valent cage might have very exciting magnetic properties.

The synthesis is entirely reproducible, and huge single crystals of the compound can be made. They are sufficiently large for neutron diffraction, and the structure which results suggests the correct formula is $[Cr_{12}O_9(OH)_3(O_2CCMe_3)_{15}]$ **10** (Figure 8). The dodecanuclear core again consists of a centred trigonal prism capped on all five faces by further chromium atoms. The central chromium is bound to the remainder of the cage through six μ_4-oxides. The exterior of **10** is stabilised by pivalate bridges and six further μ_3-oxygen atoms. In the X-ray structure these were assigned as oxides, however the neutron structure indicates that a half-weight hydrogen atom is associated with each site. This indicates that all the chromium centres are Cr(III).

The magnetic properties of **10** are interesting[19]. Susceptibility measurements (Figure 9) show two maxima in a $\chi_m T$ against T plot; one at 150 K, the second at low temperature which suggests a spin ground state of around S = 6 (observed 21.6 cm^3 K mol^{-1}, calc. 21 cm^3 K mol^{-1}). This is supported by EPR spectroscopy at K- and Q-band (Q-band spectrum shown in Figure 10), where approximately 12 lines centred at g = 1.99 are found due to fine structure within the ground state. The zero-field splitting is around |0.85| cm^{-1}. There are also spin-forbidden transitions observed at low field (Figure 10).

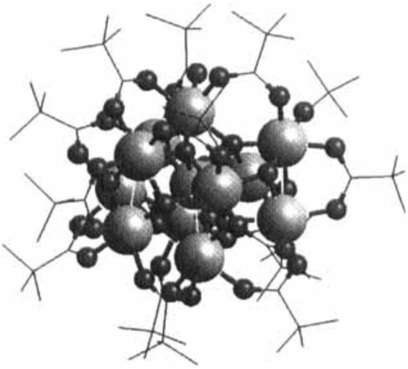


Figure 8 The structure of **10**

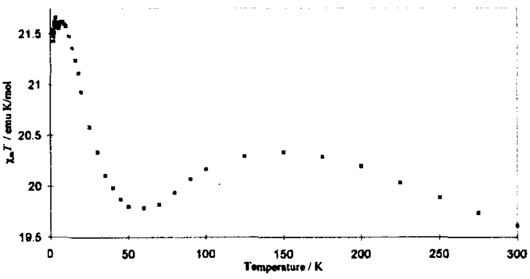


Figure 9 Plot of χ_mT *vs*. T for **10** measured in a 1000 G field

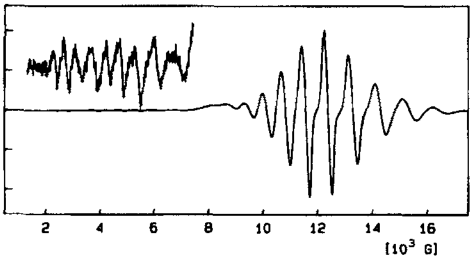


Figure 10 Q-band (34.2 GHz) EPR of **10** at 15 K

The reaction scheme seemed applicable to other carboxylates, and perhaps other metals, so we have examined it further. We also felt it was worthwhile to characterise the starting material for this chemistry more closely. Mixing chromium nitrate and sodium pivalate or benzoate in water produces a precipitate which is soluble in non-polar solvents. Electrospray mass spectrometry (ES-MS) of these solutions (generally in

1:10 CH_2Cl_2/MeOH) indicate that the predominant species present are oxo-centred trimers of formula $[Cr_3O(O_2CR)_6(OH)(H_2O)_2]$.

Where the carboxylate is benzoate the resulting product depends on the temperature to which the reactant is heated[20]. Heating to 200°C removes water and results in an octanuclear wheel:

$$8\ [Cr_3O(O_2CPh)_6(H_2O)_2(OH)] \rightarrow 3\ [Cr_8(OH)_8(O_2CPh)_{16}] + 8\ H_2O$$

The structure of $[Cr_8(OH)_8(O_2CPh)_{16}]$ **11** (Figure 11) shows each Cr...Cr vector bridged by one μ_2-hydroxide and two 1,3-bridging benzoates. Heating the reactant to 400°C, as for the reaction which produces **10**, leads to another new cage:

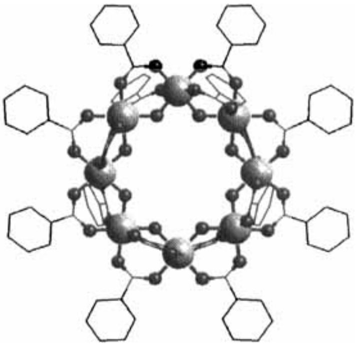


Figure 11 The structure of **11**

$$8\ [Cr_3O(O_2CPh)_6(H_2O)_2(OH)] \rightarrow 3\ [Cr_8O_4(O_2CPh)_{16}] + 20\ H_2O$$

More water has been eliminated and the resulting cage, $[Cr_8O_4(O_2CPh)_{16}]$ **12**, has a structure based on a distorted $\{Cr_4O_4\}^{4+}$ cubane core where each μ_4-oxide bridges to a further Cr atom creating a larger Cr_4 tetrahedron (Figure 12).

Twelve of the benzoate ligands are 1,3-bridging, with the final four benzoates chelating to the chromium sites of the larger Cr tetrahedron. ES-MS indicates that these last four benzoate groups are weakly bound and offer potential sites for further chemistry on this molecule.

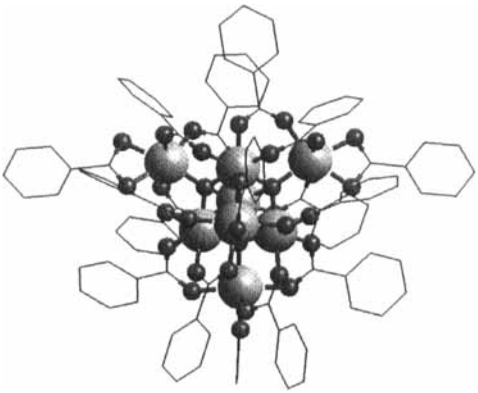


Figure 12 The structure of **12**

Clearly neither **11** nor **12** belong to the family of tricapped-trigonal prisms, however both are members of other families of cages. A number of wheels similar to **11** have been reported for the metals from vanadium to nickel, including the dodecanuclear compounds **1** and **2** discussed above. **12** is the second member of an $M_8(\mu_4\text{-}O)_4$ family which is much more limited at present, the elder member being a strikingly similar mixed-valent Co(II)/(III) cage reported by Christou and co-workers in 1995, made by a solution reaction in DMF[21]. We have good infra-red and ES-MS evidence that $[Fe_8O_4(O_2CPh)_{16}]$ can be made by the route described above.

Disappointingly for both **11** and **12** preliminary susceptibility studies suggest anti-ferromagnetic exchange is the predominant magnetic interaction, leading to low spin ground states.

CONCLUSIONS AND FUTURE STUDIES

The structural complexity of polynuclear cages is surprising, and shows no sign yet of conforming to simple rules. New methods for making such cages, and for making new topologies continue to be discovered. What is also becoming apparent is that the spectroscopic properties of these cages are exciting, and that such studies will help in understanding the magnetism of the compounds.

Acknowledgements

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