
19 Macrocyclic and supramolecular coordination chemistry

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There are an ever increasing number of interesting and complex supramolecular architectures being designed and isolated. However, a slight shift is detected towards an increasing focus on the application of the supramolecular concept to the area of functional materials, sensors and components for molecular electronics and nanofabrication. An ultra-large $\{\text{Mn}_{84}\}$ wheel-shaped cluster has been isolated²⁶ that is a single-molecule magnet (SMM). Many new types of cluster frameworks have been synthesized, some notably (*e.g.* Fe_{14}) using hydrothermal methods.³⁵ Polyoxometalate clusters provide paradigms for cation capture and filtering,^{90–92} whereas ligand design has allowed access to a vast range of molecular grids,¹⁴¹ cubes,^{131,132} boxes¹²⁹ and other complexes with interesting functionality *e.g.* solvatochromism,¹⁷⁸ Zn(II)-sensors¹⁶³ and a nanovalve.¹³⁹

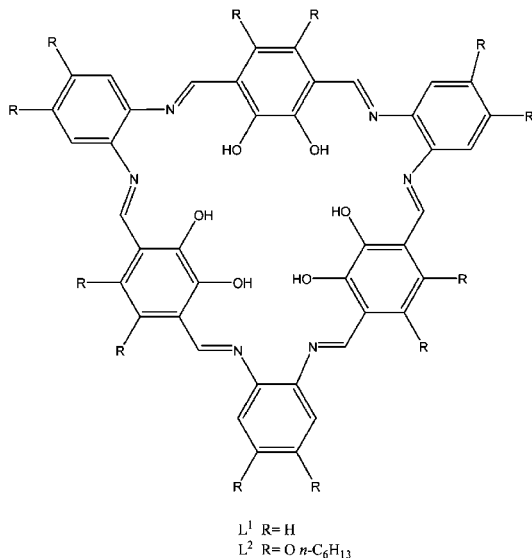
1 Introduction and scope

This report focuses on the development in design, synthesis and self-assembly of metal-based architectures and on the 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 and interesting ligands or metal-based moieties are discovered that are of consequence to the general area. Furthermore, a section on supramolecular and macrocyclic devices has been included to reflect a broader transition in the field to increasingly exploit and create functional devices and materials.

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/size 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.

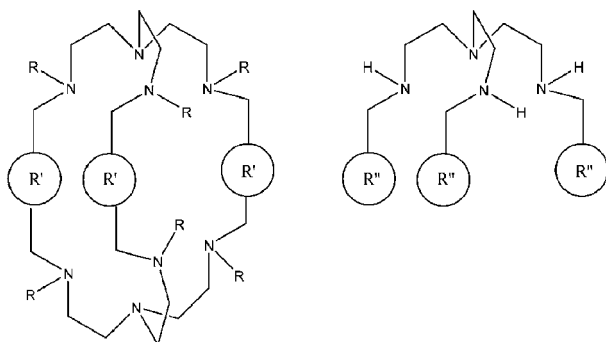
2 Macrocyclic ligands

The ion-induced assembly of tubular conjugated Schiff-base macrocycles into supramolecular assemblies has been accomplished using a new, well-defined conjugated macrocycle.² These macrocycles (L^1 and L^2) contain three tetradentate $\{N_2O_2\}$ binding sites organized in an equilateral triangle, as well as a pocket in the centre that is surrounded by six phenolic oxygen atoms resembling [18]crown-6. Complexation with a range of small cations ($M^+ = Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+$) causes a change in the physical properties that can be attributed to the formation of ionic assemblies.



The efficiency of a series of amino-azacryptands (L^3 – L^{16}) for encapsulation and extraction of the oxoanions pertechnetate and perrhenate (Fig. 1) from aqueous solution were investigated and compared with that of their open-chain counterparts.³ The aqueous formation constants for oxoanion association with the cryptands were determined by pH potentiometry and NMR and X-ray studies providing evidence for encapsulation. Interestingly, the extractabilities could not be explained solely on the basis of ligand lipophilicity; the level of protonation also plays an important role.

Anion effects in selective bifunctional metal salt extractants based on aza-thioether macrocycles has been examined whereby coordination of a metal cation to L^{17} breaks internal hydrogen bonding to allow anions to bind to the inner urea hydrogen site on the attached pendant arm.⁴ No anion binding occurs in the absence of a bound metal ion. Two-phase metal extraction studies with AgX salts and L^{17} confirm that the anion plays an important role, although it is likely that solubility of the resulting metal complexes in the organic phase is the predominant factor. The related macrocycle, L^{18} , where a sulfur donor replaces the ether oxygen in L^{17} , produces very similar results to those found for L^{18} with all of the Ag salts used. This indicates that



L^3 R = H R'' = p-xylyl
 L^4 R = CH₃ R'' = p-xylyl
 L^5 R = H R'' = o-xylyl
 L^6 R = CH₃ R'' = o-xylyl
 L^7 R = H R'' = 2,5-furanyl
 L^8 R = CH₃ R'' = 2,5-furanyl
 L^9 R = H R'' = 2,6-pyridyl
 L^{10} R = CH₃ R'' = 2,6-pyridyl

L^{11} R = benzyl
 L^{12} R = 2-pyridyl
 L^{13} R = 3-pyridyl
 L^{14} R = biphenyl
 L^{15} R = 2-naphthyl
 L^{16} R = 1-naphthyl

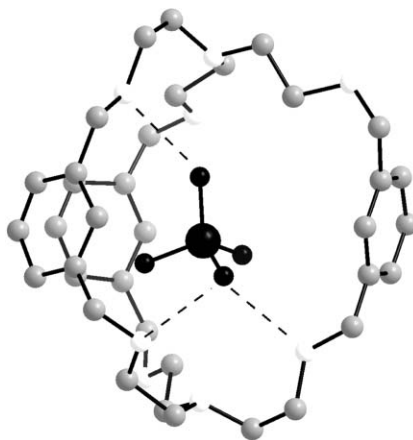
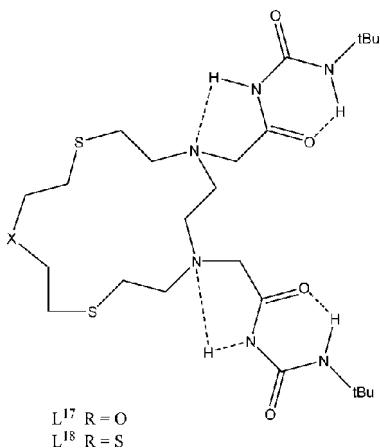


Fig. 1 Structure of L^5 complexed to ReO_4^{2-} via hydrogen-bonded interactions (dashed lines).

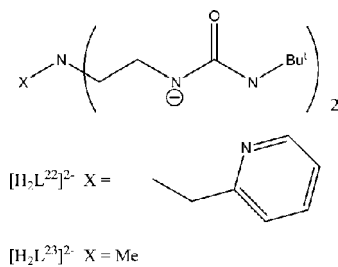
L^{18} also functions as a heteroditopic ion-pair receptor for $AgNO_3$ and $AgClO_4$. Indeed, chelate ring sequence effects on thermodynamic, kinetic and electron-transfer properties of heteroleptic ligands has recently been discussed.⁵

Primary and secondary coordination to scandium(III) has been examined with the crown ethers 15-crown-5 (L^{19}), 18-crown-6 (L^{20}) and 12-crown-4 (L^{21}) whereby hydrated scandium nitrate and the crown ethers react in ethanol solution to form a surprisingly diverse range of structural types containing the crown ethers hydrogen-bonded to the scandium-aquo-nitrato or scandium-aquo-hydroxo-nitrato complexes.⁶

The development of bio-inspired chelates with hydrogen-bond donors has been accomplished with the synthesis of the new multidentate tripodal compounds



bis[*N'*-*tert*-butylureido)-*N*-ethyl]-2-pyridylmethylamine (H_4L^{22}) and bis[*N'*-*tert*-butylureido)-*N*-ethyl]-*N*-methylamine (H_4L^{23}).⁷



These ligands contain two ureaethylene arms that, when deprotonated, bind to a metal ion and position two hydrogen-bond donors near the metal centre so that formation of intramolecular H-bonds with coordinated species is possible. The structure of the monomeric metal acetate complexes of H_4L^{22} and H_4L^{23} contain an intramolecular hydrogen bond (Fig. 2).

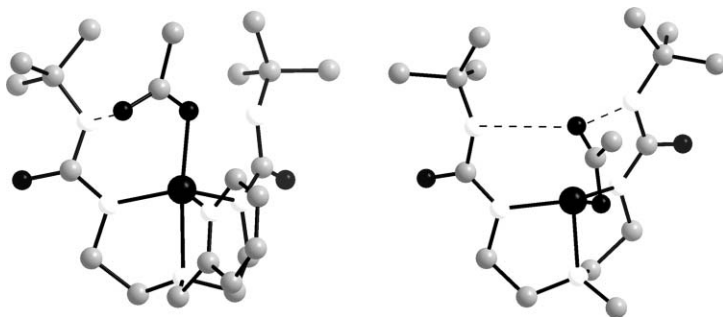
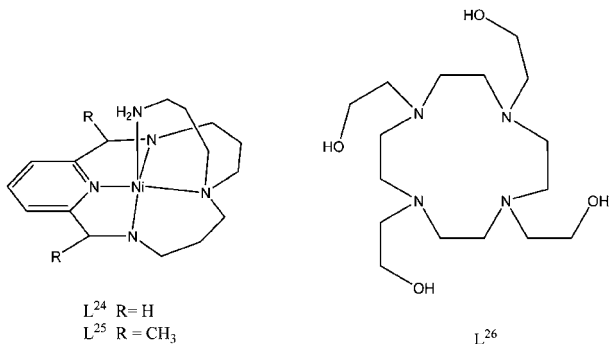
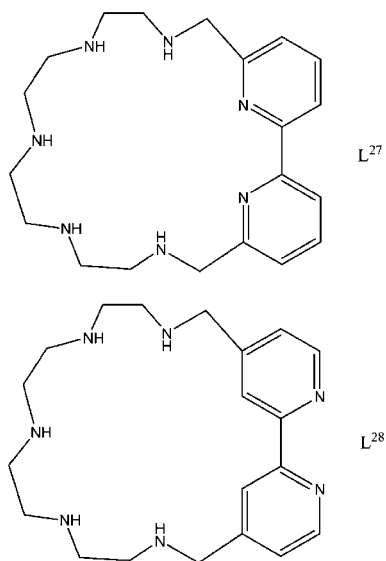


Fig. 2 Structure of L^{22} complexed to $Fe(OAc)$ (LHS) with one intramolecular H-bond, and structure of L^{23} complexed to $Fe(OAc)$ (RHS) with two intramolecular H-bonds.

Pyridine-containing macrocycles bearing aminopropyl pendant arms (L^{24} , L^{25}) have been synthesized by template condensation.^{8,9} This template condensation was carried out with nickel(II) and copper(II) salts. Demetallation of the nickel(II) macrocycles yielded stable pentadentate ligands that were used for the preparation of the copper(II) complexes. Also the cyclen derivatised with hydroxyethyl pendant arms (L^{26}) forms a diverse range of mononuclear and polynuclear lanthanide(III) complexes.¹⁰



The complexation of dipyrindine-containing macrocyclic polyamines L^{27} and L^{28} with different binding units has been examined.¹¹



Coordination of these macrocycles to copper(II) and nickel(II) salts has been investigated with potentiometric and spectrophotometric UV-vis titrations in aqueous solutions (Fig. 3). While in L^{27} all the nitrogen donor atoms are convergent inside the macrocyclic cavity, in L^{28} the heteroaromatic nitrogen atoms are located outside.

The stability and structure of mono- and di-nuclear Cu(II), Ni(II) and Zn(II)

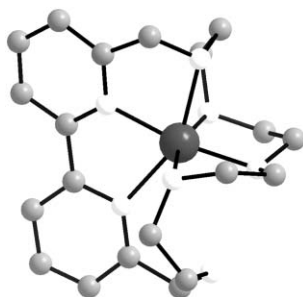
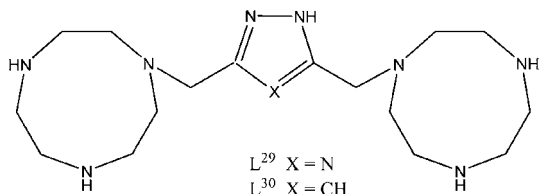
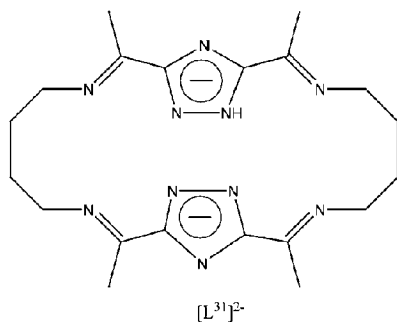


Fig. 3 The structure of L^{27} complexed to copper(II) is shown.

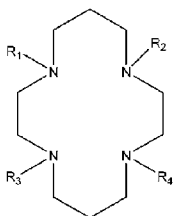
complexes of pyrazole- and triazole-bridged bis-macrocycles has been examined.¹² The two ligands L^{29} and L^{30} complex with copper(II), nickel(II) and zinc(II) salts to form a series of mononuclear $[ML^{29-30}H_m]^{(n+2)+}$ ($n = -3, -2, -1, 0, 1, 2$) and dinuclear species $[M_2L^{29-30}H_m]^{(m+4)+}$ ($m = 0, -1, -2, -3$).



A new Schiff-base macrocycle is obtained by the lead(II) ion-templated [2 + 2] condensation of 3,5-diacetyl-1*H*-1,2,4-triazole and 1,4-diaminobutane in the presence of sodium hydroxide.¹³ Transmetalation of the resulting di-lead complex, $Pb_2(L^{31})(ClO_4)_2$, in acetonitrile with two equivalents of $CoCl_2 \cdot 6H_2O$ leads to the isolation of an orange, six-coordinate complex, $[Co^{II}_2(L^{31})(NCO)_2]$, which is the first structurally characterized complex of a triazolite-containing macrocycle to date (Fig. 4).



The interaction of a series of successively *N*-benzylated derivatives of cyclam, L^{32} – L^{36} , with selected transition and post-transition metal ions has been investigated.¹⁴



- L^{32} R1 = benzyl, R2,R3,R4=H
 L^{33} R1, R3 = benzyl, R2, R4 = H
 L^{34} R1, R2 = benzyl, R3, R4 = H
 L^{35} R1, R2,R3 = benzyl, R4 = H
 L^{36} R1-R4 = benzyl

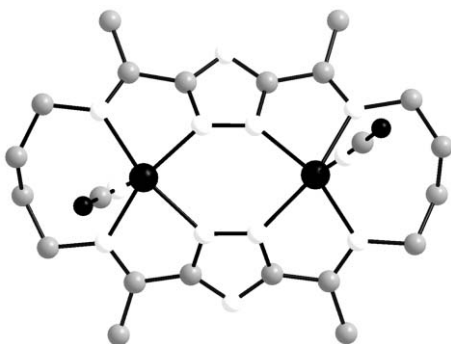
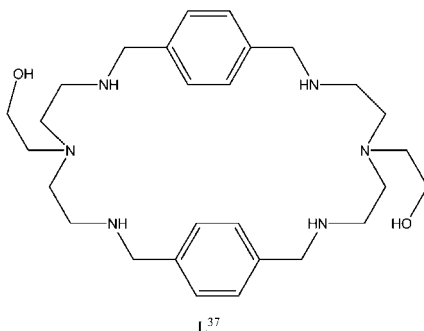


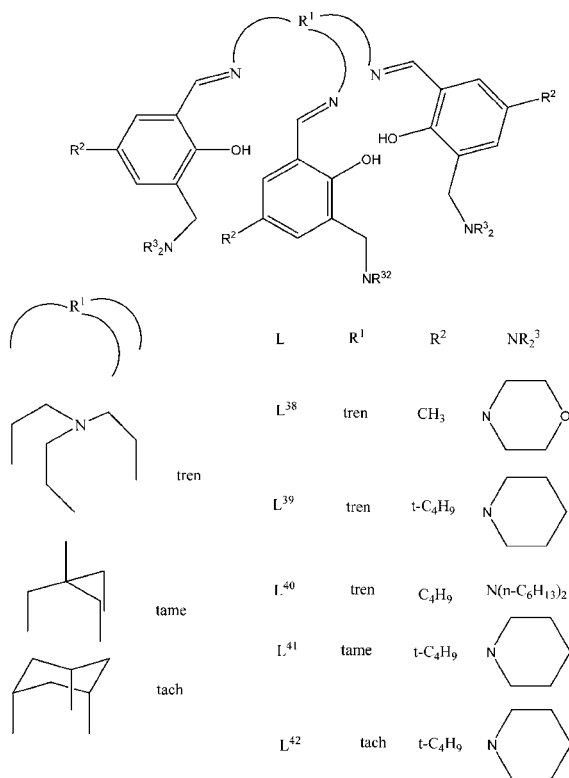
Fig. 4 Representation of the structure of $[Co^II_2(L^{31})(NCO)_2]$.

A novel imidazolate-bridged heterodinuclear $Cu(II)-Zn(II)$ complex has been derived from a macrocyclic ligand, L^{37} , with two hydroxyethyl pendants.¹⁵



Hexadentate tris-salicylaldimine ligands (L^{38-42}) bearing *ortho-N*-dialkyl-aminomethyl substituents have been shown to function as ditopic ligands for $NiSO_4$ or $NiCl_2$.¹⁶ The incorporation of the Ni ion into the $[N_3O_3]^{3-}$ site templates

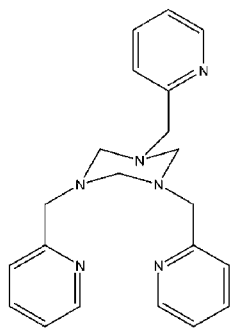
the pendant alkylammonium groups to allow them to hydrogen bond to the attendant anion(s). Formulation as complexes of the trianionic/tricationic ligand is supported by X-ray structure determinations of solvated forms of the complexes $[\text{Ni}(\text{L}^{41})\text{SO}_4]$ and $[\text{Ni}(\text{L}^{41})\text{Cl}]\text{Cl}$. The kerosene-soluble ligand L^{40} functions as a good extractant for nickel salts, showing high selectivity for recovery of NiCl_2 over NiSO_4 and demonstrates the potential of these novel zwitterionic extractants for nickel(II) salts.



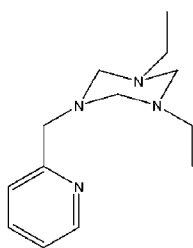
The syntheses of several novel copper(I) and copper(II) compounds containing triazacyclohexanes with one or three 2-pyridylmethyl substituents (L^{43} , L^{44}) are described.¹⁷ In particular, the complex of L^{44} reacts with dioxygen to form a complex with a $\text{Cu}_4(\text{OH})_4$ cubane core.

The potentially nonadentate ligand H_3L^{45} has been synthesized and complexed with several lanthanide ions.¹⁸ The resulting complexes have high water solubility and show highly rigid C_3 -symmetric solution structures. Furthermore, all the complexes present mononuclear nine-coordinated solid-state structures and the coordination polyhedron is a slightly distorted, tri-capped trigonal prism.

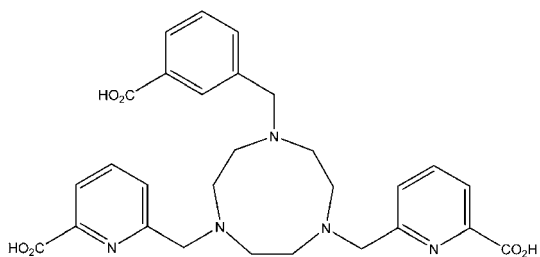
A unique trinickel(II) complex has been synthesized using the novel triple-salen ligand H_6L^{46} , which bridges three Ni(II)-salen units through a *meta*-phenylene linkage.¹⁹



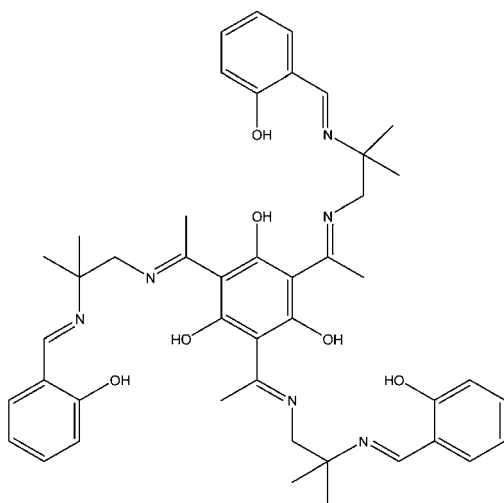
L⁴³



L⁴⁴



H₃L⁴⁵



H₆L⁴⁶

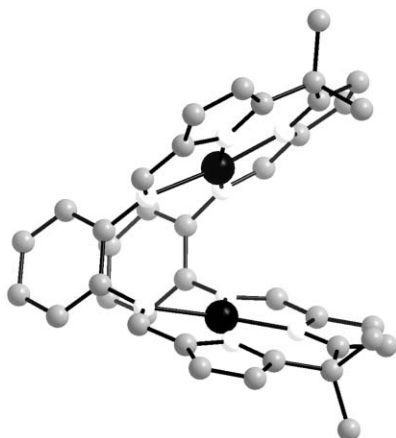
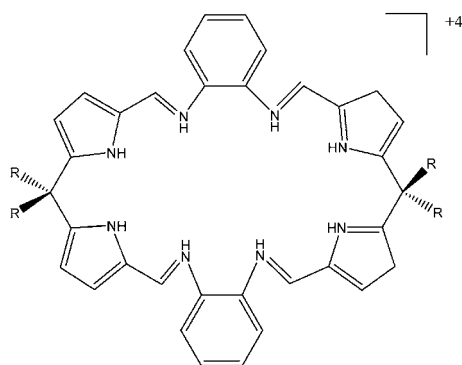
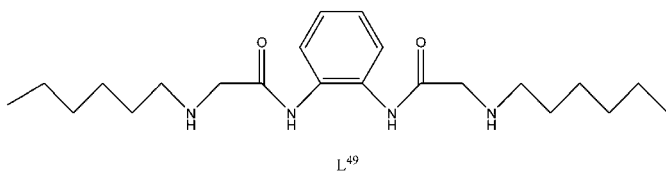


Fig. 5 Representation of the structure of $[\text{Pd}_2(\text{L}^{47})]$.

The complexation of palladium(II) by a unique family of [2 + 2] diiminodipyrromethane macrocycles (L^{47} , L^{48}) yields compounds that adopt structures reminiscent of Pac-Man porphyrins (Fig. 5).²⁰

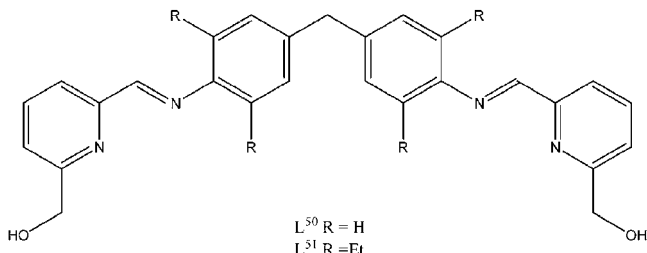


A novel family of redox-active, dinuclear transition metal-based cryptands self-assembled from dithiocarbamate ligands (L^{49}) has been synthesized.²¹ Further, depending upon the nature of the spacer groups, these new cryptand systems have been shown, *via* electrochemical studies, to recognise the binding of cations or anions.

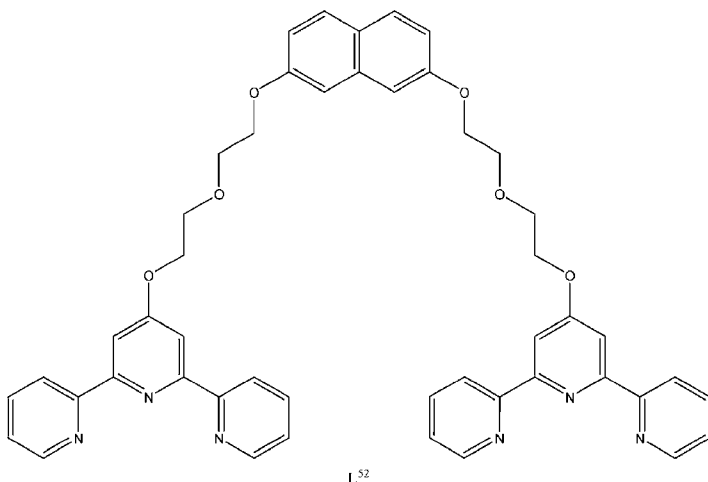


L^{49}

The aggregation of metallo-supramolecular *meso* and helical dimeric architectures has been observed when the periphery of the ligands L^{50} or L^{51} are derivatised with a hydroxy ligand.²² The hydrogen-bond sites aggregate the architectures into polymeric arrays, with the selection of anion determining whether this is self-H-bond aggregation or anion-mediated H-bond aggregation.

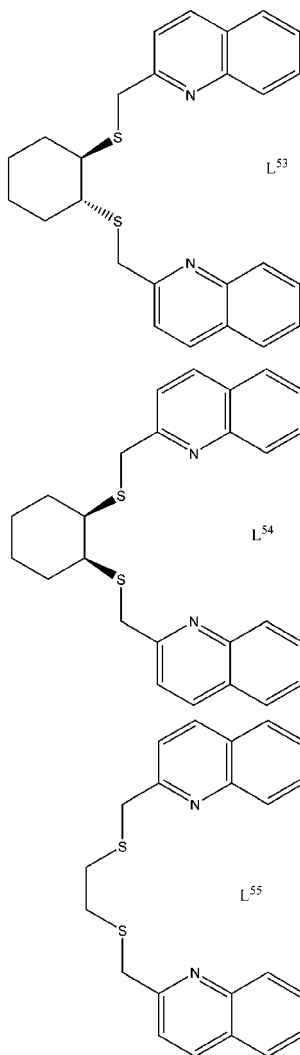


A new ditopic ligand based upon a 2,7-disubstituted naphthalene bearing two terpy-terminated bis(ethyleneoxy) substituents, L^{52} , has been prepared and shown to give a conformationally locked [1 + 1] macrocycle upon reaction with iron(II) salts (Fig. 6).²³



The new ligands *R,R-trans-S,S'*-bis[methyl(2'-quinolyl)]-1,2-dithiacyclohexane (L^{53}), *cis-S,S'*-bis[methyl(2'-quinolyl)]-1,2-dithiacyclohexane (L^{54}), and 1,6-bis(2'-quinolyl)-2,5-dithiahexane (L^{55}) have been synthesized and their complexes with copper(I) and copper(II) prepared.²⁴ The ligand/metal systems are bistable, as the complexes with copper in both its oxidation states are stable under the same conditions as solids and in solution.

A series of structurally characterized copper complexes of two pyridazine-spaced cryptands in redox states + (I,I), (II,I), (II), (II,II) are reported. The hexa-imine cryptand L^{56} [formed by the 2 + 3 condensation of 3,6-diformylpyridazine with tris(2-aminoethyl)amine (tren)] is able to accommodate two non-stereochemically



demanding copper(I) ions, resulting in $[\text{Cu}^{\text{I}}_2L^{56}](\text{BF}_4)_2$, or one stereochemically demanding copper(II) ion, resulting in $[\text{Cu}^{\text{II}}L^{56}](\text{BF}_4)_2$. The structurally characterized, octa-amine cryptand L^{57} , prepared by sodium borohydride reduction of L^{56} , is therefore more flexible (Fig. 7).²⁵

3 Metallomacrocycles and cyclic clusters

The largest single-molecule magnet (SMM), a $\{\text{Mn}_{84}\}$ cluster wheel of composition $[\text{Mn}_{84}\text{O}_{72}(\text{O}_2\text{CMe})_{78}(\text{OMe})_{24}(\text{MeOH})_{12}(\text{H}_2\text{O})_{42}(\text{OH})_6]$, has recently been discovered

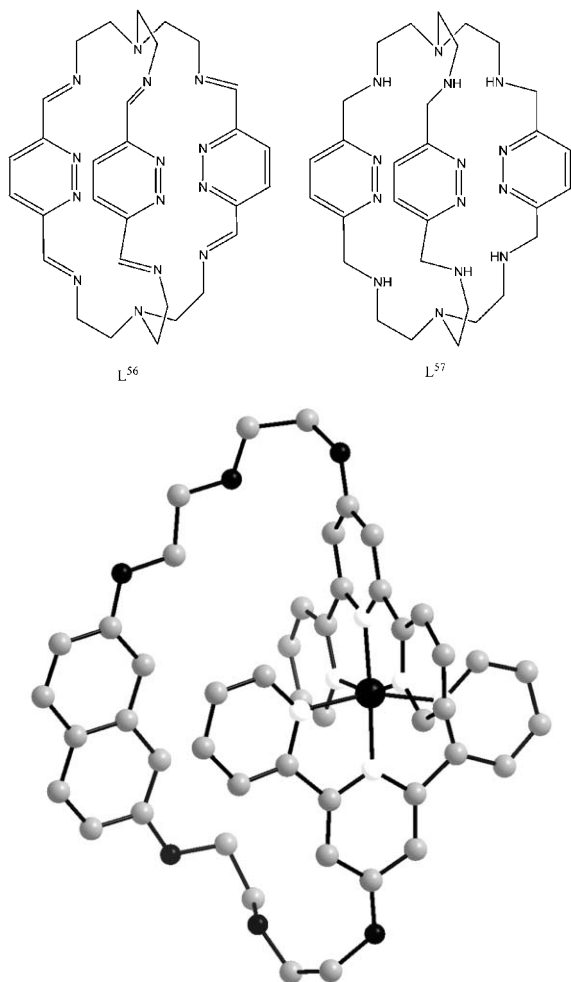


Fig. 6 Representation of the structure of $[\text{Fe}(\text{L}^{52})]^{2+}$.

(Fig. 8).²⁶ This represents the largest wheel cluster comprising first row transition metal ions and has an inner diameter of 1.9 nm and an outer diameter of 4.2 nm, and is 1.2 nm thick. This was synthesized using $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4]$ as a precursor. The wheels line up in the solid state to reveal a nanoporous supramolecular nanotube, and magnetic studies of this cluster reveal SMM-type behaviour at 1.5 K.

The formation of several new wheel-type clusters derived from the parent $[\text{Cr}_8\text{F}_8(\text{O}_2\text{CCMe}_3)_{16}]$ has been accomplished. If this $\{\text{Cr}_8\}$ wheel is synthesized in the presence of a secondary amine then a new type of open ring, or horseshoe, of the formula $[\text{Cr}_6\text{F}_{11}(\text{O}_2\text{CCMe}_3)_{10}]^{3-}$ ($\text{O}_2\text{CCMe}_3 = \text{L}^{58}$) is generated (Fig. 9).²⁷ However, if a second metal ion that does not favour an octahedral geometry is added, further new structural types are formed, e.g. $[\text{Cr}_6(\text{VO})_2\text{F}_8(\text{O}_2\text{CCMe}_3)_{15}]$, when the reaction is

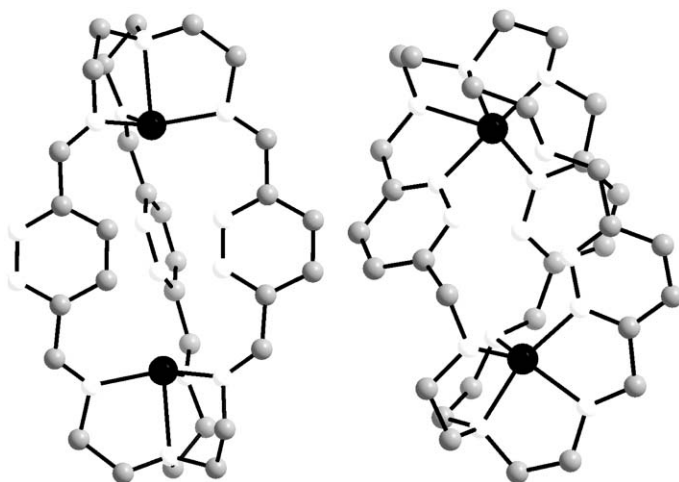


Fig. 7 Representation of the structure of $[\text{Cu}_2\text{L}^{56}]$ (LHS) and $[\text{Cu}_2\text{L}^{57}]$ (RHS).

carried out in the presence of vanadyl acetate. A new distorted structural type is formed in the presence of basic copper carbonate in the form of $[\text{Cr}_{10}\text{Cu}_2\text{F}_{14}(\text{O}_2\text{CCMe}_3)_{22}]^{2+}$. The inclusion of zinc(II) causes the formation of a regular wheel $[\text{Cr}_7\text{ZnF}_8(\text{O}_2\text{CCMe}_3)_{16}]^{2+}$ whereby the zinc(II) can be located within the ring (Fig. 9).

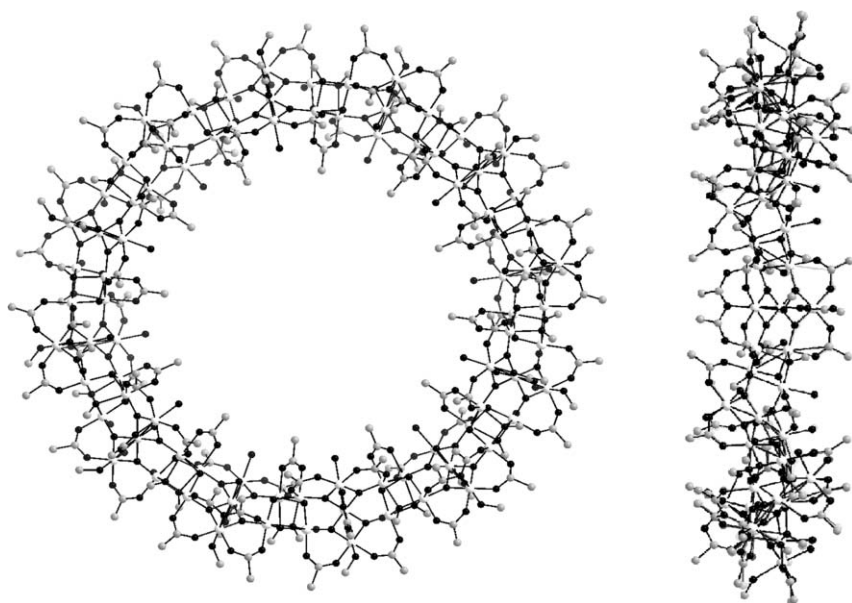


Fig. 8 Representations of the structure of $\{\text{Mn}_{84}\} = [\text{Mn}_{84}\text{O}_{72}(\text{O}_2\text{CMe})_{78}(\text{OMe})_{24}(\text{MeOH})_{12}(\text{H}_2\text{O})_{42}(\text{OH})_6]$ wheel cluster (top view LHS, side view RHS).

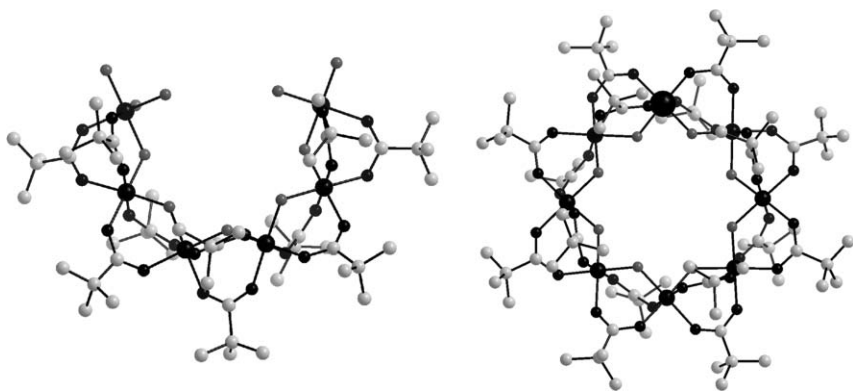


Fig. 9 Structure of the $[\text{Cr}_6\text{F}_{11}(\text{O}_2\text{CCMe}_3)_{10}]^{3-}$ horseshoe (LHS) and the structure of $[\text{Cr}_7\text{ZnF}_8(\text{O}_2\text{CCMe}_3)_{16}]^{2+}$ (RHS) (the F atoms are shown as dark grey spheres). The hydrogen-bonded amine molecule is omitted from the centre of the cluster for clarity and the Zn(II) ion is shown by the large black sphere.

A novel anion encapsulation process has been found to give rise to neutral supramolecular assemblies of cyclic copper(II)-based complexes.²⁸ In this work a series of five polymerization isomers, $[\{\text{cis-Cu}^{\text{II}}(\mu\text{-OH})(\text{L}^{59})\}_n]$ ($n = 6, 8, 9, 12,$ and 14 ; $\text{L}^{59} = \text{pz}$), is formed (Fig. 10). The metallacyclic ring sizes are not dependent upon the nature of the encapsulated anion: 6-membered rings are part of the structures

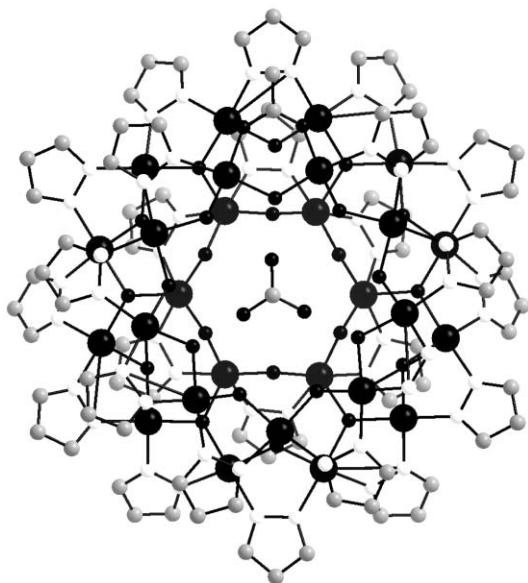


Fig. 10 The $\{\text{Cu}(\mu\text{-OH})(\mu\text{-L}^{59})\}_{6+12}$ compound is shown here, in which a carbonate ion is encapsulated between this unit and a 9-membered ring.

where $n = \{6 \text{ and } 12\}$ and when $n = 6, 12$ and 9 , whereas 9-membered rings are encountered when $n = \{6, 12\}$ and 9 and $n = \{18, 14, \text{ and } 9\}$. The aggregation of metallacycles is specific to the encapsulated anion: the smaller chloride finds a snug fit between two 6-membered rings, and the planar carbonate requires a 6- and a 9-membered ring, whereas the tetrahedral sulfate is encapsulated among 8-, 9- and 14-membered rings. The structures of the series of metallacycles $\{[cis-Cu(\mu-OH)(\mu-L^{59})]_n\}$ ($n = 6, 8, 9, 12, \text{ and } 14$) resemble those of crown ethers and natural ionophores and can be considered as fully protonated, copper-containing metallacrowns.

The generation of 'XMY' species as potential monomers for forming $[M(\mu-X)(\mu-Y)]_n$, an oligomer or polymer based on the edge-connectivity of a tetrahedron, was recently shown to produce a diverse range of complexes.²⁹ In this way, it could be expected that the controlled aggregation of low-coordinate, transition metal complexes can lead to the generation of unusual oligomers, polymers or clusters based on $[(^tBu_3Si)FeX]_n$. For instance, $[Fe(\mu-Cl)(\mu-SSi^tBu_3)]_{12}$ was formed (Fig. 11) using this idea along with the related $[Fe(\mu-I)(\mu-SSi^tBu_3)]_{14}$.

A $D_{y10}(OC_2H_4OCH_3)_{30}$ ($OC_2H_4OCH_3 = L^{60}$) has been self-assembled that represents the largest lanthanide ring to be obtained without some kind of template.³⁰ This demonstrates that large rings also occur for the lanthanides even with simple oxygen donor ligands without template effects (Fig. 12).

A metallamacrocycle containing 12 Zn^{2+} ions, making it the largest member of a family of pyrazole-bridged cyclic metal clusters, has been synthesized from the reaction of $[Zn(ClO_4)_2]$ with 5-methyl-3-phenylpyrazole, 2-mercaptoethanol, and

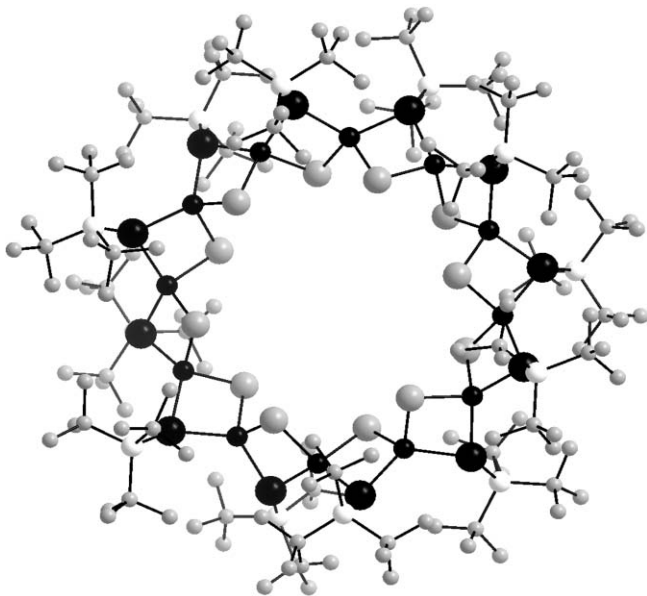


Fig. 11 Representation of the structure of $Fe(\mu-Cl)(\mu-SSi^tBu_3)]_{12}$.

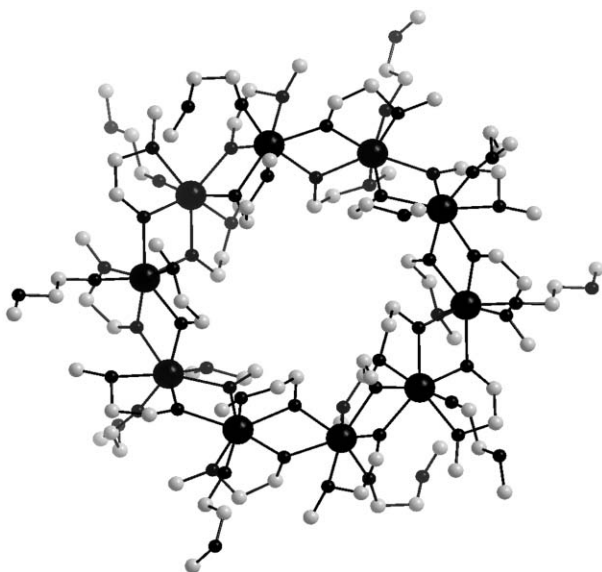


Fig. 12 Representation of the structure of $\text{Dy}_{10}(\text{OC}_2\text{H}_4\text{OCH}_3)_{30}$.

NaOH to give the hexameric, dodecanuclear metallamacrocycle $[\text{Zn}_2(\text{L}^{61})_2(\text{OCH}_2\text{CH}_2\text{S})_6]$ ($\text{L}^{61} = 5\text{-methyl-3-phenylpyrazole}$). The cluster is formally neutral as the +24 charge of the 12 Zn^{2+} centres is balanced by the 12 deprotonated pyrazole rings and the six doubly-deprotonated 2-mercaptoethanol molecules.³¹

Alcoholysis of $[\text{Fe}_6\text{O}_2(\text{OH})_2(\text{O}_2\text{C}^t\text{Bu})_{10}(\text{L}^{62})_2]$ affords ferric wheels of different nuclearities (L^{62-} = the anion of 2-(hydroxyethyl)pyridine). Hydrolysis in methanol yields $[\text{Fe}_{10}(\text{OMe})_{20}(\text{O}_2\text{C}^t\text{Bu})_{10}]$, whereas phenol gives the structurally unprecedented wheel $[\text{Fe}_8(\text{OH})_4(\text{OPh})_8(\text{O}_2\text{C}^t\text{Bu})_{12}]$, and is the first to contain phenoxide.³² Whereas alcoholysis of preformed tetranuclear and hexanuclear iron(III) clusters has been employed for the synthesis of four higher-nuclearity clusters, treatment of $[\text{Fe}_4\text{O}_2(\text{O}_2\text{CMe})_7(\text{bpy})_2](\text{ClO}_4)$ with phenol affords the hexanuclear cluster $[\text{Fe}_6\text{O}_3(\text{O}_2\text{CMe})_9(\text{OPh})_2(\text{bpy})_2](\text{ClO}_4)$. Reaction of $[\text{Fe}_6\text{O}_2(\text{OH})_2(\text{O}_2\text{CR})_{10}(\text{hep})_2]$ ($\text{R} = ^t\text{Bu}$ or Ph ; hep = deprotonated 2-(2-hydroxyethyl)pyridine) with PhOH affords the new 'ferric wheel' complexes $[\text{Fe}_8(\text{OH})_4(\text{OPh})_8(\text{O}_2\text{CR})_{12}]$ ($\text{R} = ^t\text{Bu}$ or Ph).³³

The reaction of the sodium salt dihydrate of 2-mercaptocotinic acid (H_2L^{63}) with di-*n*-butyltin dichloride in benzene affords a novel 18-tin-nuclear macrocyclic complex, which is a highly centrosymmetric 48-member macrocycle containing two centrosymmetric ladders of hydrolysis (Fig. 13).³⁴

4 Cluster frameworks

A tetradecametallic Fe^{II} cluster has been synthesized under hydrothermal conditions by heating a solution of $[\text{Fe}_3\text{O}(\text{O}_2\text{CMe})_6(\text{H}_2\text{O})_3]\text{Cl}$ in methanol in the presence of the potential bridging ligand benzotriazole (BtaH; HL^{64}) at 100 °C for 12 h. The cluster

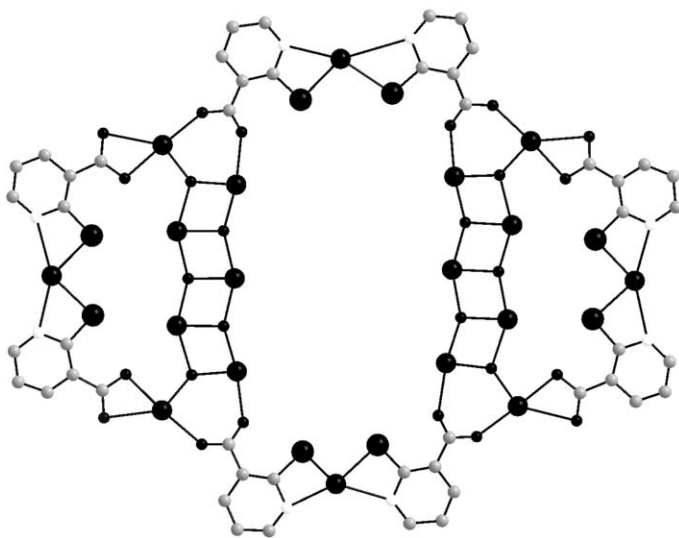


Fig. 13 Depiction of the structure of the $\{\text{Sn}_{18}\}$ macrocyclic cluster.

has the composition, $[\text{Fe}_{14}(\text{L}^{64})_6\text{O}_6(\text{OMe})_{18}\text{Cl}_6]$ (Fig. 14). The complex has pseudo-three-fold symmetry and the metallic core can be described as a hexa-capped hexagonal bipyramid with the caps on alternate faces. Preliminary magnetic investigations suggest that this cluster has a magnetic ground state where $S = 23$ representing the highest spin state so far found for a pure-iron cluster.³⁵

Phosphonate-based ligands have recently been utilised in the formation of polymetallic iron complexes by the reaction of the well-known Fe(III) carboxylate

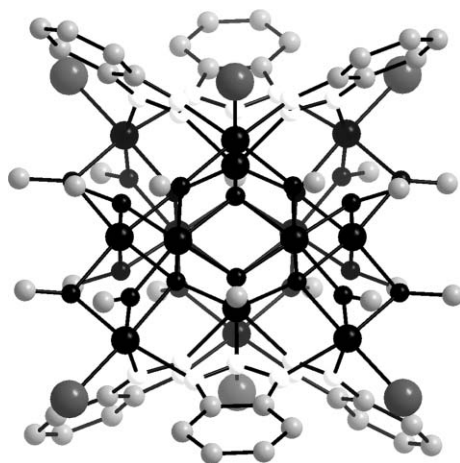


Fig. 14 Representation of the structure of $[\text{Fe}_{14}(\text{L}^{64})_6\text{O}_6(\text{OMe})_{18}\text{Cl}_6]$; the chloride ions are shown as dark grey spheres.

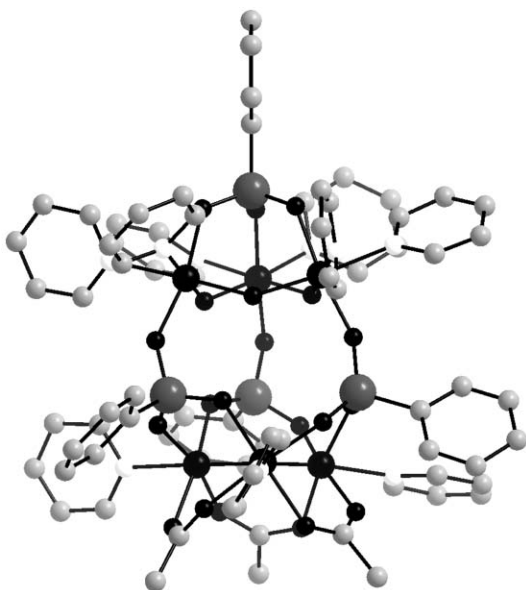
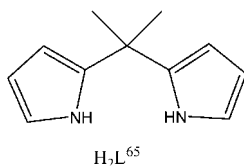


Fig. 15 Depiction of the structure of $[\text{Fe}_6\text{O}(\text{OH})_3(\text{O}_2\text{CMe})_3(\text{O}_3\text{PPh})_4(\text{py})_9](\text{NO}_3)_2$; the phosphorus atoms are shown in dark grey.

triangles $[\text{Fe}_3\text{O}(\text{O}_2\text{CR})_6(\text{H}_2\text{O})_3]\text{X}$, ($\text{R} = \text{H}, \text{CH}_3, \text{Ph}$ or CMe_3 ; $\text{X} = \text{NO}_3^-$ or Cl^-) with phenylphosphonate. The variation of R and X gives rise to a number of cages, *e.g.* $[\text{Fe}_6\text{O}(\text{OH})_3(\text{O}_2\text{CMe})_3(\text{O}_3\text{PPh})_4(\text{py})_9](\text{NO}_3)_2$, Fig. 15, ($\text{R} = \text{CMe}_3$, $\text{X} = \text{NO}_3^-$), and $[\text{Fe}_4\text{OCl}(\text{O}_2\text{CPh})_3(\text{O}_3\text{PPh})_3(\text{py})_5]$ ($\text{R} = \text{Ph}$, $\text{X} = \text{Cl}^-$). Further variation in the amount of pyridine changes the reaction path yielding several more complexes.³⁶ The use of phosphonate ligands has been extended to cobalt(II) and alkali metal ions whereby the ligands ‘encourage’ a Platonic relationship between cobalt(II) and alkali metal ions. The metal core has a high symmetry related to a Platonic solid and the choice of alkali metal used in the base used for deprotonation appears to influence the resulting structures.³⁷

The dipyrroliide ligand H_2L^{65} promotes the formation of a unique tetranuclear iron(II) compound that contains both diazaferrocenyl and distorted-tetrahedral iron centres.³⁸



Two distinct types of iron coordination are observed: one is distorted tetrahedral in which the iron is σ -bound to four pyrroliide nitrogens; the other octahedral with η^5 -bonding to two pyrroliide rings so forming a diazaferrocene unit (Fig. 16).

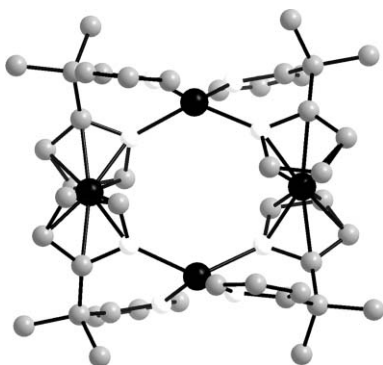


Fig. 16 Depiction of the structure of $[\text{Fe}(\text{L}^{65})_4]$.

The reaction of anhydrous FeCl_3 with HL^{65} in MeOH produces the pentanuclear complex $[\text{Fe}_5\text{O}_2(\text{OMe})_2(\text{L}^{64})_4(\text{HL}^{64})(\text{MeOH})_5\text{Cl}_5]$, containing a distorted tetrahedron of four Fe ions centred on a fifth Fe. The central Fe is antiferromagnetically-coupled to the peripheral Fe ions resulting in an $S = 15/2$ spin ground state.³⁹ The reaction of $[\text{NEt}_4]_2[\text{Fe}_2\text{OCl}_6]$ with sodium benzoate, 4,6-dimethyl-2-hydroxypyrimidine (L^{66}), and 1,1,1-tris(hydroxymethyl)ethane (H_3L^{67}) gives the undecametallic compound $[\text{NEt}_4][\text{Fe}_{11}\text{O}_4(\text{O}_2\text{CPh})_{10}(\text{L}^{67})_4(\text{L}^{66})_2\text{Cl}_4]$. Magnetic measurements indicate an $S = 11/2$ ground state with the parameters $g = 2.03$ and $D = -0.46 \text{ cm}^{-1}$. Single-crystal magnetic studies show hysteresis of molecular origin at $T < 1.2 \text{ K}$ with fast quantum mechanical tunnelling at zero field.⁴⁰

The reaction of cobalt(II) with citrate ions $[\text{L}^{68}]^{4-}$ yields a hexameric complex with the formula $\{[\text{Co}_4(\text{L}^{68})_4[\text{Co}(\text{H}_2\text{O})_5]_2]\}^{4-}$ (Fig. 17). Magnetic measurements show that this cluster behaves as a single-molecule magnet, displaying the largest energy barrier to reorientation of the magnetization for a non-manganese-based SMM.⁴¹ Increasing the crystallisation temperature of $[\text{Ni}_8(\text{L}^{68})_6(\text{OH})_2(\text{H}_2\text{O})_2]^{10-}$ causes a desolvation

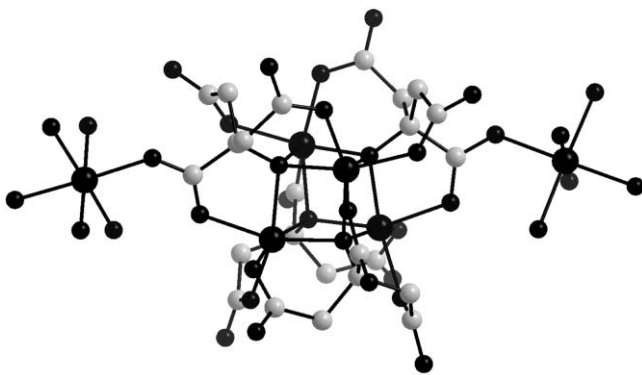


Fig. 17 Representation of the structure of $\{[\text{Co}_4(\text{L}^{68})_4[\text{Co}(\text{H}_2\text{O})_5]_2]\}^{4-}$.

process that leads to structural rearrangement of the cluster to $[\text{Ni}_8(\text{L}^{68})_6(\text{OH})_2]^{10-}$ with distinct magnetic properties.⁴²

A range of nickel(II)-based clusters has been characterized including tetranuclear nickel(II) complexes with μ_3 -1,1,3- and μ_4 -1,1,3,3- azide bridges,⁴³ a range of oximate-bridged tetranuclear nickel(II) rhombs,⁴⁴ and some hydroxyquinoline-bridged cobalt and nickel cubanes.⁴⁵ Furthermore, some novel cluster topologies for nickel(II) have also been found with the incorporation of alkaline-earth metals in the formation of $[\text{Ni}^{\text{II}}_6\text{Mg}^{\text{II}}_2]$ and $[\text{Ni}^{\text{II}}_8\text{M}^{\text{II}}]$ ($\text{M} = \text{Sr}, \text{Ba}$) cages⁴⁶ and novel trinuclear dipyrindylamido complexes of the first-row transition metals, $\text{M}_3(\text{dpa})_4\text{Cl}_2$ [dpa^- is the anion of di(2-pyridyl)amine = L^{69-} ; $\text{M} = \text{Cr}, \text{Co}, \text{Ni}, \text{Cu}$], have been reported. These compounds are interesting as they allow examination of possible induction metal-metal bonded interactions when the complexes are reduced.⁴⁷

An extended tritopic picolinic dihydrazide ligand with terminal oxime groups (H_4L^{70}) undergoes spontaneous self-assembly in the presence of copper acetate to produce a unique $\{\text{Cu}_{36}\}$ cluster of the form $[\text{Cu}_{36}(\text{L}^{70})_{12}(\mu_3\text{-OH})_8]^{16+}$ (Fig. 18) which

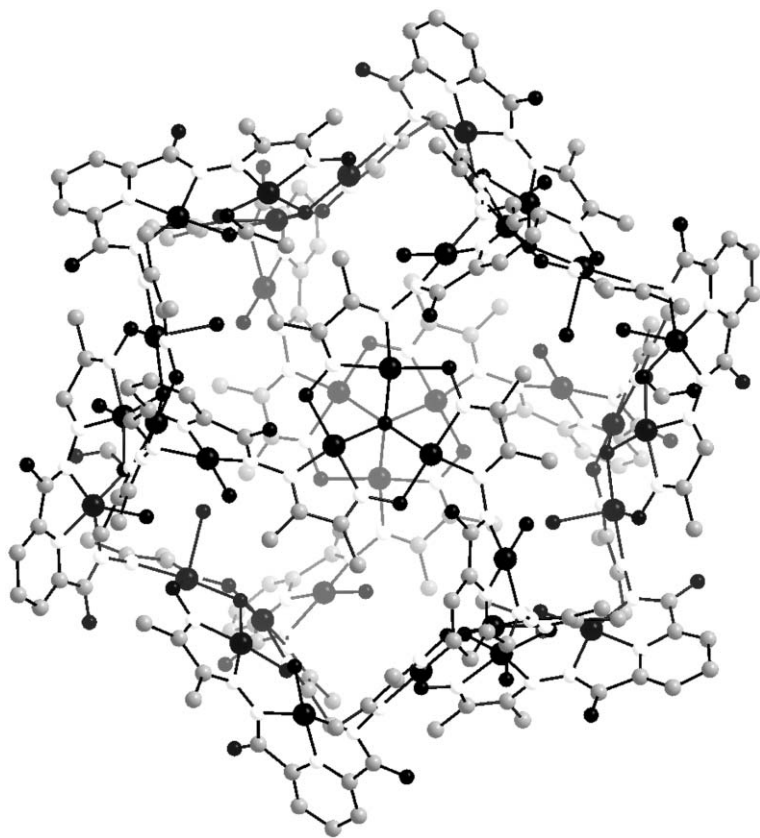
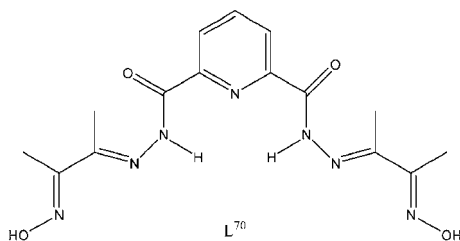


Fig. 18 Representation of the structure of $[\text{Cu}_{36}(\text{L}^{70})_{12}(\mu_3\text{-OH})_8]^{16+}$.

exhibits magnetic properties that utilise intramolecular antiferromagnetic exchange pathways.⁴⁸



A range of lower-nuclearity copper(II) complexes has also been identified. For instance, a hexa-copper(II) ‘barrel cluster’ with a spin ground state $S = 3$ has been constructed with eight chelating L-prolinato-type ligands, which in turn provide the eight oxygen donors trapping a sodium ion in the centre. The structure of the $[\text{Cu}_6\text{Na}]$ unit in the discrete system and in the infinite cluster-chain are essentially the same and both display intra-unit ferromagnetic super-exchange.⁴⁹ In a further study, trimethyltriazacyclohexane was used as a bridging ligand for triangular⁵⁰ units, and C–H hydride abstraction was observed to occur in a Cu_6 cluster when complexation of $[\text{Cu}(\text{MeCN})_4](\text{BF}_4)$ with N,N',N'' -trimethyl-1,3,5-triazacyclohexane in CH_2Cl_2 was performed. As such this leads to two⁵¹ clusters containing the triazacyclohexane as a ligand to triangular⁵⁰ units with the abstraction and incorporation of chloride and hydride.⁵² In a copper(II)-based⁵⁰ triangle, symmetry lowering and electron localization of a doublet spin state was observed, this being the one of the simplest forms of a spin-frustrated equilateral triangular lattice.⁵³ Many types of tetranuclear clusters have been isolated with many new types being discovered.^{54–58}

Further, the formation of an interesting heterometallic cluster was reported when the encapsulation of paramagnetic vanadium(IV) in an antiferromagnetically-coupled dodecanuclear copper(II) cage was accomplished. A $\{\text{Cu}_{12}\}$ cluster is formed around a $\{\text{VO}_5\}$ giving the overall formula $[\text{Cu}^{\text{II}}_{12}\text{V}^{\text{IV}}\text{O}_5\text{L}^{71}]_6$ $\{\text{H}_3\text{L}^{71}$ is N,N' -(2-hydroxypropane-1,3-diyl)bis(salicylaldehyde)) (Fig. 19).⁵⁹

The first example an oxo-bridged $\{\text{Zn}_6\}$ octahedron with a central zinc(II) cation has been isolated from the hydrothermal reaction of N -(phosphonomethyl)- N -methylglycine, $\text{MeN}(\text{CH}_2\text{CO}_2\text{H})(\text{CH}_2\text{PO}_3\text{H}_2)$ (H_3L^{72}), with zinc(II) acetate. The cluster has the formula $\{\text{Zn}_6\text{L}^{72}_6(\text{Zn})\}^{4-}$ in which seven zinc(II) cations form an unusual $\text{Zn}_6(\text{Zn})$ -centred octahedron with six of its Zn_3 triangular faces each further capped by a phosphonate group.⁶⁰ Several interesting silver(I)-based clusters have also been synthesized including supramolecular triangular and linear arrays of metal-radical solids using pyrazolato-silver(I) motifs,⁶¹ and highly luminescent trimetallic $\text{Ag}(\text{I})$ complexes.⁶²

The pace of development in manganese cluster chemistry has accelerated during the past months, one of the highlights of which was the isolation of the $\{\text{Mn}_{84}\}$ wheel (see Section 3).²⁶ A large $\{\text{Mn}_{30}\}$ cluster has also been synthesized by the same group which also utilises the archetypal $\{\text{Mn}_{12}\}$ SMM as a precursor to yield $[\text{Mn}_{30}\text{O}_{24}(\text{OH})_8(\text{O}_2\text{CCH}_2^1\text{Bu})_{32}(\text{H}_2\text{O})_2(\text{MeNO}_2)_4]$ (in which the oxidation states can be assigned as follows: 3Mn^{II} , 26Mn^{III} , Mn^{IV}). The structure of a central backbone is a



Fig. 19 Structure of $[\text{Cu}_{12}\text{V}^{\text{IV}}\text{O}_5\text{L}^{71}_6]$; the central V atom is shown as a large black sphere.

near-linear $[\text{Mn}_4\text{O}_6]$ unit, to either side of which are attached two $[\text{Mn}_{13}\text{O}_9(\text{OH})_4]$ units (Fig. 20).⁶³ Magnetic investigations demonstrate that the cluster is a SMM but no clear steps characteristic of quantum tunnelling of magnetization are observed.

The reaction of the neutral triangle $[\text{Mn}_3\text{O}(\text{PhCOO})_6(\text{py})_2(\text{H}_2\text{O})]$ with 1,1,1-tris(hydroxymethyl)ethane (H_3L)⁶⁷ affords novel dodecanuclear and octanuclear manganese complexes with unusual ladder-like cores built from edge-sharing

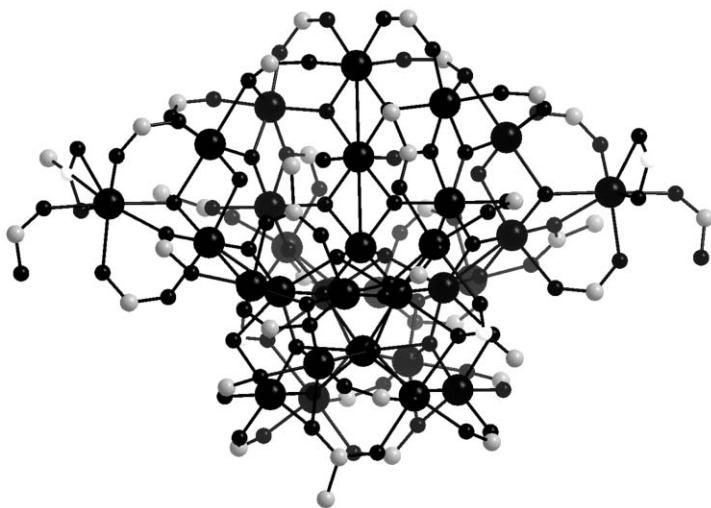


Fig. 20 Representation of the structure of the $\{\text{Mn}_{30}\}$ cluster.

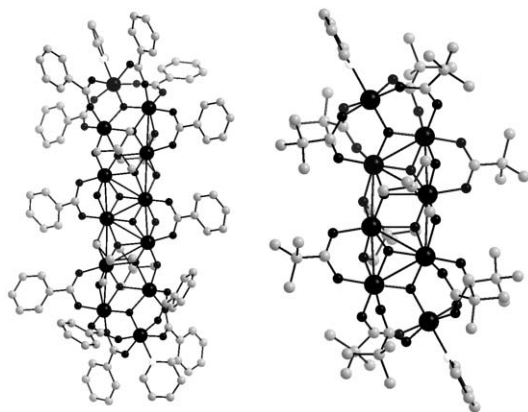


Fig. 21 Structure of the $\{Mn_{12}\}$ (LHS) and the $\{Mn_8\}$ (RHS).

triangles and with SMM-like behaviour (Fig. 21).⁶⁴ High-nuclearity cages can also be constructed *via* the dimerisation of a manganese triangle under solvothermal conditions.⁶⁵

A large variety of other Mn complexes have been found including hexanuclear manganese(II) single-molecule magnets based on the reaction of $Mn(O_2CMe)_2$ with salicylaldehyde which yields $[Mn_6O_2(O_2CMe)_2(L^{73})_6EtOH_4]$ (HL^{73} is salicylaldehyde).⁶⁶ Also, a trigonal-bipyramidal cyanide cluster with SMM properties⁶⁷ and a $\{Mn_8\}$ -based mixed-valence ($Mn^{IV}_6Mn^{III}_2$) compound have been reported,⁶⁸ as well as novel octa- and tetra-nuclear clusters formed in reactions with di-2-pyridyl ketone and phenyl 2-pyridyl ketone oxime.⁶⁹ Reaction of manganese salts with di-pyridyl ketone oxime yields a cationic 24-MC-8 manganese cluster of the form $[Mn^{II}_4Mn^{III}_6Mn^{IV}_2(\mu_4-O)_2(\mu_3-O)_4(\mu_3-OH)_4-(\mu_3-OCH_3)_2(L^{74})_{12}](OH)(ClO_4)_3$ (L^{74} = di-pyridyl ketone oxime).⁷⁰ The classical $\{Mn_{12}\}$ unit has even been derivatised with mixed carboxylate-sulfonate ligation: $[Mn_{12}O_{12}(O_2CMe)_8(O_3SPh)_8(H_2O)_4]$.⁷¹ Furthermore, a heterometallic hexanuclear cluster $\{Mn_4Ni_2\}$ with an $S = 8$ spin ground state has been synthesized,⁷² and polynuclear manganese complexes with the dicarboxylate ligand *m*-phenylenedipropionate have been used to generate a number of other clusters with different nuclearities and oxidation states.⁷³ Routes to high-nuclearity, fluoride-based octametallac and tridecametallic clusters of manganese have also been accessed,⁷⁴ as well as a range of other Mn-based clusters.^{63,75–77}

5 Polyoxometalates

The non-cyclic polyoxo(thio)molybdate(v)-sulfite $[[Mo_2^v(\mu-S)_2O_2]_6(\mu_3-SO_3)_4(\mu-SO_3)_{12}]^{20-}$ was prepared by self-condensation of the $[Mo_2^v(\mu-S)_2O_2]^{2+}$ building block. The overall cluster contains 12 Mo^v centres within the main structural unit. Each molybdenum atom has octahedral coordination and is bonded to a terminal oxo group, two $\mu-S_2$ ions and three sulfite (two $\mu-$ and one μ_3-) oxygen atoms. The 12 Mo^v atoms form six binuclear units $[Mo_2^v(\mu-S)_2O_2]^{2+}$ with a Mo^v-Mo^v separation of

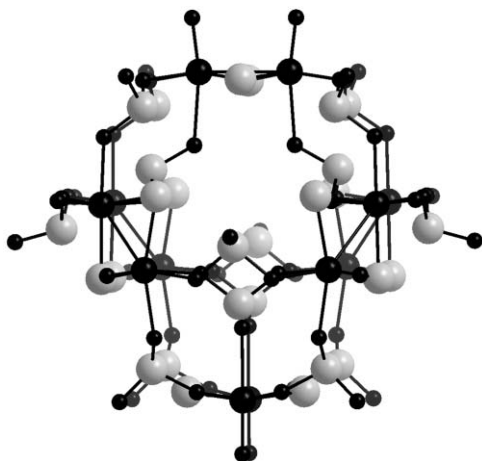


Fig. 22 Structure of $[[\text{Mo}_2^{\text{v}}(\mu\text{-S})_2\text{O}_2]_6(\mu_3\text{-SO}_3)_4(\mu\text{-SO}_3)_{12}]^{20-}$; the sulfur atoms are shown in grey.

2.828(7) Å (indicative of a single bond). Furthermore, the six $[\text{Mo}_2^{\text{v}}(\mu\text{-S})_2\text{O}_2]^{2+}$ moieties are connected to each other by 16 sulfite ligands. This compound demonstrates the versatility of the sulfite anion in the formation of polyoxometalate clusters⁷⁸ (Fig. 22).

A new family of Dawson-based $\{\text{Mo}_{18}\}$ polyoxometalate clusters has been discovered that incorporates two pyramidal C_{3v} anions rather than the normal T_d anions of the form $[\text{Mo}_{18}\text{O}_{54}\text{SO}_3]^{4-}$. In this case the SO_3^{2-} anions exhibit interesting supramolecular S...S interactions and the new clusters demonstrate thermochromic behaviour between 77 and 500 K⁷⁹ (Fig. 23).

A tetranuclear, manganous, Wells–Dawson sandwich-type polyoxometalate has been synthesized by the reaction of $\alpha\text{-Na}_{12}(\text{As}_2\text{W}_{15}\text{O}_{56})$ with an aqueous solution of

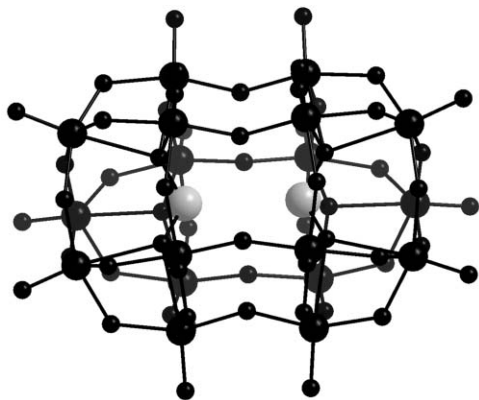


Fig. 23 Structure of $[\text{Mo}_{18}\text{O}_{54}\text{SO}_3]^{4-}$; the sulfur atoms are shown in grey.

MnCl₂, and has the structure $\alpha\beta\beta\alpha\text{-Na}_{16}(\text{Mn}^{\text{II}}\text{OH}_2)_2\text{Mn}^{\text{II}}_2(\text{As}_2\text{W}_{15}\text{O}_{56})_2$ (**1**). Electrochemical studies reveal that the presence of arsenic shifts the Mn waves to more positive potentials. Catalytic studies confirm that **1** is a significantly better catalyst for the H₂O₂-based epoxidation of *cis*-cyclooctene, cyclohexene, and 1-hexene than its counterpart containing P in place of As.⁸⁰

A new synthetic approach to the synthesis of new low-nuclearity polyoxometalate (POM) clusters has been achieved using ‘shrink wrapping’ counter ions in the synthesis of anionic POM clusters. This approach appears to allow the formation of cluster frameworks with unsymmetrical topology, low symmetry, and high negative charge such as [H₂Mo₁₆O₅₂]¹⁰⁻. The formation of symmetrical aggregates appears to be restrained and the [H₂Mo₁₆O₅₂]¹⁰⁻ cluster demonstrates a high nucleophilicity and can bind two divalent transition metal ions (Fe^{II}, Mn^{II}, Co^{II}, Ni^{II}, or Zn^{II}) to its framework yielding a family of isostructural complexes, [Fe₂(H₂O)₈H₂Mo₁₆O₅₂]⁶⁻⁸¹ (Fig. 24).

A derivatised, Anderson-type POM cluster has been synthesized using a solvothermal reaction to yield a cationic heteropolyoxovanadium(IV) cluster, [Mn^{II}V^{IV}₆O₆{(OCH₂CH₂)₂N(CH₂CH₂OH)}₆]²⁺, containing a fully reduced new cyclic {MnV₆N₆O₁₈} core with the Anderson structure. Interestingly, one pendant arm of each one of the six triethanolamine ligands (L⁷⁵) projects outward from the

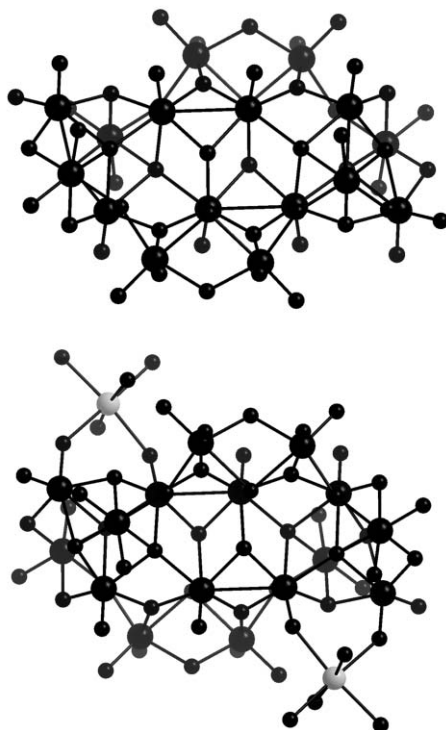


Fig. 24 Depiction of the structures of [H₂Mo₁₆O₅₂]¹⁰⁻ (top) and [Fe₂(H₂O)₈H₂Mo₁₆O₅₂]⁶⁻ (bottom); the Fe ions are shown as light grey spheres.

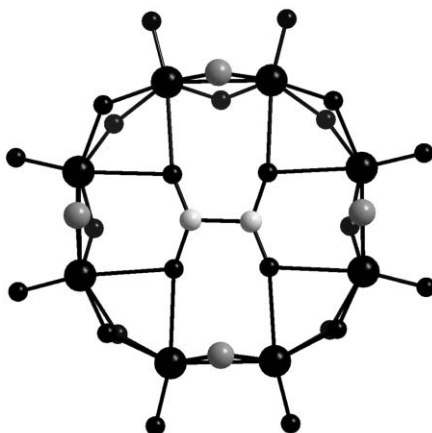
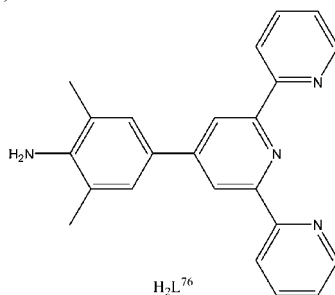


Fig. 25 Structure of $[\text{Mo}_8\text{S}_4\text{O}_{12}(\text{OH})_8(\text{C}_2\text{O}_4)]^{2-}$; the sulfur atoms are shown as large grey spheres.

hexagonal ring and is involved in hydrogen bonding with two spectator, charge-balancing chloride ions.⁸² A supramolecular tetradecanuclear copper(II) polyoxotungstate has been discovered that is comprised of four trivalent tungsten-based POM Keggin clusters of the form $\{[(\text{SiW}_9\text{O}_{34})(\text{SiW}_9\text{O}_{33}(\text{OH}))(\text{Cu}(\text{OH}))_6\text{Cu}]_2\text{X}\}^{23-}$, where X is Cl or Br and acts a central template bridging six copper(II) ions.⁸³ The inclusion of a large number of first row transition metal ions in these clusters is interesting and may provide a basis for further development. A hydrothermally synthesized new octameric ring, $[\text{Mo}_8\text{S}_4\text{O}_{12}(\text{OH})_8(\text{C}_2\text{O}_4)]^{2-}$, has been synthesized and characterized whereby the ring-shaped anion is built up by novel $[\text{Mo}_2\text{SO}_3]$ building blocks *via* edge-sharing connections (Fig. 25).⁸⁴

A terpyridine ligand is covalently linked to a hexamolybdate cluster through the Mo–N imido bond to yield an interesting hybrid POM–ligand complex (Fig. 26). The derivatised ligand (H_2L^{76})



is connected to the cluster *via* a Mo–N triple bond. This result opens the way for the preparation of hybrids containing covalently bonded transition metal complexes and polyoxometalate clusters.⁸⁵

Indeed, the formation of hybrid POM-based materials continues to be explored with the formation of networks based on $[\text{Mo}_6\text{O}_{19}]^{2-}$ POMs and crown ethers,⁸⁶

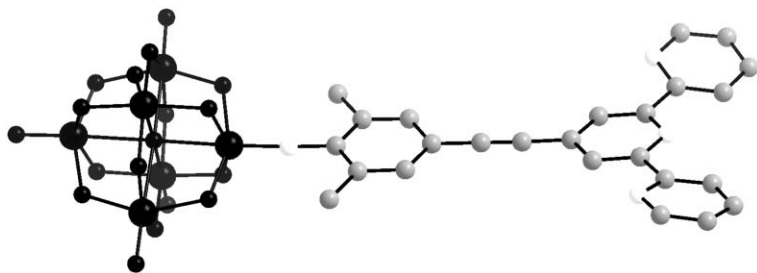


Fig. 26 Structure of the hybrid POM $[\text{Mo}_6\text{O}_{18}(\text{L}^{76})]$.

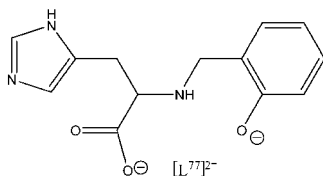
tungsten-based Keggin and copper(II)(bipy) complexes.⁸⁷ There are also some interesting POM-based spiral architectures based on the linkage of Anderson-based POMs with $\text{Cu}(\text{II})\text{bipy}$ ⁸⁸ units as well as a one-dimensional infinite double helicate formed by the bridging of $\text{Mo}(\text{VI})$ and $\text{Gd}(\text{III})$ ions by L-tartrate to yield an enantiopure, left-handed double helical chain.⁸⁹

There have been a number of advances in the synthesis of ultra-large polyoxometalate clusters including the isolation of a new type of inclusion species $[\text{Mo}^{\text{VI}}_{114}\text{Mo}^{\text{V}}_{32}\text{O}_{429}(\text{H}_2\text{O})_{50}(\text{KSO}_4)_{16}]^{30-}$. This comprises 16 encapsulated K^+ and SO_4^{2-} ions and shows an unusual 64-membered $\{\text{K}(\text{SO}_4)\}_{16}$ ring embedded into a wheel-shaped-type cluster host (Fig. 27). This is interesting as it means that the archetypal mixed-valence Mo wheels can be derivatised in extremely subtle ways to produce complex inclusion compounds.⁹⁰

Further developments in ultra-large spherical POM clusters with the composition $(\text{pent})_{12}(\text{linker})_{30} \cong \{(\text{Mo})\text{Mo}_5\text{O}_{21}(\text{H}_2\text{O})_6\}_{12}\{\text{Mo}_2\text{O}_4(\text{ligand})\}_{30}$ have been possible by manipulating the linker groups. When the linker is SO_3^{2-} or HPO_4^{2-} the cluster is able to take up cations so the uptake leads to stoichiometric preferences, *i.e.* $\{\text{Mo}_9\text{O}_9\}$ pores can function like a type of crown ether. Furthermore, these pores can act like primitive ion channels allowing the assembly of ions within and below the pore (Fig. 28).⁹¹ In addition, the $(\text{pent})_{12}(\text{linker})_{30}$ clusters have been found to be interesting vessels in which to study the assembly of water and small cations.⁹²

6 Capsules, threaded molecules and porphyrin assemblies

A molecular capsule has been synthesized that traps pyridine molecules *via* a combination of hydrogen bonding and copper(II) coordination. The capsule comprises an octameric $\text{Cu}(\text{II})$ complex, $[\text{Cu}_8(\text{L}^{77})_8(\text{py})_4(\text{H}_2\text{O})_8]$, synthesized from the tetradentate deprotonated ligand (L^{77}) (Fig. 29).⁹³



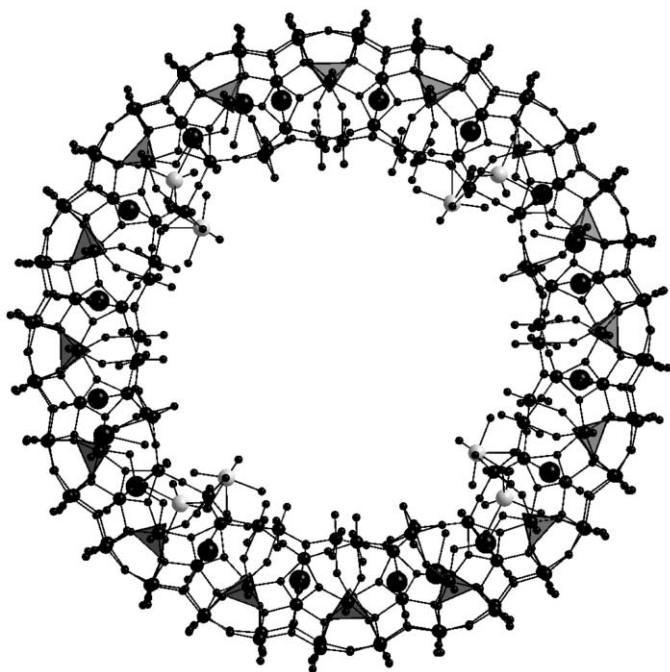
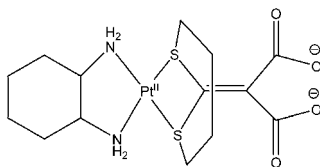


Fig. 27 Representation of the structure of $[\text{Mo}^{\text{VI}}_{114}\text{Mo}^{\text{V}}_{32}\text{O}_{429}(\text{H}_2\text{O})_{50}(\text{KSO}_4)_{16}]^{30-}$.

The platinum-based building block L^{78} complexes with copper(II) to yield a complex that contains a metal-centre hydrophobic pocket that has been shown to recognise pyridine.⁹⁴



$[\text{L}^{78}]^{2-}$

Ligand-directed molecular architectures have been assembled with cavities that can include anionic guests with the combination of L^{79-81} with silver(I) salts (Scheme 1).

These cavities comprise two-dimensional rectangular metallacycles and three-dimensional trigonal or tetragonal prisms.⁹⁵ Silver-based triangular cages have also been produced using more flexible ligands (L^{82} , L^{83}).⁹⁶

Bowl-shaped superstructures have been constructed by intra-clipping of resorcin-[4]arene derivatives (L^{84}) with two equivalents of $(\text{en})\text{Pd}(\text{NO}_3)_2$ in water and this cavity encloses several nitrate anions (Fig. 30).⁹⁷

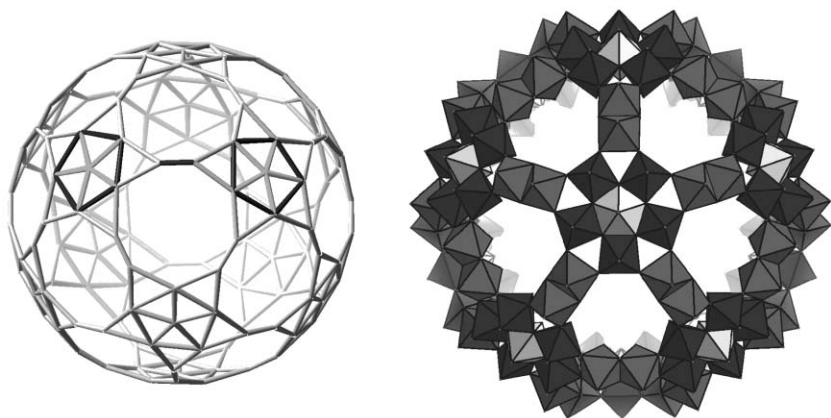


Fig. 28 Representations of the structure of the $(\text{pent})_{12}(\text{linker})_{30}$ cluster. A stick representation is shown on the LHS and a polyhedral representation of the RHS. In both case the $\{\text{Mo}_9\text{O}_9\}$ 'pores' are visible.

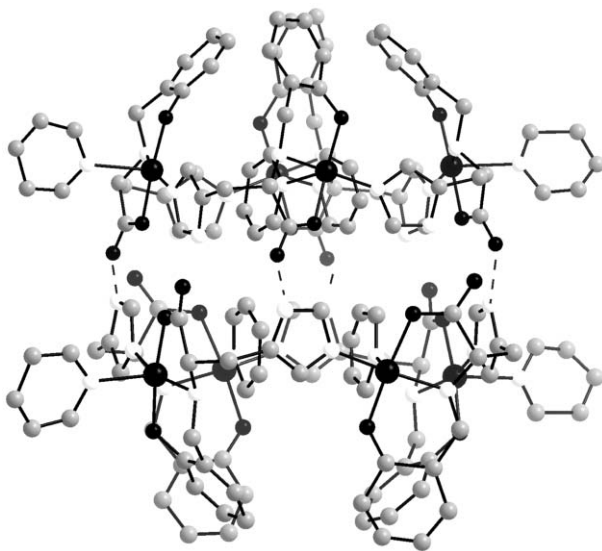
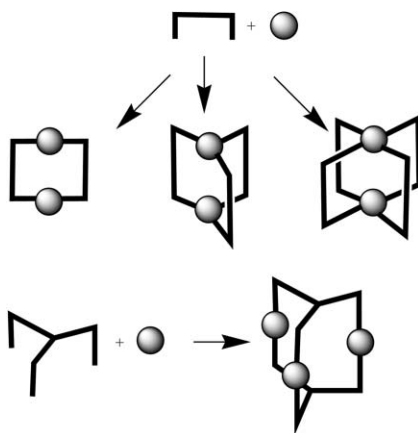
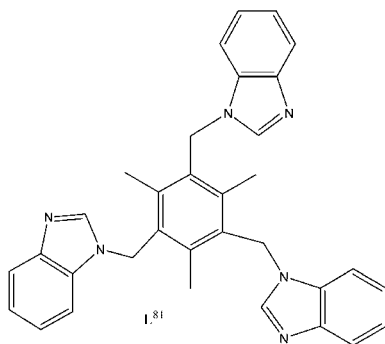
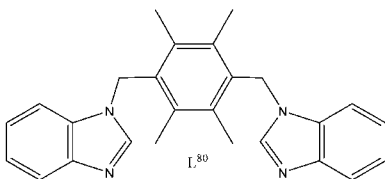
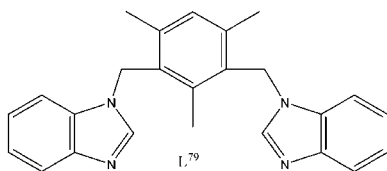


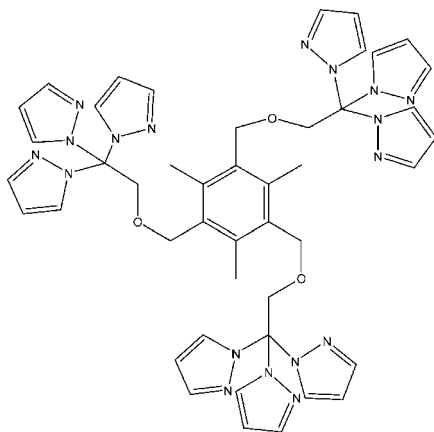
Fig. 29 Representation of the $[\text{Cu}_8(\text{L}^{77})_8(\text{py})_4(\text{H}_2\text{O})_8]$ hydrogen-bonded capsule.

Bowl-shaped cavitands have also been shown to self-assemble on surfaces to produce nano-structures.⁹⁸ Calixarenes continue to be explored as novel cavity-defining ligands, increasingly with harder metal ions such as titanium and europium ions bound to phenolate moieties.^{99–101}

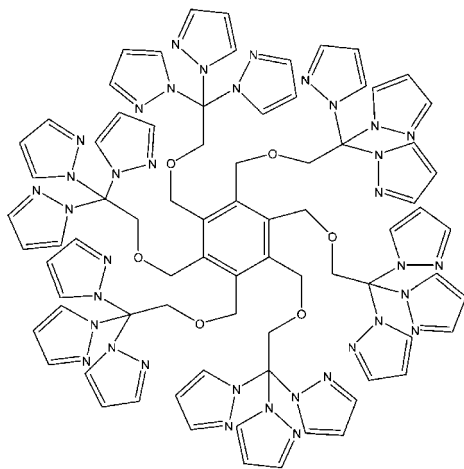
A simple general ligand system for assembling octahedral metal-rotaxane complexes has recently been described producing complexes of the form $(\text{ML}^{85}\text{L}^{86})(\text{ClO}_4)_2$. This is interesting as the imine-based ligand appears to assist in the efficient assembly of [2]rotaxanes around octahedral metal ions in a



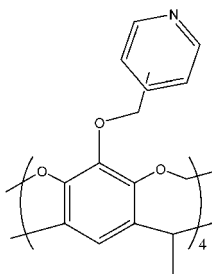
Scheme 1



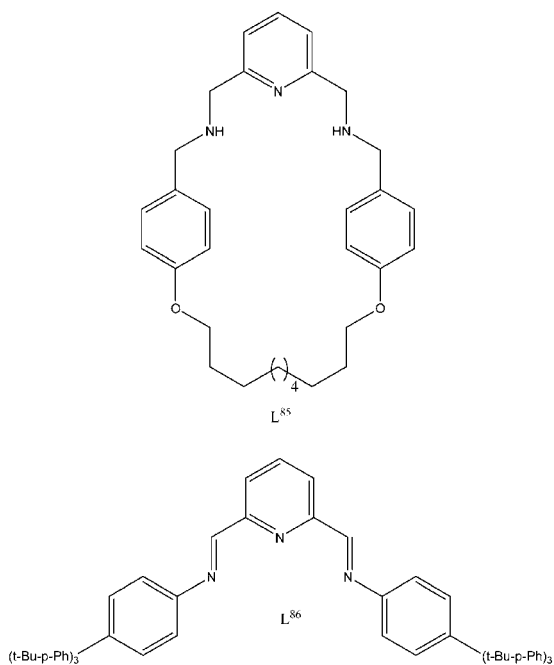
L⁸²



L⁸³



L⁸⁴



five-component self-assembly reaction, producing rotaxanes under true thermodynamic control (Fig. 31).¹⁰²

A polymeric rotaxane has been constructed from the inclusion complex of β -cyclodextrin (L^{87}) and 4,4'-dipyridine (L^{88}) by coordination of nickel(II) ions.¹⁰³ A [2]catenane has been constructed around a $Ru(\text{diimine})_3^{2+}$ which has been utilised as

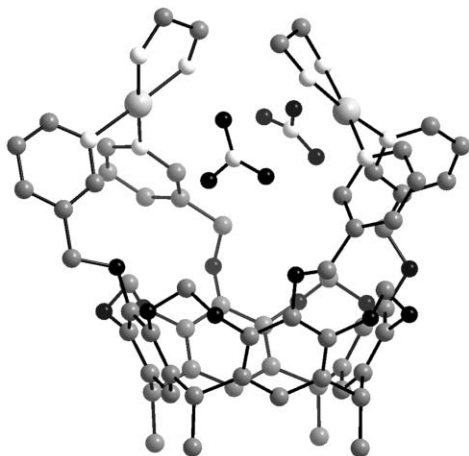


Fig. 30 Representation of the structure of $\{[Pd(en)_2][L^{84}]\}^{4+}$ with two nitrates present in the cavity.

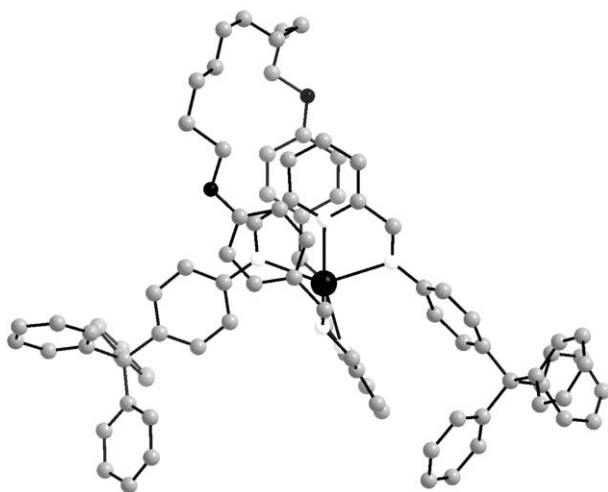
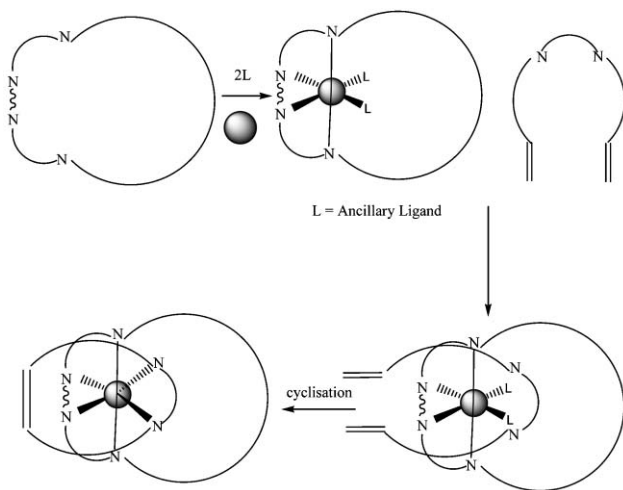


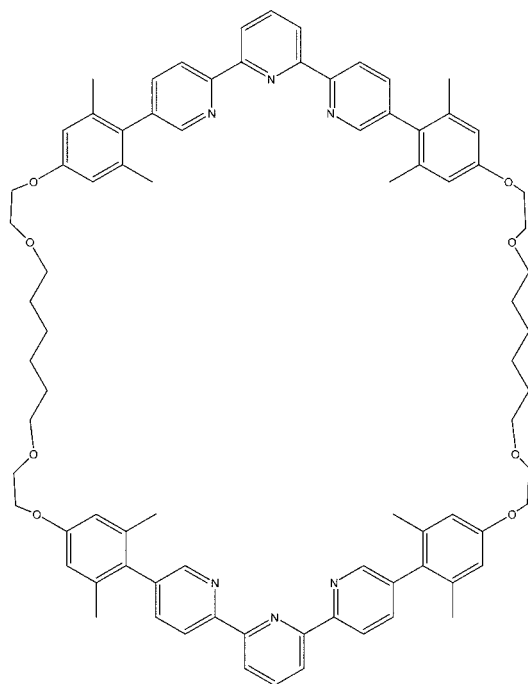
Fig. 31 Representation of the crystal structure of the [2]rotaxane $[(ML^{85}L^{86})]^{2+}$; the t Bu groups have been omitted for clarity.



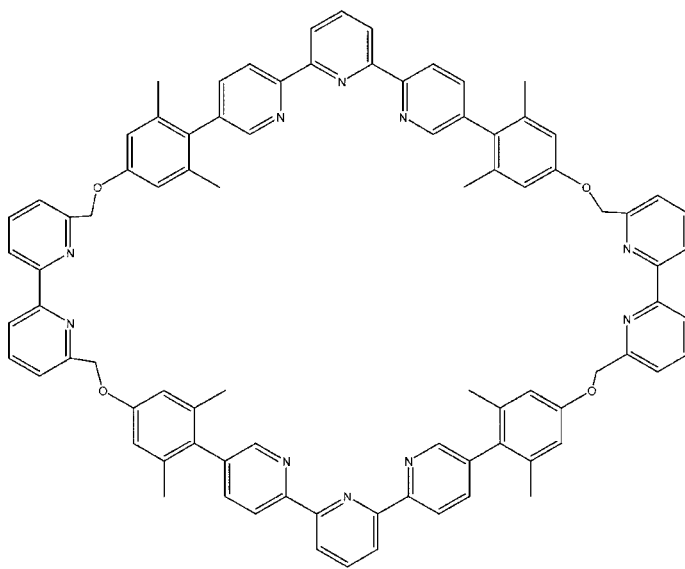
Scheme 2 Depiction of the synthetic strategy to form a [2]catenane using a coordination template route.

a template (Scheme 2). In this way a macrocycle with one bidentate chelate is formed once threaded through the macrocycle with two bidentate chelates, and cyclisation completes the formation of the complex,¹⁰⁴ although other routes involving reactions at the periphery of coordinated units have also been developed.¹⁰⁵

The synthesis of the two-ring intermediate *en route* to a Borromean link in the orthogonal-ring has been reported. This is interesting as the threaded system containing L^{89-90} represents a precursor to the Borromean link (Fig. 32).¹⁰⁶



L⁸⁹



L⁹⁰

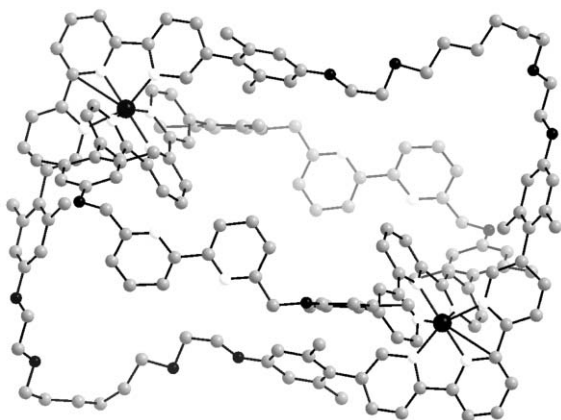
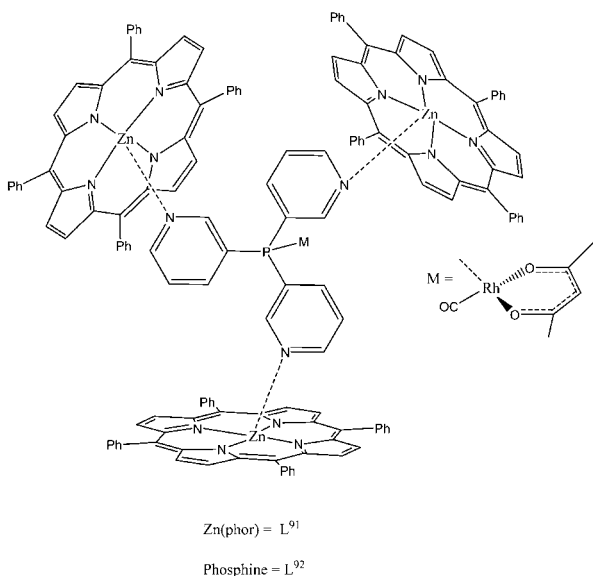


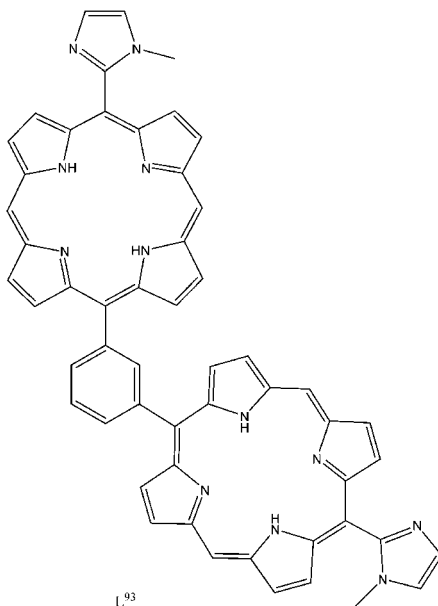
Fig. 32 Presentation of the structure of $[\text{Ru}_2(\text{L}^{89})(\text{L}^{90})]^{4+}$.

Encapsulated transition metal catalysts have been formed *via* a simple self-assembly processes involving porphyrin and pyridylphosphine-based ligands (L^{91} , L^{92}). These form new types of encapsulated catalysts with increased turnover and selectivity for the rhodium-catalyzed hydroformylation of 1-octene.^{107,108}



A hexameric assembly of porphyrins has been designed as a light-harvesting antenna mimic, $(\text{L}^{93}\text{Zn})_6$.¹⁰⁹ The complex was shown to have a circular topology, constructed from interlocking *m*-gable-porphyrins by slipped-cofacial dimer formation without the need for a protein matrix. These may be important in the construction of

light-harvesting complexes; indeed, another study has shown that it is possible to observe efficient excitation energy transfer in long, *meso-meso*-linked Zn(II) porphyrin arrays.¹¹⁰

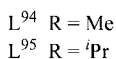
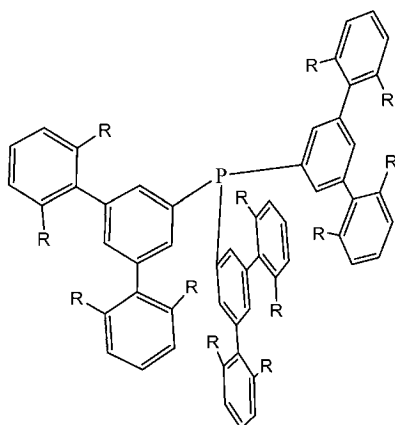


A supramolecular assembly of linear tri-nickel complexes incorporating metalloporphyrins has been assembled using L⁹¹ and L⁶⁹,¹¹¹ and a modified tetraphenyl porphyrin has been used to form a supramolecular capsule in which a {Au₅₅} cluster has been encapsulated.¹¹² Further, a range porphyrin monomer, dimer and oligomeric stacked Eu(III) complexes has been constructed and investigated electrochemically.¹¹³ In addition, a rhodium(III) porphyrin cyclic tetramer and cofacial dimer have been synthesized,¹¹⁴ as well as a porphyrin–cyclodextrin assembly with a molecular wedge.¹¹⁵

7 Squares, triangles, boxes and grids

Increasingly, the concepts of ligand design and self-assembly are being exploited in a well-defined manner to create enormous and intricate molecules, in what can be understood as a type of cooperative process.¹¹⁶ The bowl-shaped triarylphosphane ligands L⁹⁴ and L⁹⁵ react with Pd(II) salts to give an interesting trinuclear complex, [(PdX₂)₃(L⁹⁴⁻⁹⁵)₂], whose formation appears to be facilitated by the bowl shape of the ligands.¹¹⁷ Tri- and hexa-nuclear platinum complexes have been assembled that are rather dendrimer-like to give a {Pt₁₈} cluster dendrimer.¹¹⁸

Platinum(II) terpyridyl-capped, carbon-rich molecular rods with alkynic spacers have been synthesized wherein two Pt centres are linked by a (C≡C–C≡C) unit and



capped with a terpyridyl-based ligand (L^{96} = ${}^t\text{Bu}_3\text{-tpy}$ = 4,4',4''-tri-*tert*-butyl-2,2':6',2''-terpyridine). The complexes, of the type $[\text{L}^{96}\text{Pt-C}\equiv\text{C-C}\equiv\text{C-PtL}^{96}]^{2+}$ were found to have interesting luminescent properties (Fig. 33).¹¹⁹

The use of a ligand with two non-equivalent binding sites, L^{97} , leads to a hexanuclear cage complex $[\text{M}_6\text{L}^{97}\text{X}](\text{X})_5$ [$\text{M} = \text{Cu}(\text{I}), \text{Ag}(\text{I}); \text{L}^{97} = 6,6'\text{-bis}(4\text{-ethynylpyridine})2,2'\text{-bipyridine}; \text{X} = \text{BF}_4^-, \text{SbF}_6^-$]. This has been prepared using a self-assembly approach and encapsulates anions in the solid state and is fluxional in solution (Fig. 34).¹²⁰

Potential polynuclear platinum antitumor complexes have been designed using a polydentate ligand system based on dipyridylamine and 1,3,5-trimethylenebenzene to give the hexadentate ligand, *N,N,N',N',N'',N''*-hexa(2-pyridyl)-1,3,5-tris(amino-methyl)benzene (L^{98}). The trinuclear Pt(II) complex $[\text{Pt}_3\text{L}^{98}\text{L}^{99}]$ (L^{99} = cyclobutane dicarboxylic acid) shows a high affinity for DNA.¹²¹

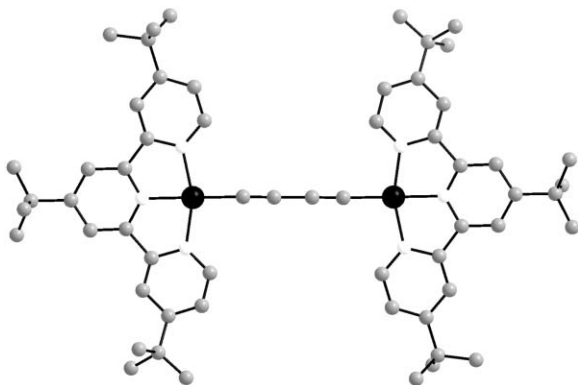


Fig. 33 Structure of the rod-shaped $[\text{L}^{96}\text{Pt-C}\equiv\text{C-C}\equiv\text{C-PtL}^{96}]^{2+}$ complex.

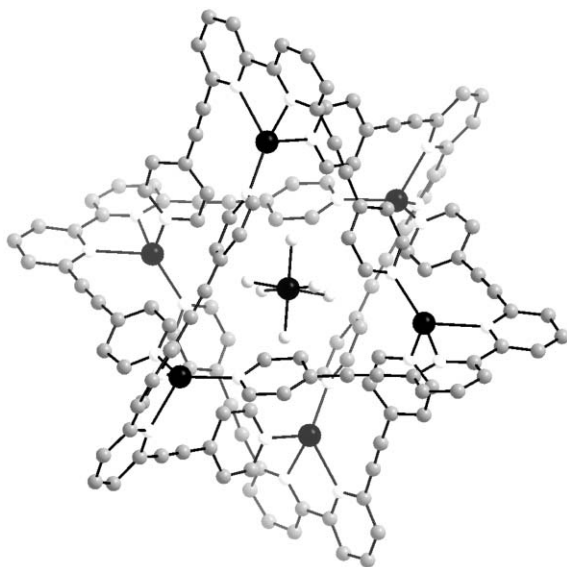
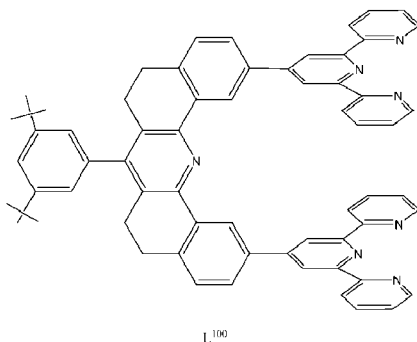
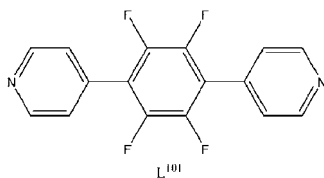


Fig. 34 Depiction of the structure of $[Ag_6L^{97}SbF_6]^{5+}$.

Molecular receptors consisting of either two parallel, cofacially disposed, terpyridyl-Pd-Cl⁺ or terpyridyl-Pt-Cl⁺ units, $[L^{100}(MCl)_2]^{2+}$, and their interaction with a range of guests have been recently investigated.¹²² The association constants found for the neutral guest with the palladium and platinum receptors are large and it is suggested that metal-metal interactions contribute to the molecular recognition.

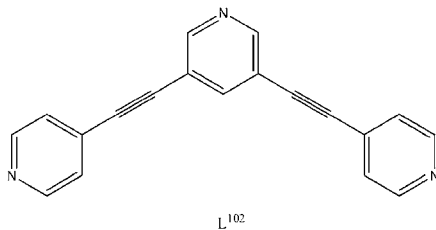


The new fluorinated rigid ligand 1,4-bis(4-pyridyl)tetrafluorobenzene (L¹⁰¹) was used in combination with different diphosphine Pd(II) and Pt(II) triflates to build metallo-supramolecular assemblies. Complex equilibria between triangular and square entities were detected for all the cases and the square/triangle ratio was seen to depend upon several factors, such as the nature of the metal corners, the



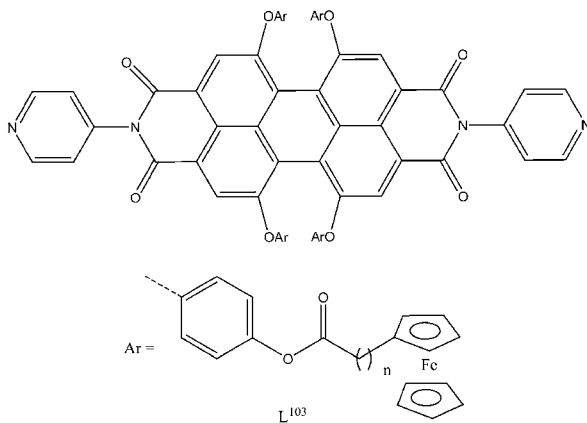
concentration, and the solvent,¹²³ although ligand design can be used to synthesize ligands that exclusively form triangular architectures.¹²⁴

A supramolecular dimeric rhomboid and its trimeric counterpart, a hexagon, are generated by design *via* the directional bonding methodology of self-assembly using L¹⁰² as a building block.



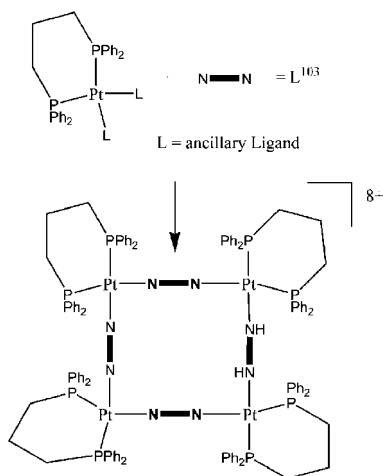
The different-sized supramolecular macrocycles formed by Pt-coordination undergo a concentration- and temperature-dependent dynamic equilibrium.¹²⁵ A range of other similar architectures is also accessible.^{126–128}

A novel tetra-ferrocenyl-substituted ligand, L¹⁰³, has been designed that can form molecular squares on complexation with Pt(II) salts.

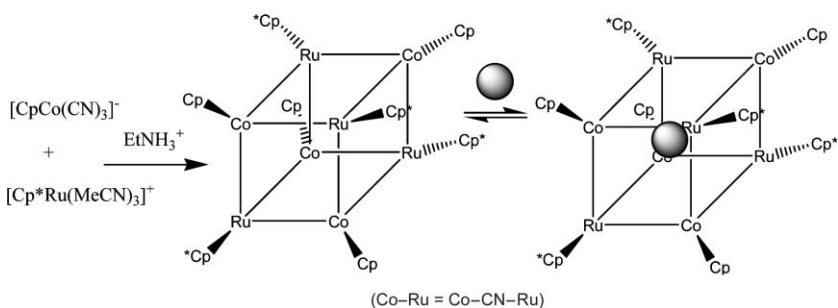


Formation of the molecular square assembles 16 ferrocenyl groups in one molecular network (Scheme 3). Electrochemical investigations of these unprecedented multiredox-active dendritic molecular squares show that the redox behaviour of the ferrocene units is influenced by the square superstructure.¹²⁹

The reaction of [CpCo(CN)₃]⁻ with [Cp**Ru*(MeCN)]⁺ in the presence of EtNH₃⁺ causes the formation of a molecular box (Scheme 4) with a large empty void of *ca.*



Scheme 3



Scheme 4

135 Å³. Furthermore, this [Ru₄Co₄] box is able to bind various, large mono-valent cations ranging from Cs⁺ to MeNH₃⁺.¹³⁰ Further studies showed that it was possible to produce ‘defect’ boxes (Fig. 35).¹³¹

The stepwise assembly of a tetranuclear species that contains four identical cobaltacarborane clusters and features a planar octagonal (tetratruncated square) {C₁₆B₈} macrocycle has been realised.¹³² This has a planar geometry and electrochemical studies reveal significant intramolecular electronic communication (Fig. 36).

A supramolecular cube, [(Cp*WS₃Cu₃)₈Cl₈(CN)₁₂L₄], has been synthesized with linking cyanide anions that connect the Cp*WS₃Cu₃ clusters to form a cube. The ‘cube’ dimensions as judged by the separation of W centres are 9.64 × 10.10 × 10.10 Å (Fig. 37). Preliminary photochemical and photophysical investigations of the cube reveal very interesting photoluminescent properties in the solid state at ambient temperature (Fig. 37).⁵⁰

Reaction of the bis-bidentate ligand L¹⁰⁴, having two bidentate pyrazolyl–pyridine termini, with Co(II) or Zn(II) results in formation of the complexes [M₈(L¹⁰⁴)₁₂]X₁₆

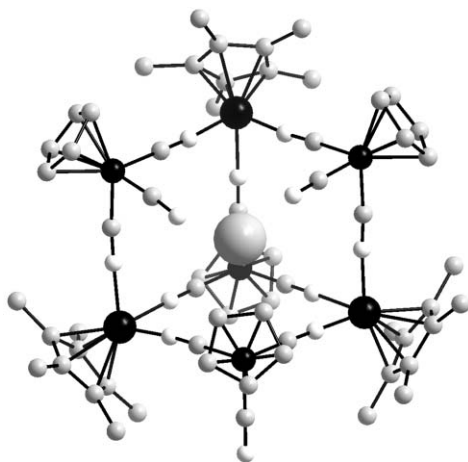


Fig. 35 Representation of the structure of the defect box, $\{\text{Cs}[\text{Cp}^*\text{Rh}(\text{CN})_3]_4[\text{Cp}^*\text{Ru}]_3\}$.

(X = perchlorate or tetrafluoroborate); $[\text{Zn}_8(\text{L}^{104})_{12}](\text{ClO}_4)_{16}$ has been structurally characterized and is a cube with a metal ion at each corner, a bridging ligand along each edge, and an anion in the central cavity. Interestingly, the cube has S_6 symmetry and is distorted (Fig. 38).¹³³

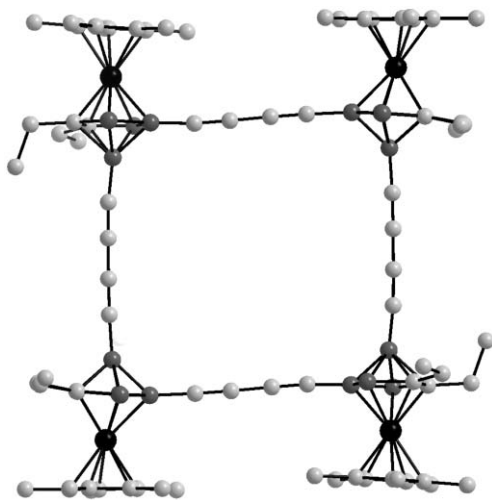
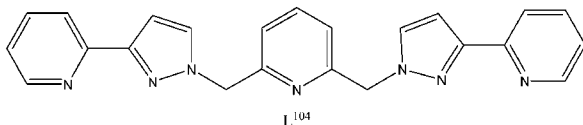


Fig. 36 Depiction of the structure of the $\{\text{C}_{16}\text{B}_8\}$, $[\text{Cp}^*\text{Co}(2,3\text{-Et}_2\text{C}_2\text{B}_4\text{H}_3\text{-5-C}\equiv\text{C-7-C}\equiv\text{C})_4]$.

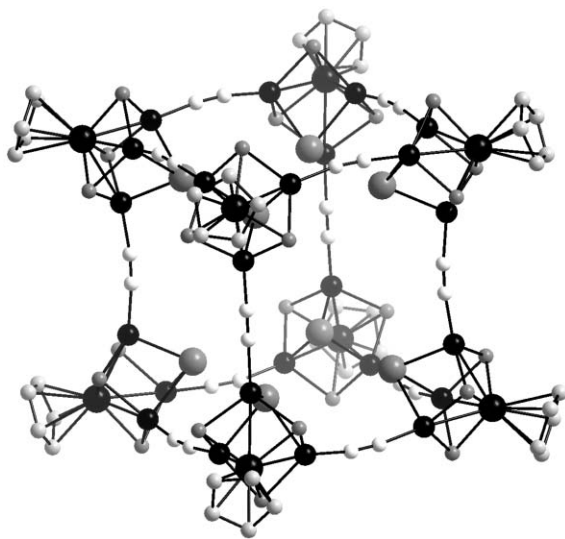


Fig. 37 Structure of the cube cluster $[(\text{Cp}^*\text{WS}_3\text{Cu}_3)_8\text{Cl}_8(\text{CN})_{12}\text{Li}_4]$.

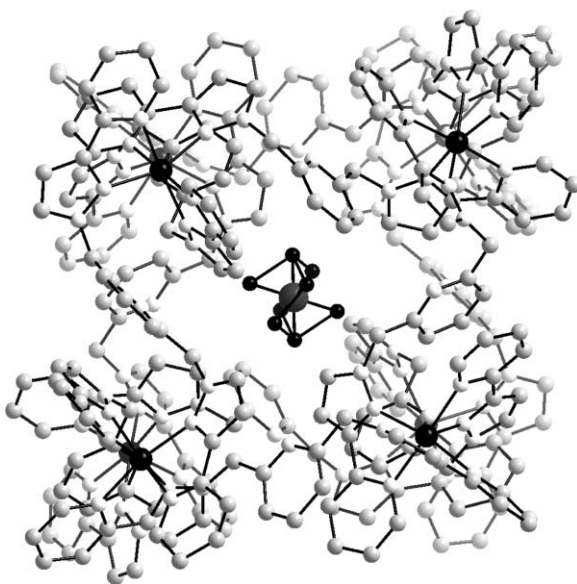


Fig. 38 Representation of the structure of $\{[\text{Zn}_8(\text{L}^{104})_{12}](\text{ClO}_4)\}^{15-}$.

The use of *cis,cis*-1,3,5-triaminocyclohexane ($\text{tach} = \text{L}^{105}$) as a capping ligand in generating metal–cyanide cage clusters with accessible cavities is demonstrated *via* the reaction of $[(\text{tach})\text{M}(\text{CN})_3]$ ($\text{M}^1 = \text{Fe}, \text{Co}$) and $[\text{M}^2(\text{H}_2\text{O})_6]^{2+}$ ($\text{M}^2 = \text{Ni}, \text{Co}$) to yield $[(\text{tach})_4(\text{H}_2\text{O})_{12}\text{M}^1_4\text{M}^2_4(\text{CN})_{12}]^{8+}$ [Fig. 39(left)]. The compound $[(\text{tach})\text{Cr}(\text{CN})_3]$

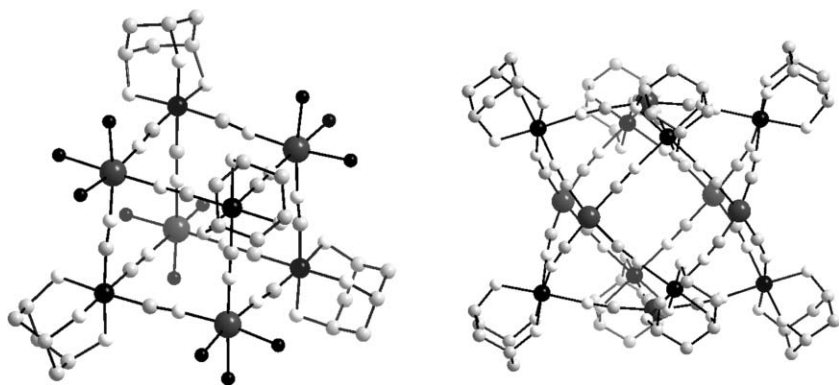
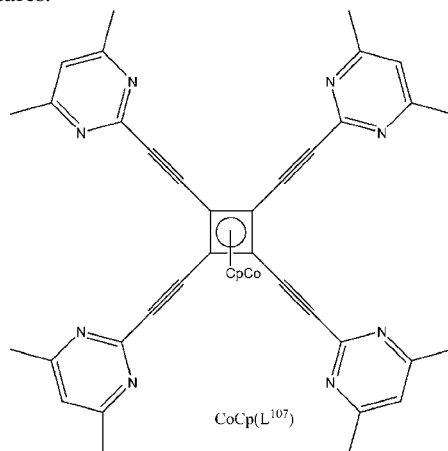


Fig. 39 Representation of the structures of $[(\text{tach})_4(\text{H}_2\text{O})_{12}\text{Co}_4\text{Ni}_4(\text{CN})_{12}]^{8+}$ (LHS) and $[(\text{tach})_8\text{Cr}_8\text{Ni}_6(\text{CN})_{24}]^{12+}$ (RHS). In both cases the nickel(II) ions are shown as grey spheres.

reacts with $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ in aqueous solution to produce $[(\text{tach})_8\text{Cr}_8\text{Ni}_6(\text{CN})_{24}]^{12+}$, featuring a structure based on a cube of Cr^{III} ions with each face centred by a square planar $[\text{Ni}(\text{CN})_4]^{2-}$ unit [Fig. 39(right)].¹³⁴ In another study the other isomer of tach, *cis,trans*-1,3,5-triaminocyclohexane (t-tach = L^{106}), has been used in the assembly of a variety of Pd(II)-based architectures from monomers, to trimeric and hexameric Pd(II) complexes.¹³⁵

A new tetrakis[(2-pyrimidinylethynyl)cyclobutadiene][(cyclopentadienyl)cobalt] complex has been synthesized (CoCpL^{107}) which is extremely well preorganized to form molecular squares.



Complexation with HgCl_2 yields $[(\text{CoCpL}^{107})\text{HgCl}_2]$ wherein the mercury is in an unusual square planar coordination environment, and two DCM molecules are bound into the square by hydrogen-bonded interactions (Fig. 40).¹³⁶ It is worth noting a few other square-like complexes have also been synthesized containing $\text{Ru}(\text{II})$ ¹³⁷ and $\text{Cu}(\text{II})$.¹³⁸

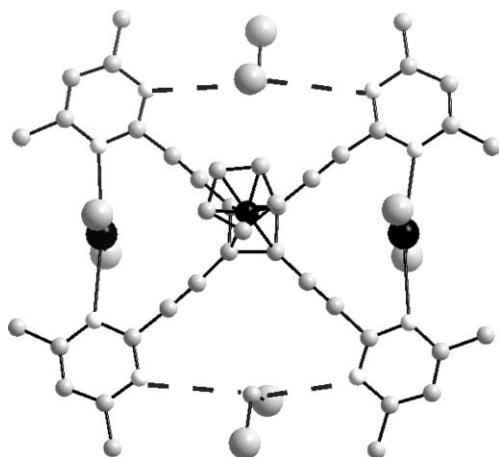
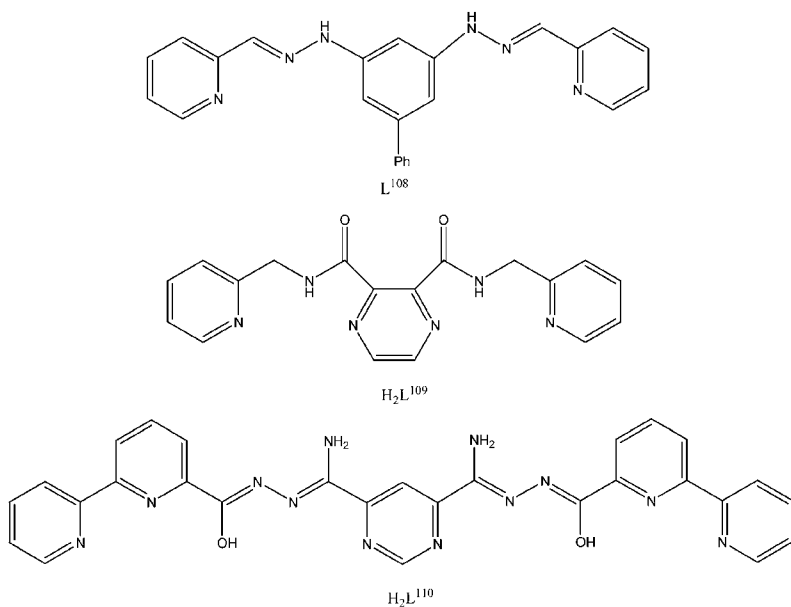


Fig. 40 Representation of the structure of [(CoCpL¹⁰⁷)HgCl₂].

A number of molecular ‘grids’ have been synthesized and characterized; for example, the new bis-hydrazone-based ligand L¹⁰⁸ forms ionisable [2 × 2] grid-type transition metal complexes whose properties may be modulated by multiple protonation/deprotonation as shown by the reversible change in optical properties of the [Co₄L¹⁰⁸]₄⁸⁺ complexes depending on their protonation state (Fig. 41).¹³⁹



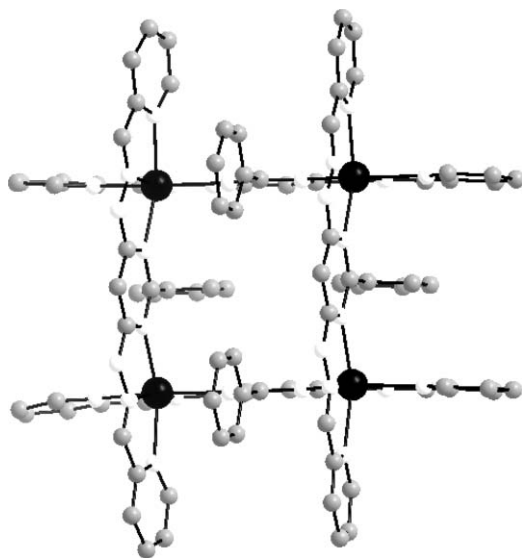
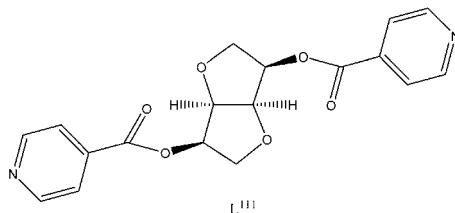


Fig. 41 Representation of the structure of $[\text{Co}^{14} 108\text{L}_4]^{8+}$.

A similar $[2 \times 2]$ grid is formed *via* the reaction of L^{109} with $\text{Cu}(\text{II})$ salts¹⁴⁰ whereas L^{110} forms a $[4 \times (2 \times 2)]\text{-}\{\text{Pb}_{16}\}$ grid structure, with an overall size of *ca.* 2.6 nm¹⁴¹ (Fig. 42) and similarly large ‘nano-grids’ have been reported by others also.¹⁴²

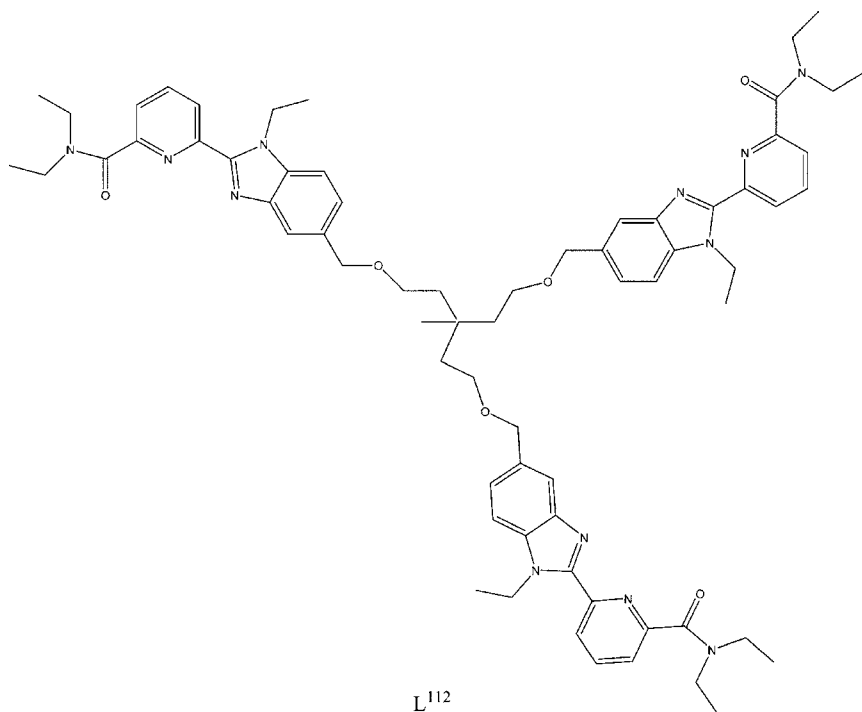
8 Helicates and extended helical frameworks

The self-assembly between a bis-monodentate tecton based on two pyridine units, L^{111} , connected to an enantiomerically pure isomannide stereoisomer and HgCl_2 leads to the formation of an enantiomerically pure triple-stranded, helical, infinite coordination network.¹⁴³



The tecton approach has also been used for double-stranded helicates.¹⁴⁴ Furthermore, a novel, extended, covalent tripod, L^{112} , designed for assembling triple-helical, nine-coordinated lanthanide(III) podates has been synthesized. Reaction with lanthanide(III) in acetonitrile produces stable and dynamically inert

C_3 -symmetrical podates $[\text{Ln}(\text{L}^{112})]^{3+}$ ($\text{Ln} = \text{La-Lu}$) in which Ln^{III} is nine-coordinate in a pseudo-tri-capped trigonal prismatic site.¹⁴⁵



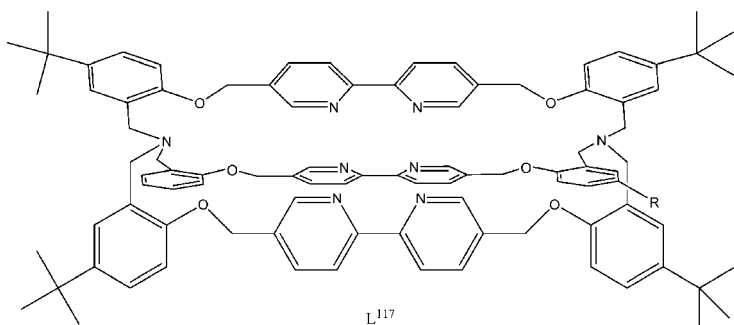
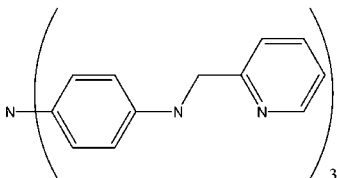
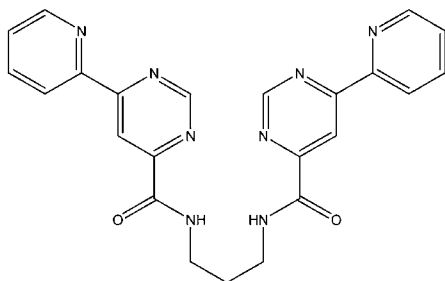
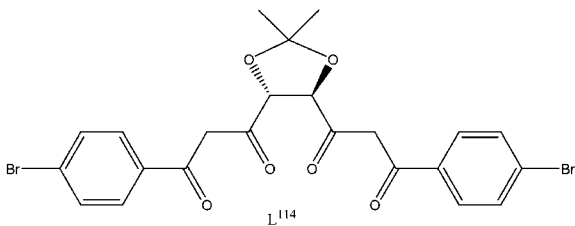
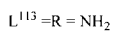
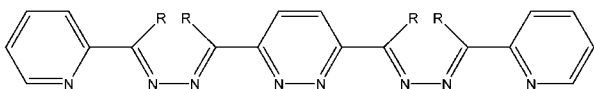
In addition, a helical complex based on the salen ligand has also been obtained.¹⁴⁶

The synthesis, structural characterization, and magnetic properties of the first triple-stranded helicate containing four metal centres $[\text{Cu}_4(\text{L}^{113})_3](\text{ClO}_4)_8$ that exhibits intramolecular magnetic exchange between metal centres has been formed through the self-assembly of L^{113} and $\text{Cu}(\text{ClO}_4)_2$ (Fig. 43).¹⁴⁷

A chiral tetraketone ligand, L^{114} , was obtained by Claisen-type condensation of 4-bromoacetophenone with the acetone ketal of L-tartraic acid diethyl ester and leads, with gallium(III) or iron(III) ions in self-assembly processes, to dinuclear helicate-type cryptands which are able to bind lithium cations.¹⁴⁸

A hexanuclear copper(II) complex with a figure-of-eight strip topology is formed by metal-directed self-assembly of tritopic ligand L^{115} , bis-bidentate glycine hydroxamic acid and $\text{Cu}(\text{II})$ ions in a 2 : 2 : 6 ratio (Fig. 44).¹⁴⁹

The synthesis and structural characterization of a novel C_3 -symmetric tris-bidentate ligand, L^{116} , featuring a triphenylamine core appended by pyridylimine coordination has been achieved. ^1H NMR compleximetric titration studies with $\text{Ag}(\text{I})$ and ESMS indicate the presence of $[\text{Ag}_3(\text{L}^{116})_2]^{3+}$ species in solution, consistent with the formation of a trinuclear double-helicate complex.¹⁵⁰ A new molecular ligand cage incorporating three bipyridyl units (L^{117}) has been synthesized by a conventional multi-step procedure using a $\text{Ni}(\text{II})$ -based templating procedure. Structural analysis



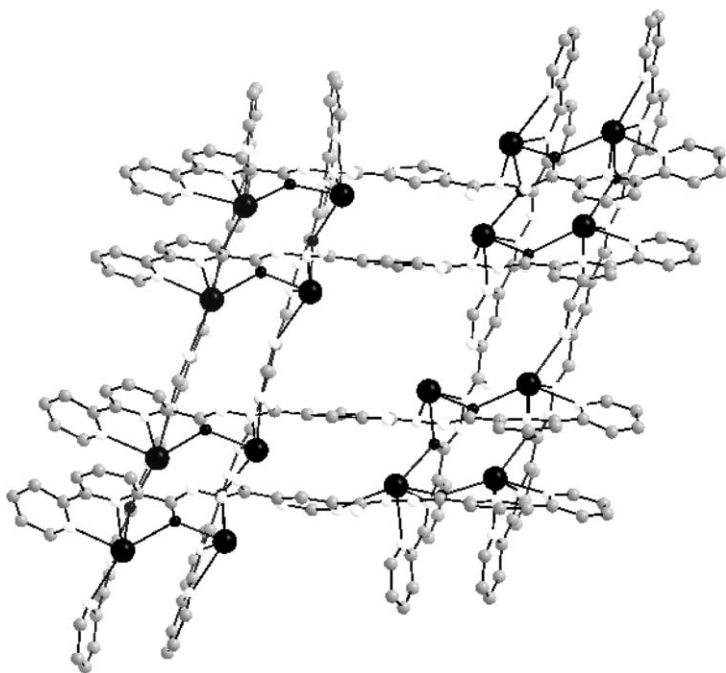


Fig. 42 Representation of the $[4 \times (2 \times 2)]\text{-}\{\text{Pb}_{16}\}$ grid structure.

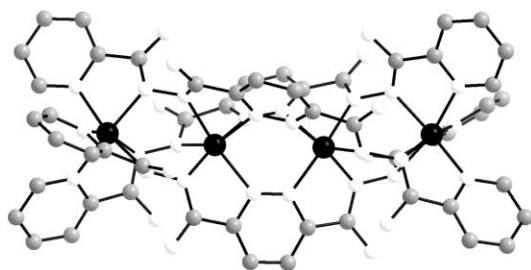
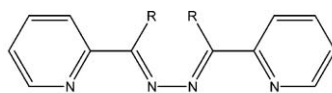


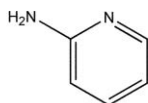
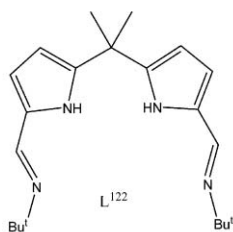
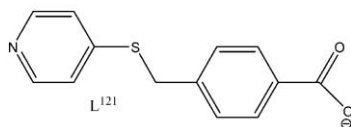
Fig. 43 Structure of the triple helicate based on L^{113} .

demonstrates that the central metal ion acts to promote a triple helical twist that extends *ca.* 22 Å along the axial length of the molecule (Fig. 45).¹⁵¹

Copper(I) coordination has been investigated for three analogous pyridine–azine ligands, in which two pyridylimine binding units are linked directly through the imine nitrogen atoms. It has been found that substituents on the imine units of the ligands influence the metallo-supramolecular architecture adopted, leading to a dinuclear double-helicate L^{118} , a trinuclear circular-helicate, L^{119} , and a polymeric array, L^{120} . In each structure the copper(I) centre is four-coordinate,¹⁵² and the effects of phenyl substituents introduced at the imine carbon (L^{120}) have been investigated.¹⁵³



L^{118} - R = Ph L^{119} - R = M L^{120} - R = H



L^{123}

A novel tubular coordination network [Zn(spcp)(OH)] (spcp = 4-sulfanylmethyl-4A-phenylcarboxylate pyridine = L^{121}) with a modest SHG activity and based on two types of homo-chiral helices was synthesized and characterized.¹⁵⁴ Double-stranded [4 × 4] helicates, of Fe(II) and Mn(II), supported by an extended dipyrroline ligand have also been synthesized. Transamination reactions between Mn and Fe

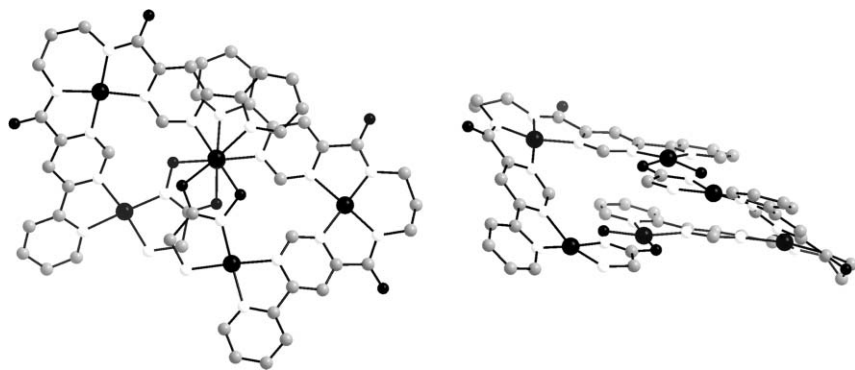


Fig. 44 Structure of the figure-of-eight complex (top view LHS, side view RHS).

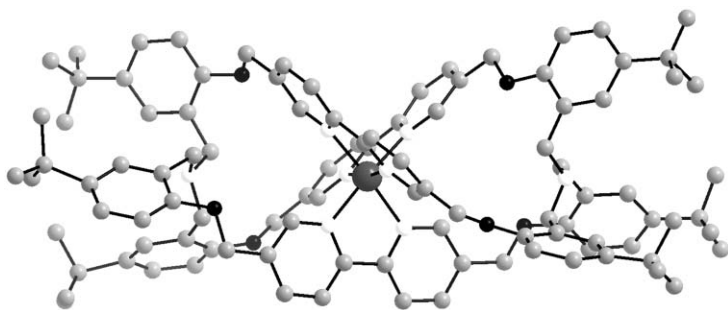
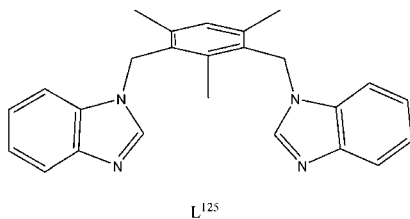


Fig. 45 Structure of the $[\text{Ni}(\text{L}^{117})_2]^{2+}$ helical complex.

amides and the diiminodipyrromethane ligand, H_2L^{122} , result in the spontaneous formation of volatile, double-stranded helicates.¹⁵⁵ Non-covalently bound ligand strands form interesting transition metal helicates that are linked *via* hydrogen-bonded interactions.¹⁵⁶

A layered zinc phosphite $(\text{C}_5\text{H}_6\text{N}_2)\text{Zn}(\text{HPO}_3)$ containing helical chains has been prepared hydrothermally from aminopyridine (L^{123}), H_3PO_4 and $\text{Zn}(\text{II})$ acetate. The structure consists of left-handed and right-handed helical chains that are connected through oxygen atoms to form an undulated sheet structure with a 4.8-net.¹⁵⁷ Hydrothermal synthesis has also been used to construct a pure molybdenum-oxide helical chain based on $[\text{L}^{124}]_2[\text{Mo}_9\text{O}_{30}]$ [$\text{L}^{124} = \text{NH}_3(\text{CH}_2)_2\text{NH}_2(\text{CH}_2)_2\text{NH}_3$].¹⁵⁸ The chains comprise two novel and symmetrically-related helices which coexist in the centrosymmetric solid, in which the two kinds of helices appear in the left-handed and right-handed enantiomorphs, respectively (Fig. 46).

Columnar supramolecular architectures were self-assembled from S_4 -symmetric coordination nanotubes encapsulating neutral guest molecules whereby a neutral coordination nanotube was assembled from four HgCl_2 units and four ditopic L^{125} ligands in a highly concerted fashion.



Two directional binding sites on the $\text{Hg}(\text{II})$ ion direct the assembly which is facilitated by the *anti*-conformation adopted by the ligand. Interestingly, the tubes are aligned such that they resemble a pipeline and these pipelines are arranged into a three-dimensional columnar architecture (Fig. 47).¹⁵⁹

$\text{Co}(\text{II})$ sulfate reacts with the flexible ligand 1,4-bis(imidazol-1-ylmethyl)benzene (L^{126}) to yield the coordination network $[\text{Co}(\text{L}^{126})_2(\text{H}_2\text{O})_2](\text{SO}_4)$, containing polymeric ribbons of rings which penetrate and catenate a 3D single frame of the

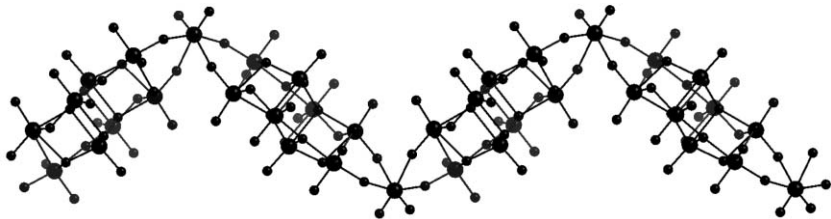


Fig. 46 Structure of $[L^{124}]_2[Mo_9O_{30}]$.

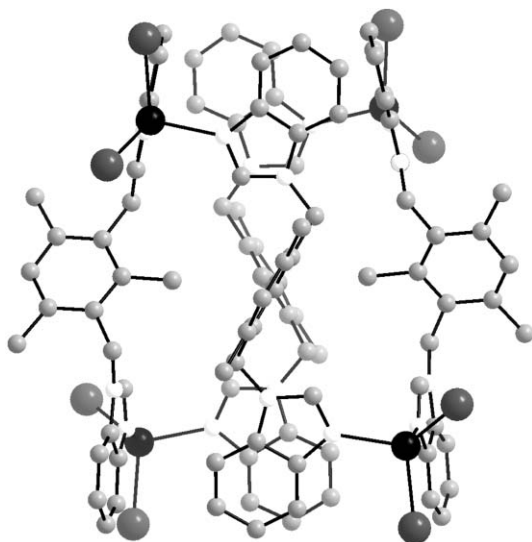


Fig. 47 Structure of $[(HgCl_2)_4(L^{125})_4]$.

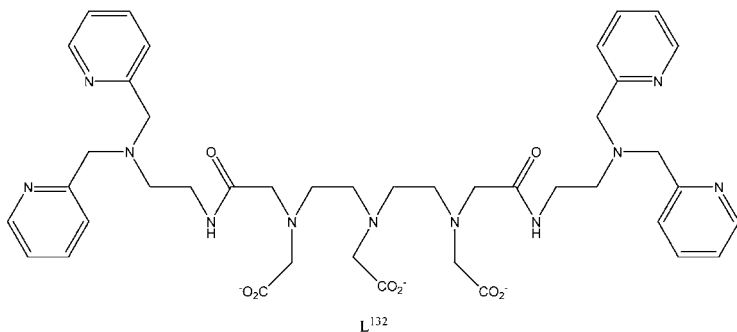
$CdSO_4$ topology, to produce an open-channel entangled architecture with nanoporous behaviour.¹⁶⁰ A new type of three-dimensional framework based on dodecanuclear $Cd(II)$ macrocycles $[\{Cd_2(L^{127})(L^{128})\}_6(L^{128})_6(L^{129})_3]_n$ [H_2L^{127} = diphenic acid; L^{128} = isonicotinic acid; L^{129} = 1,2-di(4-pyridyl)ethylene] was prepared by the hydrothermal reaction and *in situ* synthesis. The dodecanuclear $Cd(II)$ macrocycles are cross-linked by *exo*-tridentate isonicotinate ligands in their perpendicular direction to form a one-dimensional pillared framework. In this way the isonicotinate ligands serve as pillars linking the adjacent macrocycles along the z -axis through carboxylate oxygen atoms bridging between $Cd(II)$ centres of the four-membered Cd_2O_2 ring in one macrocycle and the pyridyl nitrogen atom binding to the non-semi-chelating $Cd(II)$ in the other macrocycle.¹⁶¹

A family of supramolecular inclusion solids based upon second-sphere interactions have been synthesized from $[Co(NH_3)_6]Cl_3$ and disulfonate anions. These form pillared layered structures and include guest molecules, $[\{[Co(NH_3)_6Cl](L^{130})-(H_2O)_6\}]_\infty$ [L^{130} = 1,4-piperazinebis(ethanesulfonate)] and $[\{[Co(NH_3)_6](L^{131})_{1.5}-(H_2O)_2(\text{dioxane})\}]_\infty$ (L^{131} = 2,6-naphthalenedisulfonate). The networks are sustained

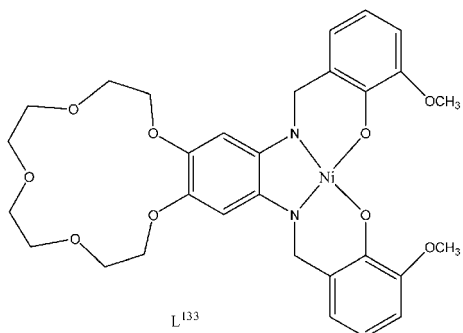
by charge-assisted hydrogen bonding and show two different assembly motifs, one based on the complementarity of the edges of the triangular triamine faces with sulfonate groups, and the other on hydrogen-bond complementarity with the centroids of the triangular faces.¹⁶²

9 Supramolecular and macrocyclic devices

A complex capable of selective detection of zinc ions with a novel luminescent lanthanide probe has been designed. Out of the Tb^{III} and Eu^{III} diethylenetriamine-pentaacetic acid (DTPA)-bisamide complexes, [TbL¹³²] gives Zn(II)-sensitive luminescence. The luminescence emission data also revealed very high selectivity for Zn^{II} ions compared with Ca^{II} and Mg^{II} ions. Notably, the luminescence emission enhancement in 100 μ M HEPES buffer (pH 7.4) containing 5 mM Ca^{II} or Mg^{II} ions showed that these ions had no effect in the presence or absence of Zn^{II} ions.¹⁶³



An acoustic wave sensor for barium based on poly[Ni(L¹³³)] recognition chemistry has been developed whereby interfacial recognition of barium by a crown ether receptor is quantified using an acoustic wave sensor, and the isotherm characteristics rationalized in terms of solution complexation chemistry and polymer materials properties. The concept of encapsulating a solution-based complex within a polymer immobilized on an acoustic wave sensor has been implemented quantitatively.¹⁶⁴

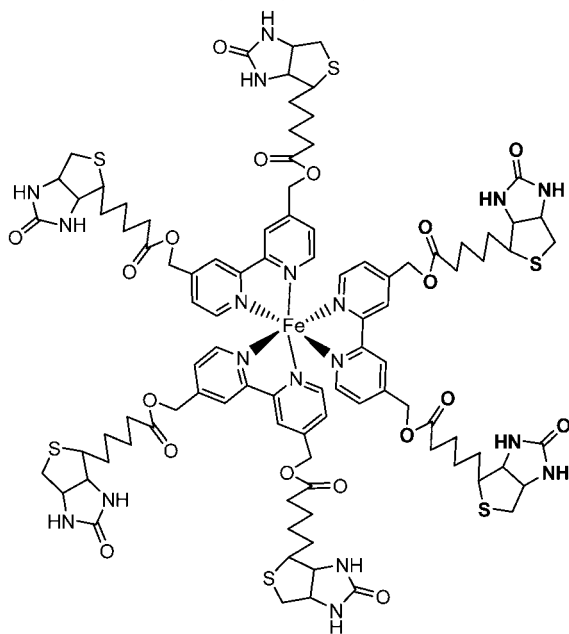


Fluorophore-capped cyclodextrins have been shown to be efficient chemical-to-light energy converters. This is because the bisbenzimidazole-capped cyclodextrins, capable of forming supramolecules, harvest chemical energy from the oxidation reaction of a bis(aryl)oxalate and emit light two orders of magnitude more efficiently than fluorescein.¹⁶⁵

In an interesting study, the supramolecular assembly of a ferrocene-porphyrin conjugate allows ferrocene-based electrochemical sensing of the metalloporphyrin axial coordination *via* a 'tail on-tail off' binding process. This was demonstrated by electrochemical methods which showed that a self-assembly phenomenon, coupled with efficient electronic communication throughout the receptor, allows an unprecedented ferrocene-based electrochemical sensing of neutral species *via* a metalloporphyrin-centred 'tail on-tail off' binding process.¹⁶⁶

The Tb^{3+} complexes of cyclen-based aromatic diaza-15-crown-5 and 18-crown-6 ether conjugates were designed as luminescent switches for sodium and potassium where the delayed Tb(III) emission, occurring as line-like emission bands between 490 and 622 nm, was 'switched on' upon recognition of these ions in pH 7.4 buffered water solution.¹⁶⁷

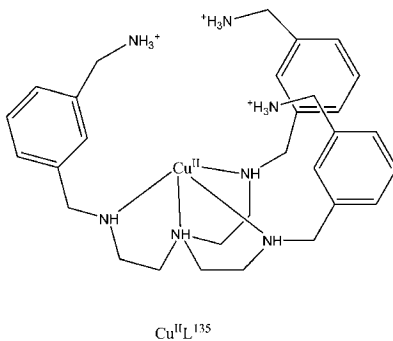
A new biotinylated tris-bipyridinyl iron(II) complex was designed as a supramolecular biosensing architecture. The bioaffine immobilization of several avidin layers on an electrode modified by a biotinylated polymer was accomplished by the first biotinylated redox bridge consisted of a tris(bipyridyl) iron(II) complex bearing six pre-oriented biotin groups. It is interesting that the biotin-labelled iron(II) complex constitutes an efficient small building block for the reproducible immobilization of several avidin layers by affinity interactions.¹⁶⁸



$Fe(L^{134})_3$

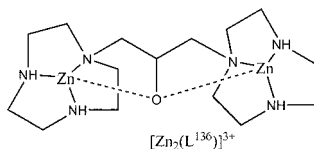
Two new copper(I) pseudorotaxanes bearing a thioctic acid appended unit have been prepared and deposited onto a gold electrode surface, leading to surface-attached electroactive pseudorotaxanes. These threaded molecules were attached onto a gold surface through the disulfide bridge and the electrochemical response in the solid state has been studied by electrochemical methods.¹⁶⁹

C_{3v} symmetric receptors were designed that show high selectivity and high affinity for phosphate ions. This was accomplished by creating cavities that are complementary to three faces of a tetrahedron.¹⁷⁰



An interesting, water-based, azophenol-based chromogenic complex has been developed and examined that is able to detect pyrophosphate.¹⁷¹

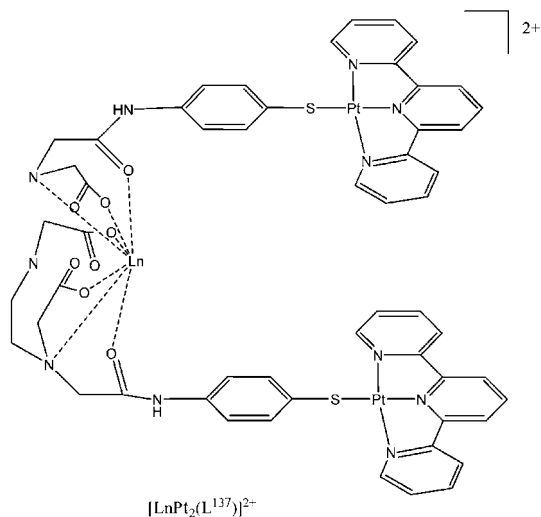
A dinuclear metal ion complex $\text{Zn}_2(\text{L}^{134})$ was synthesized and studied as a catalyst for the cleavage of the phosphate diester 2-hydroxypropyl-4-nitrophenyl phosphate (HPNP). This complex was shown, *via* a variety of studies, to be an interesting model catalyst.¹⁷²



Layer-by-layer growth of metal–metal-bonded supramolecular thin films was used in the fabrication of lateral nanoscale devices and these were directed by different substrate surfaces using monolayer templates. The thin films were studied using electrochemical techniques and the application of these multilayers as active materials for switching and other molecular devices is suggested.¹⁷³

Molecular recognition and conductance in crown ethers have been studied as model quantum conductors using theoretical techniques. It was found that cationic binding should significantly lower conductance due to quantum mechanical interference effects, and there is no correlation between conductance and ligand type. This study opens the way for experimental measurements to examine these ideas.¹⁷⁴

A ligand has been designed (L^{137}) that forms hairpin-shaped heterometallic luminescent lanthanide complexes for DNA intercalative recognition whereby the Ln–Pt₂ metallohairpins bear intercalating groups that direct the complex to DNA recognition. This leads to considerable DNA stiffening, and the lanthanide luminescent unit is ‘remote’ from the negatively-charged DNA backbone.¹⁷⁵



Building blocks for the molecular expression of quantum cellular automata have been designed and examined. These complexes met the basic requirements for a molecular QCA cell and as such contain dots consisting of metal complexes possessing two stable redox states and a planar array of four such complexes with 4-fold symmetry. This $\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_4(\eta^4\text{-C}_4)\text{Co}(\eta^5\text{-C}_5\text{H}_5)\}^+$ complex possesses sufficient through-bond or through-space interaction that the 2-electron, 2-hole mixed-valence state is stable with respect to comproportionation to lower and higher oxidation states. It shows type II or type III mixed-valence behaviour appropriate for switching (Fig. 48).¹⁷⁶

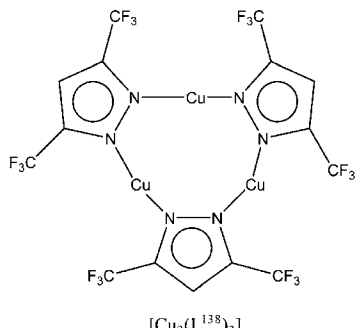
A terbium-sensitized ytterbium luminescence has been reported from a trimetallic lanthanide complex containing two terbium ions and one ytterbium ion. The complex is the first report of lanthanide-centred near-IR emission sensitized by a lanthanide ion.¹⁷⁷

A bright phosphorescent trinuclear copper(I) complex demonstrating interesting solvatochromism and ‘concentration luminochromism’ was recently reported. The trinuclear copper(I) complex $\{[3,5\text{-(CF}_3)_2\text{pz}]\text{Cu}\}_3$ {where $[3,5\text{-(CF}_3)_2\text{pz}] = L^{138}$ } exhibits multicolour, bright phosphorescent emissions that are sensitive to temperature, solvent, and concentration.¹⁷⁸

A functioning molecular machine, namely a supramolecular ‘nanovalve’ that opens and closes the orifices around ‘nanopores’ which accept and release small numbers of molecules on demand has been created. The nanopores are created using a one-step, one-pot, dip-coating technique, and they can be filled with guest molecules and



Fig. 48 Structure of the QCA complex $\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\}_4(\eta^4\text{-C}_4)\text{Co}(\eta^5\text{-C}_5\text{H}_5)\}^+$.



trapped by redox-controlled, gate-keeping supermolecules. An external reducing reagent can be used to break up the supermolecules, allowing the release of the guest molecules.¹⁷⁹

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