Coordination Chemistry of *cis,trans*-1,3,5-Triaminocyclohexane – From Mononuclear Complexes to Supramolecular Architectures

by

Georg Peter Maria Seeber

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ABSTRACT

The coordination chemistry of the rigid, aliphatic triamino ligand *cis,trans*-1,3,5-triaminocyclohexane (*trans*-tach) is investigated. With closed shell transition metals, *trans*-tach forms 1-D {Ag(OTf), $ZnCl_2$} networks and a 3-D {$AgNO_3$} coordination polymer with unprecedented topology. Coordination to the open shell transition metals {$NiCl_2$, $Ni(NO_3)_2$, $Cu(NO_3)_2$, $CuBr_2$, $CuCl_2$, CuF_2, $CuSO_4$} leads to discrete diligand complexes. Protonation of the copper(II) complexes predominantly forms monoligand species, which can aggregate into higher nuclearity clusters. Protonated $Cu(NO_3)_2$ and $CuBr_2$ complexes (HNO_3 and HBr, respectively) remain mononuclear. $CuCl_2$ and $CuBr_2$ complexes protonated with HCl, however, form trinuclear species comprising trigonal planar μ_3-chloro ligands that aggregate into 1-D trinuclear copper(II) chains *via* hydrogen-bonded interactions. Protonated CuF_2 forms a tetranuclear cubane type structure that aggregates into a 3-D nanoporous network *via* hydrogen-bonded interactions. Protonation of the $CuSO_4$ diligand complex maintains the diligand coordination, forming a 1-D nanoporous network through hydrogen-bonded interactions. Coordination to square planar palladium(II) ions forms all possible coordination motifs ('Tail' = monodentate, 'Head' = bidentate coordination). 'Head-to-Head' coordination results in diligand complexes, 'Head-to-Tail' coordination forms cyclic hexanuclear structures and 'Tail-to-Tail' coordination leads to a trinuclear species. Extension of *trans*-tach *via* Schiff base formation with pyridine-2-carboxaldehyde results in a hexadonor ligand suitable for metal coordination. Depending on the stoichiometry of the metal, mono- or polynuclear complexes are formed.

Meinen Eltern

"The essence of chemistry is not only to discover but to invent and, above all, to create."

Jean-Marie Lehn

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ABBREVIATIONS

B.p.	Boiling point
chtt	1,3,5-Cyclohexanetrionetrioxime
CI	Chemical ionisation
CN	Coordination number
COSY	Correlated spectroscopy
CSD	Cambridge crystallographic data base
dec.	Decomposition
EI	Electrical ionisation
en	Ethylenediamine
HSQC	Heteronuclear single quantum coherence spectroscopy
MALDI	Matrix assisted laser desorption ionisation
M.p.	Melting point
MS	Mass spectrometry
MS-ES+	Positive ion electrospray mass spectrometry
NOE	Nuclear Overhouser Effect
triflate, OTf	Trifluormethanesulphonate ($CF_3SO_3^-$) anion
pz	Pyrazine
rt	Room temperature
cis-tach	*cis,cis*-1,3,5-Triaminocyclohexane
trans-tach	*cis,trans*-1,3,5-Triaminocyclohexane
tbc	*cis,trans*-1,3,5-*tris*-Benzaldimino-cyclohexane
tcm	Tricyanomethanide (CCN_3^-) anion
TM	Transition metal
TOF	Time of flight
ttop	*cis,trans*-1,3,5-*tris*-(Pyridine-2-carboxaldimino)-cyclohexane

1 INTRODUCTION

1.1 Supramolecular Chemistry

"Molecular chemistry has established its power over the covalent bond. The time has come to do the same for non-covalent intermolecular forces. Beyond molecular chemistry lies the field of *supramolecular chemistry*, whose goal it is to gain control over the intermolecular bond."[1]

This consequential development represents the next step in increasing complexity beyond the molecule towards the supermolecule and organised polymolecular systems held together by non-covalent interactions. Molecular interactions form the basis of the highly specific processes that occur in biology such as recognition, reagent transport and regulation.[2,3] The design of biomimetic systems capable of processes of highest efficiency and selectivity requires correct manipulation of the energetic and stereochemical features of the non-covalent intermolecular forces within a defined molecular architecture.

The concept of 'supramolecular' stems back as early as 1906, when Paul Ehrlich recognised that molecules "do not act if they do not bind".[4] This introduced the concept of molecules acting as *receptors*. Further to this, a notion presented by Emil Fischer that binding must be selective[5] led consequently to the 'lock and key' model of steric fit, implying a certain degree of geometrical complementarity. Thus the foundations of *molecular recognition* were laid. Finally, selective binding requires interaction, an affinity between the partners that may be related to the idea of *coordination* introduced by Alfred Werner.[6] Therefore, supramolecular chemistry can be thought of as a generalization of coordination chemistry.[7] With these three concepts, *receptor*, *recognition* and *coordination*, the scientific basis for supramolecular chemistry was established.

The field began developing with the selective binding of alkali metal cations by natural[8-14] as well as by synthetic macrocyclic and macropolycyclic ligands, predominantly crown ethers[15,16] and cryptands.[17-20] A novel area of chemical research emerged by the identification of molecular recognition processes,[20] extension to intermolecular interactions and expansion into other areas - growing into supramolecular chemistry. The term 'supramolecular chemistry' was introduced in 1978[21] as a development and generalisation of earlier work[20]:

“Just as there is a field of *molecular chemistry* based on the covalent bond, there is a field of *supramolecular chemistry*, the chemistry of molecular assemblies and of the intermolecular bond.” It has been reformulated on various occasions, *e.g.* “Supramolecular chemistry may be defined as ‘Chemistry beyond the molecule’, bearing on the organised entities of higher complexity that result from the association of two or more chemical species held together by intermolecular forces.”[22] A chemical species is thereby defined by its components, by the nature of the bonds that hold them together and by the resulting geometrical and topological features. The objects of supramolecular chemistry are individual entities, *supermolecules* possessing features as well defined as those of molecules themselves. It can be postulated that supermolecules are to molecules and the intermolecular bond what molecules are to atoms and the covalent bond.[22,23] The supermolecule therefore represents the next level of complexity of matter after the fundaments of the elementary particle, the nucleus, the atom and the molecule.

In modern terminology, the meaning of *supramolecular* becomes a strategy for controlled self-assemblies, tightly linked to coordinative interactions between metals and organic ligands, which also interact through intermolecular forces.[24] These intermolecular forces, such as hydrogen bonding, donor-acceptor, van-der-Waals and π-π stacking interactions[25-30] are in general weaker than covalent bonds.[†] This means that supramolecular species are thermodynamically less stable, kinetically more labile and dynamically more flexible than molecules. The dynamic behaviour of such fast processes is important for the thermodynamic control of multi-component assemblies.[24,32,33]

Major goals of supramolecular chemistry are to mimic the structure and function of the magnificent ensembles found in molecular biology, as well as to generate new materials based on complex architectures. Approaches to the assembly of large arrays and organisation of multiple components are divided into principally different concepts: serendipity and rational design. Not limited by the boundaries of imagination, some of the polymetallic complexes with the most interesting physical properties have been made, at least initially, by accident. For example, the initial discovery of ‘single molecular magnets’ was achieved unintentionally,[34] a concept now of immense current interest due to possible applications as

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[†] Coordination bonds can have a substantial proportion of covalency.[31]

information storage devices. Serendipitous examples of such self-organised architectures are not amenable to initial design, yet allow fascinating insights into the processes that govern spontaneous supramolecular assembly.[35,36] Contrary to this, rational design utilises carefully chosen metal centres and ligand systems to facilitate the geometrical requirements for a given architecture. A common feature of such design approaches is the use of *rigid* and *polyfunctional* organic ligands as geometrically predetermined building blocks. Rigidity is an important factor to ensure the formation of the desired architecture that represents the *most favoured* structure as a function of the geometrical restraints. Elegant examples of the rational design approach can be seen in the architectures based both on the *chelating* ligands used by Raymond,[37,38] Lehn,[39,40] and Saalfrank[41,42] that show increased preorganization and high formation constants,[43] and on *monodentate* ligands,[44-48] exemplified by the work of Stang.[33,49] In his innovative work on palladium(II) coordination chemistry, Fujita[44,50] uses the concept of ‘molecular panelling’ to create polynulcear complexes containing palladium(II) fragments.

1.2 Self-assembly

Coordination driven motifs allow great directionality offered by metal-ligand coordinative bonding compared to weak electrostatic, π-π stacking or hydrogen-bonded interactions. In addition they allow great versatility due to the variety of transition-metals and multidentate ligands available as building blocks. Self-assembled multinuclear coordination structures are considered supermolecules. Although supermolecules have – in common with covalently constructed molecules – well defined molecular weight, formula, and connectivity, they also have other properties that are unique to the assembly, and unattainable with the individual component molecules.

On such basis, the following common features for metal-mediated supramolecular self-assembly can be assigned: (i) self-assembling units are held together by coordinative interactions; ii) the assembly of subunits into larger architectures is selective to form the most stable aggregate; iii) the assembled units display different properties to their individual subunits and iv) descrete assemblies are generally thermodynamically favored over polymeric systems.

Several approaches have been developed towards self-assembly of discrete multinuclear species. The two main rational design approaches are based on either control of the bonding vector direction between the building blocks (‘symmetry interaction model’) or control of the overall symmetry of interaction between the molecular components (‘molecular library model’).[33,38]

1.2.1 Design principles

1.2.1.1 ‘Symmetry interaction’ model

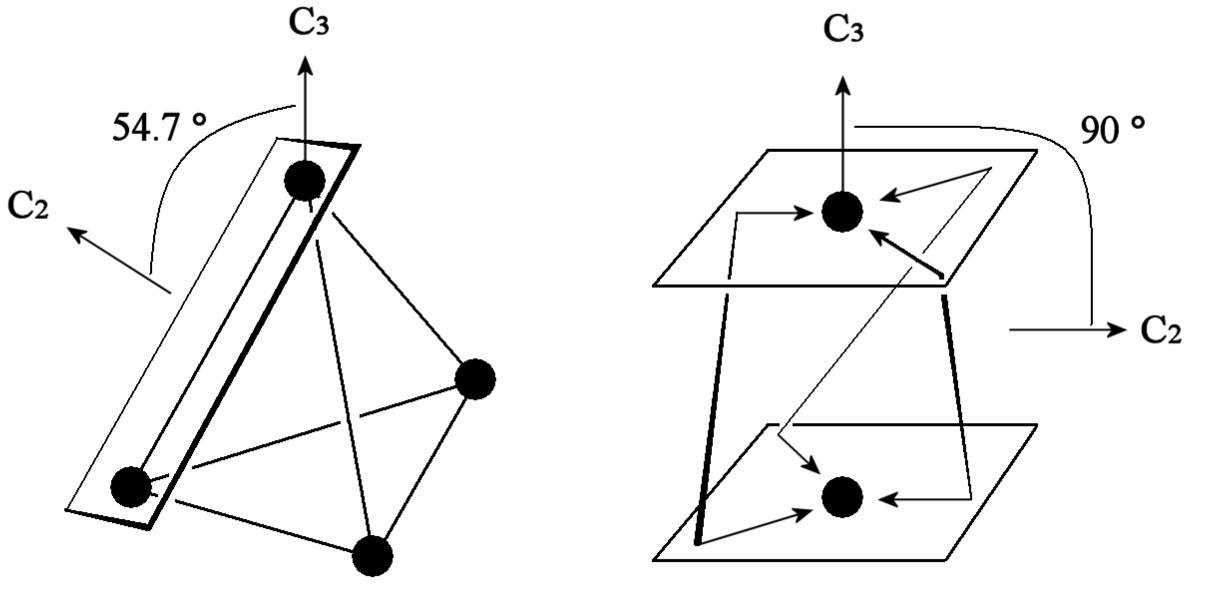


Figure 1 Geometric relationship between symmetry operations in tetrahedra (*LHS*) and helicates (*RHS*).[33]

The ‘symmetry interaction’ model takes advantage of multibranched *chelating* ligands, as exemplified by Lehn, Raymond and Saalfrank, which show increased preorganisation and stronger binding energies as a result of the chelate effect.[43] Geometric relationships between ligand and metal ion form the conceptual basis to understand the formation of a given supramolecular architecture. For example, a tetrahedron contains four C_3 and six C_2 axes (Figure 1, *LHS*). The structure may be formed from the combination of four C_3-symmetric *tris*-bidentate chelated octahedral metal centres spanned by six C_2-symmetric *bis*-bidentate ligands (M_4L_6 tetrahedron). This approach places the metal ions at the vertices of the tetrahedron and the ligands on the edges. However, not any combination of C_2-symmetric *bis*-bidentate ligands and octahedrally coordinated metal centres will generate a tetrahedron. The structure of the ligand is critical in achieving the correct orientation of symmetry elements in the target structure (*e.g.* 54.7° between the C_2 and C_3 axes for a tetrahedron).[33] Another rationally designed example is a M_2L_3 triple helicate with D_3 symmetry, where it is important that the C_3 and C_2 symmetry axes are perpendicular to each other (Figure 1, *RHS*).[33]

1.2.1.2 'Molecular library' model

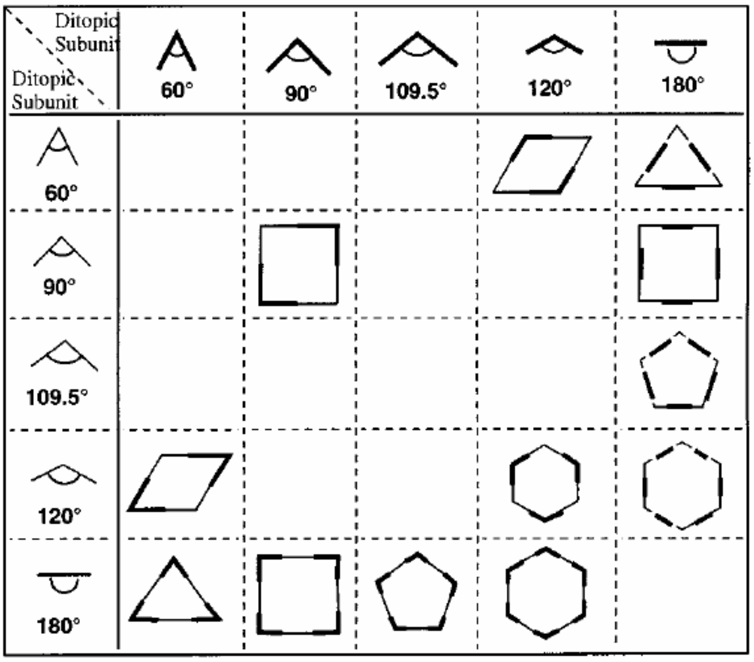


Figure 2 Molecular library of 2-D cyclic molecular polygons constructed *via* combination of ditopic building units with fixed geometry.[33]

The 'molecular library' model takes advantage of multibranched *mono*dentate ligands and was first applied by Verkade[45] and later elaborated by Fujita[44,48] and Stang.[46,47] It describes metal and ligand components as angular and linear pieces to be combined in the formation of two-dimensional polygons and three-dimensional polyhedra. A matrix of combinations of these simplified elements provides a formula for the synthesis of an array of self-assembled architectures (Figure 2). For example, a molecular square can be assembled in several different ways, such as combining four linear with four 90° angular building blocks or by combining four 90° angular subunits. Similarly, three dimensional polyhedra can be constructed where a minimum of one building unit has to be a tritopic subunit.[33]

1.2.2 2-D polygons

A variety of cyclic arrangements forming two-dimensional polygons are reported in literature. These examples vary greatly in nuclearity and a small selection of complexes is presented in this thesis.

1.2.2.1 Dinuclear assemblies

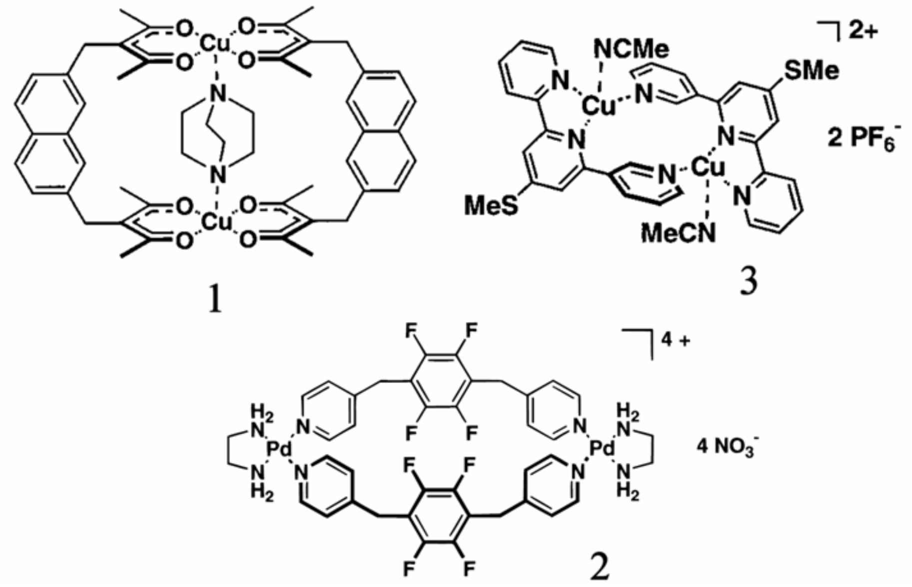


Figure 3 A selection of dinuclear metallamacrocyles.

One of the first cyclic self-assembled host molecules was reported by Maverick[51] and co-workers (Figure 3, *Top left*). This complex **1** comprises two copper(II) ions and two *bis*-(beta-diketone) ligands functioning as a host molecule for small amino bases such as pyrazine or pyridine.[51,52]

By introducing a non-linear spacer between the two pyridine rings of bipyridine, Fujita and co-workers[53] assembled the water-soluble macrocycle **2** upon coordination to [Pd(en)$(NO_3)_2$] (en = ethylenediamine), which represents a 90° corner unit by coordinative blockage of two *cis*-sites on the square planar palladium(II) centre with the ancillary ‘en’ ligand (Figure 3, *Bottom*). Due to the perfluorinated phenylene subunits, the complex was capable of recognizing electron-rich compounds, such as naphthalene, in aqueous solution.

Hannon and co-workers employed an interesting strategy to overcome the need of ancillary ligands commonly found in self-assembly processes with palladium(II) corner units.[33,44] They incorporated a chelating unit and a monodentate coordination site within one ligand system,[54] thus forming the 2:2 metal to ligand complex **3** (Figure 3, *Top right*).

1.2.2.2 *Trinuclear assemblies*

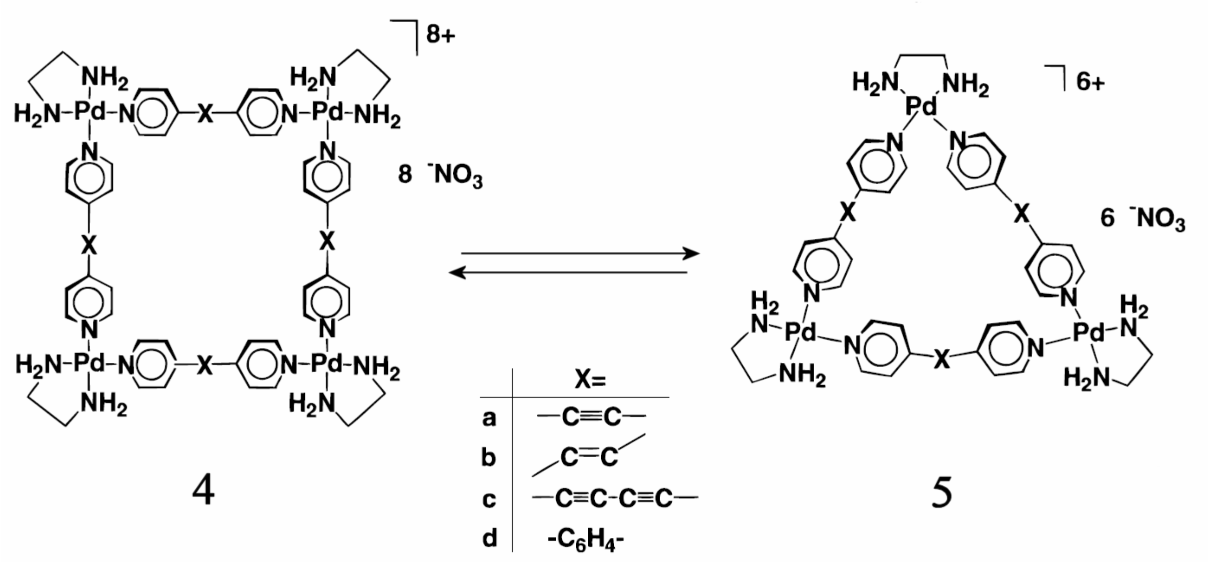


Figure 4 Equilibrium between molecular squares (**4**, *LHS*) and triangles (**5**, *RHS*) in solution.[33]

Although *de novo* construction of a molecular triangle does not seem to be synthetically complex, only a surprisingly small number of compounds have been reported. Such examples include observations by Fujita[55,56] when reacting [Pd(en)$(NO_3)_2$] with one equivalent of several *bis*-heteroaryl ligands in water (Figure 4). Under the reported reaction conditions, two different self-assembled macrocycles were observed: molecular squares **4a-d** and molecular triangles **5a-d**. The products are in equilibrium as confirmed by NMR-spectroscopy, with the major species in solution being the molecular square **4**. Assignments were supported by the observation that the equilibrium is concentration-dependent: at higher concentrations the ratio shifted towards the formation of the less strained molecular square **4**. This can be rationalized by thermodynamic considerations: molecular squares are less strained and hence more stable in terms of enthalpy, while entropically the molecular triangles are favored since they assemble from a smaller number of components.

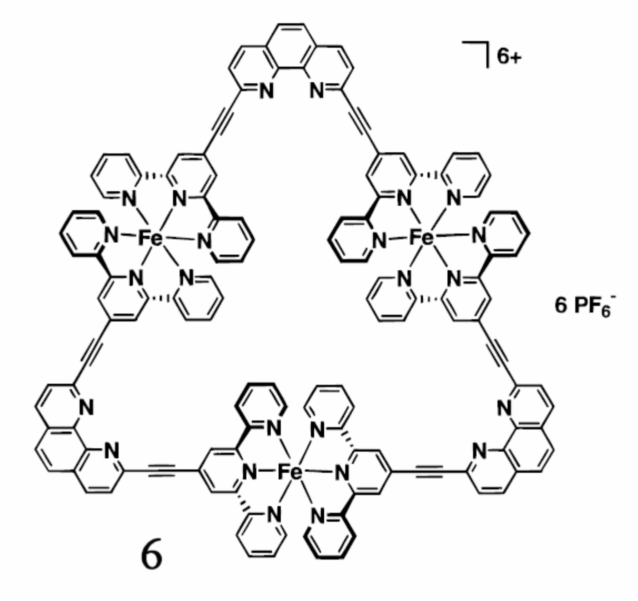
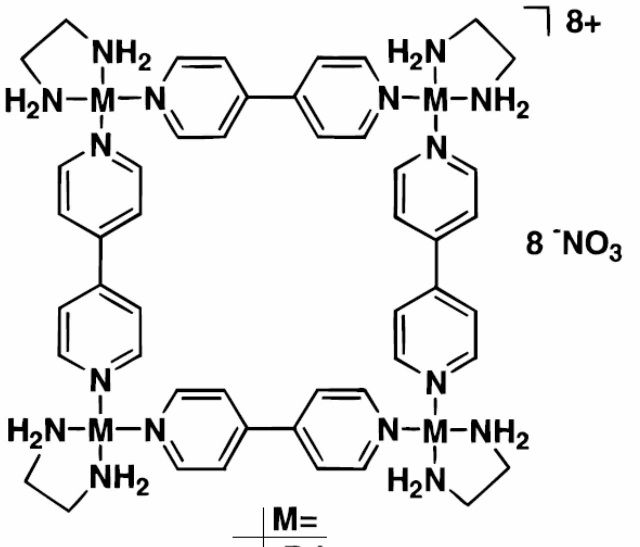


Figure 5 Molecular iron(II) triangle **6**.[57]

Similar equilibria between multinuclear species were observed by Ziessel and co-workers[57] upon formation of the trinuclear iron(II) complex **6** (Figure 5).

1.2.2.3 Tetranuclear assemblies



	M=
a	Pd
b	Pt

7

Figure 6 Molecular squares **7a** and **7b**.[55]

Molecular squares represent one of the most commonly formed supramolecular assemblies. These macrocyclic species exhibit 90° corners and therefore a wide variety of transition-metal complexes with two accessible *cis*-coordination sites are suitable to form molecular squares. These include metals with square planar, trigonal bipyramidal or octahedral coordination geometries. In addition to the earlier described equilibria between molecular squares and triangles, Fujita[55,58] also reported the quantitative formation of molecular squares by reaction of 4,4′-bipyridine and $[M(en)(NO_3)_2]$ (M = Pd (**7a**), Pt (**7b**)) in water (Figure 6). These squares show the ability for molecular recognition of neutral aromatic guests such as naphthalene and benzene. A great variety of tetranuclear molecular squares and rectangles is present in literature, including both homo- and heteronuclear assemblies.[59-65]

1.2.2.4 Higher nuclearity assemblies

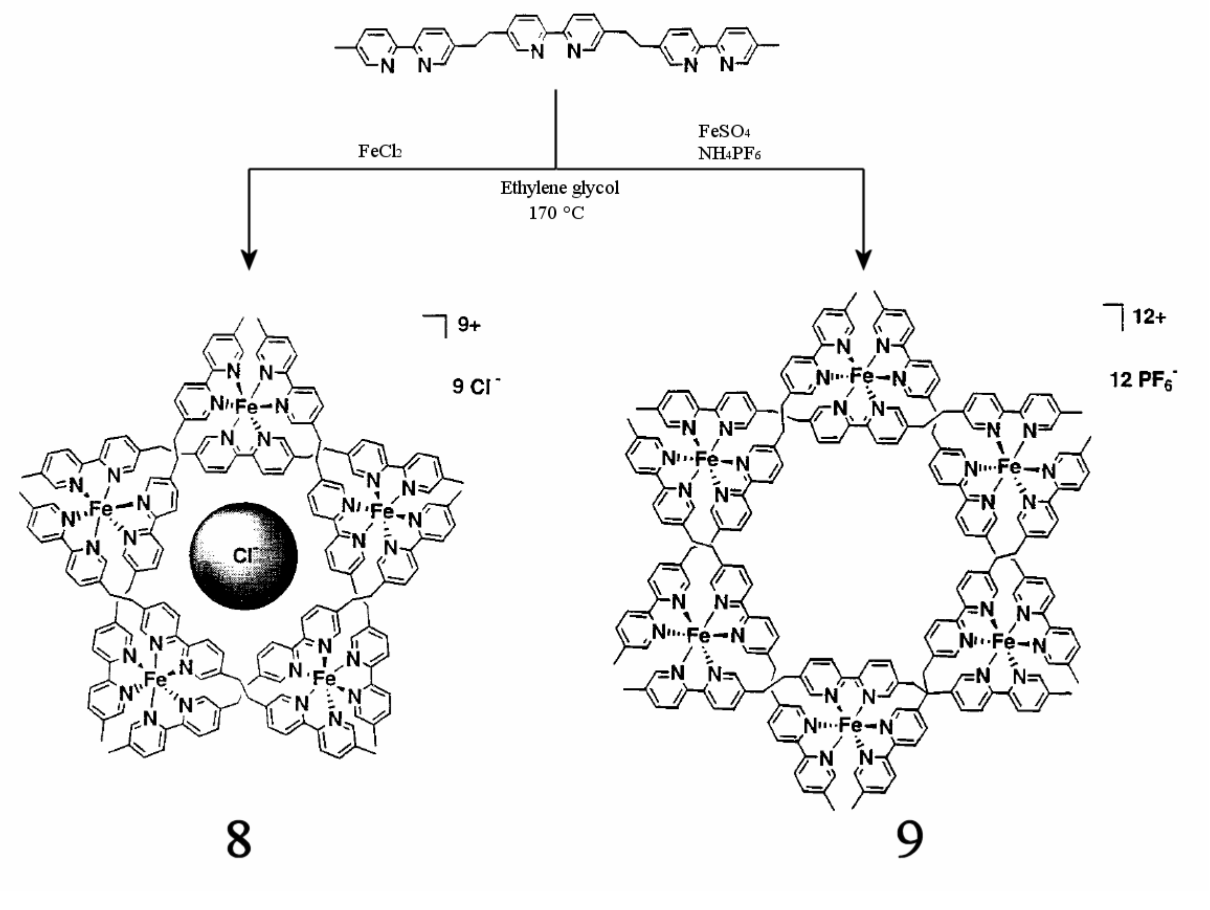


Figure 7 Anion templated formation of cyclic penta- (**8**, *LHS*) or hexanuclear (**9**, *RHS*) iron(II) clusters.[66]

Lehn and co-workers[66] have reported the self-assembly of the iron-containing molecular pentagon **8** and hexagon **9**. Both structures facilitate octahedral iron(II) centres coordinated by a *tris*-bipyridyl ligand forming circular, double-stranded helical structures (Figure 7). These reactions demonstrate the remarkable influence of anion templating effects on the formation of polynuclear assemblies. The smaller chloride ions template the formation of the smaller pentagon **8**, whereas the larger hexagon **9** is formed upon templation of the larger sulphate counterions.

Other molecular hexagons include work reported by Saalfrank (Fe_6),[67] Bernardinelli (Ag_6)[68] and Matsumoto (Cu_6).[69] Higher nuclearity assemblies such as molecular heptagons (Fe_7)[70] and octagons (Co_8, Pt_8)[71,72] reported by Köhler, McCleverty and Lin are also present in the literature. It is interesting to note that in the case of the molecular copper(II) hexagon **11** reported by Matsumoto and co-workers, the cyclic arrangement can be 'switched' on and off by controlling the pH in solution. In the mononuclear complex **10**, the ligand coordinates to one copper(II) ion in a tridentate fashion with a neutral imidazol-unit. The square planar copper(II) coordination sphere is completed by a water molecule. Deprotonation by an increase in pH results in condensation of **10** *via* coordination between the imidazolate nitrogens and copper(II) ions (Figure 8).

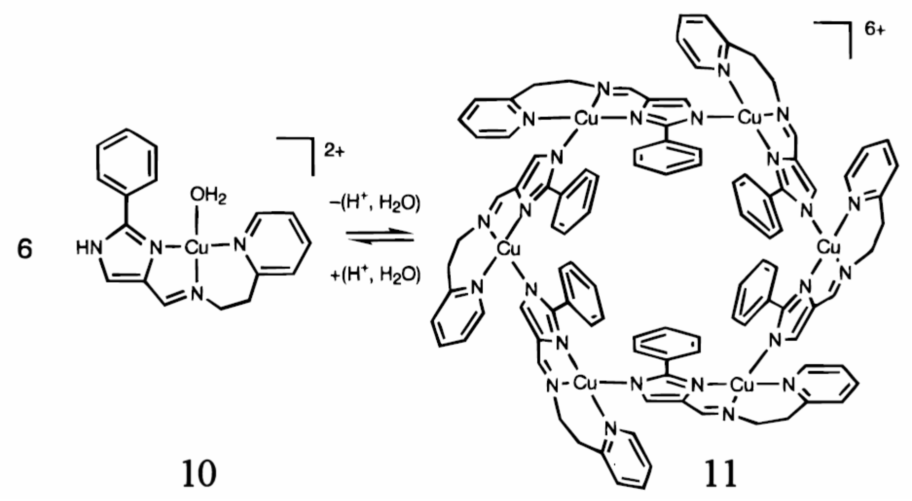


Figure 8 pH controlled reversible 'switch' from mononuclear (**10**, *LHS*) to hexanuclear (**11**, *RHS*) assemblies.[69]

1.2.3 3-D cages and polyhedra

A great number of self-assembled three-dimensional complexes has been reported in this rapidly developing field of supramolecular chemistry and are subject to a number of review articles.[33,38,44,73-79] Only a select few examples of three-dimensional polyhedra can be presented in this thesis.

1.2.3.1 Triangular prism and cylinders

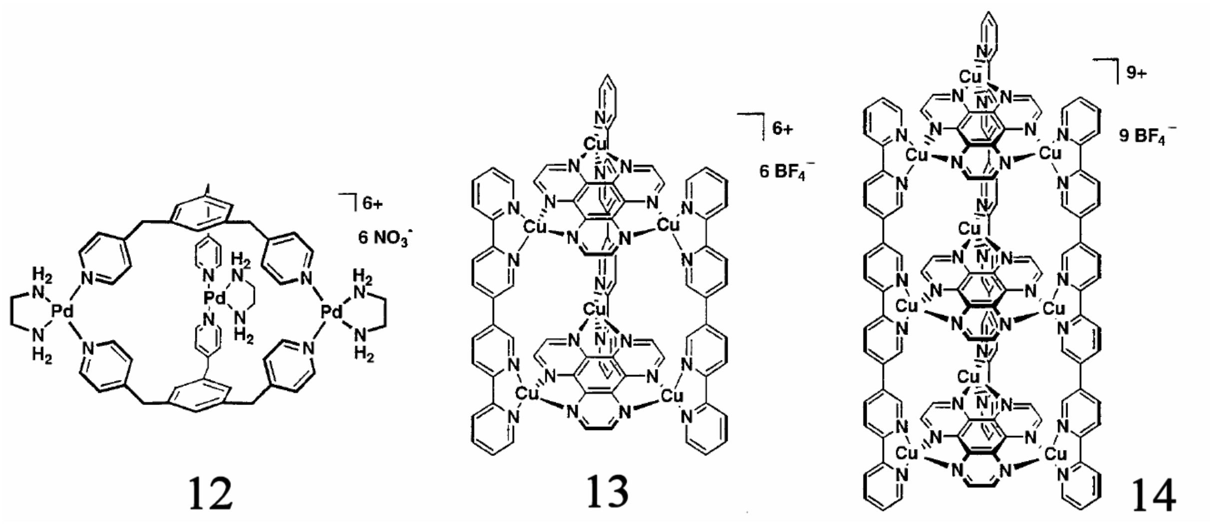


Figure 9 Selection of triangular prismatic (**12**, *Left*) and cylindrical (**13,** *Centre* and **14**, *Right*) complexes.[33]

Triangular prism represent the simplest three-dimensional architectures assembled from the fewest number of components. Their design requires only five building blocks; two angular tritopic subunits and three linear connecting units. Formation of such a cage-like molecule was reported by Fujita and co-workers,[80] whose complex **12** is preferentially formed in the presence of hydrophobic guest molecules (Figure 9, *Left*).

Further extension of triangular arrangements leads to the construction of self-assembled cylinder-type structures, which require design and choice of components that fulfil criteria such as recognition, orientation and termination. Examples involving two types of ligand and several copper(I) ions were reported by Lehn and co-workers.[81] By choosing linear *bis*- or *tris*-bipyridyl ligands in combination with suitable μ_3 bridging ligands, reaction with copper(I) resulted in the formation of the cylindrical complexes **13** and **14** (Figure 9, *Centre* and *Right*).

1.2.3.2 Tetrahedra

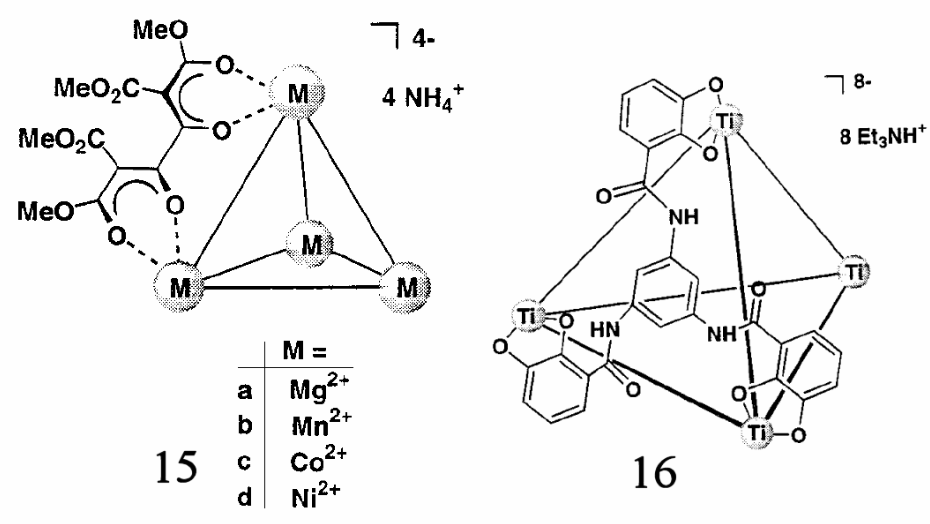


Figure 10 Molecular assemblies of M_4L_6 (**15a-d**, *LHS*) and M_4L_4 (**16**, *RHS*) tetrahedra.[33]

Two common types of tetrahedra are present in the literature: M_4L_6 and M_4L_4 clusters. In the case of M_4L_6 complexes, six C_2 symmetric *bis*-bidentate ligands form the six C_2 symmetry axes of the tetrahedron coordinating to four octahedral metal centres at the vertices (Figure 10, *LHS*). Saalfrank and co-workers[82,83] were the first to report M_4L_6 complexes, which since then have been elaborated on and more generalised by others.[84-86] The first examples were formed from dimalonic ester ligands with a variety of metal ions such as magnesium(II), manganese(II), cobolt(II) and nickel(II) (**15a-d**). Further studies led to the design principles described earlier and resulted in a great variety of tetrahedra with different metal ions and varying cavity sizes by increasing the length of the organic linker molecules.[87-90] Interestingly, it was shown that guest molecules could be incorporated in the rigid cavities of these complexes,[87,90-92] which is of great interest for guest exchange[91,92] and application of these hydrophobic pockets in catalytic processes.[93,94]

Contrary to μ_2 bridged metal centres, four C_3 symmetric *tris*-bidentate ligands coordinate to four octahedral metal centres at the vertices of M_4L_4 tetrahedra. Utilizing a *tris*-catechol ligand, the titanium(IV) M_4L_4 tetrahedron **16** is formed,[95] where each ligand represents a face of the tetrahedron (Figure 10, *RHS*). Further investigations into these types of M_4L_4 complexes were carried out by Raymond[95] and others.[96]

1.2.3.3 *Octahedra*

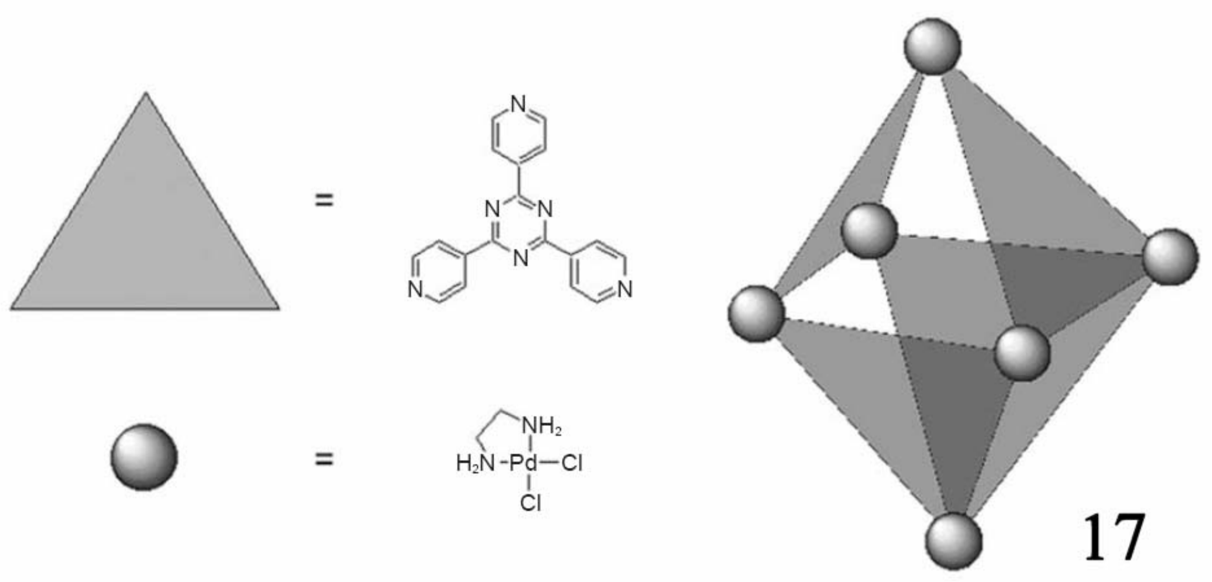


Figure 11 Molecular assembly of the M_6L_4 octahedron **17**.[50]

One of the most studied supramolecular cages is the octahedron **17** reported by Fujita and co-workers[50] This cage assembles from four 'panels', C_3-symmetric *tris*-monodentate pyridine donor ligands and six *cis*-capped palladium(II) ions (Figure 11). The large size of the host cavity allows encapsulation of multiple guest molecules that show extensive host-guest interactions. For example, Fujita reported the catalysis of styrene oxidation in aqueous solution in the presence of **17**.[93] The nano-cavity thereby acts as a phase transfer catalyst for styrene and product between organic and aqueous phase. No reaction occured when styrene was treated with the catalyst in the absence of the nanovessel, indicating the catalytic process occurring inside the cavity of **17**. Furthermore, stereoselective [2+2] photo-addition reactions are accelerated hundred-fold within the cavity of **17**.[94]

1.2.3.4 Cubes

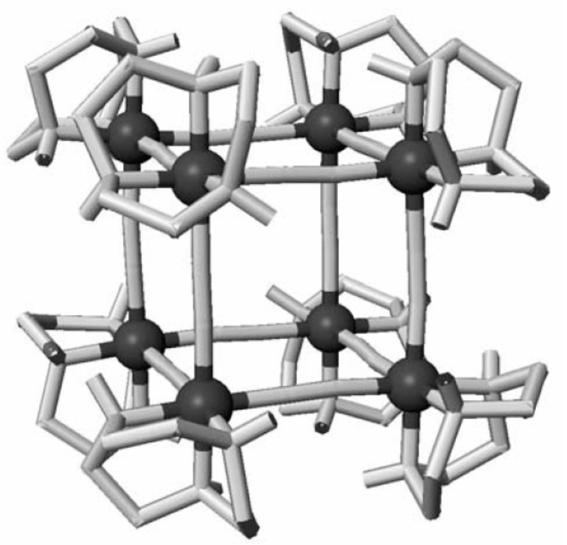


Figure 12 Molecular cubes from a variety of metal ions (dark spheres): Co(III), Cr(III) and Mo(III). The octahedral metal ions are linear bridged by cyanide ligands and face-capped to prevent oligomerization reactions.

A variety of cubic cages have been reported in literature. Long and co-workers have produced a number of discrete cubic cages with eight cobolt(III), chromium(III) and molybdenum(III) ions located at the vertices and cyanide as bridging ligands. Face capping ligands facilitated the formation of the molecular box rather than a three-dimensional network by prohibiting further coordination to the metal centres (Figure 12).[97-101]

1.2.3.5 Cuboctahedra

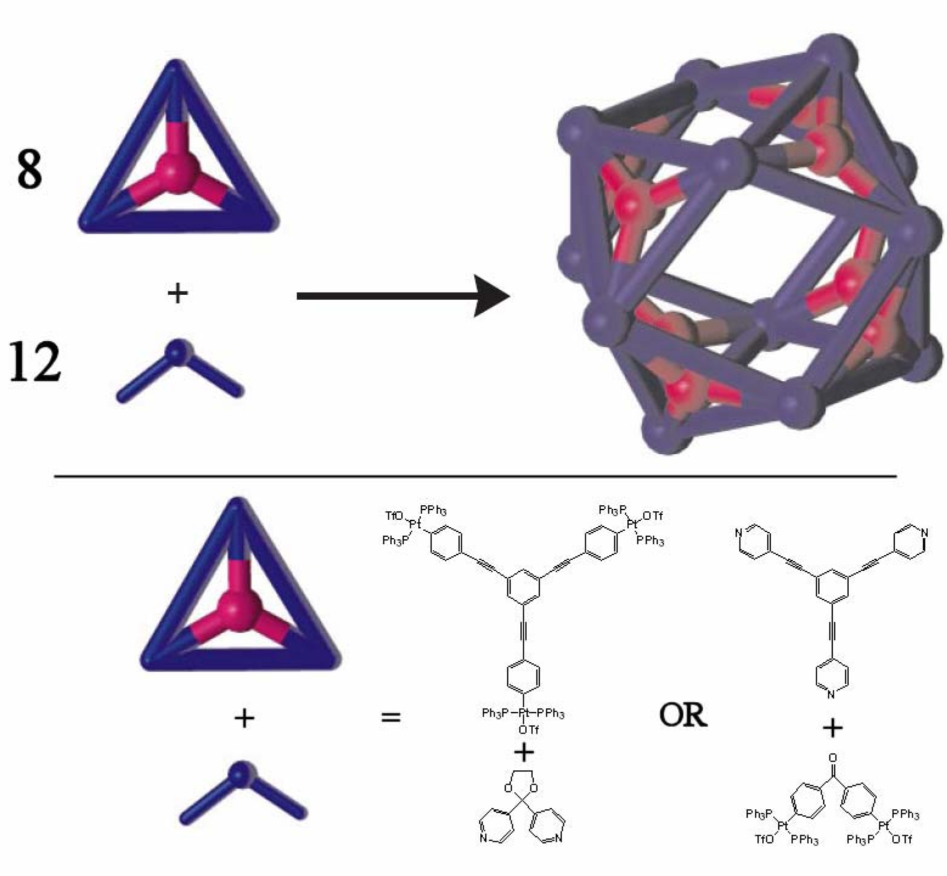


Figure 13 Formation of molecular cuboctahedra by eight tritopic and twelve ditopic building units.[102]

Stang and co-workers were the first to report the synthesis of molecular cuboctahedra.[102] These types of macromolecules are the first examples of artificial synthetic assemblies exhibiting *O*-symmetry. The complexes were formed by two different combinations of eight C_3-symmetric planar tridentate units with twelve C_2-symmetric ditopic units to spontaneously assemble the cuboctahedra (Figure 13). Both complexes were characterised in solution and their sizes were assessed to contain 5 nm voids, which makes them extremely interesting as supramolecular host molecules.

1.2.4 Helicates

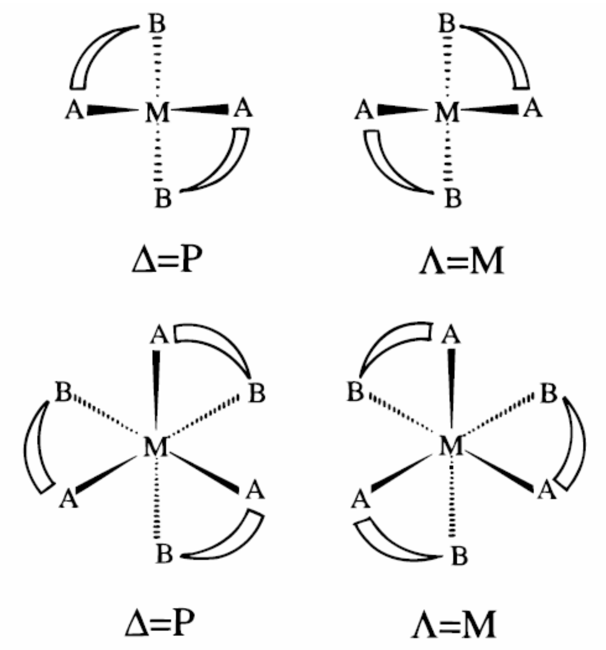


Figure 14 Absolute configurations at metal centres of *bis*-bidentate (*Top*) and *tris*-bidentate (*Bottom*) complexes. Views are along the principal axis.

The term 'helicate' was first introduced by Lehn and co-workers in 1987 as a description of a polymetallic helical double-stranded complex.[103a] The concept of helicates extends the idea of classical coordination complexes towards more complex supermolecules in which two or more metal ions lie on a helical axis.[1,103a-c] Thus, a helicate is a discrete supramolecular complex formed by one or more covalent organic strands entwined and coordinated to a series of metal-ions defining the helical axis.

Helical arrangements implicitly result in chirality of the coordinated metal ions, producing right- (Δ = P) or left-handed (Λ = M) helicity around the principal axis (Figure 14)[103b,104-107] Variations in helical arrangements can be described (i) by the number of coordinated strands, corresponding to *single*, *double* and *triple* stranded helicates and (ii) by the symmetry of the coordinating strands. Identical strands correspond to *homo*topic arrangements, whereas non-symmetrical strands represent *hetero*topic helicates, which can form isomers by different orientations of the coordinating binding units ('Head to Head' or 'Head to Tail') (Figure 15). From the myriad of reported helical structures, only a few examples are represented in this thesis.

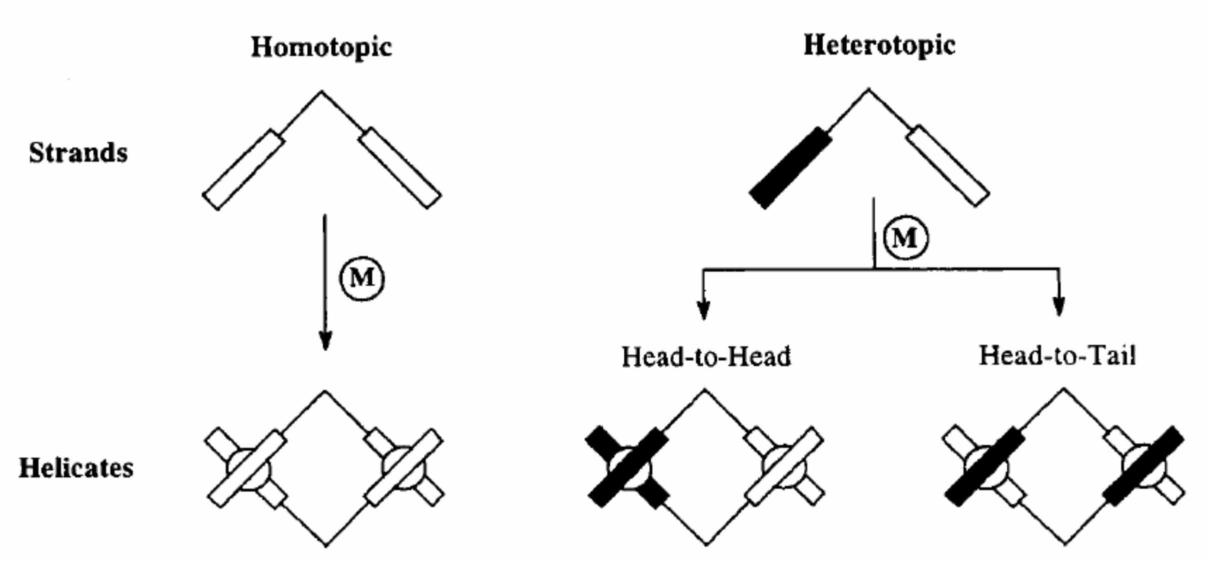


Figure 15 Overview of *homo*topic (*LHS*) and *hetero*topic (*RHS*) helical arrangements.[77]

1.2.4.1 Single stranded

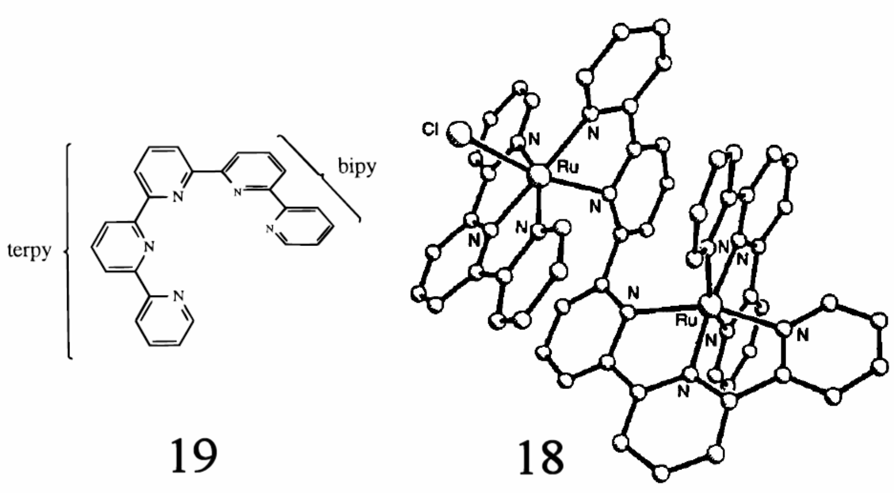


Figure 16 Representation of the single stranded helicate **18** (*RHS*) formed from quinquepyridine **19** (*LHS*) and ruthenium(II) ions.[77]

The quinquepyridine ligand **19** can form a heterotopic, dinuclear single stranded helicate with ruthenium(II) (**18**).[108] The crystal structure shows two different six-coordinate metallic sites, with one ruthenium(II) coordinated to the terpyridine subunit of **19** and the second ruthenium(II) bound to the remaining bipyridine subunit (Figure 16). The helical twist of the strand (74.9°) results from the torsion between the two connected pyridine rings of each subunit. The remaining vacant coordination sites around ruthenium(II) are occupied by one chloro and two tridentate terpyridine ligands.

1.2.4.2 *Double stranded*

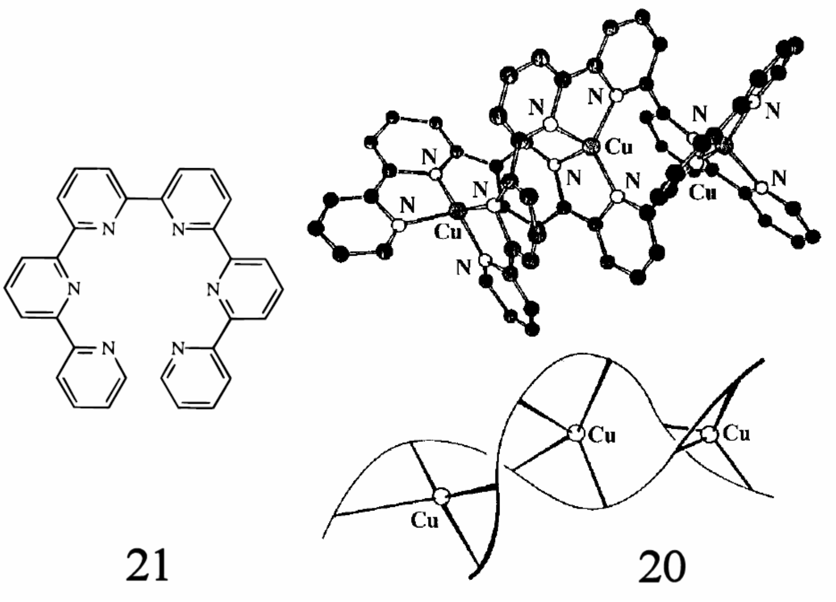


Figure 17 Representation of the double stranded helicate **20** (*RHS*) formed from sexipyridine **21** (*LHS*) and copper(I) ions.[77]

Although it was not possible to crystallise the trinuclear complex **20**, unambiguous characterisation by FAB-MS and ^{1}H-NMR (D_2-symmetric in solution) was reported by Constable and co-workers.[109,110] Two *tris*-bidentate sexipyridine ligands **21** wrap themselves around three copper(I) centres forming the trinuclear double-stranded helicate **20** (Figure 17). Other examples of double-stranded helicates are the circular penta- and hexanuclear iron(II) complexes **8** and **9** described earlier.

1.2.4.3 Triple stranded

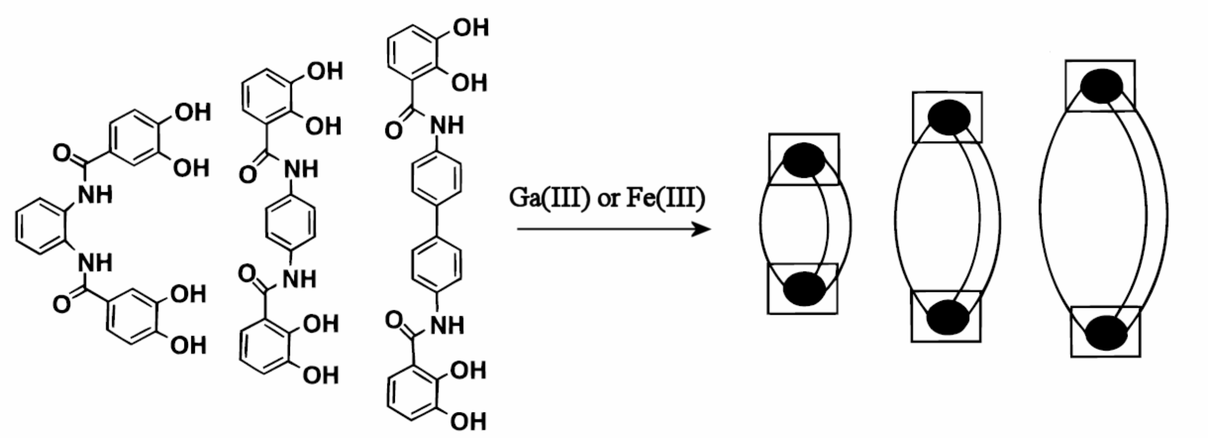


Figure 18 Self-recognition of triple stranded helicate formation (*RHS*) with *bis*-catechol ligands (*LHS*) and iron(III) or gallium(III) ions.[33]

The spontaneous, highly selective process of helicate formation has been reported to exhibit self-recognition.[111,112] In the case of gallium(III) or iron(III) coordination to *bis*-bidentate catechol ligands, Raymond and co-workers have reported the exclusive formation of complementary *homo*-triple helicates in high yield without traces of oligomeric or mixed species (Figure 18). The high degree of conformational rigidity of each donor subunit combined with differences in the distance between binding sites in each ligand provide a possible explanation for the self-recognition of the assembled complexes.

1.2.5 Interlocked structures and topology

Multi-dimensional interpenetrating networks and molecular entanglements observed in catenanes, rotaxanes and molecular knots have long fascinated chemists with beautiful examples of ingenious design. Framework solids, often accessible by self-assembly under mild conditions, are particularly interesting due to their chemical and structural diversity and challenging construction.[113] Conceptual approaches to the construction of frameworks are based on the idea of a net. Nets are abstract mathematical entities consisting of a collection of points or nodes with clearly defined connectivity or topology. The topology of a net can be described by the general term (n,p) where n is the number of nodes in the smallest closed circuit and p is the number of circuits surrounding the node. However, more complete is the Schläfli notation $n^{p(p-1)/2}$, where n is the number of nodes in the smallest closed circuits in the net and $p(p-1)/2$ represents the combinations of connections to two neighboring nodes. Thus in Figure 19 (*LHS*), the number 6 in the symbol 6^3 indicates that the smallest complete circuits in the net are hexagons, and the number 3 indicates that each node is surrounded by three hexagonal circuits. In the case of the net shown on the right hand side, the complete notation should be $4^4 6^2$. This was, however, simplified by Wells[114] to 4^4 by arbitrarily excluding circuits involving co-linear connections.

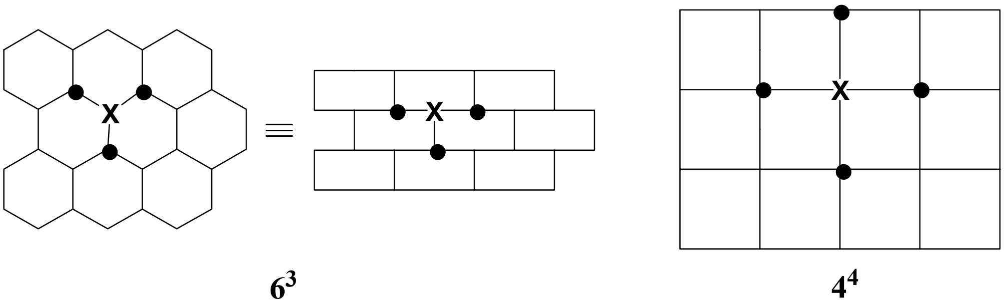


Figure 19 Network topologies for 6^3 (*LHS*) and 4^4 (*RHS*) nets.

It is interesting to note that both 6^3 nets in Figure 19 represent different geometries but identical topologies. This example illustrates the general point that nets may be geometrically deformed to any extent provided no connections are broken.

1.2.5.1 Zero-dimensional

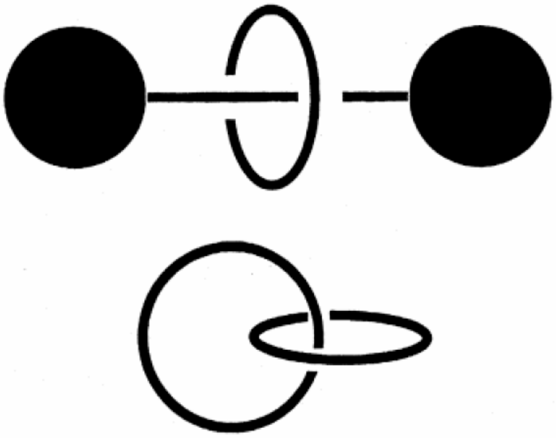


Figure 20 Topological representation of rotaxanes (*Top*) and catenanes (*Bottom*).[113]

Unlike helicates, interpenetrating zero-dimensional structures can only be disentangled by breaking of the composite strands. There are a number of ways in which these strands can be interlocked. For example, catenanes consist of two or more independent rings locked together (Figure 20, *Bottom*), whereas rotaxanes comprise a ring encircling the shank of an independent dumbbell-like component (Figure 20, Top). Molecular knots show per definition self-entanglement.[115] Synthesis and characterisation of these types of structures are particularly attractive aesthetically, and because of the challenge presented in designing interpenetrating molecular architectures. Fascinating examples of 'interlocked' cages were recently reported by Fujita and co-workers, in which two identical three-fold catenated units interpenetrate to form the overall cage structure. (Figure 21).[116]

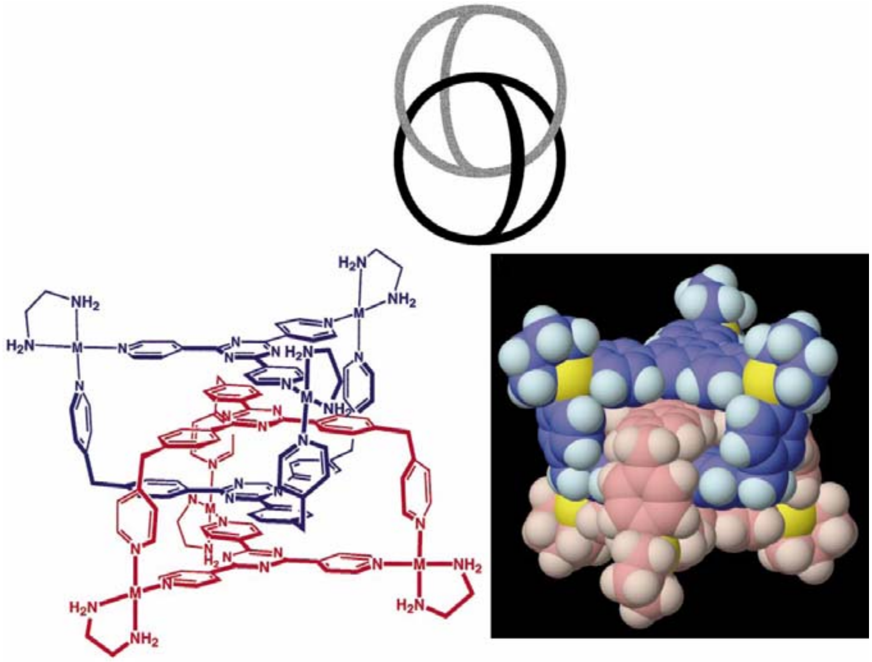


Figure 21 Two examples of three-fold catenated cages: *Top*: Topological representation; *Bottom*: Structural diagram (*LHS*) and space filling representation (*RHS*) of 'interlocked' cages, M = Pd and Pt.[116]

1.2.5.2 One-dimensional

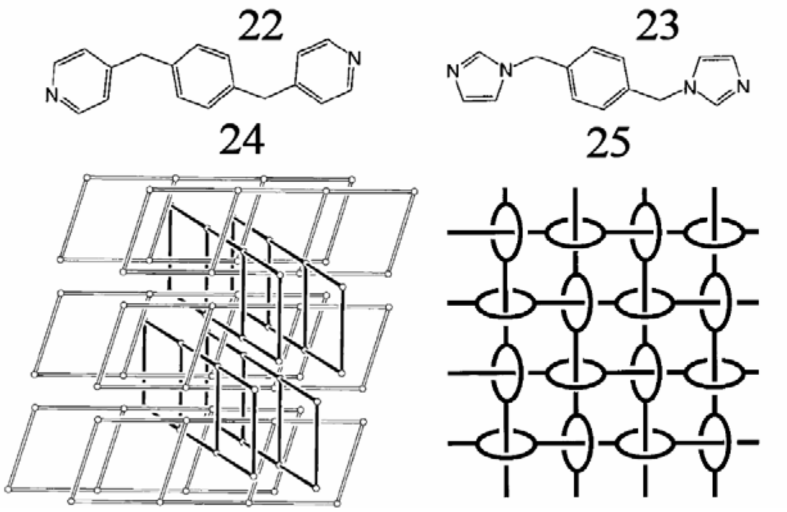


Figure 22 Topological representation of 1-D interpenetrating polymers. *LHS*: ligand **22** facilitates the formation of ladder-like chains composed of $[\mathrm{Cd}_2(\mathbf{22})(\mathrm{NO}_3)_4]$, resulting in the 3-D interlocked structure found in **23**; *RHS*: ligand **24** facilitates the formation of a polyrotaxane type architecture composed of $[\mathrm{Ag}_2(\mathbf{24})](\mathrm{NO}_3)_2$, forming the 2-D interlocked framework found in **25**.[113]

One-dimensional interpenetrating polymers are extremely rare, in fact only two examples are reported in literature. The first is based on the ligand **22** and affords infinite, 1-D ladder-like chains of the composition $[\mathrm{Cd}_2(\mathbf{22})(\mathrm{NO}_3)_4]$,[117] resulting in a three-dimensional interlocked structure (**23**, Figure 22, *LHS*). The second structure is based on the ligand **24** and forms a 1-D polyrotaxane-type coordination polymer with the composition $[\mathrm{Ag}_2(\mathbf{24})](\mathrm{NO}_3)_2$, resulting in a two-dimensional interlocked framework (**25**, Figure 22, *RHS*).[118]

1.2.5.3 Two-dimensional

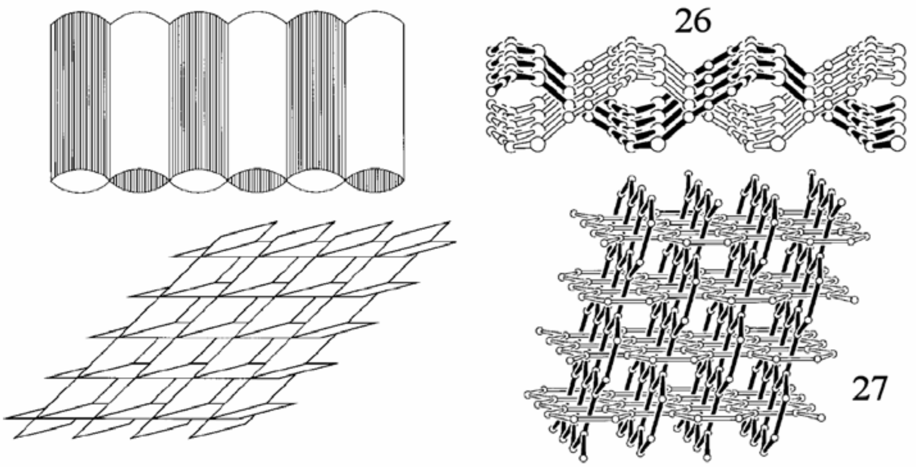


Figure 23 Topological representation of 2-D interpenetration polymers. *Top*: Parallel interpenetration resulting in the 2-D interlocked structure found in **26**, which is composed of [Ag(tcm)]; *Bottom*: Inclined interpenetration forming the 3-D interlocked framework found in **27**, which is composed of $[Cu_2(pz)_3](SiF_6)$.[113]

Two major categories of interpenetrating 2-D coordination polymers can be described as *parallel* and *inclined* interpenetration (Figure 23). Parallel interpenetration involves corrugated sheets arranged with their average planes parallel to each other, so that each is able to pass through the other an infinite number of times. The resulting structure from this interpenetration is itself two-dimensional, with the composite sheets stacked on top of one another. One example of parallel interpenetration is given in the [Ag(tcm)] (tcm = tricyanomethanide) complex forming a 6^3 net with three connected nodes provided by alternating central carbon atoms of the tcm ions and three-coordinate silver(I) centres (**26**, Figure 23, *Top right*).[119,120]

Inclined interpenetration polymers arrange one sheet in a tilted fashion with respect to another, resulting in an overall three-dimensional interlocked structure. One example of this type of interpenetration is given in the complex $[Cu_2(pz)_3](SiF_6)$ (pz = pyrazine). This complex is based on a 6^3 net with three connected nodes provided by copper(I) centres linked to three neighbouring copper(I) centres by pyrazine bridges (**27**, Figure 23, *Bottom right*).[121]

1.2.5.4 Three-dimensional

A variety of interpenetrating 3-D coordination polymers are reported. The topology varies from uniform three-, four- or six-connected nets to multi-nodal combinations of nets containing three- and five- or three- and six-connected nodes. Each notation can be further classified into subgroups with slight topological variations in the resulting network. A comprehensive review of literature examples has been published by Batten and Robson,[113] and an overview of the more theoretical aspects of topological systems is given by Wells.[114]

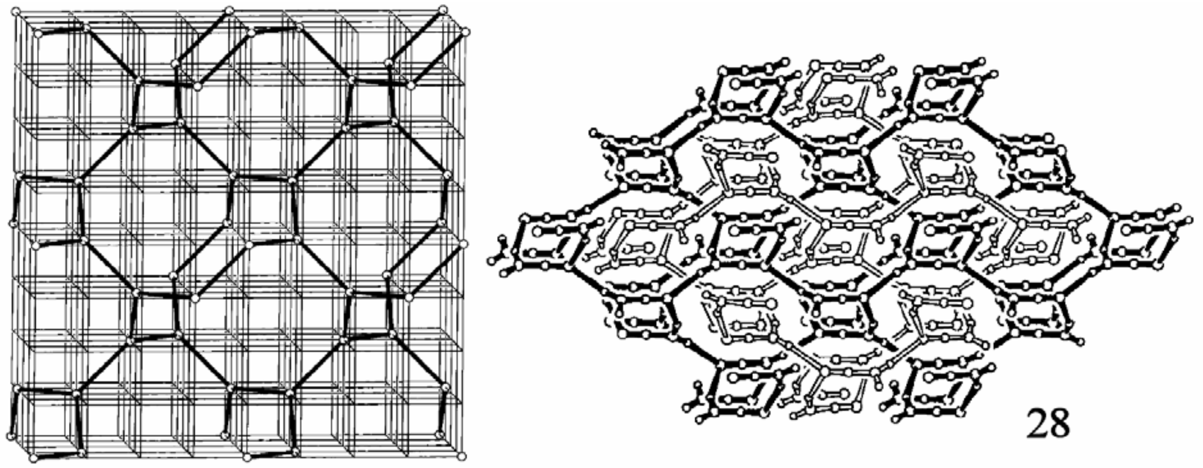


Figure 24 Topological representation of 3-D interpenetrating polymers. *LHS*: A chiral 10^3-*a* net; *RHS*: Enantiomorphic interpenetration of two 10^3-*a* nets with opposing handedness found in **28**, which is composed of $[Ag_2(2,3\text{-}Me_2pz)_3](SbF_6)$.[113]

One example of three-connected 3-D nets is represented by 10^3-*a* nets (the *a* indicates the most symmetrical of a number of possible variations). The network is shown in (Figure 24, *LHS*) in its geometrically most symmetrical cubic form. Every node shows a trigonal planar environment with 120° angles. A characteristic feature of the 10^3-*a* net is the presence of four-fold helices, all of identical handedness, running parallel with the three cubic axes. The net as a whole is therefore chiral. However, interpenetration can occur with an identical net of the same handedness[122,123] and also with a net of opposing handedness, in which case the structure represents a three-dimensional racemate. Such enantiomorphic interpenetration is found in the crystal structure of $[Ag_2(2,3\text{-}Me_2pz)_3](SbF_6)$ in which the silver(I) atoms provide the three-connected nodes for the 10^3-*a* net (**28**, Figure 24, *RHS*).[124]

1.2.6 Application and outlook

Progress in utilizing cavity-containing supramolecular hosts in catalysis raises expectations to further increasing the applicability of such systems. By providing a unique molecular environment isolated from the bulk solvent, a high local concentration of reagents is observed within the cavities. Thus, reactions of hydrophobic substrates can occur in aqueous media within the hydrophobic cavities resulting in stereospecific and catalytic reactions otherwise not observed in bulk solution. Furthermore, fixation of unstable intermediates or products[101,125,126] within these cavities can provide insight into reaction mechanism. Further application involves deposition of the catalytically active complexes onto surfaces as demonstrated by Reinhoudt and co-workers.[127]

Self-assembly has proven to be a powerful tool for the formation of large, multifunctional architectures. Most metal ions can be incorporated into supramolecular assemblies as demonstrated by various examples in literature. This rapidly growing field of chemistry routinely produces new structures that further deepen our understanding of structural design principles and give insight into the processes that govern supramolecular formation.

2 AIMS

Current interests in supramolecular chemistry lie within the synthesis and characterisation of suitable building blocks to construct supramolecular architectures. Since rigidity of a given ligand system plays an important role in rational design approaches, the main focus so far has been on aromatic ligands with in-built rigidity due to aromatic planarity, delocalisation and conjugation.[33,38,44,48] However, there are less examples that utilise aliphatic based ligands to form supramolecular assemblies.[128-130]

The aim of this work is to exploit the use of rigid aliphatic ligand systems in supramolecular chemistry and to demonstrate their usefulness in constructing supramolecular architectures. The design of such aliphatic ligand systems in this thesis is based on certain requirements: (i) rigidity must be maintained in order to rationally design supramolecular assemblies, (ii) multiple donor groups are necessary to link metal centres together *via* coordinative interactions, (iii) the binding sites must be non-interacting to ensure the formation of polynuclear complexes. Differentiating these binding sites might further prove useful in specifically addressing different parts of the molecule by (iv) dividing the donor groups into sets of binding sites with varying denticity, (v) incorporation of hard and soft donor groups, thus varying their coordination preferences, (vi) enabling second order interactions like hydrogen-bonded interactions.

Consideration of these ligand requirements leads to a set of molecules based upon the rigid cyclohexane backbone. The cyclic structure provides rigidity and the *equatorial* and *axial* positions on the chair conformation differentiate between multiple binding sites. As a starting point, the simplest case will be investigated as proof of concept. In this case, three binding sites in 1,3,5-position on the cyclohexane ring are chosen to be in a *cis,trans*-configuration. This places two donor groups in *cis* position and a third *trans*, thus generating two sets of non-interacting binding sites. Furthermore, the donor atoms are chosen to be identical, namely amino groups. Amino functionalities are excellent donor groups in coordination chemistry, which also have the ability to forming strong hydrogen-bonded interactions, particularly upon protonation.

This project investigates the coordination chemistry of *cis,trans*-1,3,5-triaminocyclohexane (*trans*-tach, **29**) and its potential as a building block in supramolecular chemistry. The coordination chemistry[131-136] and application[137-142] of its geometrical isomer, *cis,cis*-1,3,5-triaminocyclohexane (*cis*-tach, **30**) is well established; *cis*-tach acts predominantly as a tridentate chelating ligand, preferentially *facial* coordinating in octahedral complexes. This tridentate coordination mode is achieved by ring-flip from the more stable *tris*-*equatorial* to the *tris*-*axial* conformation upon complexation. Presumably entropic effects, as well as ligand-field stabilisation energies, overcome the enthalpy necessary for the transformation of one conformation into the other. Similarly it is anticipated that *trans*-tach is also capable of conformational change from the more stable bis*equatorial*-mono*axial* conformation into the bis*axial*-mono*equatorial* conformation upon complexation. This is demonstrated by the related ligands *cis*-1,3-diaminocyclohexane[143-146] and *cis*-3,5-diaminopiperidine,[147,148] where the *cis*-*axial* amino groups can act as a bidentate chelating moiety upon coordination to various metal ions. In addition to the *cis*-bidentate moiety upon ring-flip, it is anticipated that the *equatorial* amino group provides a monodentate coordination site independent from the bidentate chelating moiety. Furthermore, ligand derivatisation, *i.e.* upon Schiff base formation, are anticipated to be straightforward as demonstrated on the *cis,cis*-isomer.[149-151] These ligand systems are anticipated to exhibit modified coordination properties.[131,152]