
18 Macrocyclic and supramolecular coordination chemistry

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New macrocycles with larger compartments are being designed that may allow use in nanoscale chemistry as devices.¹⁴ Many new wheel clusters have been discovered that incorporate several types of transition metal ions³⁰ as well as some examples with lanthanides.³⁵ Ligand design has also played a major role in producing unexpected architectures^{41, 65} and functional cages that can facilitate photochemical reactions in a confined space.⁷⁴ New helical units surrounding an alkyne-based spacer⁸² have been devised as a possible molecular wire, as well as cavities that can stabilise Cu(I) complexes in aqueous solution.¹⁰² Simple inorganic ligands have been employed in the synthesis of giant clusters that are beginning to link the molecular with the nanoscale.¹⁴⁷

1 Introduction and scope

This report focuses on the development in design, synthesis, and self-assembly of metal-based architectures together with ligands designed to aid the construction of metallo-supramolecular architectures. Although particular attention will be paid to discrete molecular architectures, infinite networks and polymers will be included where new interesting ligands or metal-based moieties are discovered that are of consequence to the general area.

In the past decade supramolecular chemistry has been transformed by the revolution in small molecule crystallography and much of the interest in this area lies in the manipulation, understanding and construction of new architectures and topologies. Therefore, many crystal structures have been included in this report to aid visualisation and conceptualisation of the many interesting metallo-supramolecular architectures that have been constructed.¹ A common colour scheme is used in all the structural figures unless otherwise stated; the carbon atoms are light grey, nitrogen atoms white, metal ions large black spheres, sulfur atoms large grey spheres, oxygen atoms small black spheres.

2 Macrocyclic ligands

The design of new macrocyclic ligands continues to be an expanding area with exploration of ring size and investigation into various combinations of donor set. For

example a new macrotricyclic ligand, L^1 with an N_4S_2 donor set that encapsulates lithium and transition metal ions has been synthesized from the tetraazamacrocyclic cyclam.² This macrocycle was found to bind lithium in a peculiar linear coordination mode in the formation of a $[Li(HL^1)](ClO_4)_2$ complex with the macrocycle adopting an anti conformation, see Fig. 1.

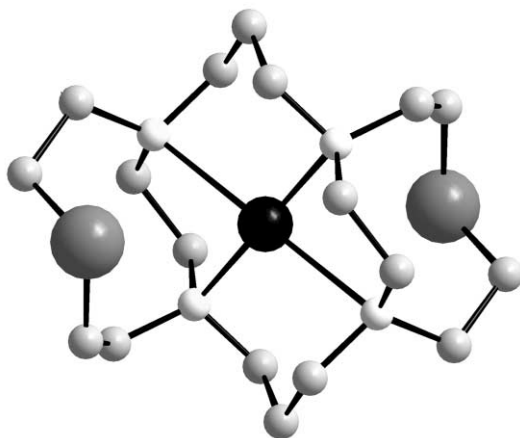
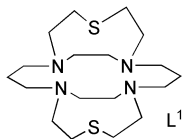
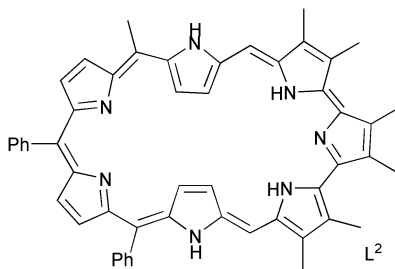


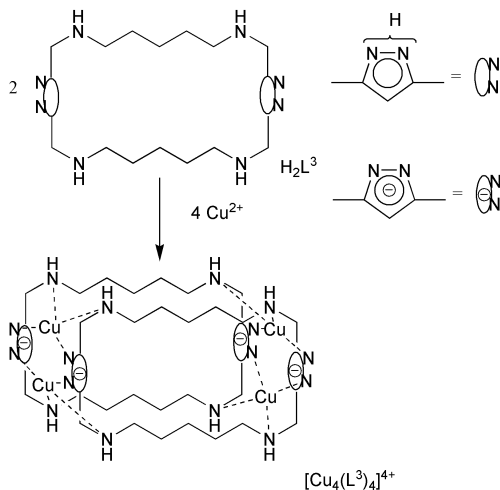
Fig. 1 Structure of $[Li(HL^1)]^{2+}$ showing the anti-conformation of the complexed macrocycle.



Also a heptapyrrolic macrocycle L^2 [30]heptaphyrin(1.1.1.1.1.0.0) has been synthesised with a structure that exhibits a 'figure eight'-like topology. This is interesting as pyrane-terpyrrole containing expanded porphyrins, such as heptaphyrins are rare and only a few known expanded porphyrins containing seven pyrroles have been described previously.³



The pyrazole containing ligand, H_2L^3 affords a tetranuclear cluster-unit when complexed with Cu(II) where the metal to ligand ratio is 2 : 1, yielding a complex of the form $[Cu_4(H_2L^3)_2]^{4+}$ where each ligand contains two pyrazole units connected by two 1,5-diaminopentane spacers. The resulting complex is a new type of metal-ion induced inorganic–organic cage.⁴



The molecular features of H_2L^3 favour an arrangement in which two molecules of L^3 are connected together by four Cu(II) metal ions. Each one of the four metal centres is bound by two secondary nitrogen and two pyrazole nitrogen atoms, and these belong to different macrocyclic subunits forming the base of a strongly distorted square pyramid. All the pyrazole fragments are deprotonated and behave as exobidentate ligands, see Fig. 2.

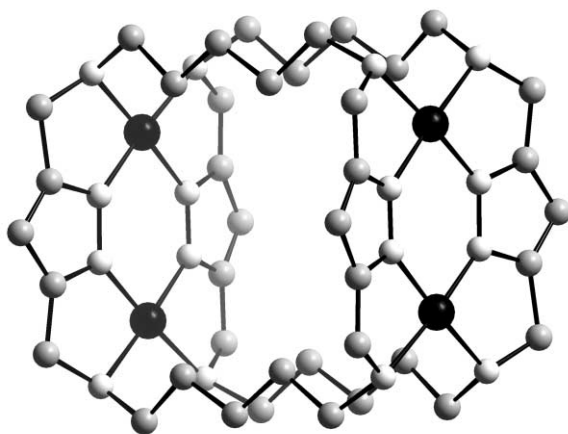
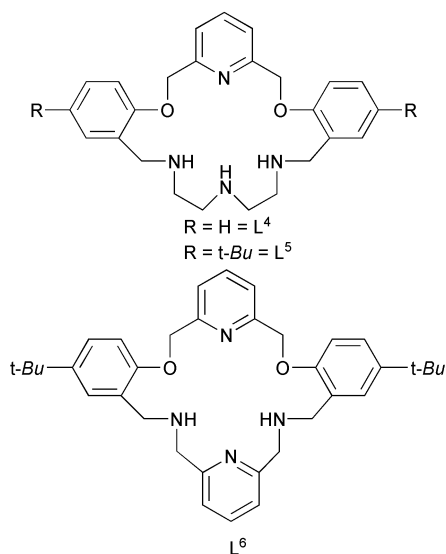


Fig. 2 The dimeric nature of the complex $[Cu_4(H_2L^3)_2]^{4+}$.



A series of complexes based on three N_4O_2 (L^4 , L^5 and L^6) mixed donor macrocycles were synthesised and the comparative investigation of the interaction of these three dibenzo-substituted macrocycles with cobalt, nickel, copper, zinc, cadmium, silver and lead has been carried out. These studies show that all the macrocycles form [1 : 1] complexes except in the case of Ag(I) with L^4 which also forms a trimeric complex, see Fig. 3.⁵

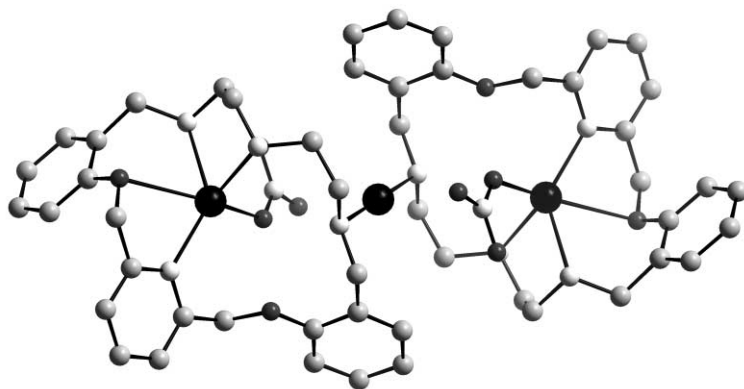
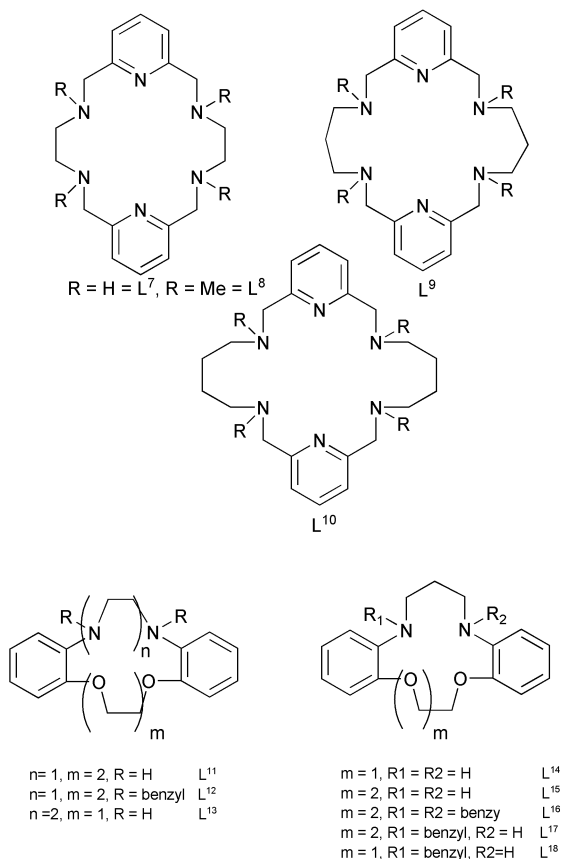


Fig. 3 The structure of the trimeric silver complex $\{Ag[AgNO_3(L^4)]_2\}^+$.

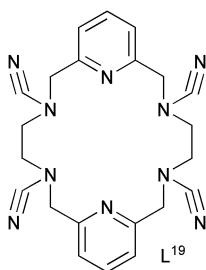
The hexaaza macrocycles L^7 , L^8 ($[18]py_2N_4$) and L^9 ($[20]py_2N_4$) and L^{10} ($[22]py_2N_4$) have been synthesised⁶ and the stability constants of complexes with a range of metal ions determined. These studies show that the stability constants decrease as the cavity size of the macrocycle is increased, taking into account the difference in basicity of the

ligands. Furthermore, the metal centre exhibits a hexacoordinate environment and the macrocycle adopts a twisted helical topology. The effect of the cage sizes of ([18]py₂N₄) and ([20]py₂N₄) on the molecular dimensions of metal complexes of both macrocycles causes a significant decrease in the helicity of complexes of the 18-membered macrocycle compared to complexes of the 20-membered ring.

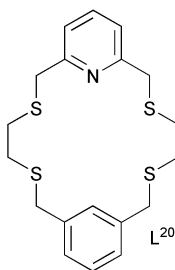


In a further study on mixed macrocyclic O/N donor sets the interaction of cobalt, nickel, copper, zinc, cadmium, silver and lead was examined with macrocycles L^{11} – L^{18} . Examples of N-benylation of individual parent macrocycles lead to enhanced discrimination for silver ions.⁷

A new pendant-armed macrocyclic ligand, L^{19} , bearing four cyanomethyl pendant groups has been synthesized by N-alkylation of the tetraazamacrocyclic precursor with bromoacetonitrile. Structural analysis of uncomplexed L^{19} shows the formation of tubular arrays, and reveals intra- and inter-molecular π -stacking interactions between the pyridyl groups of the macrocyclic backbone. Furthermore, metal complexes utilize the ring-N-donors and do not complex cyanomethyl groups.⁸



Synthesis of a mixed donor, pyS_4 – aza-thia macrocycle 2,5,14,17-tetrathia[6-(1,2)benzo[6](2,6)pyridinophane (L^{20}) produces a ligand that complexes with Ni(II) , Pd(II) , Pt(II) , Cu(II) , Cu(I) and Ag(II) . Interestingly this versatile macrocycle demonstrates a variety of coordination modes; tetradentate with Ni(II) , tetradentate plus a fifth weaker M-S interaction with Pd(II) and Pt(II) and truly pentadentate with Cu(II) , Cu(I) and Ag(I) . It is unsurprising, therefore, that this ligand appears uniformly selective for the aforementioned metal ions.⁹



Macrocycles with *exo*-metal binding groups can be used to strategically position metal ions on the outer ‘rim’ of the macrocycle. The bipy-based macrocycle L^{21-23} places two bipy units on opposite sides of the macrocycle and complexation of L^{21-23} with two equivalents of $[\text{Ru}(\text{bipy})_2\text{Cl}_2]$ affords the doubly complexed macrocycle supporting two external Ru(II) centres, see Fig. 4.¹⁰

One extremely powerful way of selecting different macrocyclic ring sizes and donor sets is *via* the application of the ‘virtual combinatorial library’ approach whereby many building blocks are accessible under a given set of reaction conditions. To use this approach a reversible and an irreversible reaction step need to be accessible; application of a selection event during the reversible stage facilitates the construction of the labile entity to be followed by a quenching event that prevents re-distribution to a range of products, see Scheme 1. For example L^{24} results from a reaction of the di-aldehyde with the diamine when $n = 2$ even when 1 equivalent of the $n = 3$ diamine is also present along with MgCl_2 . The role of the MgCl_2 as a template in selecting the desired product from the library before reduction is obvious. The scope of this thermodynamically controlled, reversible approach for macrocycle syntheses is illustrated.¹¹

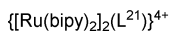
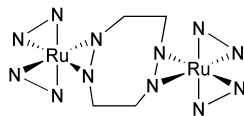
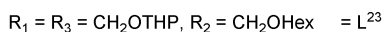
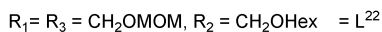
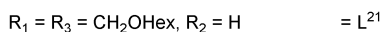
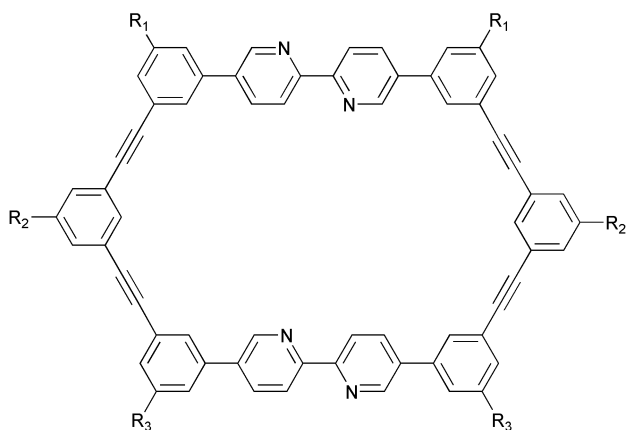
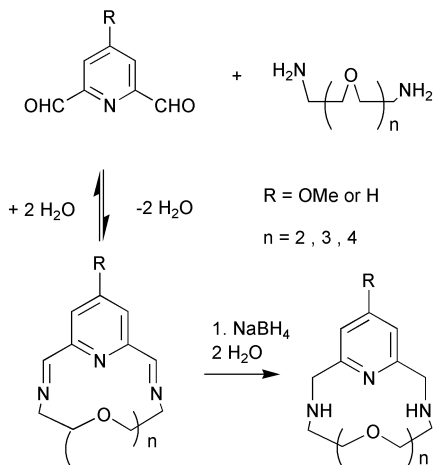


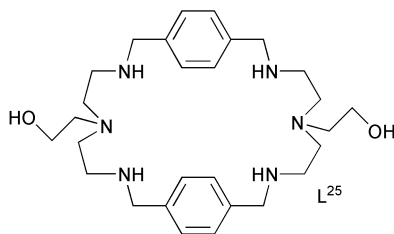
Fig. 4 A representation of L^{21-23} and the result of complexation with with Ru(II) centres.



e.g. when $R = \text{OMe}, n = 2 = L^{24}$

Scheme 1 A representation of one synthetic approach to macrocycle selection *via* a virtual combinatorial library.

A novel hexaaza macrocycle bearing two hydroxyethyl pendants (L^{25}) has been designed as a potential catalyst. Complexation with 2 equivalents of Cu(II) ions results in a dinuclear complex, whereby each pendent hydroxyethyl group is coordinated to one Cu(II) ion in addition to three nitrogen atoms and one chloride. Furthermore the coordinated hydroxyethyl group appears to be an effective nucleophile as the complex is active towards the hydrolysis of 4-nitrophenyl acetate with a second-order rate constant of $0.41 \pm 0.02 \text{ M}^{-1} \text{ s}^{-1}$.¹²



The derivatisation of 1,4,7-triazacyclononane with pendant acetophenoneoxime moieties produces a new type of ligand which is capable of forming tri-nuclear and tetra-nuclear complexes which have interesting properties. Complexation with Cu(II) yields a mononuclear complex $[\text{Cu}(\text{H}_2\text{L}^{26})](\text{ClO}_4)$ whereas complexation with Co(II) and Mn leads to mixed valence complexes of the form, $[(\text{L}^{26})_2\text{Co}^{\text{II}}\text{Co}^{\text{III}}](\text{ClO}_4)_2$ and $[(\text{LH})_2\text{Mn}^{\text{II}}(\mu\text{-O}_2\text{COCH}_3)(\text{CH}_3\text{OH})\text{Mn}^{\text{III}}](\text{ClO}_4)_2$; in the case of Mn the complex also sequesters CO_2 from the air. Furthermore, complexation with Ni(II) yields a tetra-nuclear complex of the form $[\text{Ni}_4(\text{HL}^{26})_3]^{2+}$ which exhibits irregular spin-ladder type behaviour, Fig. 5.¹³

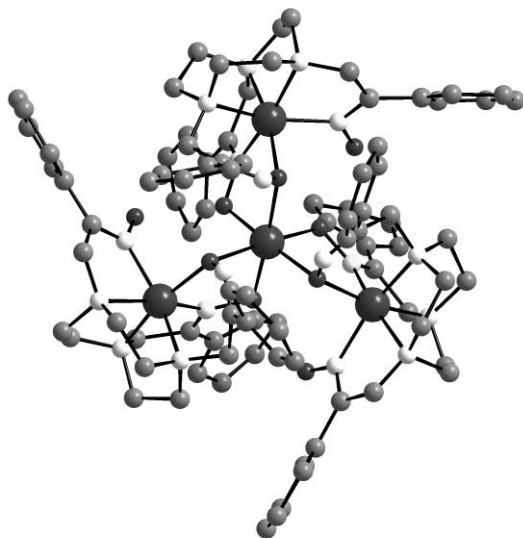
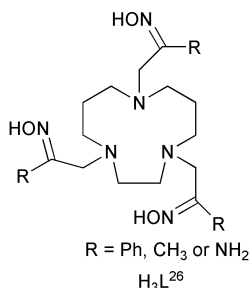
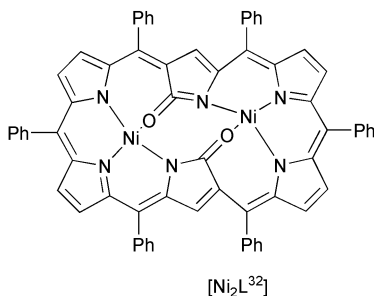
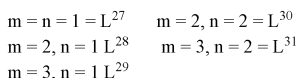
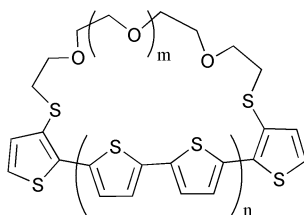


Fig. 5 Structure of the tetranuclear Ni(II) complex of L^{26} .

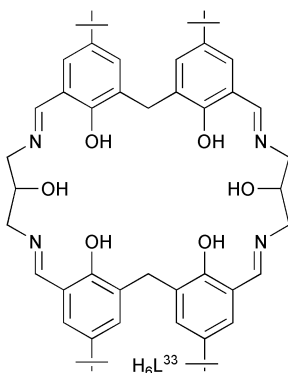


Crown-annulated quater- (4T) and sexithiophenes (6T) with oligooxyethylene chains of various lengths (L²⁷–L³¹) attached at the 3-positions of the terminal thiophene rings have been designed with cation-binding properties. Cyclic voltammetry shows that, depending on the binding constant, the presence of metal cation produces a negative or a positive shift. The compounds do not complex alkali cations but show reasonably good binding properties for alkali-earth cations. The cation-binding constant increases with the length of the polyether chain, whereas shorter polyether loops impose a stronger constraint to the conjugated system. This unusual behaviour can be understood in terms of electrostatic interactions and conformational changes associated with cation binding. Such conformational changes may even be exploited in the development of molecular devices.¹⁴



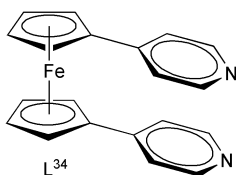
Expanded porphyrins, hexapyrrolic porphyrinoids, hexaphyrins, are promising candidates as ligands to form electronically novel *bis* complexes because such hexaphyrins can adopt a planar conformation as a result of a fully delocalized ligand

donor set. To this end the synthesis of a doubly N-confused *meso*-hexaarylhexaphyrin (L^{32}), has been achieved and a Ni(II) complex of this ligand characterised.¹⁵ The two adjacent metals are located in a large conjugated π -electron pool. Double compartment ligands are also capable of binding more than two metal ions. For instance H_6L^{33} can act as a ligand for two, three and even four metal ions within the macrocyclic framework. This ligand can be considered as an expanded calix[4]arene containing two $=NCH_2CH(OH)CH_2N=$ inserts.¹⁶

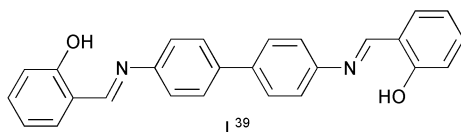
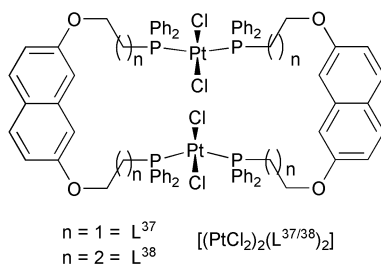
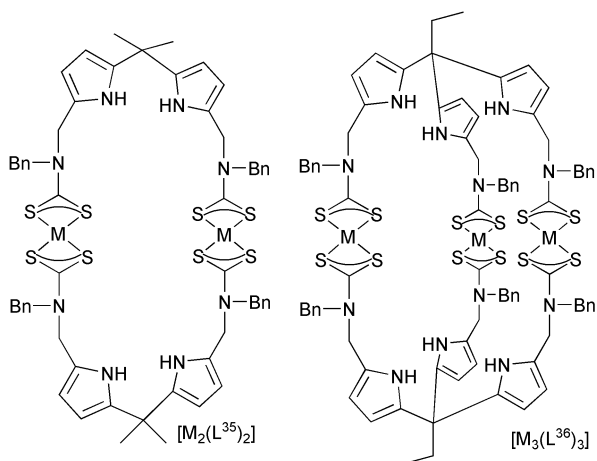


3 Metallamacrocycles

The bidentate sandwich ligand $[Fe(\eta^5-C_5H_4-1-C_5H_4N)_2]$, L^{34} has been employed in the preparation of the novel supramolecular heterobimetallic metalla-macrocycles. Reaction of L^{34} with Ag(I), Cu(II) and Zn(II) affords a macrocyclic complex of the form $[M_2(L^{34})_2]$.¹⁷ The dithiocarbamate ligands, L^{35} and L^{36} , based on a pyrrole framework,



self assemble with Zn^{2+} , Ni^{2+} and Cu^{2+} to yield dinuclear metallamacrocycles and trinuclear metallocryptands. Some preliminary anion binding studies have also been conducted, using electronic spectroscopy and electrochemistry. The nickel macrocycles show affinity for acetate, whereas the copper cryptand showed affinity for benzoate anions. Furthermore the copper cryptand also exhibited a significant electrochemical response to a range of anions.¹⁸ The bridging bisphosphanes DPPN (L^{37}) and DPEN (L^{38}) are constructed around the rigid 2,7-dialkoxy-naphthalene backbone. These show marked preference for bridging pairs of metal atoms (Pt^{II} , Mo^0) to form metallamacrocycles or oligomers.¹⁹ These complexes also show activity as hydroformylation catalysts which is comparable to monomeric catalysts. A novel



neutral mixed-valent $\{\text{Cu}^{\text{I}}(\text{Cu}^{\text{II}})_2\}$ triangular metallomacrocyclic $[\text{Cu}_3\text{L}^{39}_2(\text{HL}^{39})]$ was assembled by reaction of the tetradentate ligand, L^{39} , with copper(II) salts. This cluster is stable in solution and comprises 2 $\text{Cu}(\text{II})$ and 1 $\text{Cu}(\text{I})$ ions from magnetic investigations; the $\text{Cu} \cdots \text{Cu}$ separation in the triangle is *ca.* 11.8 Å. Each copper atom is coordinated by two oxygen atoms and two nitrogen atoms from two different bis-bidentate ligands in a heavily distorted tetrahedral geometry, while each ligand is bound to two metal ions in a bis-bidentate coordination mode.²⁰ Strong intramolecular $\pi \cdots \pi$ interactions between the ligands stabilize the triangular conformation, and electrochemical studies reveal that the mixed-valent $\text{Cu}(\text{I})\text{Cu}(\text{II})_2$ complex is the stable state in solution and communication between the copper ions might be explained on the basis of through-bond interactions. UV-vis-NIR spectral measurement demonstrates the Robin-Day class II behavior of the mixed-valence compound with weak copper–copper interactions.

A cyclic-octanuclear $\text{Ca}(\text{II})$ phosphate complex (Fig. 6) has been synthesised with a ligand, L^{40} , that contains bulky amides groups; $[\text{Ca}^{\text{II}}_8\{\text{L}^{40}\}_8(\text{O}=\text{CHNMe}_2)_8(\text{H}_2\text{O})_{12}]$.

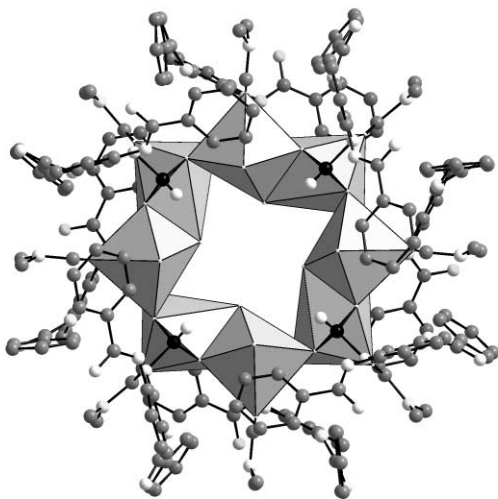
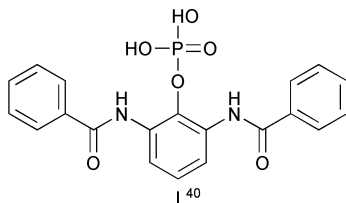


Fig. 6 A representation of the cyclic octamer, the ligands are shown in ball and stick and the metal ions as grey polyhedra.

This complex has a cyclic topology and was synthesised by the addition of DMF to a zig-zag chain precursor complex, $[\text{Ca}^{\text{II}}\{\text{L}^{40}\}-(\text{H}_2\text{O})_4(\text{EtOH})]_n$.²¹ The transformation in the $\text{Ca}(\text{II})$ complex from a zig-zag to a cyclic structure occurs by the coordination of the amide $\text{C}=\text{O}$ of DMF without changing the metal-phosphate ratio.



The zig-zag chains are stacked with each other due to the intermolecular $\text{OH} \cdots \text{O}=\text{C}$ hydrogen bonds involving the amide groups, but the DMF molecules seem to be effective in removing the interactions to the amide groups. The bulky amide ligands are able to convert the formation of the intermolecular and intramolecular hydrogen bonds and the transformation from the zig-zag structure to the cyclic-octanuclear structure is correlated with the formation of the intermolecular hydrogen-bond networks.

Four nanometer-sized cobalt azametallacrowns, have been synthesised by the self-assembly reaction of cobalt ions with N-substituted salicylhydrazide ligands, L^{41} – L^{44} to yield metallacrowns of the form $[\text{Co}^{\text{III}}_6(\text{L}^{41-44})_6(\text{MeOH})_6]$, Fig. 7.²²

The hexanuclear 18-membered ring of six cobalt ions is linked by the six hydrazide N–N groups of the six N-substituted salicylhydrazide pentadentate ligands in the metallacrowns. All four azametallacrown complexes possess non-crystallographic

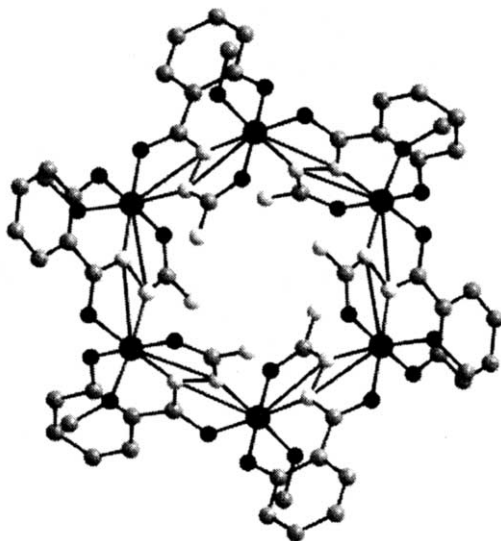
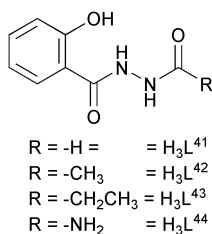


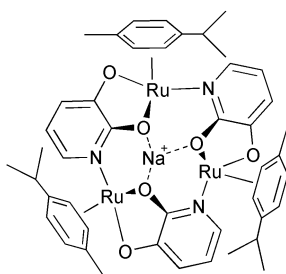
Fig. 7 The structure of the hexa-azametallacrown.



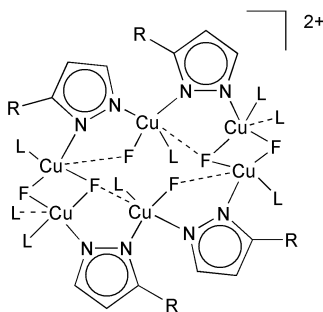
pseudo- C_{3i} symmetry and lie on crystallographic inversion centres. The chiralities of the cobalt atoms alternate between the Λ and Δ forms. The crowns can also include several solvent methanol molecules in the nanometer-sized cavity of the azametallacrown.

A complex of molecular Na_2SiF_6 , stabilised by two 12-metallacrown-3 host complexes, $\{\text{Ru}_3(\text{L}^{45})(p\text{-cymene})_3\}^+$ has been synthesized. The structure of the metallocrown shows a pseudo C_3 symmetric metallacrown complex 6 with a sodium ion coordinated to the three adjacent O-atoms of the macrocyclic ring.²³ It would appear that this metallocrown provides a steric environment that allows the inclusion of guest molecules within a well-defined framework.

The complex $[\{\text{Cu}_3(\text{Hpz}^{\text{tBu}})_4(\mu\text{-pz}^{\text{tBu}})2(\mu\text{-F})_2(\mu_3\text{-F})_2\}]_2\text{F}_2$ ($\text{Hpz}^{\text{tBu}} = 3\{5\}\text{-tert-butylpyrazole} = \text{L}^{46}$) has a cyclic, C_{2v} -symmetric hexacopper core. The two non-coordinated F^- anions are encapsulated within cavities formed by three Hpz^{tBu} ligands and it would appear that the reaction of Cu(II) salts with L^{46} depend drastically on the anion present in the reaction mixture.²⁴ This emphasises that the exogenous, hydrogen-bonded anions play an important role in templating the structures of these cluster products.



$\text{Na}^+\text{Ru}_3(\text{L}^{45})_3(\rho\text{-Cymen})_3$



$\text{R} = \text{}^t\text{Bu}$ and $\text{L} = \{5\text{-tert-butyl-pyrazole}\}$

Reaction of the novel rigid ligand *cis,trans*-1,3,5-triaminocyclohexane, (L^{47}) which contains two types of metal binding sites *trans* to each other, with palladium(II) chloride results in the self assembly of a hexanuclear ring cluster that has been characterised both in the solid state and in solution. In the formation of this cluster, both the *cis* bidentate amino moiety and the *trans* amino moiety of the ligand L^{47} are utilised to form a hexanuclear cluster with a circular topology, Fig. 8, of the form $[\text{Pd}_6(\text{L}^{47})_6\text{-Cl}_6]\text{Cl}_6$. This cluster is extremely rigid and represents the first complex to be structurally characterised using this ligand.²⁵

Methods for the self-assembly of hexaruthenium metallomacrocycles employing bis-terpyridine building blocks (L^{48}) has been achieved. Self-assembly is effected by a combination of equimolar mixtures of bismetallated and nonmetallated bis-(terpyridinyl) monomers.²⁶ In an effort to understand the distribution of a second metal into homometallic clusters, heteronuclear diethylcarbamato ($\text{L}^{49} = \text{Et}_2\text{NCO}_2$) complexes of the form $\text{Co}_n\text{Mg}_{6-n}(\text{L}^{49})_{12}$ were prepared from the isostructural homonuclear precursors $\text{Mg}_6(\text{L}^{49})_{12}$ and $\text{Co}_6(\text{L}^{49})_{12}$, *via* a solvothermal synthesis. The structures are best described as two trinuclear M_3 units cross-linked by diethylcarbamate ligands and twisted about one another, so that the complex has overall D_2 symmetry.²⁷ The X-ray data prove that the Co(II) ions migrate to one particular site in the heteronuclear complexes, Fig. 9.

A novel luminescent hexanuclear platinum(II) complex, $[\text{Pt}_2(\mu\text{-dppm})_2(\text{L}^{50})_4\text{-}\{\text{Pt}(\text{terpy})\}_4]^{8+}$ has been synthesised that has interesting photophysical properties.²⁸

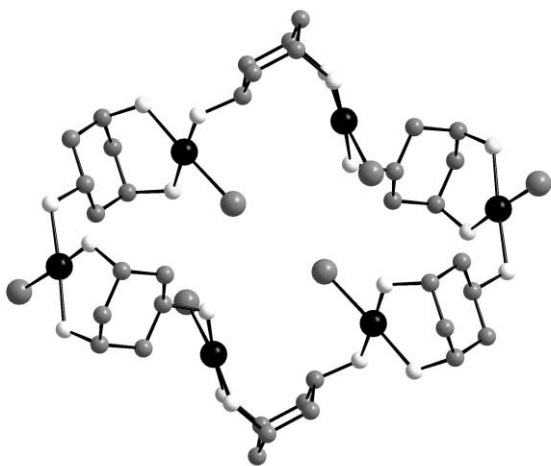
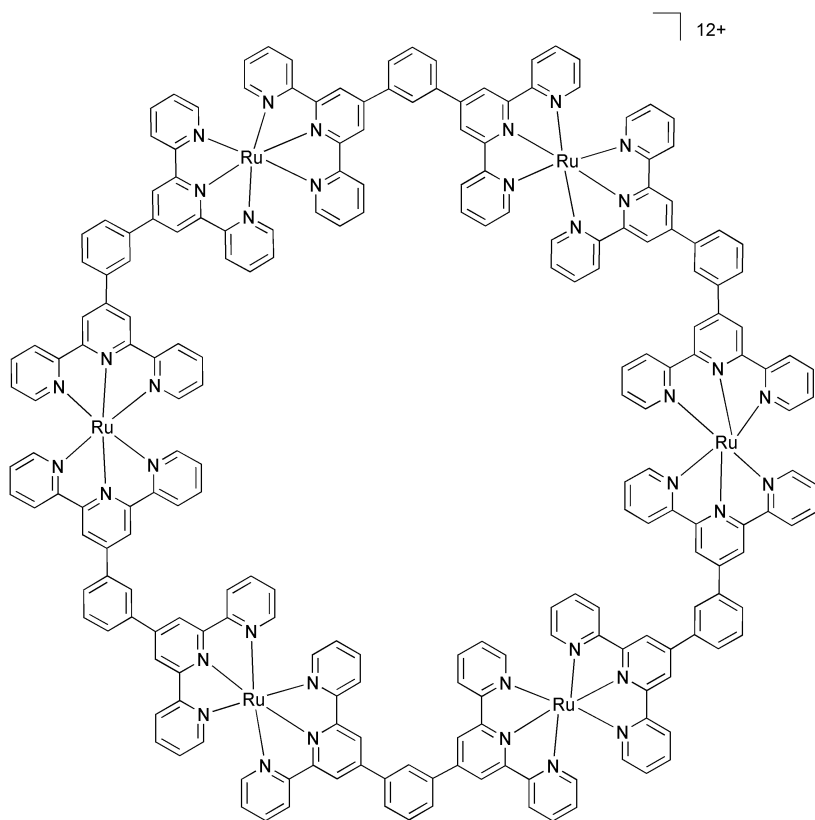


Fig. 8 The structure of the hexanuclear Pd complex of L⁴⁷ is shown. The metal ions are shown in black and the chloride ions are shown as the larger grey spheres.



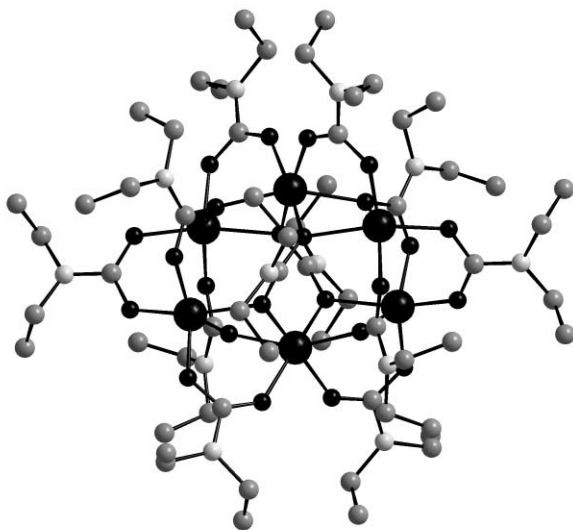
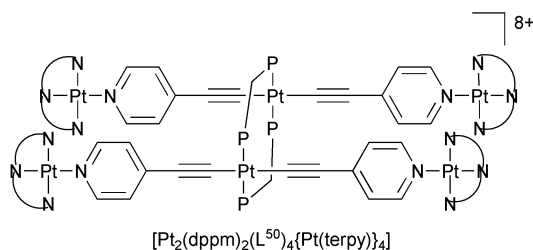


Fig. 9 The structure of the hexanuclear cluster is shown, the metal ions are shown in black and the diethylcarbamato ligands can be seen decorating the outer rim.

The complex exhibits strong luminescence at *ca.* 520 nm at 77 K in ethanol-methanol (4 : 1 v/v) glass, which arises from metal-perturbed ligand-centered phosphorescence. In the solid state at 77 K a strong luminescence at *ca.* 620 nm is also ascribed to phosphorescence derived from the ³MMLCT state. Energy transfer in luminescent molecular rods containing ruthenium(II) and osmium(II) 2,2':6',2'-terpyridine complexes linked by thiophene-2,5-diyl spacers has also been reported.²⁹

Routes to heterometallic wheels of the form [Cr₇MF₈(L⁵¹)₁₆]⁻ have been devised (L⁵¹ = O₂CCMe₃) which utilise a secondary amine as a cation. In this way wheels have been synthesised where M^{II} = Ni, Fe, Mn, Cd.³⁰ and the M...M vector in the wheel structure is bridged by a μ -fluoride and two 1,3-bridging pivalates. The M site is disordered over all possible metal sites. In all the structures the average Cr-F and Cr-O bond lengths are longer than in the parent cluster (comprising only Cr ions), Fig. 10.

In the development of new clusters, the pro-ligand 1,1,1-tris(hydroxymethyl)ethane (H₃L⁵²) has been used in the synthesis of two new types of Fe^{III}-based unsupported (*i.e.* no central metal ions) octametallac, [Fe₈(PhCOO)₁₂(L⁵²)₄] and hexadecametallic, [Fe₁₆(EtO)₄(PhCOO)₁₆(HL⁵²)₁₂]⁴⁺ ferric wheel clusters.³¹ The bridging alcoholate ligand

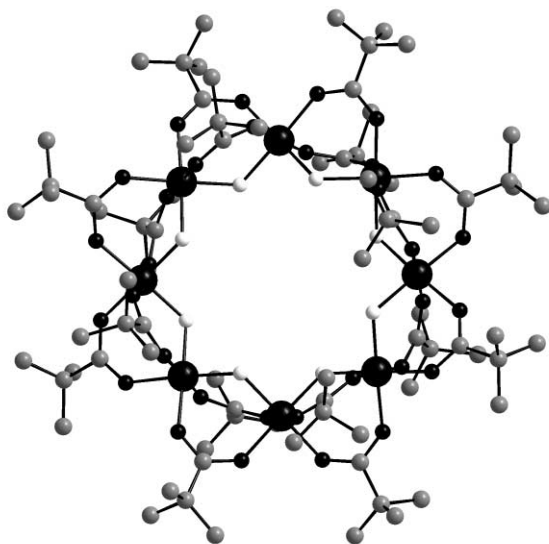


Fig. 10 The structure of the heterometallic-heptameric wheel.

(L⁵²) appears to be responsible for the formation of these clusters and shows a degree of coordinative flexibility. It is interesting that the switch from the {Fe₈} to the {Fe₁₆} wheel is accomplished by the addition of a coordinating alcohol group in the crystallisation step. A {Co₁₂} wheel, [Co₁₂(L⁵³)₁₂(O₂CMe)₁₂(H₂O)₆(THF)₆] (6-chloro-2-pyridine = HL⁵³), has been synthesised with an electronic ground state of spin $S = 6$, which corresponds to ferromagnetic interactions between the twelve Co(II) ions.³² Interestingly this wheel is isostructural to the [Ni₁₂(L⁵³)₁₂(O₂CMe)₁₂(H₂O)₆(THF)₆] analogue. The compound lies on a crystallographic $\bar{3}$ axis and includes two metal atoms in the asymmetric unit, each bound to six oxygen donors. These are derived from acetate ligands, bridging chp ligands, bridging water molecules and terminal THF molecules, Fig. 11.

A new manganese(III/IV) carboxylate cluster [Mn₁₆O₁₆(OMe)₆(OAc)₁₆(MeOH)₃(H₂O)₃]·6H₂O has been structurally characterised and shown to display net anti-ferromagnetic coupling with preliminary evidence for single-molecule magnetic behaviour.³³ The cluster consists of six Mn(IV) and ten Mn(III) ions held together by fourteen μ_3 -O²⁻, two μ -O²⁻, four μ -OMe⁻ and two μ -OAc⁻ groups to give a roughly elliptical planar {Mn₁₆} core (Fig. 12).

Two new octanuclear cages have been produced which feature formate as a bridging carboxylate, [M₈Na₂(OH)₂(L⁵³)₂(O₂CCPh₃)₈(HCO₂)₆(HL⁵³)₂(EtOAc)₂] [M = Ni(II) or Co(II)]. These clusters have been formed *in situ* from decomposition of triphenylacetate used as a ligand.³⁴ The structures comprise eight Ni or Co sites describing a C-shaped topology, with the open segment of the C containing two Na sites. All the metal sites are six-coordinate, with distorted octahedral geometries. Within the C-shape are six formate ligands and two μ_3 -OH ligands bridging Ni/Co sites within the sides of the C-shape (Fig. 13).

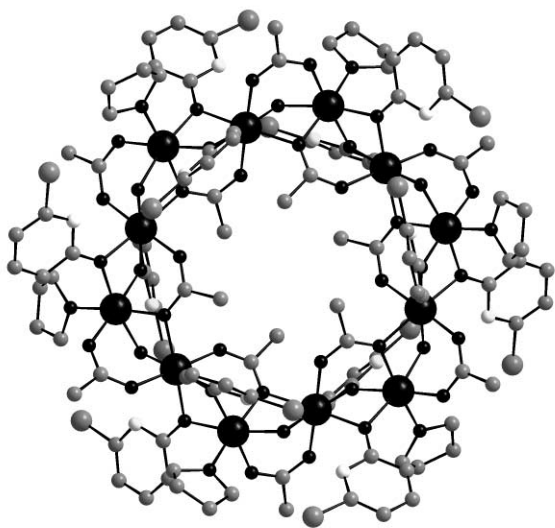


Fig. 11 The structure of the $\{Co_{12}\}$ wheel is shown and the internally bridging acetates can be seen along with the externally bridging acetates, THF and chp ligands.

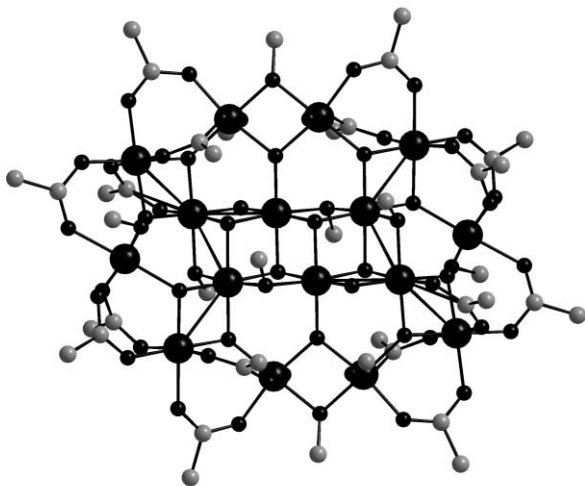


Fig. 12 The structure of the $\{Mn_{16}\}$ cluster.

The formation of intricate cages is not only limited to transition metal ions, a simple asymmetric tetradentate ligand 2,2':6',2''-terpyridine-6-carboxylic acid (HL^{54}) facilitates the self assembly of a large rare earth ring containing eight Eu(III) ions. The ring has the formulation $[Eu_8(Eu(L^{54})_2)_6]^{9+}$ in which six $Eu(L^{54})_2$ components are

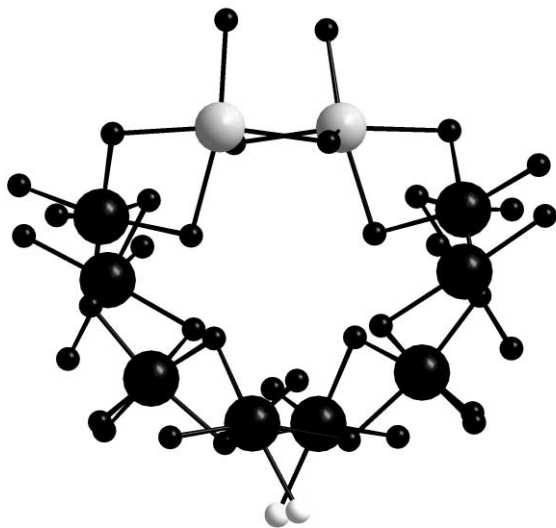


Fig. 13 The structure of the octanuclear cluster is shown with the metal ions in black and the two sodium ions in grey.

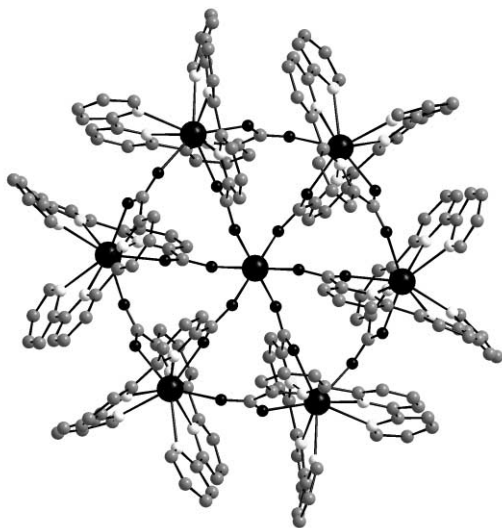


Fig. 14 The structure of $[\text{EuC}(\text{Eu}(\text{L}^{54}))_6]^{9+}$ with the wheel-like topology and the central Eu ion.

connected by six bridging carboxylates to yield a ring encapsulating an octahedral Eu(III) cation, Fig. 14.³⁵

Preliminary ^1H NMR studies indicate that the presence of additional lanthanide cations of different sizes also yields a controlled self-assembly. While the addition of

0.16 equiv. of Ln(III) ions larger than Eu(III) to an acetonitrile solution of the cluster was reported to result in a complicated mixture of species, the addition of smaller Ln(III) ions such as Ho, Tm, Yb, or Lu leads to only one other self-assembled species. The presence of two different lanthanides in organized molecules is of particular interest since it can result in new intramolecular directional energy transfers leading to light-converting devices. In the formation of an even larger lanthanide-based clusters, a series of pentadecanuclear lanthanide-hydroxo complexes possessing a common core of the formula $[\text{Ln}_{15}(\mu_3\text{-OH})_{20}(\mu_5\text{-X})]^{24+}$ (type 1 when $\text{X} = \text{Cl}^-$ and $\text{Ln(III)} = \text{Eu}$ or Nd or Gd ; type 2 when $\text{X} = \text{Br}^-$ and $\text{Ln(III)} = \text{Pr}$ or Eu) can be prepared by L-tyrosine-controlled hydrolysis of corresponding lanthanide perchlorates in the presence of added Cl^- or Br^- . The cationic cluster core comprises five vertex-sharing cubane-like $[\text{Ln}_4(\mu_3\text{-OH})_4]^{8+}$ units centred on the halide template.³⁶ Furthermore the efficient self-assembly of halide-encapsulating multi-cubane complexes and the inability to produce an analogous nitrate-containing complex demonstrate the superior templating roles played by the halide ion(s), see Fig. 15.

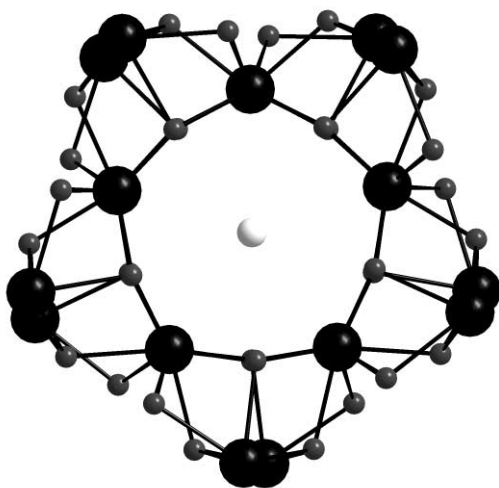
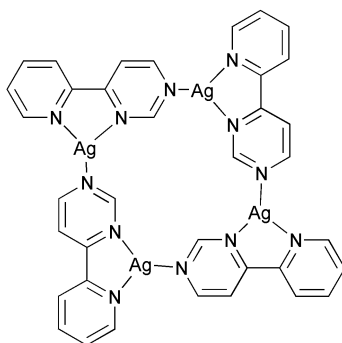


Fig. 15 A representation of the core of the $\{\text{Ln}_{15}\}$ cluster with the central halide ion shown as a white sphere showing the obvious templating role for these ions.

The ligand 4-(2-pyridyl)-pyrimidine (L^{55}) forms multinuclear Ag(I) complexes *e.g.* $[\text{Ag}_4(\text{L}^{55})_4]^{4+}$ by a combination of chelating and bridging coordination modes; molecular shape (square or rectangle) and degree of aggregation depend on the anion used. The head-to-tail aggregation of four corner residues requires that the Ag(I) ions each bind in a pseudo-trigonal planar geometry.³⁷

Reaction of Rh(I) and Zn(II) metal centers with a ligand containing salicylaldiminato and thioether-phosphine moieties, (L^{56}) results in the formation of a tetranuclear heterobimetallic molecular square. The directionality required to form these structures is imparted by both the tetrahedral and square planar metal centers acting in concert with one another.³⁸ Therefore, the resulting square is formed by cooperative



interactions throughout the molecule rather than by any specific directional bonding effect. As opposed to assembling prefabricated corners and linkers, flexible building blocks are constrained to form a rigid structure using complementary coordination geometries. It is likely that this approach can be used to create flexible macrocycles through the breakage of the weak thioether bonds.

The synthesis of a class III mixed-valence square complex has been achieved, $[(L^{57})_4-Ru_4(prz)_4]^{9+}$ (L^{57} = cyclen = 1,4,7,10-tetraazacyclododecane, prz = pyrazine), in which electron delocalization occurs between four equivalent Ru centres, see Fig. 16.

The electronic nature of the square complex was investigated spectroscopically and with preliminary electrochemical analysis which confirm the tentative assignment of a class III mixed valence complex.³⁹ In other studies, the synthesis and characterization of a family of novel chiral molecular squares based upon $[Cl(CO)_3Re(L^{58})_4]$ (where L^{58} is enantiopure 4,4'-bis(pyridyl)-1,1'-binaphthyl) has allowed the first observation of enantioselective luminescence sensing by a chiral metallocycle.⁴⁰ These chiral

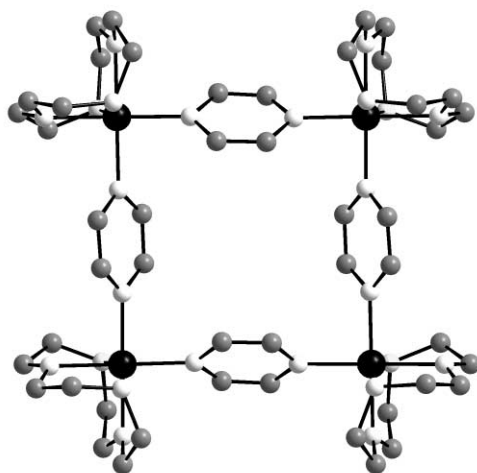
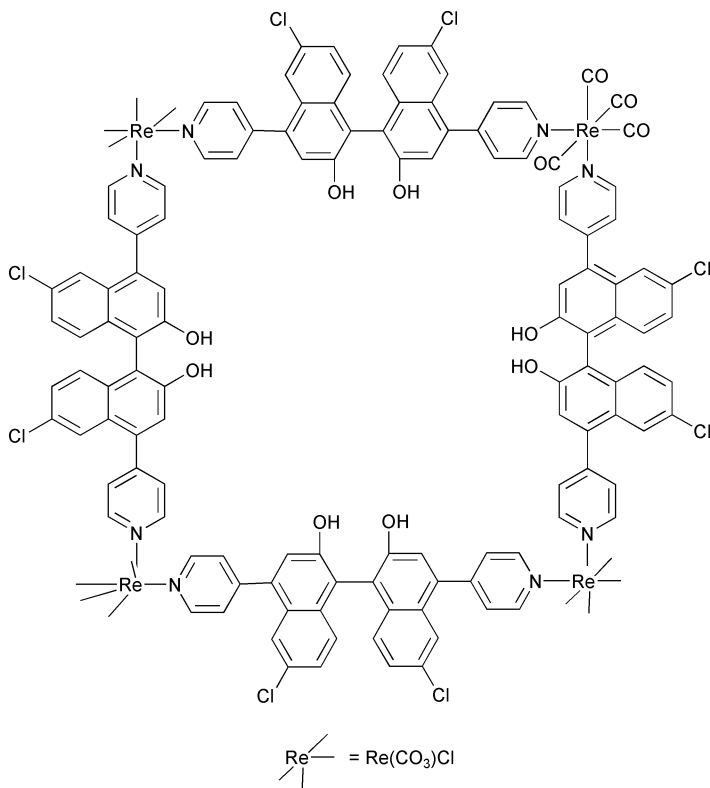


Fig. 16 The structure of this mixed-valence square is shown with the four prz linking ligands and the capping cyclen ligands.



molecular squares are readily assembled using enantiopure atropisomeric bipyridyl bridging ligands and *fac*- $\text{Re}(\text{CO})_3\text{Cl}$ corners. Such metallocycles exhibit interesting enantioselective luminescence quenching by chiral amino alcohols and higher enantioselectivity within a given family of macrocycles is probably a consequence of a better-defined chiral environment in the metallocycle.

4 Cages and related complexes

A ligand L^{59} , which comprises two bidentate pyrazolylpyridine units linked to an aromatic core through two methylene spacers has been synthesised and unexpectedly, this reacts with cobalt(II) and zinc(II) ions to generate dodecanuclear cage complexes $[\text{M}_{12}(\text{L}^{59})_{18}]\text{X}_{24}$ (where X = perchlorate or tetrafluoroborate) in which each of the 18 bridging ligands spans an edge of a truncated-tetrahedral $\{\text{M}_{12}\}$ array, see Fig. 17.⁴¹

Each of the four faces of the initial tetrahedron therefore becomes a hexagon, and the polyhedron accordingly contains four triangular and four hexagonal faces. All twelve cobalt(II) centres within each complex molecule have the same chirality but the crystal is racemic as a whole.

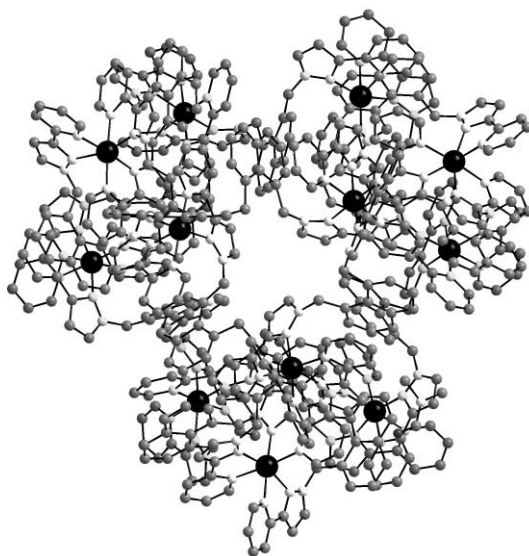
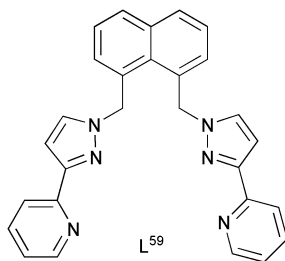


Fig. 17 The structure of the $\{\text{Co}_{12}\text{L}^{59}_{18}\}$ is depicted and shows the central cavity; this actually contains four BF_4^- anions.



A synthesis of homovalent Cu(I) clusters of the type $[\text{Cu}_{x+y}(\text{L}^{60})_x(\text{RC}\equiv\text{C})_y]$ ($\text{L}^{60} = \text{hfac} = \text{hexafluoroacetylacetonate}$) have been synthesised. The largest is a Cu_{26} , $[\text{Cu}_{26}(\text{L}^{60})_{11}(1\text{-pentynyl})_{15}]$, see Fig. 18.⁴² In addition to this, large clusters with 16 and 20 Cu(I) ions have also been characterized.⁴³ It is amazing that these clusters are very simply prepared by the addition of L^{60} to Cu_2O with excess alkyne followed by heating *in vacuo*, followed by partial oxidation to the overall cluster in the case of the $\{\text{Cu}_{26}\}$ cluster.

The self-assembly of the $\text{M}_3(\text{L}^{61})_2$ trigonal prismatic molecular cages of the type $[\{\text{CuI}_3\text{C}[\text{Cu}_3(\text{L}^{61})_2]\}_2](\text{Cu}_2\text{I}_4)$ has been achieved where L^{61} is 1,3,5-tris(benzimidazol-1-ylmethyl)-2,4,6-trimethylbenzene). Solution ^1H NMR spectroscopic studies indicate that the box structure is the thermodynamically stable but kinetically labile product, see Fig. 19.⁴⁴ The encapsulation of the $\{\text{CuI}_3\}^{2-}$ ion in the cavity is interesting and it appears to be effectively sandwiched within the cavity.

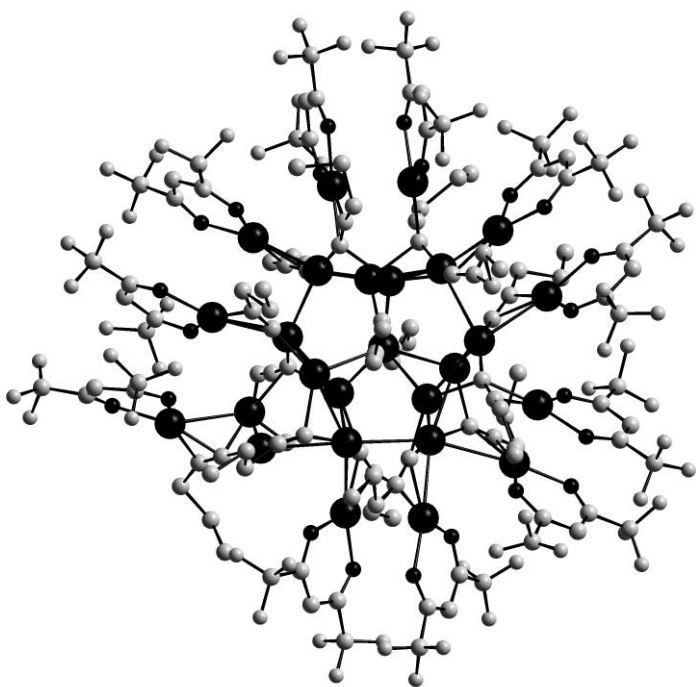
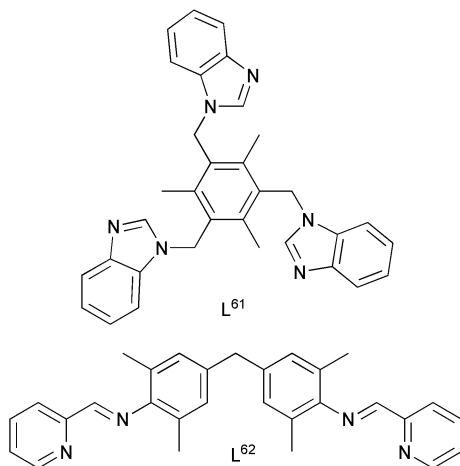


Fig. 18 The structure of the $\{Cu_{26}\}$ cluster.



The synthesis of the di-imine ligand, L^{62} , allows the synthesis of a bowl-shaped triangular $[Cu_3(L^{62})_3]^{3+}$ complex. These units aggregate in the solid state to form a ball comprising 12 L^{62} ligands and 12 Cu^{II} ions. This aggregation is also assisted by the $CH-\pi$ interactions between the complexes. The diameter of the resulting ball is

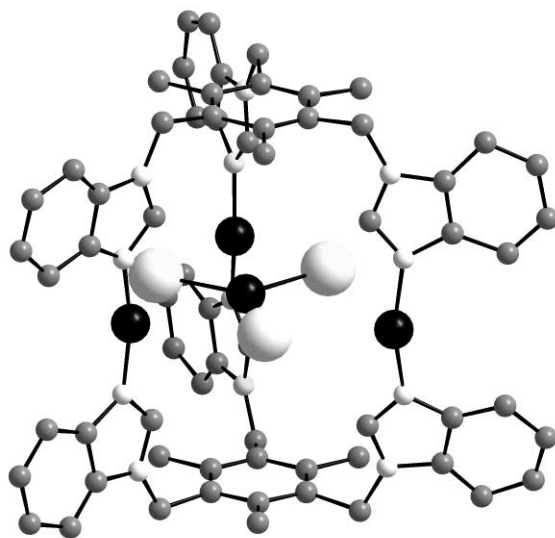
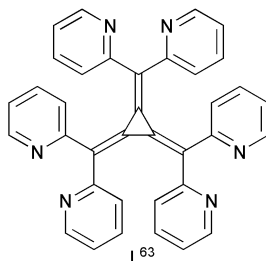


Fig. 19 The structure of the $\{M_3(L^{61})_2\}$ cage is shown along with the encapsulated $\{CuI_3\}^{2-}$ moiety whereby the iodides are shown by the large white spheres.



approximately 2.5 nm.⁴⁵ The reaction of the new ligand hexa(2-pyridyl)[3]radialene (L^{63}) with silver tetrafluoroborate results in the formation of a $\{M_6(L^{63})_2\}$ cage with an encapsulated μ_3 -fluorido anion, see Fig. 20.⁴⁶

The reaction of 2-(dimethylamino)phenylhydroxamic acid (H_2L^{64}) with $NiSO_4 \cdot 6H_2O$ gives the complex $[Ni_7(2-HL^{64})_2(L^{64})_8(H_2O)_2]SO_4$ uniquely exhibiting four distinct hydroxamate binding modes, and showing both antiferromagnetic and ferromagnetic interactions in contrast to $[Cu_5(HL^{64})_4(HSO_4)_2(MeOH)_2]$, a strongly antiferromagnetic metallocrown formed with $CuSO_4 \cdot 5H_2O$, see Fig. 21.⁴⁷

A dodecanuclear silver cluster has been synthesised with the bulky ligand and contains a 20-membered ring of alternating silver and sulfur atoms, which is compactly folded; the sulfur atoms are doubly bridging and each silver atom exhibits linear two-coordination in the primary Ag–S interactions, see Fig. 22.⁴⁸

Ligand H_3L^{65} can form a variety of $\{Cu^{II}_{12}\}$ clusters of the form $[Cu_{12}(\mu_3-OMe)_2 OMe)_6(L^{65})_6]_{22}$ (Fig. 23), which can be crystallised in a number of ways where the clusters are separated by large areas of non-interacting solvent molecules connected

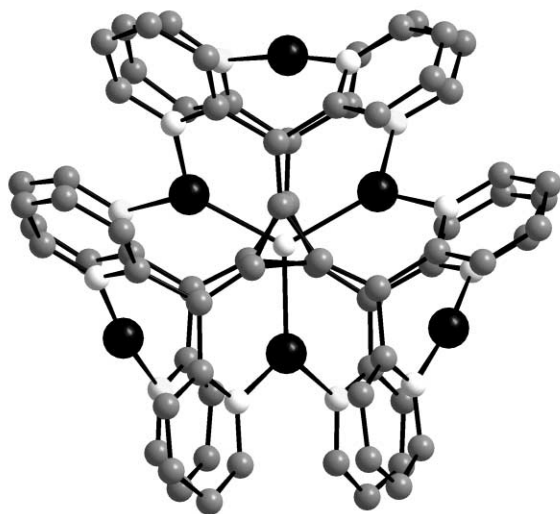


Fig. 20 The structure of the hexanuclear silver cluster is shown, the μ_3 bridging fluoride is depicted in the centre of the clusters as the small white sphere.

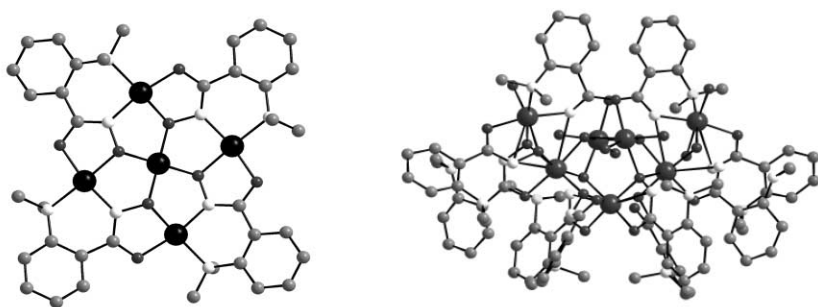
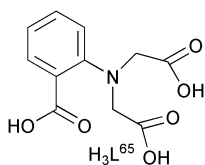


Fig. 21 Structures of the $\{\text{Cu}_5\}$ (LHS) and the $\{\text{Ni}_7\}$ (RHS) clusters based on L^{64} .



through alkali-metal ion linkages or by $\{\text{Cu}_2(\mu\text{-Ome})_2\}^{2+}$ bridges. These systems show magnetically interesting behaviour which can be examined as a function of the supramolecular array formed.⁴⁹

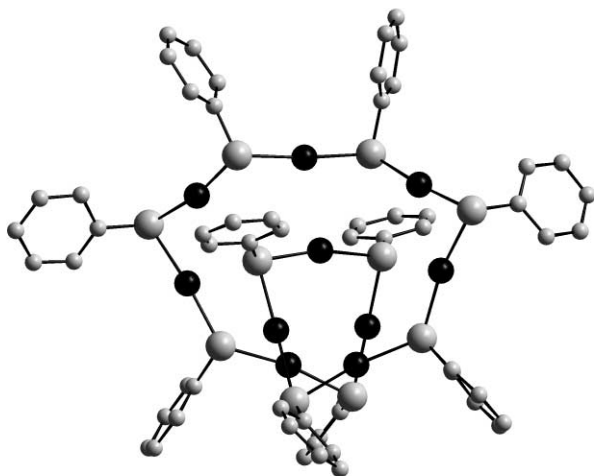


Fig. 22 The structure of the $\{Ag_{12}\}$ core is shown and the folded ring can be easily seen (the *i*-Pr groups on the phenyl rings are removed).

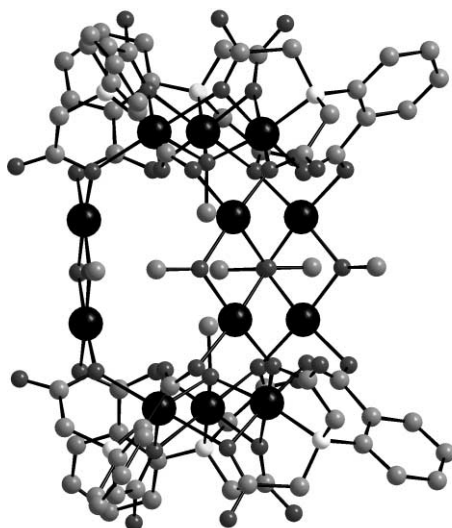
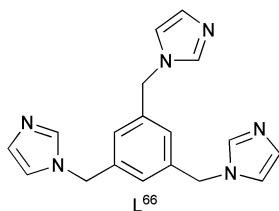
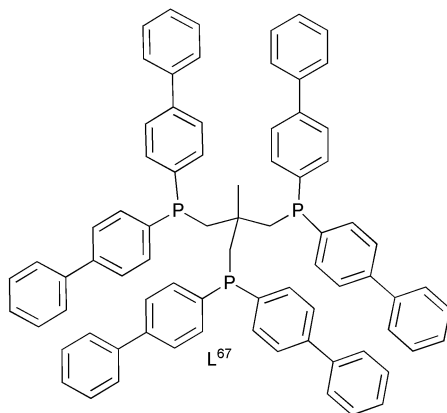


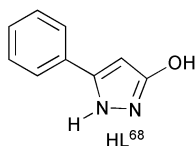
Fig. 23 The structure of the $\{Cu_{12}\}$ cluster.



The coordinatively saturated, nanometer-sized $\{M_6(L^{66})_8\}$ complex $[Pd_6(L^{66})_8]Cl_{12}$ ($L^{66} = 1,3,5$ -bis(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene) was obtained by assembly of six Pd(II) ions with eight L^{66} ligands; structural analysis shows that these eight L^{66} ligands are in a disordered cube configuration and the six Pd atoms are in a disordered octahedral configuration; the inner cavity of the cage is estimated to have a volume of 1000 \AA^3 , large enough to encapsulate eight Cl^- anions.⁵⁰ Silver salts and triphosphine ligands with biphenyl substituents, L^{67} , assemble to give coordination cages of the form, $[Ag_6(L^{67})_4(NO_3)_4]$ with four external aromatic channel receptors in a pseudo-tetrahedral arrangement.⁵¹ These receptors have been shown to complex benzene. The first $\{Mn_{14}\}$ cluster has been synthesised from pyrazolyl-type ligand,



3-phenyl-3-pyrazolin-5-one (HL^{68}) is of the form, $[Mn_{14}O_2(OH)_4(L^{68})_{18}(HL^{68})_4(NO_3)_4(MeCN)_4]$. The core is based on $\{Mn_7\}$ fragments of which each contains a $\{Mn_3O_4\}$ distorted incomplete cubane, lacking one Mn site. Two of the O-centres within this unit are hydroxide. It is interesting to note that this is a new nuclearity for Mn-based cages.⁵² The reaction of $[Mn_3O(OAc)_6(py)_3]$ with 1,1,1-tris(hydroxymethyl)ethane



(H_3L^{52}) gives the $Mn^{IV}_3Mn^{III}_4Mn^{II}_2$ complex $[Mn_9O_7(OAc)_{11}(L^{52})(py)_3(H_2O)_2]$ (Fig. 24), which has an $S = 17/2$ ground state and displays characteristics of a single-molecule magnet, see Fig. 24.⁵³ A new family of Mn_{12} clusters with 2-(hydroxymethyl)pyridine has been produced that also act as single molecule magnets.⁵⁴

Even higher nuclearity manganese clusters can be formed by the reaction of MnF_3 with benzotriazole (HL^{69}) in hot MeOH, giving the Mn^{III} complex $[Mn_{26}O_{16}(OH)_{10}(OMe)_6(F)_{10}(L^{69})_{20}(HL^{69})_2(MeOH)_{13}(H_2O)]$ which displays hysteresis and temperature-independent magnetization relaxation at low temperature.⁵⁵ However organo-metallic Mn-based clusters can be produced by the reaction of manganocene, Cp_2Mn ,

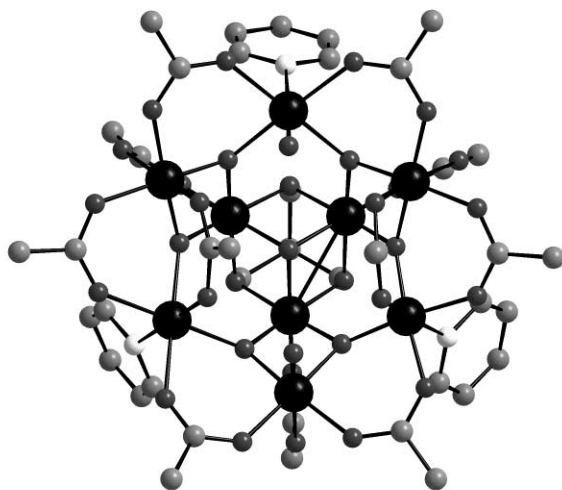
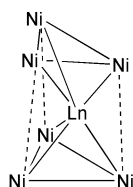


Fig. 24 The structure of the $\{Mn_9\}$ cluster.

with 2-aminopyridine (HL⁷⁰) or 2-amino-3-bromo-5-methylpyridine (HL⁷¹) to give the novel hexanuclear and octanuclear Mn(II) amido cage compounds $[Cp_2Mn_3(L^{70})_4]_2$ and $[Mn_8(L^{71})_{12}(\mu_4-O)_2]$; their structural and magnetic properties have been investigated.⁵⁶ The use of carboxylates can also allow access new spin clusters. For example the conversion of $[Ni_8(L^{72})_6(OH)_2(H_2O)_2]^{10-}$ to $[Ni_8(L^{72})_6(OH)_2]^{10-}$ $\{H_4L^{72} = C(OH)(CO_2H)(CH_2CO_2H)_2\}$ has been achieved by manipulation of temperature and this indicates how the formation of high nuclearity nickel(II) citrate spin clusters can be triggered by desolvation and ligand reorganisation.⁵⁷ In addition, heptanuclear trigonal-prismatic polyhedra, $Na_4[PrNi_6(Gly)_9(\mu_3-OH)_3(H_2O)_6]^{7+}$ and four related com-



plexes has been constructed with Gly as a ligand (HL⁷³). A Ln^{3+} ion is in the centre of the prism formed by six nickel atom and it coordinates to nine oxygen atoms. Its coordination polyhedron may be best described as a tricapped trigonal prism. The five complexes all have a core of $[LnNi_6(Gly)_6(\mu_3-OH)_3(H_2O)_6]^{6+}$ and were obtained through the edge-ligand exchange of the three μ_2-OH_2 ligands of $[LnNi_6(Gly)_6(\mu_3-OH)_3(H_2O)_6(\mu_2-OH_2)_3]^{6+}$ partly or wholly by glycine or Cl^- .⁵⁸

The reaction of HL⁷⁴, *N*-(2-methylthiazole-5-yl)-thiazole-2-carboxamide, with zinc acetate produced the tetrametallic zinc cluster $[Zn_4O(L^{74})_4(OAc)_2]$. When the 3-methyl-substituted analogue HL⁷⁵ was allowed to react under identical conditions

with zinc acetate, another tetra-zinc cluster was produced that is isostructural to the cluster produced with L^{74} . However, iron(II) acetate under aerobic conditions reacts with HL^{74} to produce a cluster which comprises two connected tri-metallic clusters, $[\{Fe_3O(L^{74})_2(OAc)_4\}_2O]$, see Fig. 25.⁵⁹

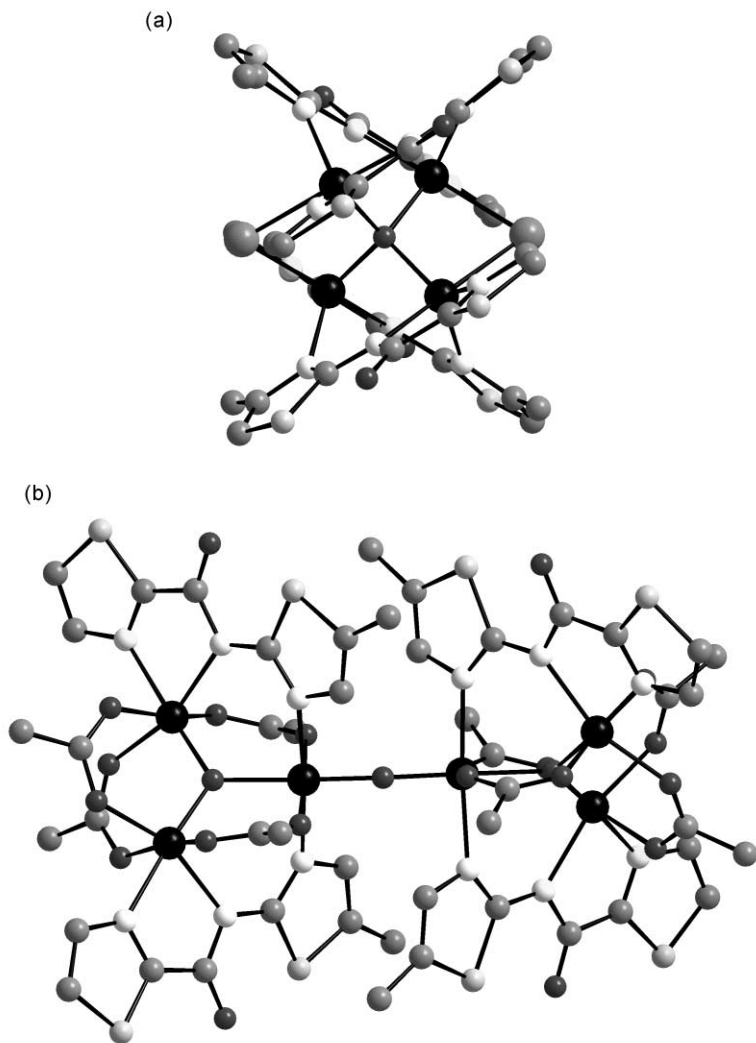


Fig. 25 A representation of the $\{Zn_4\}$ complex is shown on the TOP and the $\{Fe_3\}_2$ cluster is shown on the BOTTOM.

Self-assembled tetrahedral $[M_4(L^{76})_6]^{8+}$ ($M = Cu^{2+}$ or Zn^{2+}) clusters were generated from the reaction of L^{76} with the zinc(II) or copper(II) perchlorate salts in a 3 : 2 ratio. A perchlorate ion anion is encapsulated within the tetrahedral cluster, see Fig. 26.⁶⁰

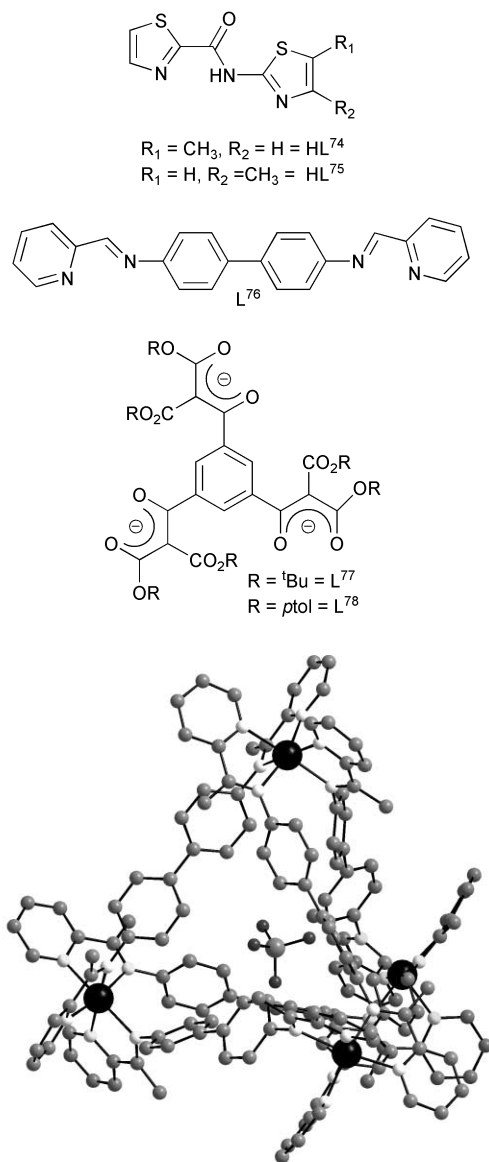


Fig. 26 The structure of $[\text{M}_4(\text{L}^{76})_6]^{8+}$ demonstrating a tetrahedral topology.

Self-assembly of tetrahedral and trigonal antiprismatic clusters can be achieved *via* the combination of the components required to form L^{77} and L^{78} and iron(II) dichloride. The *in-situ* formation of $[\text{Fe}_4(\text{L}^{77})_4]$ and $[\text{Fe}_6(\text{L}^{78})_6]$ has been proven by crystallography and the oxidation of the iron(II) centres to iron(III) was proven by Mossbauer spectroscopy, see Fig. 27.⁶¹

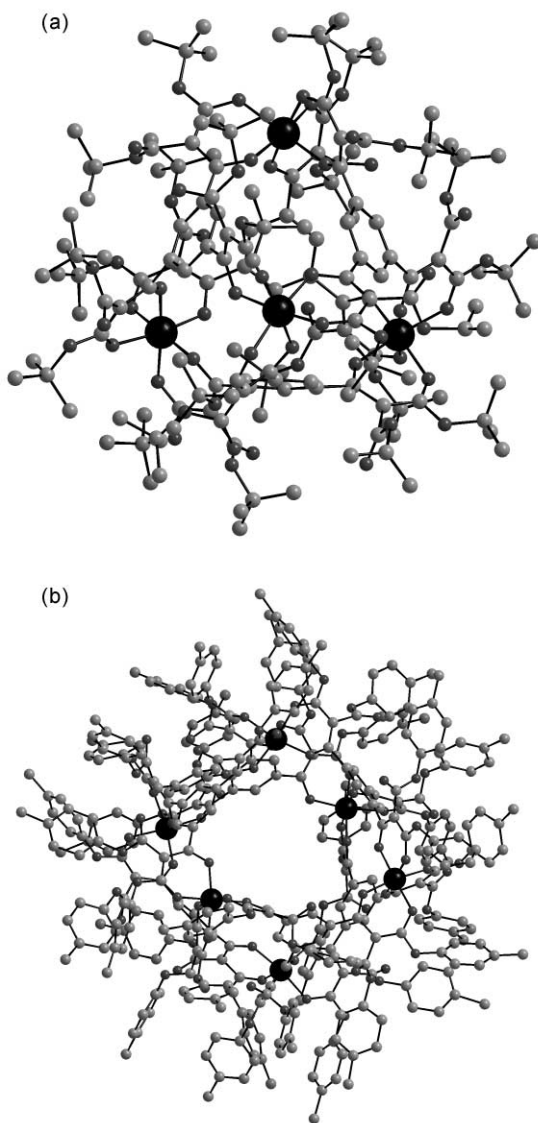


Fig. 27 The structures of $[\text{Fe}_4(\text{L}^{77})_4]$ (TOP) and $[\text{Fe}_6(\text{L}^{78})_6]$ (BOTTOM).

A series of heptanuclear rare-earth-centered trigonal prism clusters of the form $[\text{LnCu}_6(\mu\text{-OH})_3(\text{HL}^{79})_2(\text{L}^{79})_4]^{2+}$ ($\text{Ln} = \text{La-Ho}$ and Y ; H_2L^{79} = iminodiacetic acid) have been synthesised which utilize the central rare earth cation as a template. The central $\text{Ln}(\text{III})$ ion is nine-coordinate and the coordination polyhedron can be described as a tricapped trigonal prism and the $\text{Cu}(\text{II})$ ions in the complex are all five-coordinate, exhibiting a distorted tetragonal pyramidal geometry. These complexes were

assembled using a rare-earth cation as the template, and the process is also affected by the μ_3 -bridged hydroxyl groups resulting from the slow hydrolysis of the rare earth ions.⁶² Heterometallic heptanuclear clusters were synthesised from the reaction of $[\text{Mn}(\text{L}^{80})\text{OH}_2]^{2+}$ and $[\text{Ni}(\text{L}^{80})\text{OH}_2]^{2+}$ ($\text{L}^{80} = 1,4\text{-bis}(2\text{-pyridylmethyl})\text{-}1,4,7\text{-triazacyclononane}$). In each case the cyano ligands of the ferricyanide facilitate the assembly of heteropolynuclear cations around the cyanometalate core and reduction of Fe(III) to Fe(II). In $[\{\text{Mn}(\text{L}^{80})\text{CN}\}_6\text{Fe}\}^{8+}$ and $[\{\text{Ni}(\text{L}^{80})\text{CN}\}_6\text{Fe}\}^{8+}$, ferrocyanide is encapsulated by either six Mn^{II} or Ni^{II} L^{80} moieties, as shown in Fig. 28.⁶³

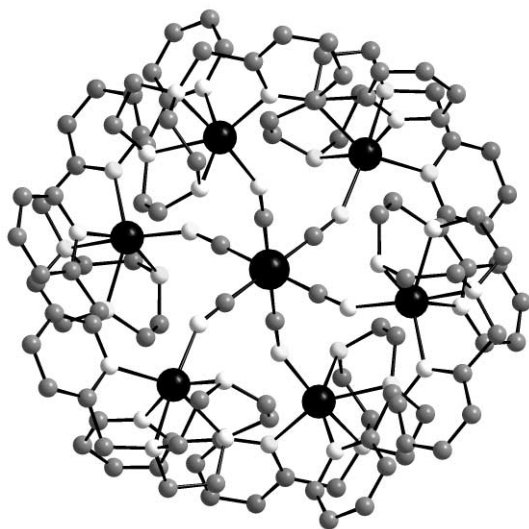


Fig. 28 The structure of the Mn substituted cluster is shown and the Ni cluster is isostructural. The central black sphere represents Fe and the other spheres are either Mn or Ni.

The reaction of ZnCl_2 with *tert*-butylphosphonic acid and 3,5-dimethylpyrazole (HL^{81}) affords a trinuclear molecular zinc phosphonate $[\text{Zn}_3\text{Cl}_2(\text{L}^{81})_4(\text{t-BuPO}_3)_2]$. The structure of this compound contains a planar tri-zinc assembly containing two bi-capping $\mu_3[\text{t-BuPO}_3]^{2-}$ ligands and terminal pyrazole and chloride ligands. The analogous reaction of ZnCl_2 with phenylphosphonic acid and 3,5-dimethylpyrazole affords a hexanuclear zinc phosphonate $[\text{Zn}_6\text{Cl}_4(\text{L}^{81})_8(\text{PhPO}_3)_4]$, see Fig. 29.⁶⁴

Two new metal-cyanide clusters, $[(\text{L}^{82})_{12}\text{Cr}_{12}\text{Ni}_{12}(\text{CN})_{48}]^{12+}$, with high nuclearities can be assembled by a reaction involving L^{82} ($\text{L}^{82} = \text{N},\text{N}',\text{N}''\text{-trimethyltriazacyclononane}$) $[(\text{L}^{82})\text{Cr}(\text{CN})_3]$, Ni(II), and KCN in aqueous solution. The structure of this 24-metal cluster features a cube of eight Cr^{III} centers linked along the edges by 12 *trans*-coordinated $[\text{Ni}(\text{CN})_4]^{2-}$ units, and capped on four faces by $[\text{Cr}(\text{L}^{82})]^{3+}$ moieties, see Fig. 30. A larger cluster, $[(\text{L}^{82})_{14}\text{Cr}_{14}\text{Ni}_{13}(\text{CN})_{48}]^{20+}$, was obtained from a related reaction excluding the addition of KCN⁶⁵ and a similar architecture has been reported with mixed Mo/Ni ions.⁶⁶

A disc-shaped ligand, L^{83} forms both 2-D and 3-D complexes with silver(I) salts. The Ag(I) complexes of L^{83} were proven to assume both sandwich-shaped

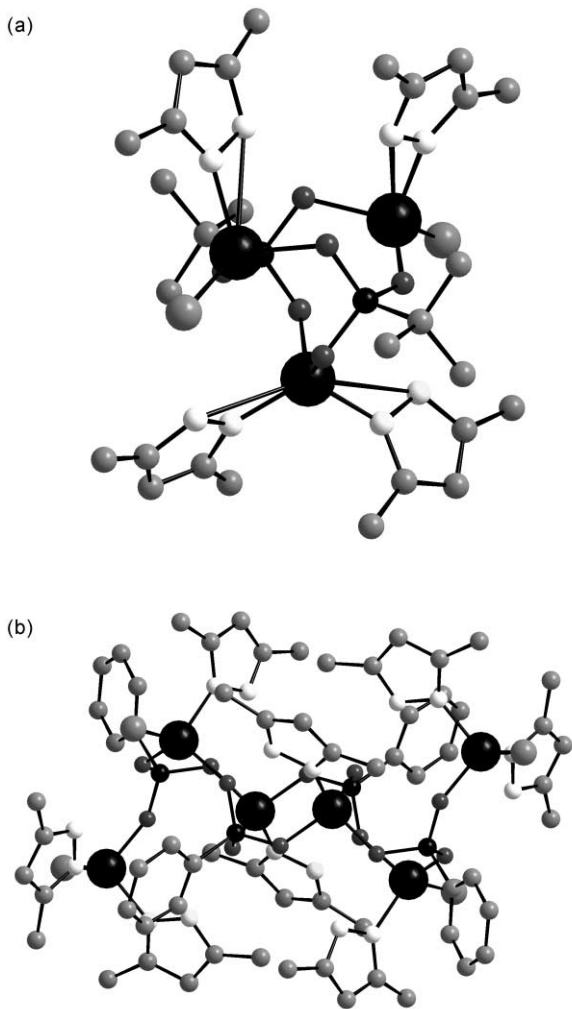
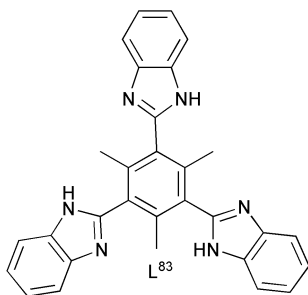


Fig. 29 The structures of the tri-nuclear and hexa-nuclear zinc-phosphonate-based clusters.



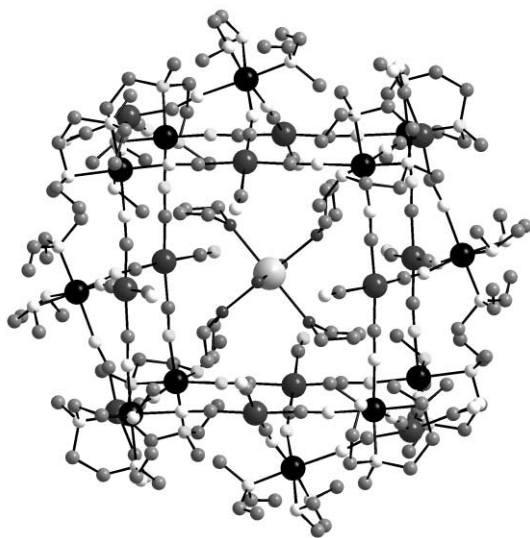
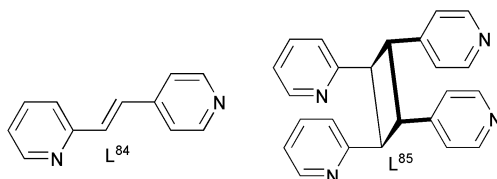


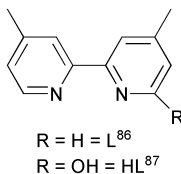
Fig. 30 A representation of the crystal structure of $[(L^{82})_{12}Cr_{12}Ni_{12}(CN)_{48}]^{12+}$ cube cluster.

$[Ag_3(L^{83})_2]^{3+}$ and tetrahedral $[Ag_4(L^{83})_4]^{4+}$ structures which are in a controllable dynamic equilibrium in solution, depending on the ratio of L^{83} to $Ag(I)$ ions.⁶⁷

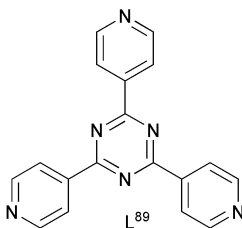
A linear template based on resorcinol is used to direct a regiocontrolled synthesis in a molecular solid, $2(4\text{-Cl-res}), 2(L^{84})$ (4-Cl-res = 4-chlororesorcinol; L^{84} = *trans*-1-(2-pyridyl)-2-(4-pyridyl)ethene), to give the product, *rctt*-1,2-bis(2-pyridyl)-3,4-bis(4-pyridyl)cyclobutane (L^{85}). This ligand complexes with transition-metal-ions to form a hexanuclear cage, $[Cu_6(L^{85})_6(H_2O)_6]^{12+}$, with a structure that conforms to a trigonal antiprism.⁶⁸



Several interesting cubane, and cubane like architectures have been synthesised,^{69,70} however the first tetranuclear manganese cluster containing a $[Mn_4(\mu-O)_5]^{6+}$ core has recently been reported.⁷¹ This is a manganese complex of the form, $Mn_4(\mu-O)_5(L^{86})_4(L^{87})_2]^{4+}$.



A range of interesting Pd/Pt-based architectures have been synthesised which have a topology that resembles that of a molecular bowl as analogues of calix[3]arenes based on 4,7-phenanthroline, L^{88} . Cages based on the $[Pd_6(L^{89})_4]^{12+}$ (where L^{89} is 2,4,6-tri-(4-pyridyl)-1,3,5-triazine) have also been shown to facilitate the stereoselective [2+2]



photodimerisation of acenaphthylenes and naphthoquinones within coordination cages, see Fig. 31.⁷² These types of molecule have also been shown to allow the shape-selective enclathration of neutral guests in the cage.⁷³

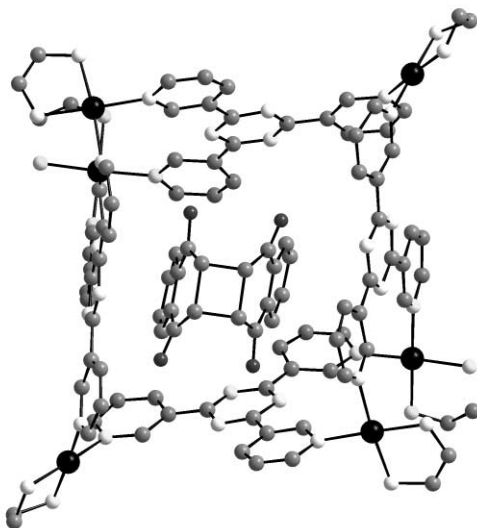


Fig. 31 Structure of $[Pd_6(L^{89})_4]^{12+}$ along with the [2 + 2] photodimerised guest is shown.

In addition this versatile nanometer cage has also been used in the electrochemically driven clathration/declathration of ferrocene.⁷⁴ A Pd(en) complex of a ligand based upon pentakis(*m*-phenylene) incorporating two pyridine units at opposite ends of the ligand, L^{90} can undergo chirality induction through the reversible catenation of coordination rings.⁷⁵ Furthermore it has been found that solventless reactions involving L^{89} with Pd(II) salts dramatically accelerates supramolecular self-assembly from days to minutes.⁷⁶ Other $\{Pd_3L_2\}$ -based cages have been synthesised using a subphthalocyanine cage that undergoes chiral self-discrimination during the assembly process.⁷⁷

A series of hetero- and homometallic square complexes bridged by a photoactive 4,4'-azopyridine (L^{91}) or 1,2-bis(4-pyridyl)ethene (L^{92}) ligand, cyclobis{[*cis*-(dppf)M](μ - L^{91})₂(*fac*-Re(CO)₃Br)}(OTf)₄ (M = Pd) were prepared by thermodynamically driven self-assembly processes. Upon irradiation at 313 or 366 nm, Pd(II)-Re(I)-containing tetranuclear squares undergo photoisomerization and convert to their corresponding dinuclear complexes whereas Pt(II)-Re(I)-based squares only show slow square disassembling processes.⁷⁸ A molecular triangle of palladium(II)⁷⁹ was synthesised from the ligand 4(3*H*)-pyrimidone (HL⁹³) and forms a bowl-like molecular triangle, [$\{Pd-(bu_2bipy)(\mu-L^{93})\}_3\}^{3+}$ ($bu_2bipy = 4,4'$ -di-*tert*-butyl-2,2'-bipyridine), with the deprotonated ligand (L^{93}). This triangular complex acts as a host for binding of several anionic guests including nitrate, HSO_3^- , perchlorate and triflate. An equilibrium mixture of triangular and square supramolecular species results when the flexible, ditopic donor unit, *trans*-bis(4-pyridyl)ethene (L^{94}), is reacted with the ditopic acceptor unit, *cis*-(Me₃P)₂Pt(OTf)₂, in a one-to-one ratio.⁸⁰

5 Helicates

The preparation of a double metallahelicate containing 28 copper atoms in seven different donor environments with an overall stoichiometry of [Cu₂₈L⁹⁵(OAc)₁₀-Cl₄(MeOH)₅(H₂O)₃] where the copper-ligand (1-norvaline hydroxamic acid, H₂L⁹⁵)-chloride ratios are 5 : 4 : 2 has been reported.⁸¹ A new class of helicate comprising a double helix of sp³ carbons has been self assembled around a sp carbon chain and has the form, [(C₆F₅)(*p*-tolyl₃P)₂Pt(C≡C)₄Pt(P*p*-tol₃)₂(C₆F₅)]. Such molecules are excellent models for insulated molecular-scale devices and wires, see Fig. 32⁸²

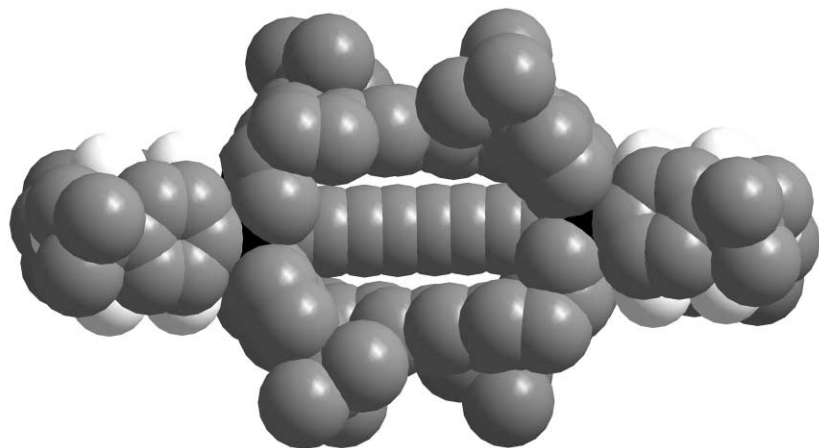
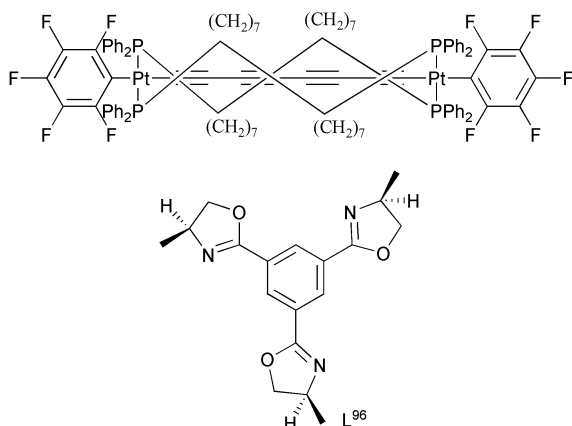
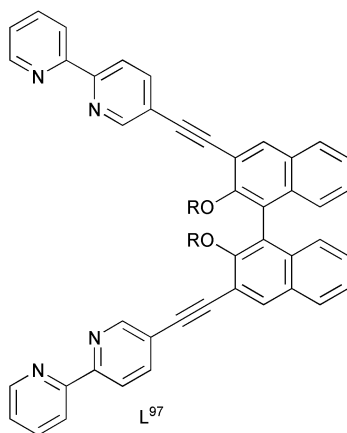


Fig. 32 The space filling modelling of the structure of the double helicate surrounding the central molecular wire, alkyne-based spacer.

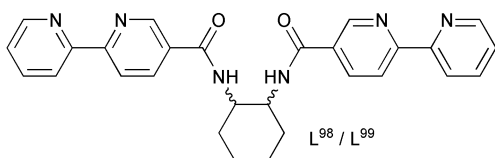
An enantiomerically pure propeller-shaped supramolecular capsule based on the stereospecific self-assembly of chiral tris(oxazoline) ligands of the type L^{96} , around three Ag(I) ions, has been constructed.⁸³ These chiral tris(oxazoline) ligands have been

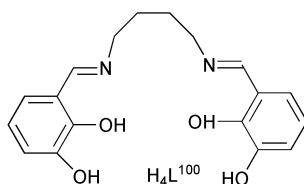


used to induce a predetermined chiral helicity because it is easy to introduce chirality and rigidity within the self-assembled superstructure from simple chiral amino alcohols. Complexation of L^{97} with $Zn(BF_4)_2$ forms a dinuclear triple stranded helicate. Structural analysis showed unambiguously that the dinuclear complex adopts a structure containing an overall D_3 -symmetric P-configured triple-stranded helicate with a complex of the form, $(\Delta, \Delta)\text{-}[Zn_2(L^{97})]_3^{4+}$.⁸⁴ Self-assembled triple helicites with pref-

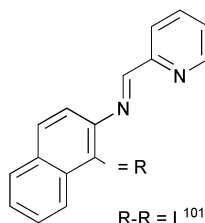


erential helicity⁸⁵ can be assembled from the enantiomerically pure ligands $L^{98}(RR)$ and $L^{99}(SS)$ N,N' -bis(-2,2'-bipyridyl-5-yl)carbonyl-(1*S*/*R*,2*S*/*R*)-(±)-1,2-diaminocyclohexane). A bis-helical [4 + 4 + 4] trinuclear copper(II) complex was formed by the reaction of H_4L^{100} with copper(II) salts to give $[Cu_3(H_2L^{100})(L^{100})]$.⁸⁶ Enantiopure

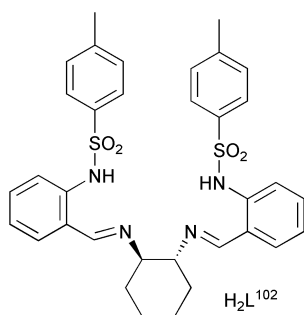




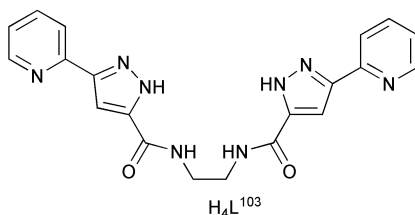
dinuclear silver(I) double helicates, $[\text{Ag}_2(\text{L}^{101}R/S)_2]^{2+}$ can be prepared by the reaction of the *R* or *S* enantiomers of L^{101} . These chiral ligands predetermine the chirality of the helicates: the *R* link gives a *P* helicate and the *S* spacer an *M* helicate.⁸⁷ However,



the N_4 Schiff base ligand, L^{102} complexes with divalent metal ions (Fe, Co, Ni, Cu, Zn and Cd) to form 'mono-helical' complexes $[\text{M}(\text{L}^{102})]$. If the cyclohexane unit in L^{102} is replaced with a flexible unit double helicates can result.⁸⁸ The novel polydentate ligand



N,N'-bis[5-(2-pyridyl)-4*H*-pyrazole-3-carbonyl]-1,2-diaminoethane (H_4L^{103}) possesses four bidentate chelating units and can bind metal ions in bis(binucleating) or tetradentate modes.⁸⁹ Ligands $\text{L}^{104-106}$ also form dinuclear triple helicates with $\text{Ag}(\text{I})$ whereas L^{107} forms di-nuclear double helicates with $\text{Cu}(\text{I})$.⁹⁰ The tris-tridentate



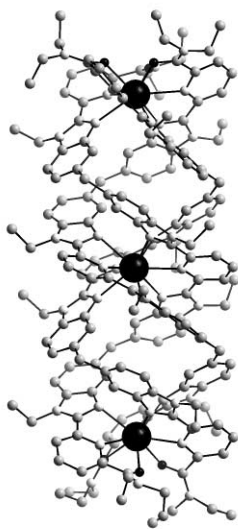


Fig. 33 The structure of the lanthanide-based triple helicate.

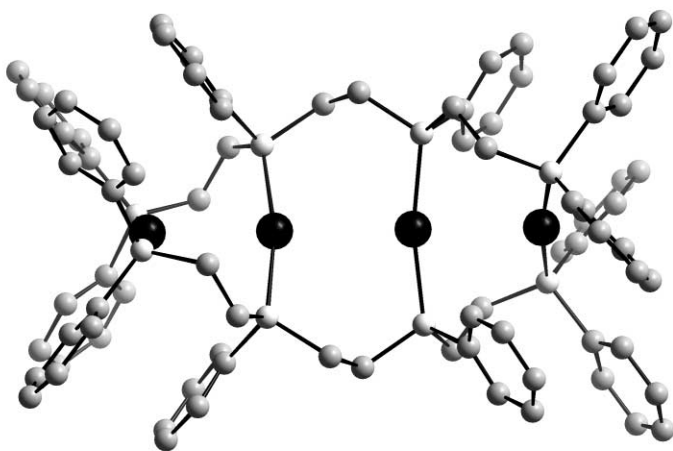
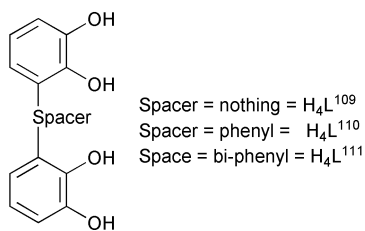
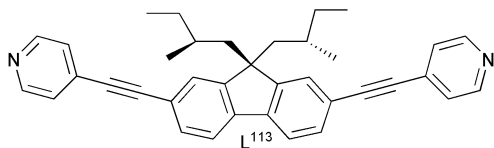


Fig. 34 A representation of the $\{Au_4\}$ cluster.

6 Grids

A chiral square-grid has been synthesised by treating L^{113} , a chiral fluorene-based ligand with copper(II) nitrate to yield, $[\text{Cu}(L^{113})_2(\text{NO}_3)_2]$, an infinite grid-network with dimensions of $25 \times 25 \text{ \AA}$.⁹⁴ The complexation of the spiro-bridged bisphen ligand, L^{114} , with one equivalent of Cu(I) salts yields a tetranuclear complex, $[\text{Cu}_4(L^{114})_4]^{4+}$



where the four copper ions are tetrahedrally coordinated to two phen subunits belonging to two independent ligands. Interestingly this unit seems able to complex anthracene, see Fig. 35.⁹⁵

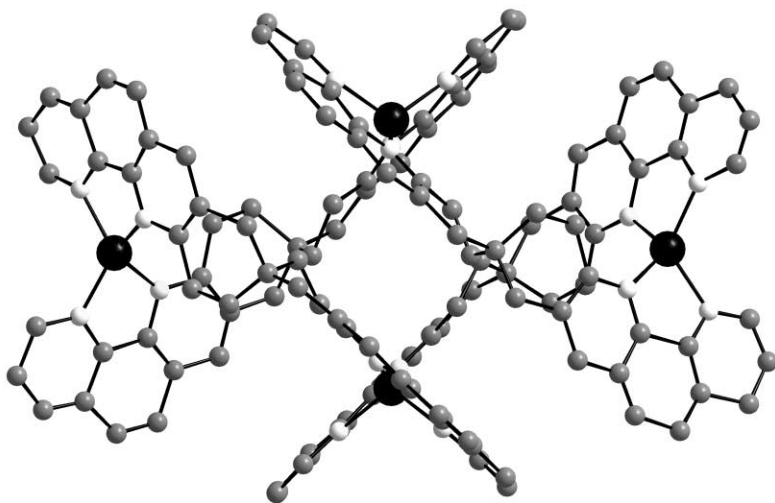
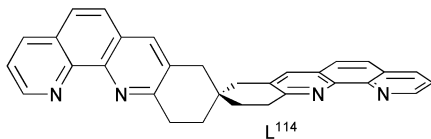
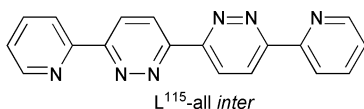
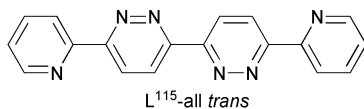
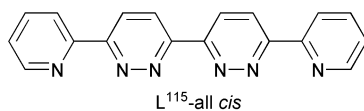
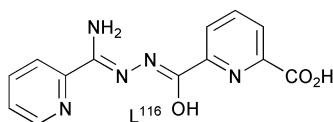


Fig. 35 The structure of complex $[\text{Cu}_4(L^{114})_4]^{4+}$, notice the cavity which can include aromatic molecules such as anthracene.

The formation of discrete $[3 \times 3]$ grids of the form $\{(\text{L}^{115})_6\text{Ag}_9\}^{9+}$ has been achieved with L^{115} and the mechanism of formation has been studied in detail; this gives some insights into the assembly process and demonstrates a degree of co-operativity during

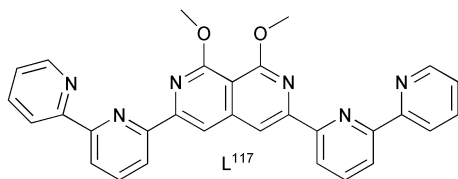


assembly.⁹⁶ Significantly the reversibility of the system demonstrates that it has potential to search the many possibilities of the free-energy hypersurface and this has significance for the design of dynamic supramolecular architectures. A homoleptic, self-assembled $[2 \times 2]$ square $\{Cu_4\}$ is formed when L^{116} is complexed with $Cu(II)$ salts. The carboxylic acid-substituted picolinic hydrazone ligand (L^{116}) forms a homoleptic $[2 \times 2]$ tetranuclear (Cu^{II})₄ complex with four six-coordinate $Cu(II)$ centers bridged by μ -O alkoxide groups in a square grid structure. The terminal carboxylic groups



complete the six-coordinate structures at each copper centre, capping off external coordination positions, with two functioning as carboxylates, and two in neutral carboxylic acid form. Intramolecular ferromagnetic exchange with $J = 7.2 \text{ cm}^{-1}$ is present and the complex has a $S = 4/2$ magnetic ground state, see Fig. 36.⁹⁷

A similar tetranuclear $[2 \times 2]$ square containing $(Co^{II})_4$ has also been constructed with a bis(bipyridine)dimethoxynaphthyridine ligand, L^{117} . The ligand helps produce a regular internal cavity which is 11 Å deep and 7 Å wide.⁹⁸



Larger grids have also been synthesised, for instance a dodecanuclear copper(II) ‘picture frame’ held in a $[4 \times 4]$ grid-like assembly has been reported.⁹⁹ This is constructed using H_2L^{118} yielding a grid of the form: $[Na \subset Cu_{12}(L^{118})_8]^{9+}$ and encapsulates a single sodium cation. Several other $[2 \times 2]$ and $[3 \times 3]$ grids have also have been reported using poly-terpy type ligands.^{100,101}

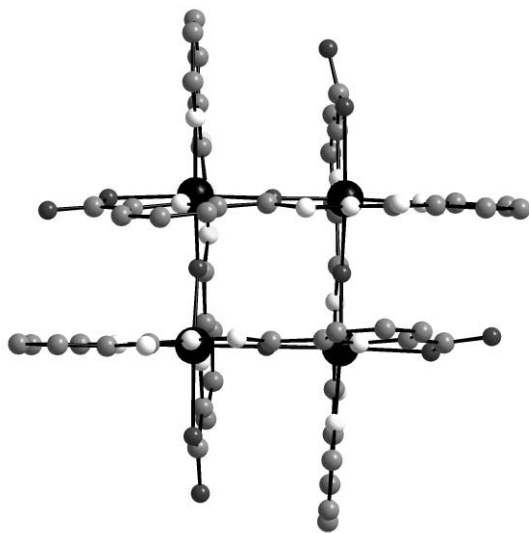
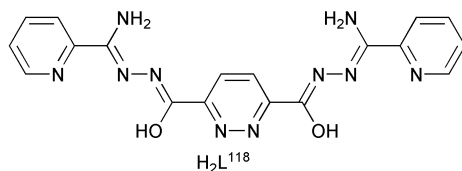
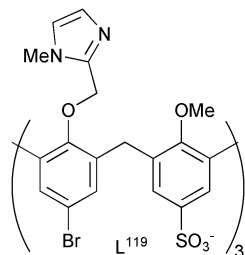


Fig. 36 The structure of the Cu-based $[2 \times 2]$ complex.



7 Cavities and bowls

The encapsulation of metal ions with a cavity or superstructure offers many possibilities for control of reactivity and the development of host guest chemistry. For instance a water soluble calix[6]arene derivatised with methylimidazole, L^{119} , binds copper(I) in aqueous solution to give a $N_3Cu(I)$ complex.¹⁰² The fourth binding site is



accessible for an exogeneous ligand with a strong affinity for the metal ion such as CO. A trimeric metallomacrocyle complex $[Cp^*Ir(C_5H_3NO_2)]_3$ forms a pocket that can selectively recognise LiF .¹⁰³ The accessibility of the Li center is controlled by the steric

requirements of the host. The small fluoride anion is able to enter the cavity whereas larger anions are efficiently blocked. In this way a highly specific receptor is obtained, see Fig. 37.

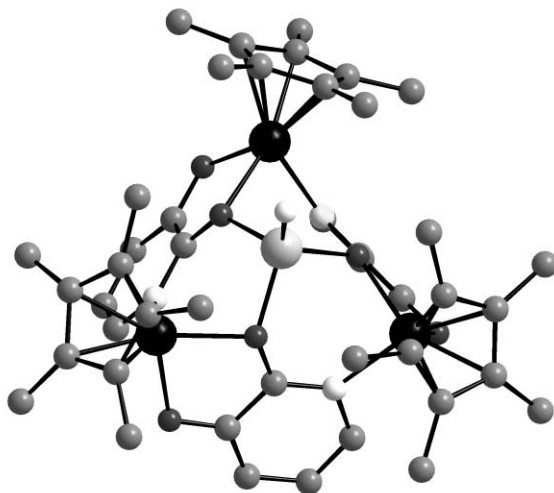
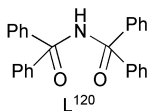


Fig. 37 The structure of the metallocene LiF receptor.

Tetra- and hexa-nuclear mercury(II) complexes have been formed from the complexation of tetrathiacalix[4]arene and tetramercaptotetrathiacalix[4]arene and are new diagonal and trigonal receptors of the Koiland type.¹⁰⁴ In addition thiacalix[*n*]pyridines are soft hosts and can complex soft metal ions such as Cu(I), see Fig. 38.

Structural motifs incorporating trivalent lanthanoid ions and *p*-sulfonato-calix[4]arene have been synthesised including host molecules and without host molecules. These systems include polymers and a molecular capsule which is held together by two adjacent metal ions.¹⁰⁵ Similar systems comprising bipyridyl-sulfonato-calix[4]arene, in the presence of trivalent lanthanide ions, are able to capture 4,13-diaza-18-crown-6 molecules.¹⁰⁶

The assembly of hydrophobic shells around lanthanide ions, for example [Eu(L¹²⁰)₃] has utility in the formation of a complex that blocks all water from approaching the metal meaning that these ligands can be useful for sensitising luminescence. This is



because the aryl-functionalised imidodiphosphinate ligands (HL¹²⁰) provide a bidentate anionic site that leads to hexa-coordinate lanthanide complexes in which the aryl groups surround the ion, excluding water molecules from the central lanthanide ion.¹⁰⁷

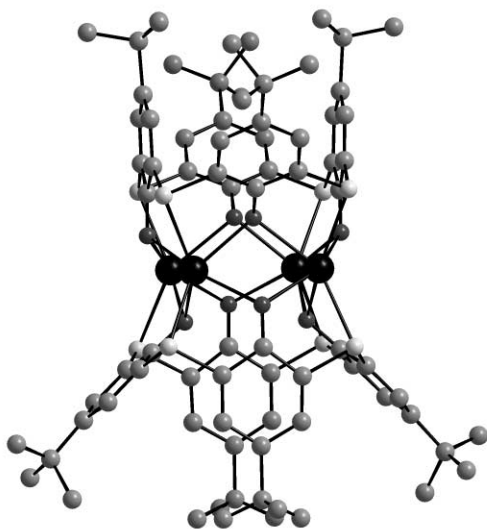


Fig. 38 The structure of the tube-like Hg-based Koilands.

Cucurbituril (L^{121}) has also been used as an encapsulating ligand for lanthanide ions, for example the complex $\{[\text{Gd}(\text{NO}_3)(\text{H}_2\text{O})_4](L^{121})\}^{2+}$. The crystal structures show a packing of 1 : 1, 2 : 2, and 2 : 3 in the (cucurbituril)lanthanide complexes in which cucurbituril plays a bidentate ligand role, and water molecules of the (aqua)lanthanide complexes form hydrogen bonds with carbonyl groups of the cucurbituril molecule.

A new class of potassium-selective ionophore, based on bis calix[4]arene–calix[4]-tubes has been designed. These molecules proved highly selective for complexation of potassium over all group I metal cations and barium. Modification of the upper calix[4]arene allows manipulation of the rate of potassium uptake.¹⁰⁸ Hybrid metallocoronates or one-dimensional oxo-bridged metal strings are formed by self-assembly, coordination number controlled product formation, have been synthesised and these include caesium ions within the metallocoronate.¹⁰⁹

8 Interlocking molecules

A number of interesting interlocking rotaxanes and catananes involving metals have been developed. For example interlocking of molecular rhombi into a 2D polyrotaxane network *via* π – π interactions has been achieved using Cu(II) complexes of phen ligands in the complex $[\text{Cu}_2(L^{122})_2(\text{phen})_2(\text{H}_2\text{O})]_2 \cdot 2\text{H}_2\text{O}$ (L^{122} = biphenyl-4,4'-dicarboxylate).¹¹⁰ A proton-controlled inter-conversion between an achiral discrete molecular square and a chiral interpenetrated double-chain architecture has been reported where an achiral Cu(II) molecular square, and a 1D spontaneously resolved chiral interpenetrated double-chain with $\{\text{Cu}_4\}$ cavities, based on bis(3-propionyl-oxo)-1,5-diazacyclooctane (H_2L^{123}) has been observed.¹¹¹

The reversible cross-catenation of two different coordination rings (Pd(II)- and Pt(II)-linked rings) has been achieved by using the labile nature of the Pd–N interaction and efficient hydrophobic contact between the rings.¹¹² Interestingly a striking strategy to synthesize molecular necklaces, in which a number of small rings are threaded onto a large ring, utilizing the principles of self-assembly and coordination chemistry as been reported. This strategy involves threading a molecular “bead” with a short “string” to make a pseudorotaxane and then linking the pseudorotaxanes with a metal complex with two cis labile ligands acting as an “angle connector” to form a cyclic product. The molecular components are 1,4-diaminobutane or 1,5-diaminopentane, cucurbituril (L¹²¹) and Pt(en)Cl₂. Also gold(I) macrocycles have been used to form chiral catenanes, see Fig. 39.¹¹³

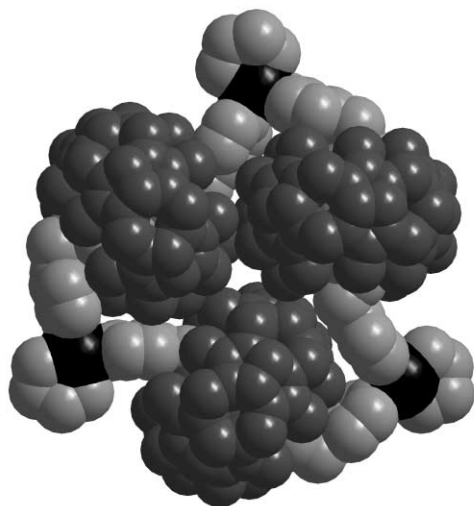
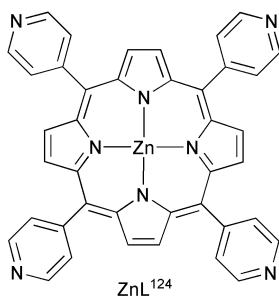


Fig. 39 A depiction of the structure of the threaded thread with the ‘cucurbituril’ beads.

9 Assemblies of porphyrins

Open network architectures have been constructed from the self-assembly of AgNO₃ and 5,10,15,20-tetra(4-pyridyl)porphyrin (H₂L¹²⁴) building blocks.¹¹⁴ For instance,



polymeric frameworks obtained from the self-assembly of AgNO_3 with H_2L^{124} or $\text{Zn}(\text{L}^{124})$, to give a 2D species $[\text{Ag}_4(\text{H}_2\text{L}^{124})_3]^{4+}$ and $[\text{Ag}_2(\text{H}_2\text{L}^{124})(\text{NO}_3)]^+$ as well as the 3D network $[\text{Ag}_8(\text{Zn}(\text{L}^{124})_7(\text{H}_2\text{O})_2)]^{8+}$. $[\text{Ag}_2(\text{H}_2\text{L}^{124})(\text{NO}_3)]^+$ contains 2D square-grid layers, whereas the other complexes are comprised of networks with new topologies. However all the compounds are robust and exhibit large free voids (>50%) full of removable guest solvent molecules. A large $[\text{Re}_6(\mu_3\text{-S})_8(\text{ZnL}^{125})_6]^{2+}$ (H_2L^{125} is 5-(4-pyridyl)-10,15,20-tritolylporphyrin) cluster has been synthesized which assembles 6 porphyrins around a hexarhenium cluster.¹¹⁵ These clusters are interesting as the cores can be seen as a giant octahedral center, since the six terminal ligands are oriented in such a manner that each pair of neighboring ligands are arranged vertically to each other. A similar set of architectures have also been reported with S replaced by Se in the core unit, see Fig. 40.¹¹⁶

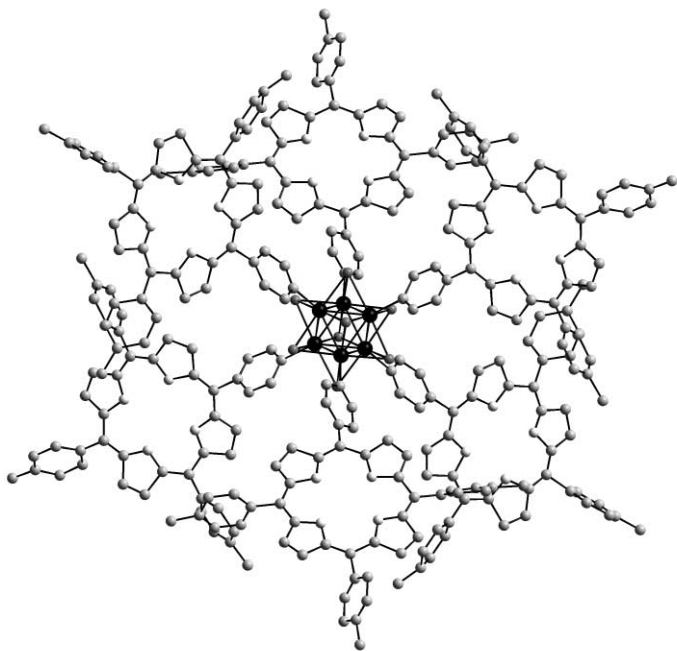


Fig. 40 The structure of the porphyrin cage built around the cluster core.

A fluorinated Zn porphyrin, ZnL^{126} $\{\text{L}^{126} = [5,10,15,20\text{-tetrakis}(4\text{-}n\text{-propylamino-}2,3,5,6\text{-tetrafluorophenyl)porphyrin}]\}$ undergoes self-assembly to a two-dimensional network of amine-functionalized, hexacoordinated Zn porphyrins where each porphyrin is linked to four orthogonally-oriented chromophores, see Fig. 41.¹¹⁷

However the use of co-directing units can help organise higher dimensionality assemblies for instance, the targeted synthesis of new supramolecular motifs of metalloporphyrins in crystals by a concerted mechanism of molecular recognition in three dimensions, aided by organic ligands, is presented; it involves induced assembly of L^{127} zinc species ($\text{L}^{127} = \text{tetrakis}(4\text{-hydroxyphenyl)porphyrin}$) by a combination of

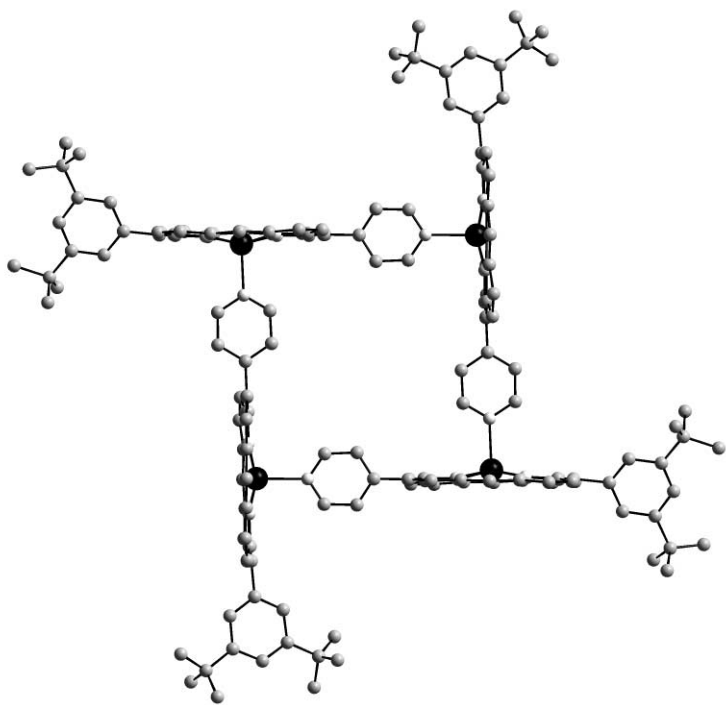
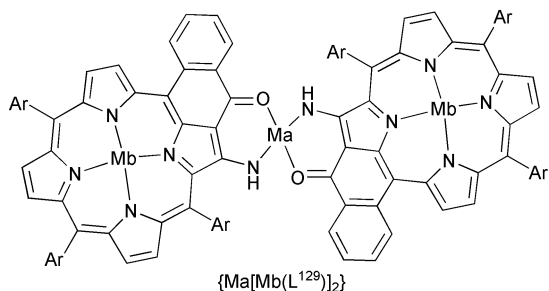


Fig. 41 The structure of the square porphyrin cluster.

axial coordination through bridging bipyridyls and of lateral hydrogen bonding.¹¹⁸ Covalently linked boxes have also been assembled to form meso-meso-linked bis (L^{128}) porphyrinato zinc(II)}¹¹⁹ where L^{128} = 5-*p*-pyridyl-15-(3,5-di-octyloxyphenyl)-porphyrin. Similar frameworks have been synthesised which comprise Ru and Rh linking units.^{120,121,122}

The preparation, isolation, and characterization of several new peripherally functionalized monomeric porphyrins [H_2L^{129}] and metalloporphyrins and of porphyrin dimers, are obtained by linking two monomeric porphyrins with metal ions bearing at their periphery an enaminoketone chelate fully conjugated with the aromatic ring. These molecules have interesting optical properties and may find application as new dyes.¹²³



10 Miscellaneous coordination complexes

An interesting $\{\text{Cu}_8\}$ cluster is formed when a methanolic solution of HL¹³⁰ (0.125 equivalents) is mixed with copper(II) nitrate. The copper ions are antiferromagnetically coupled in this cluster yielding a $S = 0$ ground state.¹²⁴ Fig. 42.

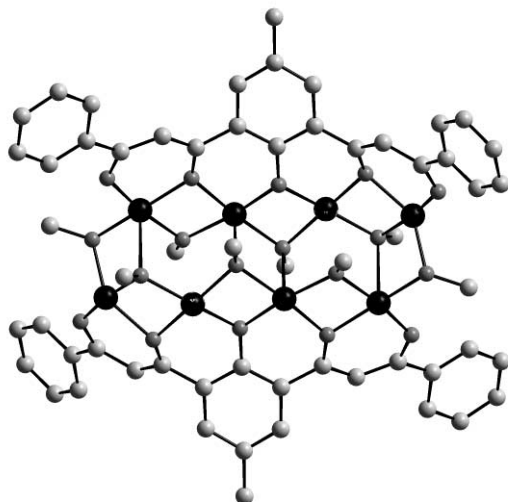
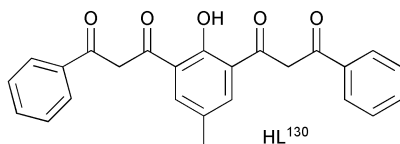
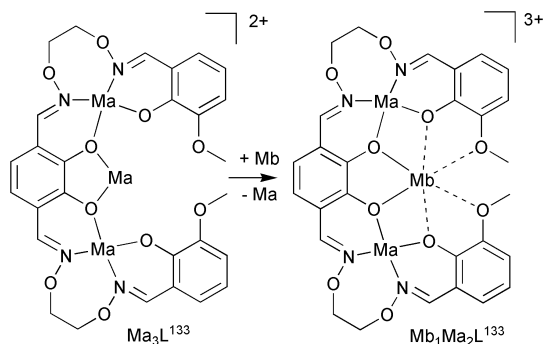


Fig. 42 Shows the two sets of lines of the Cu(II) ions found in the $\{\text{Cu}_8\}$ cluster.



A tetranuclear mixed-valent $\{\text{Mn}^{\text{II}}_3\text{Mn}^{\text{IV}}\}$ compound with a $(\mu_4\text{-O})\text{Mn}_4$ core in the tetranuclear cluster $[\text{Mn}^{\text{II}}_3\text{Mn}^{\text{IV}}(\text{O})(\text{L}^{131})_4(\text{L}^{132})_4]$ has been synthesised (L^{131} = di(2-pyridyl)ketonoxime, L^{132} = 3,4-dichlorophenoxy acetic acid). This is the only example of a manganese tetranuclear cluster with a $2e^-$ difference between the oxidation states of the metal ions and it is the first example of a manganese tetranuclear cluster with four metal centers interacting through a $\mu_4\text{-O}$ bridging atom. The central $\{\text{Mn}_4\}$ core is best described as a distorted Mn_4 tetrahedron.¹²⁶ Tetranuclear manganese carboxylate complexes have also been reported.¹²⁵ Also, an unprecedented mixed-charged state in a supramolecular assembly of ligand-based mixed-valence redox isomers has been reported¹²⁷ and a novel $\{\text{Co}^{\text{III}}(\mu\text{-O})_2\text{Co}^{\text{III}}\}$ complex has been stabilised by hydrogen bonds at room temperature.¹²⁸

A novel synthetic approach to trinuclear 3d–4f complexes has been devised that allows specific exchange of the central metal of a trinuclear zinc(II) complex of a tetraoxime ligand, H_4L^{133} , with a lanthanide(III) ion.¹²⁹ Pendent $-\text{OMe}$ groups at the periphery of the complex help recognise the larger, more highly charged Ln^{III} ions. A



trimacrocyclic derivative of 1,4,7-triazacyclononane (L^{134}) has been used to synthesise trimeric and hexameric copper(II) complexes whereby the hexameric complexes comprise copper(II) ions connected by hydroxo bridges.¹³⁰ Further trimeric copper(II) complexes have been synthesised with N,N,N',N' -tetramethylethylenediamine (L^{135}) and this is one of several examples of copper(II) trimers reported.^{131,132} A novel triangular complex $[\text{Ni}(\text{SCN})_2L^{136}]_3$ was generated *via* self-assembly from $\text{Ni}(\text{SCN})_2$ and the readily prepared imine-based ligand L^{136} , $(\text{C}_5\text{H}_4\text{N})-\text{CH}=\text{N}-\text{N}=\text{CH}-(\text{C}_5\text{H}_4\text{N})$. Hydrogen-bonded hexamers in crystals comprising complexes of the type $[L^{137}]\text{-M}(\text{CO})_3\text{L}'$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{L}' = \text{CO}, \text{CN}t\text{Bu}$) have been prepared and characterised ($L^{137} = 4\text{-}[(\text{pyridine-2-ylmethylene})\text{amino}]\text{phenol}$).¹³³ This aggregation of the complexes in the solid state follows general patterns due to the formation of multiple hydrogen bonds giving infinite chains, dimers and a cyclic hexamer, see Fig. 43.

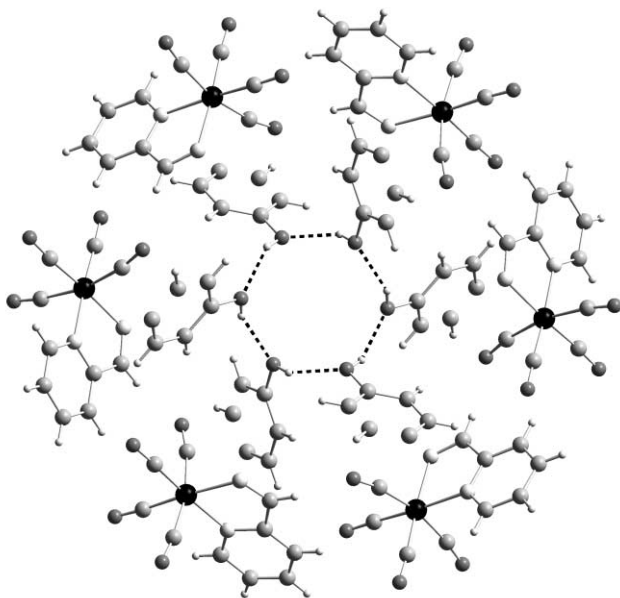


Fig. 43 The hydrogen-bonded hexamer is shown above.

A conjugated bimetallic Pd(II) complex has been synthesised *via* oxidative complexation and a tetracyclic Pd(II) complex *via* self-assembling complexation.¹³⁴ The conjugated homobimetallic palladium(II) complex $[(L^{138})Pd(qd)Pd(L^{138})]$ ($qd =$ quinonediiimine, $H_2L^{138} = N,N'$ -bis(2-phenylethyl)-2,6-pyridinedicarboxamide) was obtained in a one-pot reaction by the *in-situ* oxidative complexation of 1,4-phenylenediamine with the palladium(II) complex $[(L^{138})Pd(MeCN)]$ while in the absence of an additional ligand $[(L^{138})Pd(MeCN)]$ was converted to the amide-bridged macrocyclic tetramer $[Pd(L^{138})]_4$. It is interesting that the qd bridged complex appears to be stabilised, at least in part by $\pi-\pi$ interactions, see Fig. 44.

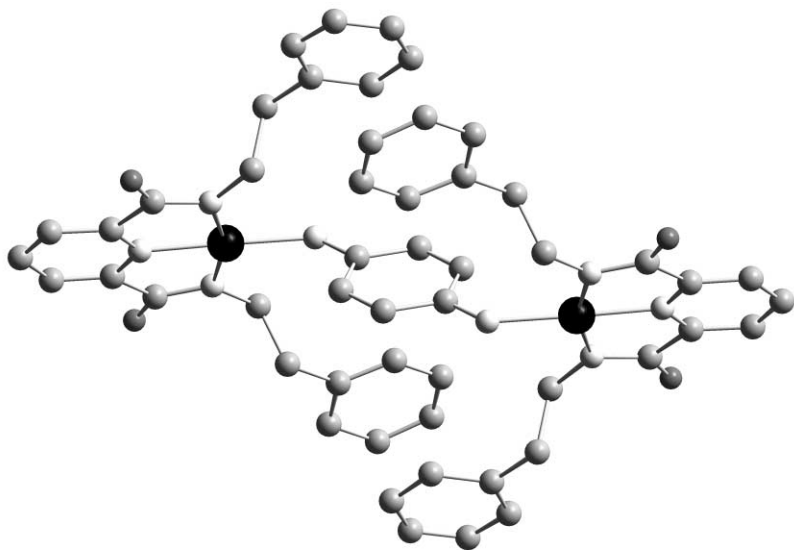
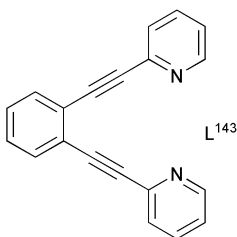
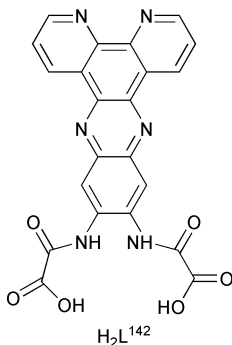
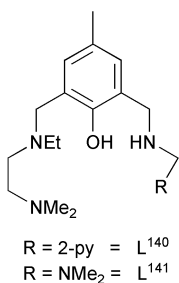


Fig. 44 The structure of the Pd dimer complex based on L^{138} .

A new approach to the transport of metal salts *via* the encapsulation of anions in dinuclear Cu(II) complexes has been developed where $[Cu_2(L^{139})_2SO_4][SO_4]$ ($L^{139} = 2,2'$ -[1,6-hexanediy]bis[(methylimino)methylene]]bis[4-*tert*-butyl-6-(phenylazomethyl)-phenol]).¹³⁵ Using this ligand design approach both the metal ion and anion can be complexed in the same ligand framework.¹³⁶ Dinuclear, tetranuclear and pentanuclear nickel(II) complexes of the related, reduced asymmetric compartmental ligands ($L^{140/141}$) (have been synthesised.^{137,138,139} The assembly of the dinuclear complex includes one $-OH$ bridge whereas the pentanuclear nickel(II) complexes includes 3- OH bridges and the tetranuclear nickel(II) complex contains an intramolecular $[H_3O_2]_2$ bridge. A new ligand, H_2L^{142} , bearing four coordination sites that may be metallated in a stepwise manner has been synthesised and complexed with Cu(II) and Fe(II) salts. This ligand is interesting as it incorporates three different types of coordinating sites and may have utility in the formation of trimetallic complexes in a controlled manner.¹⁴⁰ An interesting *trans*-chelating bis-pyridine ligand (L^{143}) has been synthesised and forms monomeric and bis ligand complexes with Pd salts.¹⁴¹



Oxidation of Ni₃(L¹⁴⁴)₄Cl₂ (L¹⁴⁴ = di-2,2'-pyridylamide) and exchange of the coordinating chloride ligands to Ni₃(L¹⁴⁴)₄(PF₆)₃ results in a complex where the Ni distances are 2.284(1) Å, indicating partial bonding character. Such molecules have been suggested as a possible precursor to polynickel molecular wires and devices, see Fig. 45.¹⁴² and this idea has been extended by use of an related tripyridyl rather than dipyridyl ligand. This has produced an unsymmetrical linear pentanuclear nickel string complexes.¹⁴³

Spontaneous resolution induced by self-organization of chiral self-complementary cobalt(III) complexes with achiral tripod-type ligands containing three imidazole groups has been achieved.¹⁴⁴ This work demonstrates an interesting evolution in chirality, that is, the progression from the synthetically simple achiral ligand, to the isolated chiral complex, to the homochiral assembled 2D layer, and then to the conglomerate. The synthesized Co(III) complexes have been synthesised with capped- and tripod type ligands containing three imidazole groups, [Co(H₃L^{145/6})]³⁺. This work

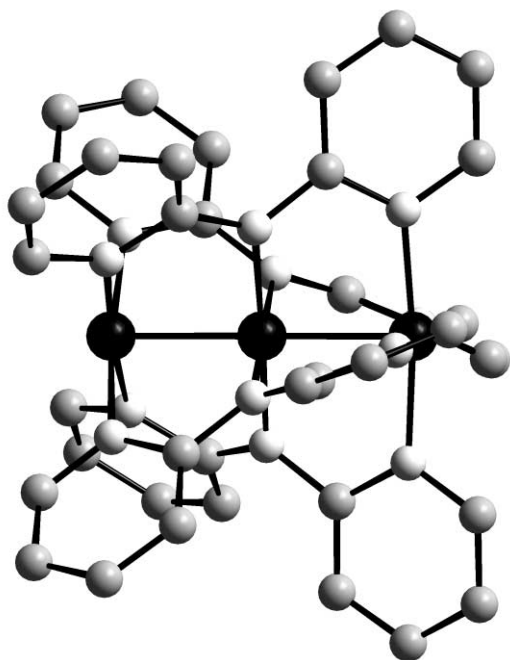
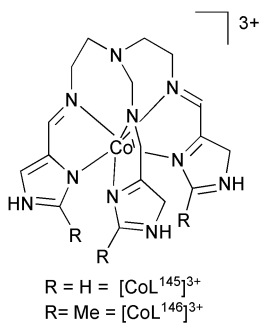


Fig. 45 Structure of the nickel three trimer and 'protecting' ligands.

addresses a central problem through metallocsupramolecular assembly, namely how to generate chirality from achiral components and how to force racemates of chiral molecules to undergo spontaneous resolution.¹⁴⁴ Extended architectures have been synthesised using the triply deprotonated $L_{-3H}^{145/146}$ complexes of cobalt(III) in combination with hydroquinone or resorcinol that form 1 : 3 adducts respectively through hydrogen bonding.¹⁴⁵



11 Ultra large polyoxomolybdate clusters

This area of metallosupramolecular chemistry is interesting as it appears that the dominant control in the overall supramolecular architecture lies with the oxidation state of the metal centres and the degree of condensation (*i.e.* degree of polymerisation of the Mo–O-based polyhedra) rather than the use of specific ligand design elements to control the aggregation and assembly of the structure through direct means. For instance the reduction of molybdate in the presence of Eu(III) ions at pH 1–2 with *ca.* 20% of the added molybdate reduced to Mo(V) leads to a giant wheel shaped cluster, similar to the archetypal $\{\text{Mo}_{154}\} = [\text{Mo}_{154}\text{O}_{462}\text{H}_{14}(\text{H}_2\text{O})_{70}]^{14-}$ but this time the inclusion of the Eu(III) ions leads to the assembly of a giant elliptical cluster dimer $\{\text{Mo}_{256}\text{Eu}_8\} = [2\{\text{Mo}_{128}\text{Eu}_4\text{O}_{388}\text{H}_{10}(\text{H}_2\text{O})_{81}\}]^{20-}$ with a diameter of *ca.* 4 nm, see Fig. 46. It appears that the inclusion of the Eu(III) ions causes a dramatic increase in curvature, when compared the original $\{\text{Mo}_{154}\}$ wheel which results in the elliptical shape of the new cluster.¹⁴⁶

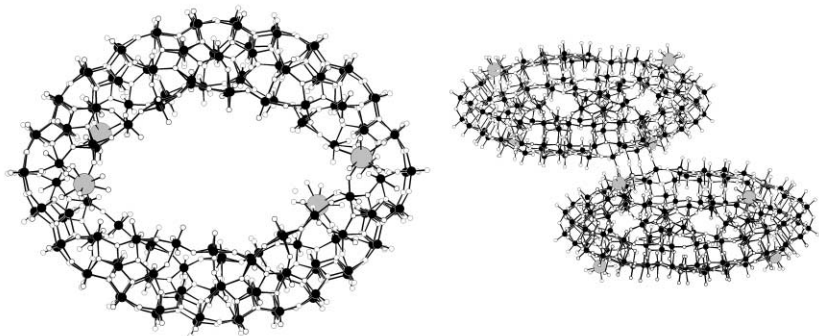


Fig. 46 The structure of the elliptical $\{\text{Mo}_{128}\text{Eu}_4\}$ wheel (LHS) and the structure of the full dimeric $\{\text{Mo}_{256}\text{Eu}_8\}$ cluster unit (RHS); the Eu(III) ions are depicted as grey spheres.

In a further dramatic development a new $\{\text{Mo}_{368}\}$ ‘lemon’ shaped cluster was synthesized with the approximate formula $[\text{H}_{16}\text{Mo}_{368}\text{O}_{1032}(\text{H}_2\text{O})_{240}(\text{SO}_4)_{48}]^{48-}$.¹⁴⁷ This cluster was synthesized from a solution acidified with sulfuric acid and this allowed the incorporation of the sulfate anion within the cluster framework dramatically altering the cluster framework compared to the wheel type clusters which are synthesized under similar conditions.¹⁴⁶ In this case the ‘lemon’ shaped cluster was synthesised at low pH (1–3) and with 30% of the available molybdate reduced to Mo(V). Thus the ‘lemon’ cluster is more highly reduced than most ‘Mo-blue’ species isolated to date and includes 48 sulfate anions on the inner sphere of the cluster. The cluster incorporates both positively and negative curved surfaces and has a maximum diameter of *ca.* 5 nm, see Fig. 47.

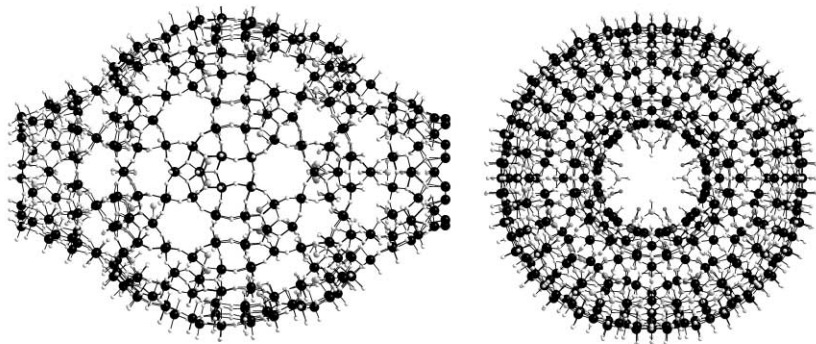


Fig. 47 The structure of the $\{\text{Mo}_{368}\}$ 'lemon' cluster. The side view is shown (LHS) and the top view is also shown (RHS).

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