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New Self-Assembled Structural Motifs in Coordination Chemistry

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I. Introduction

A feature of modern coordination chemistry is its expanding ability to mimic form and structure in biology. This has largely been achieved using a principle which has itself been borrowed from biology: the spontaneous self-assembly of well-defined and complex molecular entities from constituent subunits in solution. Unlike biology, however, self-assembly in coordination chemistry occurs through the formation of coordinate bonds rather than weak inter- or intramolecular interactions. The same principle—a thermodynamic drive to lower energy—nevertheless generally applies, so that coordination chemistry provides a useful tool in the elucidation of the self-assembly process itself.

While much has been written about the similarities of biology and coordination chemistry in this regard, this topic has not been explored in great detail. The aim of this work is 3-fold: (i) to highlight the diversity of architectural motifs currently known in coordination chemistry, (ii) to review the role of metal-directed self-assembly in their formation, and, in doing these, (iii) to establish general principles for the description of structural complexity in coordination compounds along the lines of that employed in biology—a field in which extensive structural complexity is the norm.

Recent reviews have comprehensively covered coordination compounds displaying double- and triple-helical structures, the so-called helicates,[1,2] as well as geometrically shaped metallocyclic complexes[3] and network coordination polymers.[4] This work is designed to be complementary to those reviews and therefore specifically considers nonhelicate complexes up to the size of small, noninfinite metal clusters which have been self-assembled by metal–ligand coordination. To comprehensively include the different motif types, representative examples of geometric metallocycles have also been included.

An emphasis has necessarily been placed on molecular structure and the role of self-assembly in the

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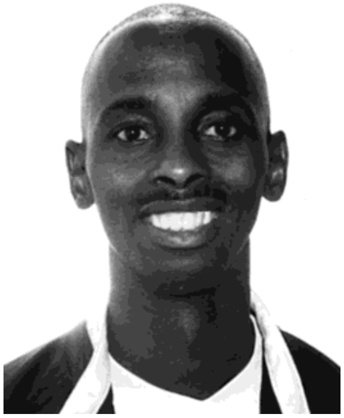

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formation of complexes rather than on physico–structural relationships per se. Where these are of particular interest however, this topic has been explored, as has the incidence of complexes displaying novel architectures obtained via nonmetal-mediated self-assembly. The literature coverage extends to September 1999; a concluding note (section XI) covers the period to April 2000.

II. Higher Structure in Biology and Coordination Chemistry

The structure of biological materials such as proteins is typically characterized by levels of organization. While the covalent interconnections between individual atoms in proteins (i.e. the sequence of amino acids) is known as primary structure, secondary structure can be observed in the distinct architectural motifs (e.g. α-helices or β-sheets) into which sequences of individual units spontaneously arrange. The organization of these secondary structures within a single entity (i.e. a polypeptide chain in a folded protein) is referred to as tertiary structure, while quaternary structure describes the manner in which individual entities are organized relative to each other.

The issue of structural complexity has not hitherto been considered important in coordination chemistry because the discipline has traditionally focused on variations in the type and arrangement of bonds within simple compounds. However, the recent self-assembly of complexes displaying double- and triple-helical structure[5,6] has definitively established the fact that higher levels of structural organization are possible. Indeed, the past decade has seen a proliferation in the reports of complexes displaying distinct, nonsimple architectures. For example, coordination compounds exhibiting motifs reminiscent of grids, racks, ladders, triangles, squares, hexagons and other polygons, various polyhedra/boxes, cylinders, rods, metallodendrimers, coordination oligomers, rotaxanes, catenanes, knots, and circular helicates, inter alia, are today known in addition to the helicates referred to earlier.

Lehn and Stoddart have separately suggested that structural complexity in coordination chemistry can be considered comparable to that in biology if the coordination bonds formed during the self-assembly process are viewed in the same light as the weak inter- or intramolecular interactions formed during biological self-assembly.[7a,b] This is reasonable given the fact that the term “self-assembly” is generally agreed to involve the spontaneous assembly of molecules into stable, noncovalently joined aggregates displaying distinct 3-D order.[8,9] While coordinate bonds are highly directional and of greater strength (bond energies ca. 10–30 kcal mol^{-1}) than the weak interactions of biology (bond energies ca. 0.6–7 kcal mol^{-1}), they are nevertheless noncovalent in nature. Indeed, they can be considered to have intermediate properties when compared to covalent bonds (strong and kinetically inert) and the interactions of biology (weak and kinetically labile). Their formation therefore offers unique opportunities to generate securely fastened compounds having distinctive and elaborate architectures using a self-assembly process.

Thus, according to Lehn,[7a] a helicate, like a protein, exhibits primary structure (1°) in the covalent interconnectedness of the individual atoms in the reacting building blocks (also known as “tectons”[7c]) and secondary structure (2°) in the helical motif into which the complex as a whole is twisted (Figure 1). The resulting compound displays two hierarchies of structural organization and is therefore termed a “supermolecule” according to Stoddart’s nomenclature.[7b] As in biology, the secondary structure arises from the steric and bonding constraints associated with the assembly process, which, in this case, involves the formation of coordination bonds rather than weak inter- or intramolecular interactions. Also as in biology, the secondary structure of such compounds

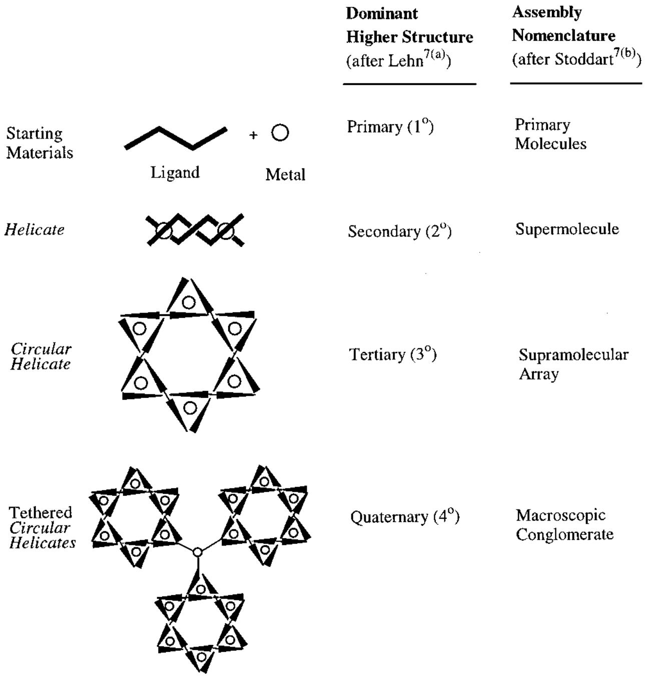


Figure 1. Schematic illustration of organizational hierarchies in the structure of coordination compounds. Note: the depicted tethered circular helicate assembly is a hypothetical compound which has been included for illustrative purposes only.

consists of recognizable repeat subunits, although these are usually present in lesser, often unitary quantities. A greater diversity of repeat units is moreover possible because a wider variety of metal ions and ligands are available in coordination chemistry—a fact which this review aims to highlight. Finally, the secondary structure of such coordination compounds is—as in biology—best observed when several elements of the ligand primary structure are viewed from afar.

Where two or more distinct secondary structural elements have been formed in a coordination compound, tertiary structure (3°) must also exist to describe their arrangement relative to each other.[7a] Alternatively, if one or more secondary structural elements impose a further distinct and more encompassing motif on the molecule as whole, tertiary structure (3°) is necessary to describe this arrangement. Thus, a complex such as a circular helicate, in which the two ends of a metal—ligand double-helix are connected to each other in a closed loop (Figure 1), can be seen to display primary structure (covalent interconnectedness in the ligands), secondary structure (the double-helix), and tertiary structure (the closed loop).[7a] Such a molecule exhibits three levels of structural hierarchy and is therefore referred to as a “supramolecular array” in Stoddart's terminology.[7b] As in biology, the tertiary structure constitutes the dominant structural motif and is best observed when the secondary structure is viewed from afar.

If several separate circular helicates were to be formed and tethered to each other by the in-situ formation of coordination bonds during a self-assembly, the resulting molecule would have four levels of structural organization, with quaternary structure (4°) required to describe the arrangement of the individual circular helicates relative to each other (Figure 1). As in biology, the quaternary structure would be the most macroscopic architectural motif and would be best observed from that perspective. If such an ensemble was known, it would conform with Stoddart's definition of a “macroscopic conglomerate”.[7b] Many network coordination polymers can be considered to display quaternary structure.

Since current coordination chemistry involves compounds that are generally much simpler than biological compounds, their levels of higher structure are often not as obvious as those of proteins. Lehn's nomenclature extending the hierarchy of protein structure to coordination chemistry nevertheless provides a useful means of describing the nascent structural complexity in this field to date. For this reason it has been employed in this review to unify what would otherwise constitute an apparently disparate collection of work. Its inclusion, like the discussion on self-assembly which follows, is intended to highlight the new directions in which coordination chemistry is advancing.

While the concepts described here are framed in the context of coordination chemistry, they are applicable to self-assembling systems in general, regardless of whether these involve coordinate, π donor—acceptor, hydrophobic/hydrophilic, hydrogen bonding, ion-pairing, or van der Waals interactions.

III. Self-Assembly in Coordination Chemistry and Biology

Coordination complexes displaying helicate motifs have traditionally been obtained by treating a semiflexible linear polydentate ligand with a kinetically labile metal ion which is too small for the binding cavity that would be present if the ligand was in a planar conformation.[10] The resulting mismatch between the geometry of the ligand binding site and the preferred geometry of the metal ion destabilizes the monomeric complex,[11] so that twisted bi- or polymetallic compounds having the characteristic helicate secondary structure are instead favored. An example of such a reaction is shown in Figure 2a, which depicts the spontaneous formation of the trisilver(I) helicate $[Ag_3(\mathbf{1})_2]^{3+}$ from three Ag(I) ions and two tris(bipyridine) ligands **1** having semiflexible linkers.[12]

A characteristic feature of these and, indeed, of all “strict” or “thermodynamic” self-assembly processes is that a kinetically rapid, reversible thermodynamic equilibrium exists between the starting materials and the products at all times and for all steps. The proportion of each product obtained in the final mixture is then determined by its relative thermodynamic stability. As the equilibrium is reversible, the process is self-correcting; a bond which is initially formed “incorrectly” can therefore dissociate and reassociate “correctly”. To be practically useful, however, a thermodynamic self-assembly process should generate one product which is substantially more stable than any of its competitors; this ensures a near-quantitative yield of that substance.[13]

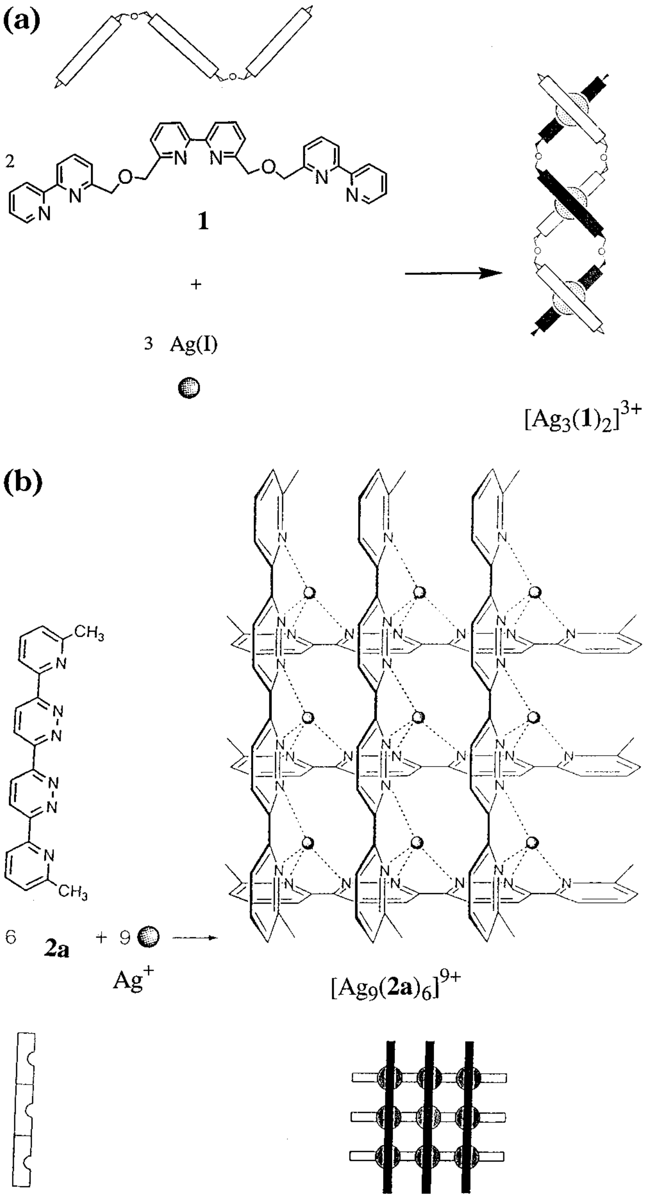


Figure 2. (a) Helicates. Schematic representation of the formation of a double-stranded, trimetallic helicate of Ag(I) with a semiflexible tris(bipy) ligand (bipy = 2,2′-bipyridyl). (Reproduced and adapted with permission; ref 12. Copyright 1990 Royal Society of Chemistry.) (b) Grids. Schematic representation of the formation of a 3 × 3 inorganic supramolecular grid of Ag(I) with a rigidly linear hexadentate ligand containing three bipy-like binding sites. (Reproduced and adapted with permission; ref 19. Copyright 1994 Wiley-VCH.)

While thermodynamic self-assembly is particularly common in coordination chemistry, other forms of self-assembly also exist. From the biological literature, Lindsey[9] has identified six further self-assembly processes: (i) irreversible self-assembly; (ii) assisted self-assembly; (iii) directed self-assembly; (iv) precursor modification followed by assembly; (v) self-assembly with post-modification; (vi) self-assembly with intermittent processing.

Irreversible self-assembly involves a cascade of irreversible reactions which are kinetically guided down a particular pathway. Since an equilibrium never exists, the capacity for self-correction is absent from such processes and every bond must be formed correctly the first time for the assembly to be successful. As this is statistically rare, the fidelity of an irreversible self-assembly process can generally be expected to decrease with an increase in the number of bond-forming steps involved. The products of each step in such a self-assembly are kinetically stable.

Assisted self-assembly involves the presence of an external agent which typically does not direct the assembly process nor appears in the final product but which acts by preventing the formation of intermediates leading to nonfunctional components.

Directed self-assembly requires the presence of a temporary scaffolding or template which directs the course of the assembly but does not appear in the final product. The external element may thermodynamically stabilize an association of subunits (or destabilize a competing one) or kinetically channel the assembly along a particular pathway.

Self-assembly processes involving various modifications (i.e. classes iv and v above) typically involve one of the earlier classes of self-assembly followed or preceded by irreversible, conventional reactions. For example, self-assembly with precursor modification (class iv) can, in coordination chemistry, be considered analogous to completing the synthesis of the precursors before carrying out the assembly. Similarly, self-assembly with post-modification (class v) involves carrying out an irreversible reaction on a self-assembled intermediate, usually in order to lock the structure into a kinetically stable state. Self-assembly with intermittent processing (class vi) involves combinations of the above classes into a single overall process.

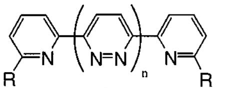
The majority of the compounds featured in this review have been obtained by thermodynamic self-assembly. However examples of irreversible and directed self-assembly, as well as self-assembly with post-modification, are also known and discussed. All known knot, most catenane,[14,15,16] and some kinetically stable helicate[17] coordination compounds have, for example, been formed by self-assembly with post-modification.

IV. Development of New Motifs via Thermodynamic Self-Assembly and Their Significance

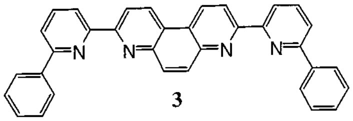
A. Virtual Combinatorial Libraries (VCL’s) in Self-Assembly Reactions

In a kinetically rapid, strict self-assembly reaction all possible products are continuously being formed and dissociated in a thermodynamic equilibrium. A combinatorial library of products—each having its own structural architecture—therefore exists in such solutions, although most of the individual members may be present in only minuscule proportions (thereby rendering the library virtual).[18] Each member of such a library nevertheless represents the whole of the library since it can be disassembled and reassembled into every other member.[18] Thus, a change in an external influence which crucially affects the thermodynamic stabilities of the members of such a library can dramatically alter their relative propor-

Chart 1



2a R = Me; n = 2
2b R = Ph; n = 2
2c R = Me; n = 1
2d R = H; n = 1



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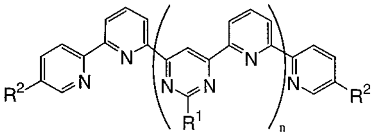


4a $R^1 = R^2 = H$; n =1
4b $R^1 = Me$; $R^2 = H$; n = 1
4c $R^1 = R^2 = Me$; n =1
4d $R^1 = R^2 = H$; n = 2
4e $R^1 = Me, Ph$; $R^2 = H$; n = 2
4f R^1 = 9-anthracyl; $R^2 = H$; n =1

tions. For example, variations in the temperature or the counterion employed, the presence of interacting third-party species or modifications to the ligand structure, or the stereochemical preferences of the metal ion can result in the selective favoring of a library member displaying a novel and unique structural motif. Lehn has therefore described thermodynamic self-assembly in coordination chemistry as a form of dynamic combinatorial chemistry in which the establishment of a virtual combinatorial library (VCL) permits the formation of structures having hitherto unknown features.[18]

This concept has proved exceedingly useful in the preparation of new structural motifs in coordination chemistry. For example, if one can imagine the modification of ligand **1** by fusion of adjacent halves of its bipyridyl binding sites into rigidly planar pyridazine rings, then it becomes ligand **2a** (Chart 1). When treated with Ag(I), **2a** forms the gridlike complex $[Ag_9(\mathbf{2a})_6]^{9+}$ depicted in Figure 2b and not the helicate structure shown in Figure 2a.[19] This is because removal of the flexible linkers between the binding sites in the ligand leaves the system with little option other than the formation of a grid; grids are the thermodynamically most stable motif when a tetrahedral metal ion is combined with a planar polytopic ligand containing inflexible linkers. As in biology, new secondary structure in coordination chemistry therefore may arise from and be a pronouncement of thermodynamic stability.

B. Programmed Self-Assembly Using Interactional Algorithms

The chief factor favoring the formation of one motif over another in a thermodynamic self-assembly in coordination chemistry is the interplay between the structure of the ligand(s) and the stereochemical preferences of the metal ion(s). As noted above, the combination of particular stereochemical and structural features in the ligands and metals can drive the self-assembly process toward a certain motif. These features can therefore be considered to be instructions, analogous to those of an algorithm which drives a computer program.[20] In this case, the structural and stereochemical features of the ligand and metal establish an interactional algorithm according to which higher structure is generated.[20] Thermodynamic self-assembly can consequently be visualized as the programmed formation of higher structure using instructed components. This concept is not restricted to self-assembly in coordination chemistry; the primary structure of proteins typically “instruct” their folding in exactly the same way.

The inclusion of several different instructed features in the starting materials may establish several such interactional algorithms as separate subroutines of the same self-assembly program.[21] For example, the combination of a tetrahedral metal ion with a composite ligand containing both semiflexible binding domains (which typically generate helicates) and rigidly planar binding domains (which typically generate grids) may deliver a complex containing both grid and helicate motif types. Such a compound has recently been prepared in just such a multiple subroutine self-assembly process (vide infra, section V.E).

While the idea of programmed self-assembly is appealing, it must be acknowledged that it assumes invariance in many factors which can significantly affect the self-assembly process. These include the possible formation of kinetic products, or solvent, concentration, pH, or temperature effects, or the presence of sterically or electronically demanding groups remote from the interacting sites. In practice, a variety of such determinants may play a role,[22] so that interactional algorithms of this type are seldom straightforward. In biology the invariance of physiological conditions (e.g. temperature and pH) enhances the reproducibility of self-assembly and can be considered to simplify the individual algorithms involved.

C. Unique Selectivity of Thermodynamic Self-Assembly

In a strict self-assembly, the thermodynamically most-favored compound is formed regardless of the presence—even large-scale presence—of other species. Thus, separate and discrete helicate and grid compounds can be simultaneously and selectively formed within a single vessel from a mixture which contains the applicable metals and ligands in low proportions.[23,24] This unique selectivity often bestows an astounding fidelity upon self-assembly in coordination chemistry—a fact which has been noted in many of the examples included in this review. It is, indeed, also the basis of many biological processes so that, in this respect, self-assembly in coordination chemistry also closely resembles that in biological systems.

D. Role of Self-Assembly in Generating New Structure

The effect of coordinate bond formation during a self-assembly process can be anything from a pivotal

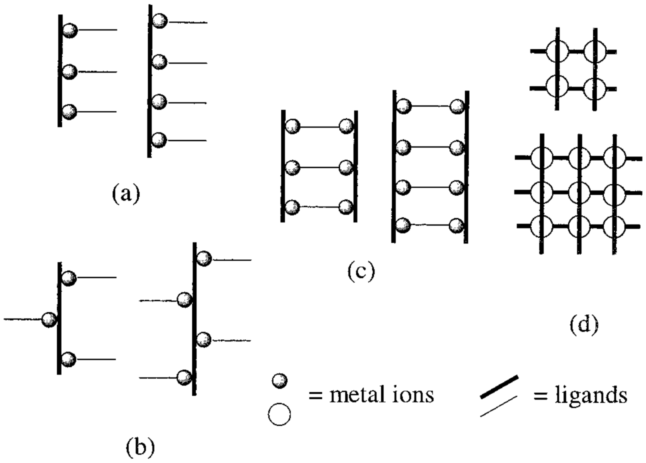


Figure 3. Racks, ladders, and grids. Schematic illustrations of (a) *syn*-rack, (b) *trans*-rack, (c) ladder, and (d) grid architectures.

to an inconsequential event in terms of the structure formed. For example, a self-assembly process is structurally trivial where a metal ion and an extensively preorganized ligand are combined to generate a product whose motif is due entirely to the structure of the ligand. By contrast, it is central in a reaction drawing numerous separate components into a new, highly ordered entity. Because this review seeks to emphasize the potential of self-assembly in the creation of new structure, it highlights examples in which coordinate bond formation is the key step in the creation of new motifs. Examples where it plays a lesser role are also mentioned, although largely only in the interests of completeness.

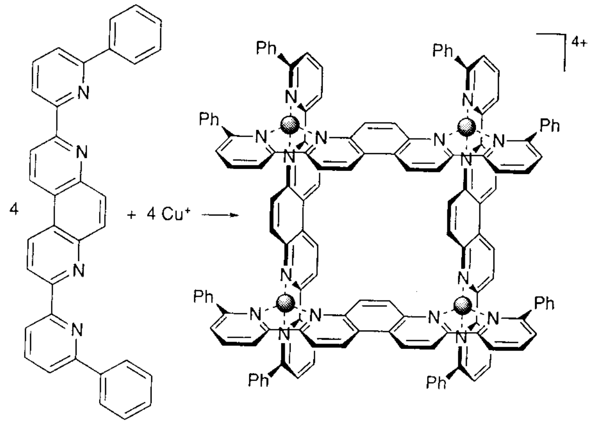
E. Practical Importance of Self-Assembly

The self-assembly process therefore offers a valuable means of preparing, in an often rational and highly selective manner, coordination compounds whose structural complexity starts to approach that common in biology. As in biology, such compounds may exhibit novel physical and chemical properties with interesting and useful associated applications. Self-assembly in coordination chemistry consequently provides an important and powerful entry into supramolecular engineering and the associated fields of solid-state and crystal engineering.[25] It potentially also affords novel catalytic systems,[26] which may ultimately be induced to offer the selectivity and usefulness of biological catalysts.

V. Motifs in Coordination Compounds Displaying Higher Structure

A. Latticed Motifs

Latticed motifs include the grid, rack, and ladder structures schematically illustrated in Figure 3,[27] as well as 2-D network coordination oligomers/polymers (termed coordination arrays) incorporating exclusively orthogonal or near-orthogonal binding. A characteristic common to all of these motifs is the formation of coordination bonds at alternating right angles to each other. In grids, this is generally achieved by the combination of tetrahedrally or octahedrally disposed metal ions with rigidly linear ligands having multiple chelating sites down their length. The presence of these two components ensures that a rigid, orthogonal architectural element is described when separate ligands are bound to a single metal ion. Ladders and racks typically involve the presence of an additional ligand having binding sites at one or both ends. In coordination arrays several rigid ligands having binding sites organized in various right-angled arrangements are usually employed.



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$[Cu_4(\mathbf{3})_4]^{4+}$

Figure 4. Grids. A self-assembled inorganic [2 × 2]G. The shaded circles represent Cu(I) ions (Reproduced with permission; ref 34. Copyright 1997 Royal Society of Chemistry.)

1. Grids

Grids are described using the nomenclature [$n \times n'$]G, in which ligands having n and n′ binding sites respectively combine with $n.n'$ metal ions to form a complex containing $n + n'$ ligands in a grid arrangement.[19]

A variety of coordination complexes displaying grid secondary structural motifs have been reported. These include [2 × 2]G[28−33] (e.g. Figure 4),[34] [2 × 3]G (e.g. $[Ag_6(\mathbf{2c})_3(\mathbf{2a})_2]^{6+}$ in Figure 9),[35] and [3 × 3]G (e.g. Figure 5).[19,36a] Ligands **2**−**6** (Charts 1 and 2) have thus far been employed in grid formation or been prepared with the aim of synthesizing grids. These ligands are characteristically planar and contain rigidly linear spacers between their binding sites. Bidentate heteroaromatic linkers, such as pyrimidines or pyridazines, have commonly been used; the heteroatoms in these spacers typically participate in separate, adjacent binding sites.

While tetrahedral metal ions such as Ag(I) (Figures 2 and 5) or Cu(I) (Figure 4) have been most widely employed for grid formation,[19,30,34−35] octahedral metal ions, such as Co(II) or Cu(II), have also proved effective when treated with hexadentate bis(bipyridyl)pyrimidine ligands such as **4a**−**c** or with diimine ligands such as **5**.[28−29,31−32] Figure 6 illustrates the [2 × 2]G, $[Co_4(\mathbf{4b})_4]^{8+}$.[36a] The Cu(II)-containing grid $[Cu_4(\mathbf{5})_4]^{4+}$ was found to be stabilized by phenoxo-bridging of the metal centers as shown in Figure 7.[31]

Ni(II)- and Cd(II)-containing [2 × 2]G's have also been reported,[28,32] while a Zn(II)-containing grid has

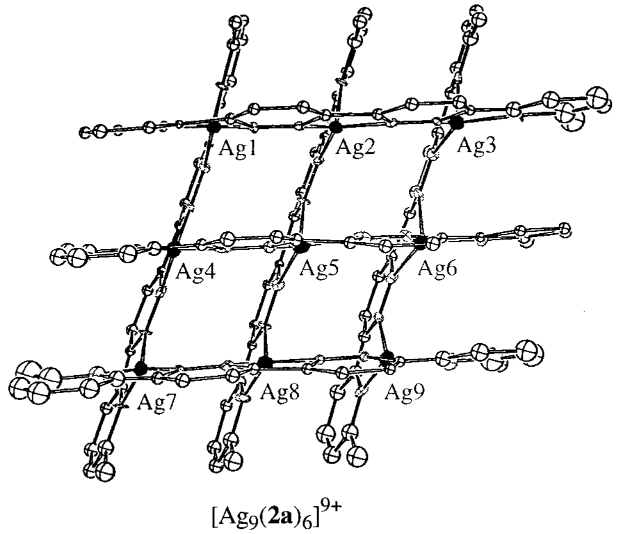


Figure 5. Grids. ORTEP of the self-assembled [3 × 3]G $[Ag_9(\mathbf{2a})_2]^{9+}$ (Reproduced with permission; ref 19. Copyright 1994 Wiley-VCH.)

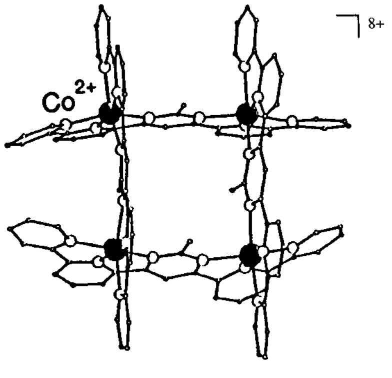


Figure 6. Grids. ORTEP of $[Co_4(\mathbf{4b})_4]^{8+}$. (Reproduced with permission; ref 36. Copyright 1998 American Chemical Society.)

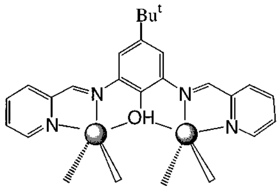


Figure 7. Grids. Phenoxide-bridging in the grid $[Cu_4(\mathbf{5})_4]^{4+}$.

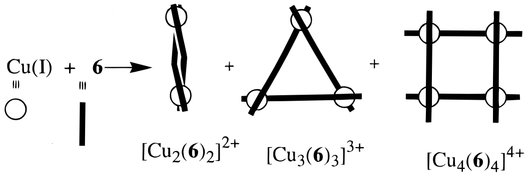


Figure 8. Grid self-assembly. The reaction of Cu(I) and ligand **6** generates an equilibrium mixture of helicate, triangle, and grid complexes in dichloromethane. Crystallization using a nonpolar solvent induces selective crystallization of the helicate in the solid state.

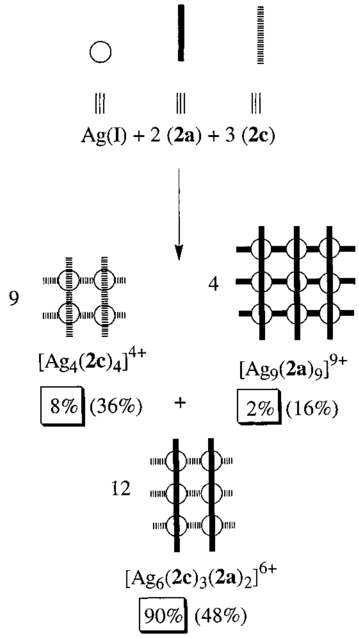
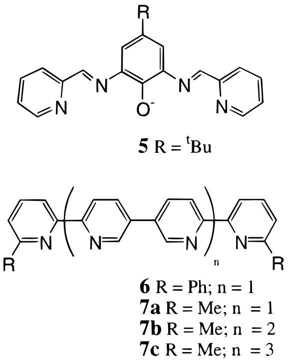


Figure 9. Grids. Possible self-assembly products for a mixture of Ag(I), **2a**, and **2c**. The relative product proportions are given in parentheses (statistically expected proportions) and blocks (actually observed proportions).

Chart 2



been mentioned in passing without any further discussion.[28]

a. Grid Self-Assembly. All known grids have been formed by thermodynamic self-assembly. Several studies have examined the processes involved.

An interesting solvent effect was observed in the self-assembly of the 2 × 2 grid $[Cu_4(\mathbf{2d})_4]^{4+}$. When 1 equiv of Cu(I) and 2 equiv of **2d** were mixed in benzene, the [2 x 2]G formed immediately.[30] This material could be recrystallized from acetone−diethyl ether without any change to its structure. However, when the formation reaction was performed in acetone, a deep green polymeric material was obtained. This polymer was converted back to the grid upon dissolution in CD_3CN. The reason for this behavior was not fully investigated; however, it appears likely that, when present in large excess, the acetone stabilized the polymer by competing with the ligand donors for coordination of sites on the metals.

A similar effect was noted in the reaction of Cu(I) and **6** in dichloromethane.[33] The equilibrium mixture contained the 2 × 2 grid $[Cu_4(\mathbf{6})_4]^{4+}$ as a low-yield reaction product, along with the helicate $[Cu_2(\mathbf{6})_2]^{2+}$ and the triangle $[Cu_3(\mathbf{6})_3]^{3+}$ (Figure 8). The mixture could be transformed into the helicate by selective crystallization using a nonpolar solvent. However, crystals of the helicate immediately regenerated the equilibrium mixture when redissolved in dichloromethane.[33]

The selectivity of self-assembly in the formation of grid complexes was neatly illustrated in the reaction of 6 equiv of Ag(I) with a mixture of 3 equiv of the ditopic ligand **2c** and 2 equiv of the tritopic ligand **2a** (as illustrated in Figure 9).[35] Statistically one would expect a product mixture containing 36% of the 2 × 2 grid $[Ag_4(\mathbf{2c})_4]^{4+}$, 16% of the 3 × 3 grid $[Ag_9(\mathbf{2a})_9]^{9+}$, and 48% of the 2 × 3 grid $[Ag_6(\mathbf{2a})_2(\mathbf{2c})_3]^{6+}$. Instead product ratios of 8%:2%:90% were obtained, respectively. The heteroligand assembly was therefore strongly thermodynamically favored over the homoligand assemblies. This may have been due to the relatively poorer stability of the [3 × 3]G which contained the least stable metal−ligand coordination site; because of the size of the metal ion and the geometry of the pyridazine ring, which is not a perfect hexagon, Ag(I) coordination in grids of these types is generally considered to be less stable than that involving Cu(I).[35]

An interesting feature of ligand **3** is that it formed the grid $[Cu_4(\mathbf{3})_4]^{4+}$ (schematically shown in Figure 4) when phenyl substituents were present on the 2-position of the terminal pyridines of **3** but not when H or Me substituents were present.[34] Oligomeric mixtures and insoluble coordination oligomers were instead obtained in those cases. The steric bulk of the phenyl group therefore appears to be necessary to destabilize the competing oligomers. This grid is also interesting because it selectively traps guest solvent molecules in the grooves between the parallel ligands in the solid state; some tetragonal distortion is consequently observed in the X-ray crystal structure.[34]

X-ray structure determinations show that several of the other grids are also not completely orthogonal but tetragonally distorted. Figure 5 depicts the structure of one such species, $[Ag_9(\mathbf{2a})_6]^{9+}$.[19] Grids containing Ag(I) ions appear to be particularly prone to such distortions when combined with ligands containing pyridazine linkers.[19,35,36]

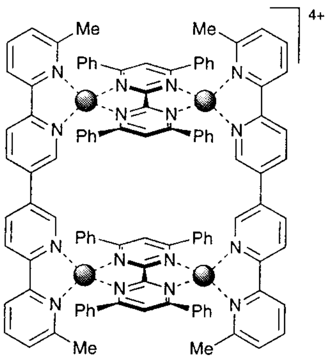
Complexes simultaneously containing both grid and helicate secondary motifs have also been self-assembled; these are discussed in section V.E (Metal-Directed Mixed-Motif Complexes).

2. Ladders and Racks

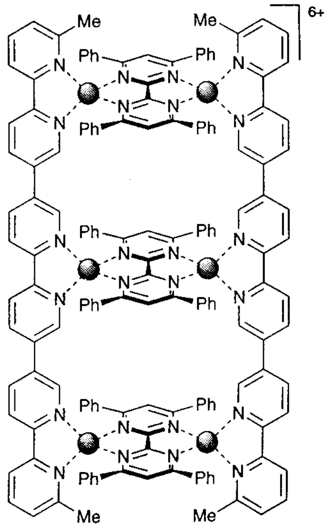
Ladders and racks resemble grids in that multiple coordination occurs down the length of a linear polydentate ligand. However they differ in that a second, mono- or bidentate ligand is always necessary; this ligand must have binding sites at either one (ladder) or at both ends (rack).

Ladders are described using the nomenclature [2 × *n*]L, where *n* refers to the number of "rung" ligands present. Like grids, ladders are structurally rigid. All known ladders have been formed as secondary structural motifs by thermodynamic self-assembly processes.

Several [2 × 2]L and [2 × 3]L have been reported;[37] these include the complexes illustrated in Figure 10.[37] To form these ladder compounds, the bidentate bipyrimidine **8** (Chart 3) was used as a "rung" ligand. A mixed-ligand self-assembly process must therefore have occurred in the reaction; such a process involves recognition between the constituent particles, followed by growth and finally termination, giving the discrete complexes.



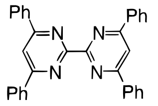
$[Cu_4(\mathbf{7a})_2(\mathbf{8})_2]^{4+}$



$[Cu_6(\mathbf{7b})_2(\mathbf{8})_3]^{6+}$

Figure 10. Ladders. Self-assembled tetranuclear and hexanuclear ladders. The shaded circles depict Cu(I) ions. (Reproduced with permission; ref 37. Copyright 1996 Royal Society of Chemistry.)

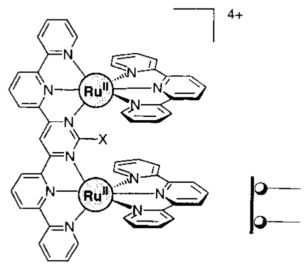
Chart 3



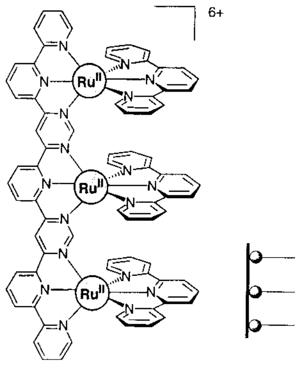
8

Racks are designated as [*n*]R, where *n* refers to the nuclearity of the species (or the number of "rung" ligands present). Since racks have only one linear polytopic ligand present, they may display structural isomers if the linkers in that ligand permit rotational freedom. The syn isomer illustrated in Figure 3a involves an eclipsed conformation of metal ions and "rung" ligands down one side of the central ligand. The trans isomer depicted in Figure 3b contains the metal ions and "rung" ligands alternatively coordinated on opposite sides of the central ligand.

Several compounds having [2]R[38] and [3]R[39] (Figure 11)[39] rack secondary structure have been re-



$[Ru_2(\mathbf{4a}\text{ or }\mathbf{4f})_1(tpy)_2]^{4+}$
(X = H, 9-anthracyl)



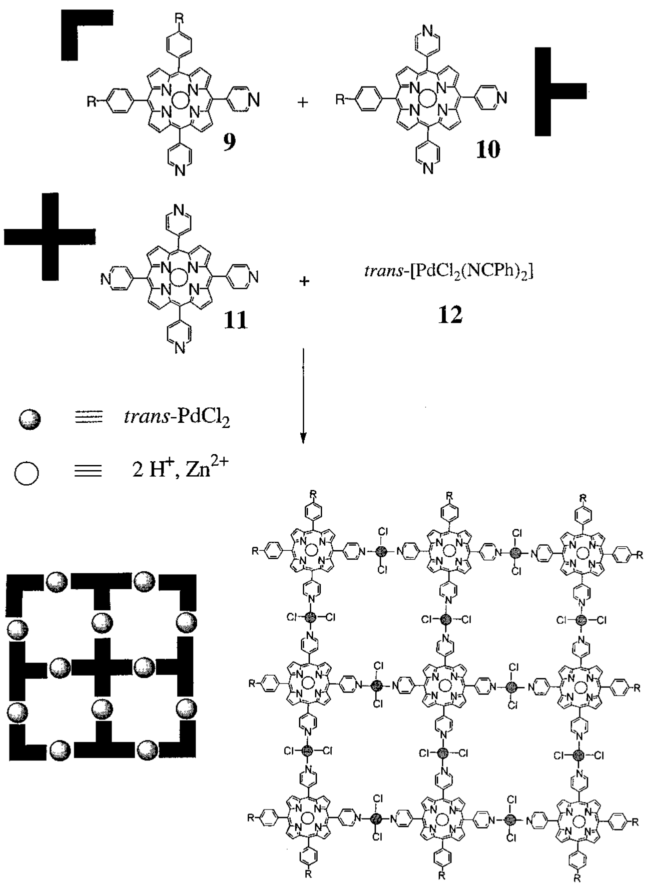
$[Ru_2(\mathbf{4d})_1(tpy)_3]^{6+}$

Figure 11. Racks. Self-assembled bi- and trinuclear racks (tpy = 2,2′:6′6″-terpyridine). (Reproduced with permission; ref 39. Copyright 1995 Wiley-VCH.)

ported; all were obtained by thermodynamic self-assembly. A series of syn- and trans-racks incorporating pseudorotaxane motifs have also been described; these are discussed in section V.E (Metal-Directed Mixed-Motif Complexes).

3. Other Noninfinite Coordination Arrays

The compound $[Pd_{12}Cl_{24}(\mathbf{9})_4(\mathbf{10})_4(\mathbf{11})_1]$ depicted in Figure 12 displays a discrete square array secondary structure. It was obtained by the reaction of 12 equiv of *trans*-bis(benzonitrile)palladium(II) **12** with 4 equiv of the porphyrin-containing "L-shaped" unit **9**, 4 equiv of the "T-shaped" unit **10**, and 1 equiv of the "X-shaped" unit **11**.[40] In this reaction, the 4-pyridyl substituents of the porphyrins coordinatively replaced the benzonitrile coligands on the Pd(II) ions, with the L-shaped units forming the corners of the array, the T-shaped units the sides, and the X-shaped unit the central core. Thus, four different types of molecules spontaneously self-assembled to form a 21-membered array which covered an area of 25 nm^2. The complex was obtained in 90% yield after 30 min, when the components were added at room temperature in an overall concentration of 10 μM. At 20 μM the yield was reduced to ca. 70% under similar conditions. Smaller, molecular square versions of compounds of this type have also been produced.[41]



$[Pd_{12}Cl_{24}(\mathbf{9})_4(\mathbf{10})_4(\mathbf{11})_1]$

Figure 12. Coordination arrays. Self-assembly of a square array containing 12 Pd(II) ions and 9 porphyrins (R = Me, ^{t}Bu). (Reproduced with permission; ref 40. Copyright 1998 Wiley-VCH.)

4. Properties and Applications of Latticed Compounds

Intramolecular antiferromagnetic coupling has been noted in the [2 × 2]G, $[Co_4(\mathbf{4b})_4]^{8+}$ (Figure 6).[29] The magnetic properties of an isomorphous Ni(II)-containing [2 × 2]G involving the same ligand also exhibited intramolecular ferromagnetic coupling. These grids form a near perfect quantum spin system of four and are therefore ideal systems in which to study magnetic interactions in a discrete entity. A potential application of such species is as individually addressable units in a future information storage and processing nanotechnology.[28] Highly ordered thin films of various [3 × 3]G have been prepared at an air−aqueous interface to investigate this application.[36]

The similarity of grids to quantum dots has also been noted.[29] Grids have the advantage, however, of consisting of ion dots of smaller size than quantum dots, which additionally do not need microfabrication. Extended 2-D and 3-D architectures of such grids could theoretically act as digital supramolecular chips for information storage.[19]

The photophysical properties of the *syn*-[2]R rack complex $[Ru_2(\mathbf{4f})(tpy)_2]^{4+}$ illustrated in Figure 11 (X = 9-anthracyl; tpy = 2,2′:6′,2”-terpyridine)[39] is also unusual. In this complex the anthracyl substituent was interposed between the tpy coligands.[42] The complex, which luminesces in the infrared, is one of the lowest energy emitting Ru(II) compounds known. In addition, it displays an abnormally long excited-state lifetime considering the low energy of its emitting state.[42]

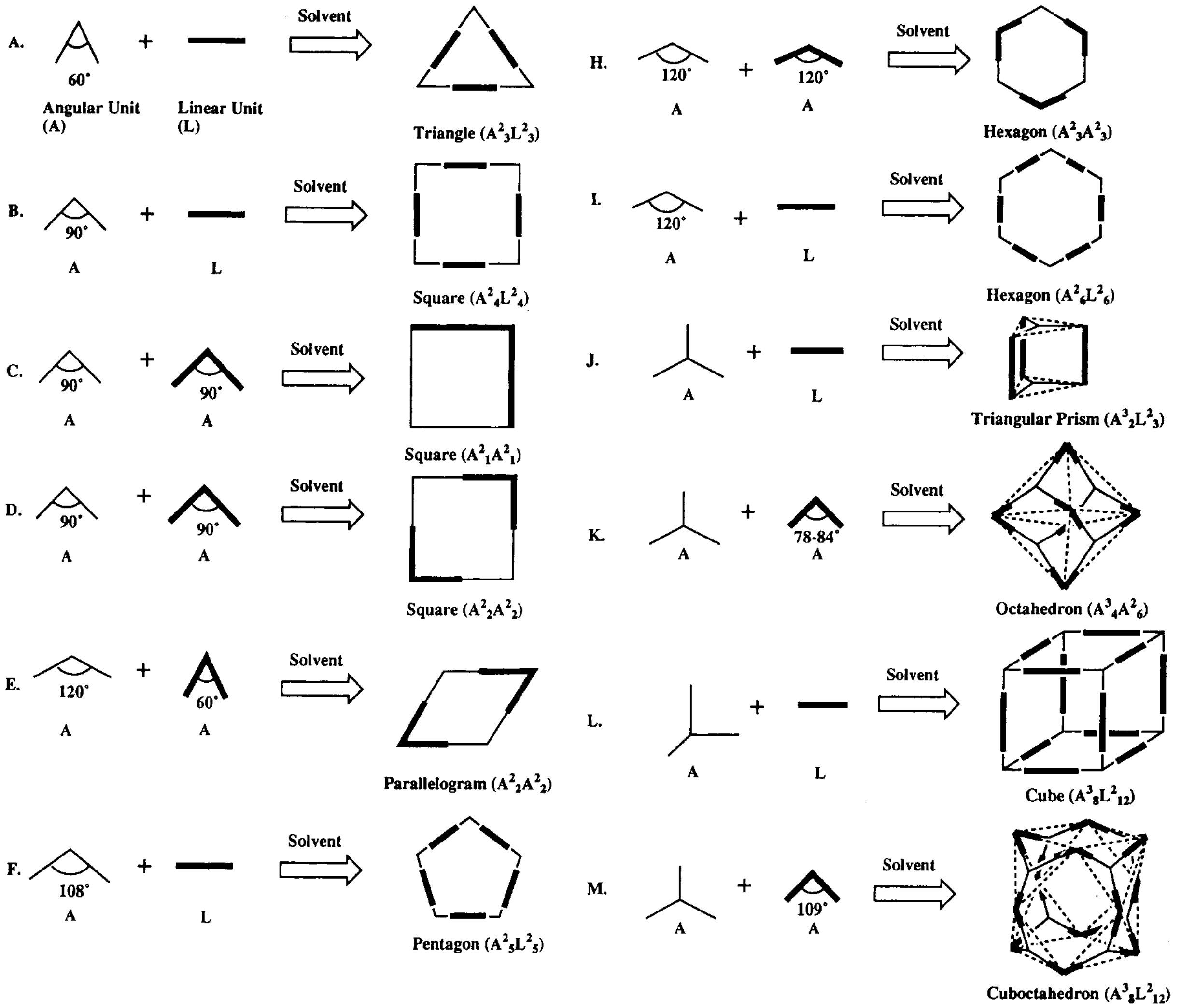


Figure 13. Rational design of geometrically shaped metallocycles, molecular library method: Schematic depiction of routes for the self-assembly of coordination oligomers exhibiting cyclic polygonal or polyhedral motifs. (Reproduced with permission; ref 46a. Copyright 1997 American Chemical Society.)

B. Cyclic Motifs

Complexes displaying closed 2-D or 3-D structures incorporating metal ions are collectively known as metallocycles, i.e. cycles formed by the coordination of metal ions. A wide variety of such compounds are known. These range from complexes in which the metal ions and ligands are rigidly held in a structure having a distinctively geometric shape, to assemblies whose closed, cyclic nature is the only distinguishing feature. Several recent reviews have comprehensively covered various aspects of this field.[3,43−46] This section is therefore limited to representative examples of geometrically shaped metallocyclic polygons and polyhedra not appearing in earlier reviews or whose self-assembly processes are of interest. Cyclized helicates, known as circular helicates, are also discussed.

1. Rational Design and Description of Geometrically Shaped Cyclic Motifs

a. Molecular Library Approach. Figure 13[46a] schematically illustrates Stang's "molecular library" method for the rational self-assembly of various geometrically shaped metallocycles.[3a,46a] The highly directional formation of coordination bonds between suitably rigid, complementary donor (ligand-based) and acceptor (metal-based) building blocks can generate a variety of secondary structures displaying polygonal geometric structural motifs (e.g. triangles, squares, and hexagons) or polyhedral/box geometric structural motifs (e.g. triangular prisms, octahedra, and cubes). For example, the combination of a square planar metal ion having two vacant cis-coordination sites (i.e. an acceptor unit enclosing a 90° angle) with a rigidly linear ditopic ligand (i.e. a donor unit enclosing an angle of 180°) may lead to the formation of a molecular square by the path depicted in eq B of Figure 13.

In a variation on this theme, building blocks which contain both donor and acceptor elements may be induced to spontaneously self-cyclize under certain physical conditions, usually involving a particular concentration, pH, or temperature. For example, a molecule containing a ligand site rigidly angled at 90° to a metal with a vacant coordination site at its other end may self-assemble a molecular square by the complementary formation of coordinate bonds. A process of this type is illustrated in eqs C or D in

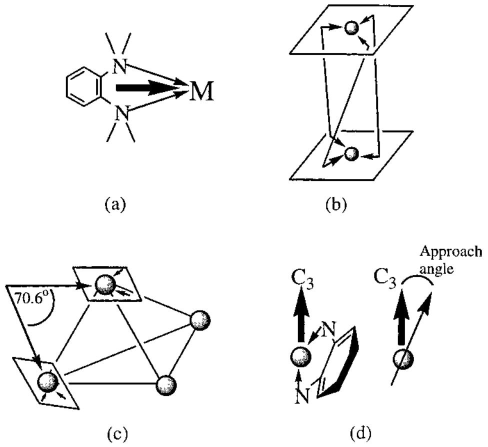


Figure 14. Rational design of geometrically shaped metallocycles, symmetry-interaction method: Schematic depictions of (a) the coordinate vector of a bidentate chelating group bound to a metal ion, (b) the chelate planes in a triple-stranded bimetallic helicate of D_3 symmetry, (c) adjacent chelate planes in a polyhedral M_4L_6 cluster (M = metal ion, L = ligand), and (d) the approach angle of a bidentate chelate and the major symmetry axis of the metal ion to which it is bound.

Figure 13 when the depicted interacting units are identical.

b. Symmetry-Interaction Approach. Another means of metallocycle formation involving rational design is the so-called "symmetry-interaction" model described by Raymond and co-workers.[3b] This approach derives from the realization that many natural supramolecular assemblies are formed in a symmetry-driven process which relies on incommensurate lock-and-key interactions.[47] By reverse engineering a desired polyhedral structure, one can therefore determine the symmetry interactions and the associated geometric relationships necessary to generate that motif from a combination of preorganized ligands and metal ions.

Several terms have been defined to describe the determinant geometric relationships in such polyhedra (Figure 14):[3b] (i) The "coordinate vector" of a chelating group is that vector which bisects the chelate in the direction of the metal ion to which it is bound. (ii) The "chelate plane" of a metal ion is that plane which contains all the coordinate vectors of the chelating groups bound to it. (iii) The "approach angle" describes the arrangement of three bidentate chelators about a metal ion; it defines the angle between the plane holding the coordinating atoms of a bidentate chelating group and the major symmetry axis of the metal center. Figure 14a illustrates the coordinate vector of a bidentate group, while chelate planes are depicted about the metal ions in Figure 14b,c. Figure 14d illustrates the approach angle of a bidentate group.

Each class of polyhedra involves different relationships between these variables. For example, chelate planes which are parallel (0°) are necessary in a triple-stranded, binuclear helicate of D_3 symmetry (Figure 14b), while an angle of 70.6° between the chelate planes is required for the formation of a tetrahedral M_4L_6 cluster (M = metal ion, L = ligand) (Figure 14c).[3b] To self-assemble these structures, ligands capable of chelating at these angles should therefore be employed with metal ions capable of accommodating them correctly. Ligands or metals having structural properties conforming to other relationships between the structural variables in these motifs may also be used.

c. Assembly Descriptors. Several descriptors have been devised to describe the formation of cyclic, geometric assemblies. The convention employed by Stang[46a] is most widely used; it involves consideration of the building blocks as either linear, L, or angular, A, components. The assembly is then symbolized by listing the numbers and type of each constituent building block, with superscripts to depict their topicity. Thus, an assembly, such as the triangle shown in eq A in Figure 13, which consists of three ditopic angular units and three ditopic linear units, is denoted $A^2{}_3L^2{}_3$. Self-cyclized species are characterized by descriptors containing only one building block, e.g. the $A^2{}_4$ square which would result if the building blocks in eq D of Figure 13 were identical and contained donor and acceptor sites at opposite ends.

These descriptors not only offer a convenient abbreviation of the self-assembly process but also provide information in regard to the number of coordination bonds formed during the reaction and the coordinative saturation of the resulting metallocycle. To form species which are enthalpically stable, the number of coordination bonds formed by the donor and acceptor elements on the building blocks must be equal and the maximum number possible.

2. Thermodynamic Factors in the Self-Assembly of Metallocycles

The requirements for a thermodynamic self-assembly of a metallocycle are that (i) coordination bonds must form between the donor and acceptor elements involved, (ii) the bonds must be kinetically labile so as to allow self-correction, and (iii) the desired assembly must be thermodynamically more favorable than any competing species.

Several studies have examined the role of thermodynamic factors in the self-assembly of metallocyclic compounds.[22a,48,51] These have generally concluded that cyclic structures are preferred over linear ones for enthalpic reasons, while small cycles are favored over large cycles (at low concentrations) for entropic reasons.

The enthalpic preference arises from the fact that an increased number of bonds are possible per subunit in a cyclic arrangement relative to a linear one. For example, a square of $A^2{}_2A^2{}_2$ formulation obtained according to eq D in Figure 13 contains four coordinate bonds, or one bond per building block. Its equivalent noncyclic $A^2{}_2A^2{}_2$ coordination oligomer is coordinatively unsaturated and therefore contains only three bonds, or 0.75 bonds per building block. To maximize the number of bonds formed, the noncyclic oligomer can polymerize; however the donor and acceptor sites at each end of the polymer will always remain uncoordinated. Thus, the ideal of one bond per building block cannot be achieved unless cyclization occurs. If cyclization is impossible, it is likely that the oligomer will polymerize until its precipitation as a kinetic product.

The entropic preference referred to above is a result of Le Chatelier's law, which states that a perturbation to a dynamic equilibrium results in a readjustment of the equilibrium to minimize its effect. Thus, dilution of a solution containing a equilibrium mixture of cyclic oligomers results in a shift of the equilibrium to increase the total number of species present. At low concentrations smaller cycles are consequently favored, with the reverse being the case at high concentrations. As most self-assembly reactions are performed in dilute solution, the smallest possible cycles are usually favored.

In coordination chemistry, the enthalpic driving forces in a self-assembly reaction invariably dominate the entropic ones because of the large enthalpy of coordinate bond formation. However, once coordinative saturation has been achieved, entropic effects may play the deciding role. Indeed, entropic influences have been employed to selectively modify or alter the architecture of complexes (e.g. see section V.D.2., Self-Assembled Catenanes).

A recent study has also examined the physical requirements for "self-cyclization" in coordination chemistry.[49] This work indicated that a critical monomer concentration (cmc) typically exists in self-cyclizing systems, below which only the self-assembled product is present. Any monomer added above the cmc produces only acyclic species. The optimum monomer concentration for the self-assembly of metallocycles was found to generally be about one-tenth of the cmc, but this varies according to the relative thermodynamics of the self-assembled species.

3. Geometric Metallocyclic Polygons

a. Triangles. *Self-Cyclized Triangles.* A^2_3 Molecular triangles have been obtained by the self-cyclization of three rigidly angular building blocks having donor elements at one end and acceptor elements at the other. One example is [Pd_3(**13a**)$_3$(OAc)$_3$] shown in Figure 15.[50] This complex was self-assembled by three Pd–bis(benzimidazolyl)benzene species **14a** which had been irreversibly formed in situ from the original mixture. The resulting triangle (or "tricorn")[50b] structure was obtained as a thermodynamically stable entity by the replacement of one acetate on the Pd(II) in **14a** by an N-donor on an adjacent complex. The cavity in the product is chiral, so that two mirror image enantiomers existed; in the solid state the cavity was occupied by an acetonitrile molecule. Compounds **13b**–**d** formed similar products.[50c]

Analogous reactions with the structurally identical ligands **15**, which contain a 2,4-pyridine spacer rather than the benzene spacer of **13**, failed to spontaneously generate tricorn structures in solution.[50c] This can be ascribed to the tripositive electrostatic charge which would exist on the tricorn; the different behaviors of **13** and **15** neatly illustrate the danger of planning self-assembly routines solely on the basis of the coordination geometry of metals and ligands.

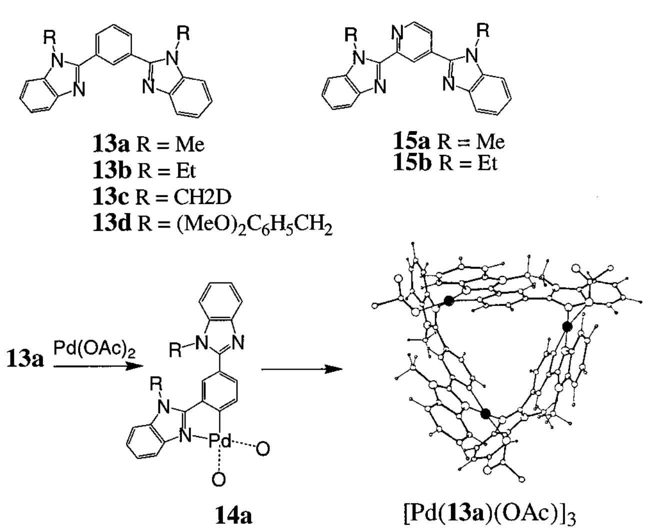


Figure 15. Triangles. Formation of, and an ORTEP of, the molecular triangle generated in the reaction of 1,3-bis-(1-methylbenzimidazol-2-yl)benzene with $Pd(OAc)_2$. (Reproduced with permission; ref 50a. Copyright 1993 Wiley-VCH.)

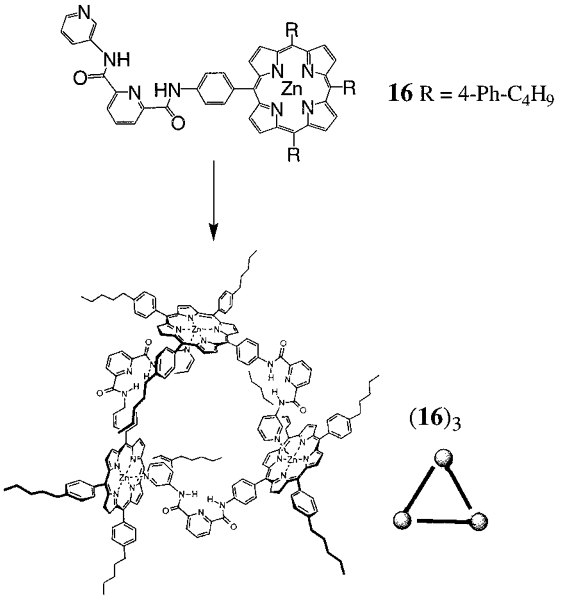


Figure 16. Triangles. Self-assembly of a porphyrin-based molecular triangle. (Reproduced with permission; ref 51. Copyright 1995 Royal Society of Chemistry.)

The self-cyclization of metalated porphyrins containing pendant donors which are flexible (**16**)[51] or inflexible (**17**)[52] may also generate complexes exhibiting an A_2^3 triangle secondary motif (Figures 16 and 17).[51,52a] In the case of (**16**)$_3$, the assembly was spontaneously formed at suitable concentrations (Figure 16). The triangles formed by **17** were, however, only obtained upon the addition of a base which deprotonated the hydroxy substituents, eliminating HCl and thereby allowing binding to the metal ion of a neighboring porphyrin.[52a]

The C_1-symmetrical chiral A_2^3 triangle **19b** (Figure 18), which involves Co(III) and a purine linker ligand, was similarly prepared as 20% of a mixture also containing the corresponding squares.[53] To overcome the poor kinetic lability of Co(III), the self-assembly process had to be initiated by the addition of NaOH which led to deprotonation of the purine amines,

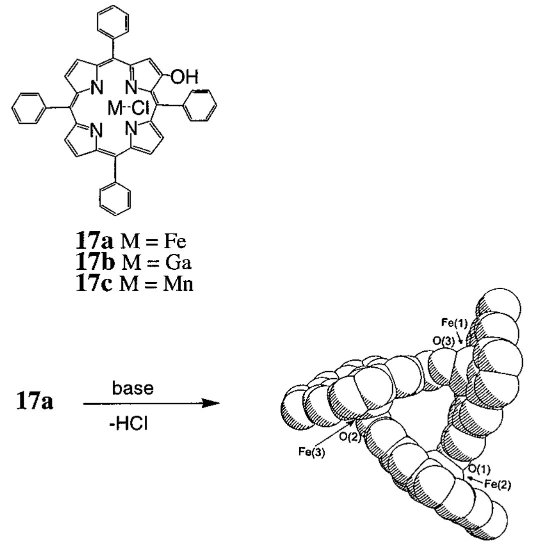


Figure 17. Triangles. Formation of, and space-filling view of, the cyclic core of the triangle spontaneously formed from **17a** upon loss of HCl. The aromatic substituent groups on the porphyrin have been omitted in the space-filling depiction for clarity. The *R*,*R*,*S* isomer of the triangle is depicted. (Reproduced with permission; ref 52a. Copyright 1997 American Chemical Society.)

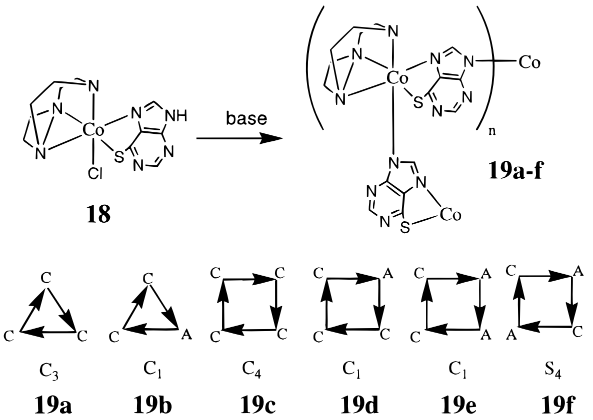


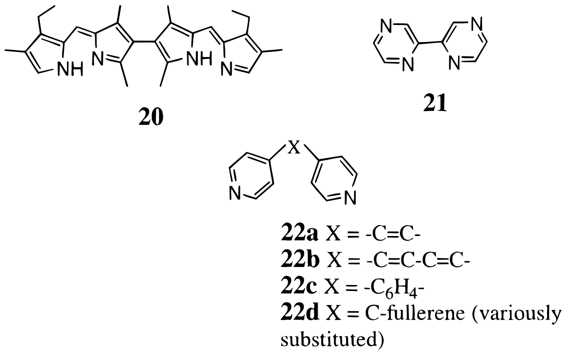
Figure 18. Triangles and squares. Schematic depicting the formation of, and possible geometric isomers of, the cyclic triangles and squares of purine-6-thione with 1,4,7-triazacyclononane−Co(III). The arrows depicted in **19a**−**f** illustrate the directionality of the linking purines. The characters at the corners of each structure, C (clockwise) and A (anticlockwise), denote the chirality of each Co(III) unit.

followed by their ready substitution of the chloride ligand on the cobalt ion. The resulting triangle was sufficiently kinetically stable to be optically resolved into its mirror image isomers by elution on a Sephadex column using a chiral eluant.

Multiple-Component Triangles. The $A^2{}_3L^2{}_3$ triangle $[Cu_3(\mathbf{6})_3]^{3+}$ was formed from Cu(I) and **6** as 30% of a mixture, which included the helicate $[Cu_2(\mathbf{6})_2]^{2+}$ and the grid $[Cu_4(\mathbf{6})_4]^{4+}$ (Figure 8).[33] The mixture could be transformed into the helicate by fractional crystallization; on redissolution, the triangle ↔ grid ↔ helicate equilibrium was reestablished.

Other $A^2{}_3L^2{}_3$ triangles have been reported to exist in an equilibrium with their corresponding squares.[54,55] Generally, these and other triangles (typically involving ligands such as **22** (Chart 4)) become favored over their squares by the presence of the following: (i) more flexible, or extended, linkers between the ligand binding sites; (ii) sterically demanding coligands; (iii) certain guest molecules to bring about induced-fit molecular recognition (via a directed self-assembly); (iv) increased solution concentrations.[54,55] Entropy effects appear to increase the thermodynamic stability of the triangles relative to the squares in the last mentioned case.

Chart 4



$A^2{}_3L^2{}_3$ triangles have been reported from the following reactions: (i) (1,4,7-triazacyclononane)Cu(II) with imidazolate;[56] (ii) Zn(II) or Co(II) with ligand **20**;[57] (iii) Pt(II) or Pd(II) with 2,2′-bipyrazine **21**;[58] (vi) (ethylenediamine)Pd(II) with **22a**−**c**.[54a,59] Certain of the latter complexes can also be considered hexagons despite the fact that they are distinctly triangular in terms of the metals present.

Several organometallic triangles are known (e.g. Hg(II)−carborane triangles).[60,72,73] While they are not coordinative species, the principles involved in their formation are similar.

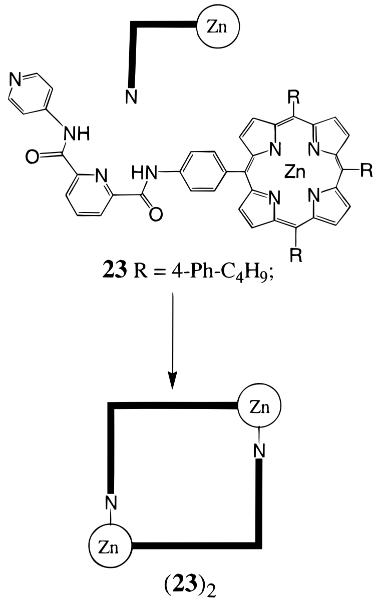
Triangles may also be formed using various nucleobases.[3e,61] The first known luminescent molecular triangle has recently been reported; it involves Re(I) corner ions.[81f]

Multiple-component molecular triangles have recently been reviewed.[3a]

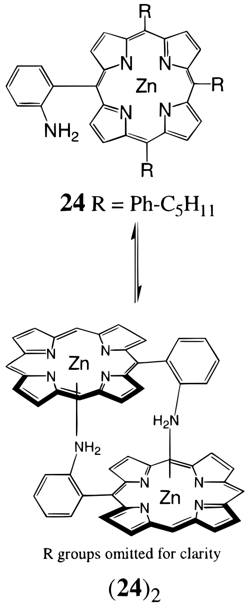
b. Squares. *Self-Cyclized Squares.* The zincated porphyrin **23**, which is the 4-pyridyl analogue of **16**, has been reported to spontaneously form the $A^2{}_2$ square $(\mathbf{23})_2$ (Scheme 1) by intermolecular Zn−N coordination at certain concentrations (10^{-7}−10^{-2} M in chloroform at room temperature).[62] The extraordinary stability of this dimer appears to be linked to the presence of intramolecular hydrogen bonding in its side chains, which reduces the angle subtended by the linkers from the 120° expected for *meta*-substituted pyridyls to approximately 96°.

Direct substitution of a porphyrin with an aniline group produces a rigid linker. While coordination of zinc by the N-donor of such an aniline is significantly weaker than that of pyridine, studies have shown that zinc aminoporphyrins do form Zn−N bound dimers in solution, provided that *o*- or *m*-aniline substituents are used (e.g. **24**) (Scheme 2).[63] In these cases, free rotation about the aniline−porphyrin bond allows the formation of a coordinate bond roughly orthogonal to the plane of the porphyrin. Rigid compounds of $A^2{}_2$ formulation which bear square secondary motifs, such as $(\mathbf{24})_2$, may then be formed

Scheme 1



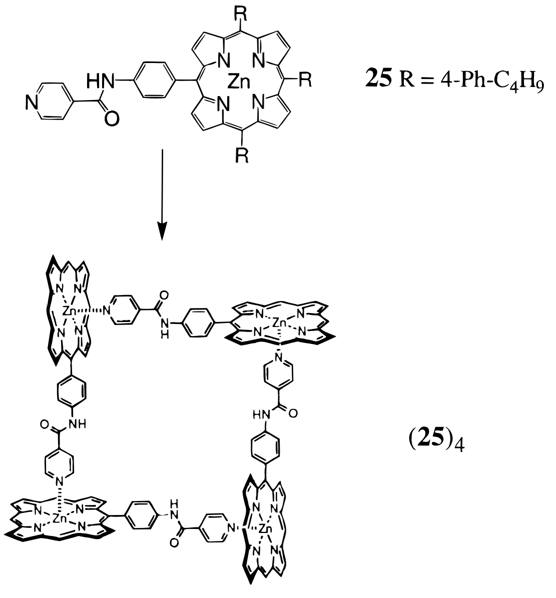
Scheme 2



at suitable concentrations. When *p*-aniline was used as a substituent, the amine N-atom was unable to coordinate orthogonally, so that coordination oligomers and polymers resulted.[63]

Zincated porphyrins with reactive, pendant pyridine or sulfoxide groups have been self-cyclized to form A^2_4 squares secured by intermolecular Zn−N(pyridyl)[51,62,64] or Zn−OS[69] coordination bonds. Figure 19 illustrates a square of the former type,[51] while Figure 20 depicts the mode of coordination in a square of the latter type.[69]

A series of S_4-symmetrical squares **19f** involving Co(III) and purine linker ligands were selectively obtained out of four possible isomers also because of stabilization arising from intramolecular hydrogen bonding (Figure 18).[53] The normally kinetically inert Co(III) was found to become labile in the presence of partially deprotonated purine under the reaction conditions.



meso substituents omitted for clarity

Figure 19. Squares. Formation of a self-assembled, porphyrin-based A^2_4 molecular square. (Reproduced with permission; ref 51. Copyright 1995 Royal Society of Chemistry.)

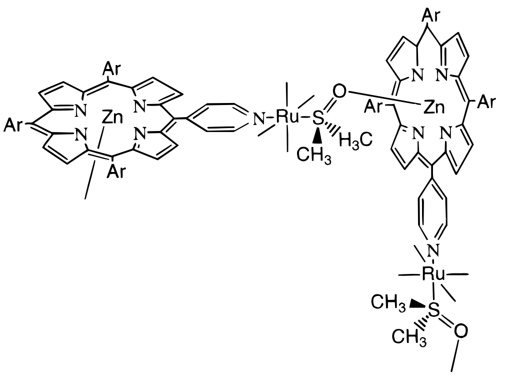


Figure 20. Squares. Depiction of Zn−OS coordination in molecular squares incorporating zincated porphyrins and Ru(II) (section V.B.3.a).

Multiple-Component Squares. The spontaneous assembly of the protonated porphyrin bearing two flexible 4-pyridyl substituents, **26**, with compound **27** containing two, zincated porphyrins tethered to each other by a terephthaloyl diamine linker (or a naphthalenediimide linker) produced the $A^2_1A^2_1$ squares [(**26**)(**27**)] (Scheme 3).[64] These discrete 1:1 complexes, secured by Zn−N coordinate bonds, were found to be highly stable despite the apparent flexibility of the side chains; intramolecular hydrogen bonding—like that in (**23**)$_2$—may have assisted.

A vast range of rigid $A^2_2A^2_2$ and $A^2_4L^2_4$ squares have been reported by Stang and other researchers using the “molecular library” technique described earlier and depicted in eqs B and D of Figure 13. This work has recently been extensively reviewed,[3] and this class of compound is consequently covered in only summary detail here.

Construction of rigid $A^2_2A^2_2$ and $A^2_4L^2_4$ squares typically involves a thermodynamic self-assembly process in which a rigidly linear or angled bidentate, ditopic ligand is combined with a labile square planar

Scheme 3

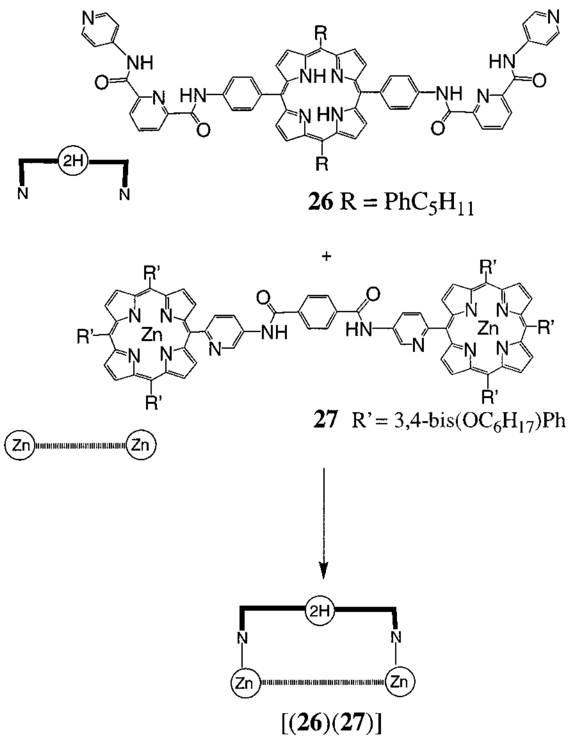
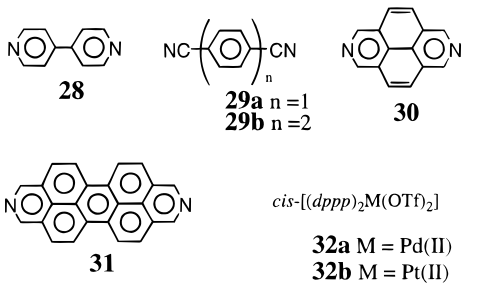


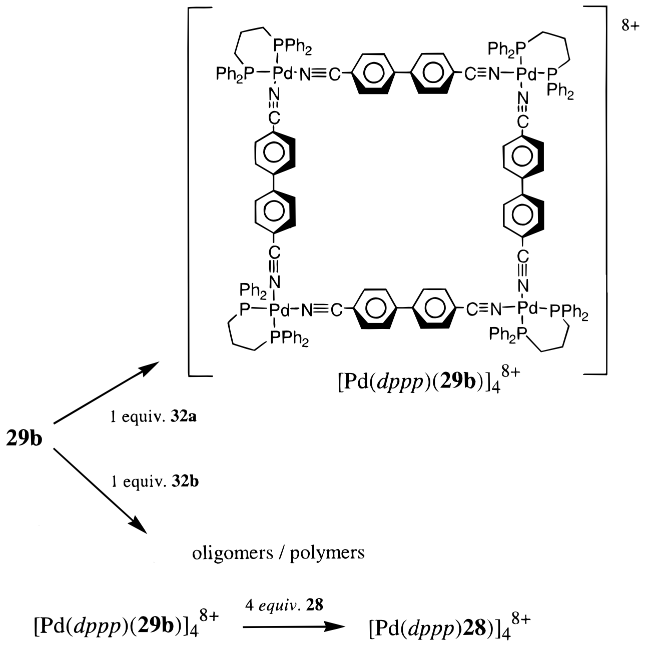
Chart 5



metal ion. When the metal ion has two cis-coordination sites securely occupied by coligands, it forms a 90° angle when new ligands coordinate the vacant sites. Rigid ligands commonly employed in such reactions include 4,4′-bipyridine (**28**), 1,4-dicyanobenzene (**29a**), 4,4′-dicyanobiphenyl (**29b**), 2,7-diazapyrene (**30**), or 2,9-diazadibenzo[cd,lm]perylene **31**[46a] (Chart 5).

The reaction of **29a** or **29b** with metal ions serves as a representative illustration of the formation and properties of molecular squares of this type. Cationic $A^2{}_4L^2{}_4$ squares were self-assembled when **29b** was treated with Pd(II) but not with Pt(II), which instead formed oligomeric products (Scheme 4).[65] This was largely ascribed to the poor lability of the Pt−NC bond, but a lack of stabilizing π-stacking interactions may also have played a role. The cyano-based squares were highly fluxional in solution, whereas the bipyridyl and related systems were more stable. Thus, the cyano-based squares could be spontaneously converted to their bipyridyl analogues by the addition of 4 equiv of free 4,4′-bipyridine **28** (Scheme 4). NMR studies indicated that electron-rich molecules, such as 1,5-dihydroxynaphthalene, were involved in host−guest interactions with the cyano-squares when present in solution.

Scheme 4



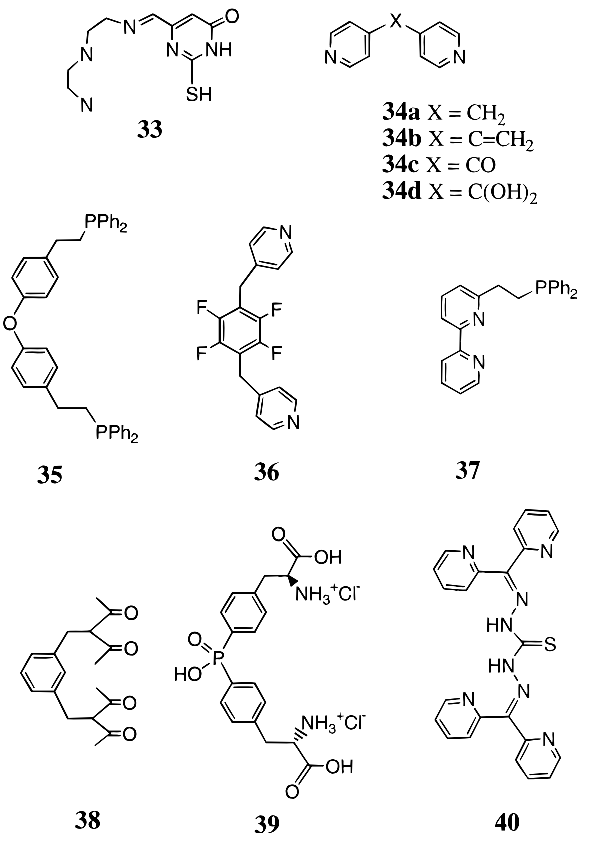
$$[\mathrm{Pd}(dppp)(\mathbf{29b})]_4{}^{8+} \xrightarrow{4\ equiv.\ \mathbf{28}} [\mathrm{Pd}(dppp)\mathbf{28})]_4{}^{8+}$$

Rigid $A^2{}_2A^2{}_2$ and $A^2{}_4L^2{}_4$ molecular squares of the following types have been prepared, inter alia: (i) heterotetrametallic Pd(II)−Pt(II) squares;[66a,b] (ii) "hybrid" squares involving T-shaped iodonium moieties at one set of opposite corners;[66c] (iii) squares made optically active by the use of chiral coligands or by helical twisting arising from the use of unsymmetrical ligands;[66d−f] (iv) squares containing tethered fullerenes;[66g] (v) a variety of rigid porphyrin-based squares;[41a−c,66h,66m] (vi) squares containing crown ethers or calixarenes within their coligands;[66h] (vii) squares having nanometer-scale sides (termed nanosquares);[66i] (viii) squares containing redox active components;[66j] (ix) "π-tweezer" squares in which Ag(I) is bound at the corners in a Ag−acetylene π-complex;[66k] (x) electron-poor cyclophane squares, which recognize electron-rich compounds such as naphthalene;[66l] (xi) silicon-bridged squares and rhomboids.[66m]

Self-Assembly of Squares. Several metal ions other than those mentioned above have also been used in the self-assembly of molecular squares. These include ruthenium,[67−69] cadmium,[70a,71] mercury,[72,73] copper,[68,71,74−76] cobalt,[71,77,78] iron,[71,79] rhodium,[80] rhenium,[81] molybdenum,[82,83] manganese,[71] nickel,[71] zinc,[71] and other examples involving silver,[70b,84] palladium,[85] and platinum.[66g] While many of these metal ions would not normally be considered kinetically labile, several studies have suggested that even nominally inert compounds can become thermally labilized under conventional synthetic conditions, thereby allowing thermodynamic self-assembly to occur. For example, the complete absence of the statistically expected but competing linear oligomers in the production of various rhenium−imine squares is strong evidence for the formation of thermodynamic and not kinetic products despite the generally accepted inertness of such linkages; molecular orbital explanations can rationalize this phenomenon.[86]

It may appear obvious that the self-assembly of geometrically shaped polygons and polyhedra must

Chart 6



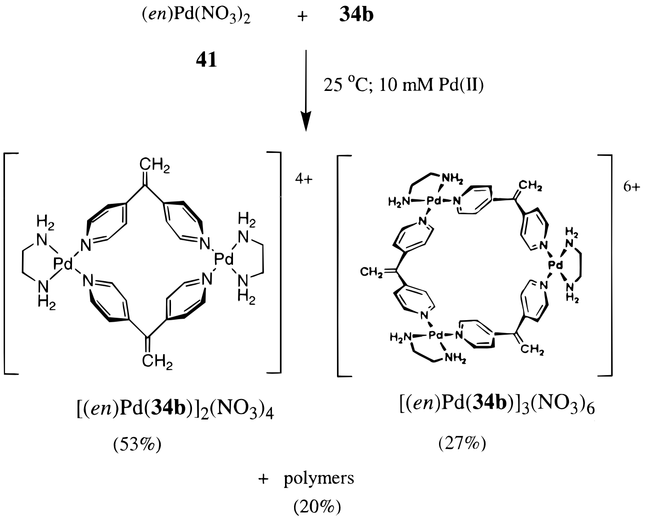


Figure 21. Squares and hexagons. Depiction of the $A^2{}_3L^2{}_3$ hexagon (right) and $A^2{}_2L^2{}_2$ square (left) obtained when bis(4-pyridyl)ethene is treated with (en)Pd^{II}. The mixture also contained oligomers (20%).

involve ligands which are somewhat conformationally inflexible. However, as mentioned above, square complexes which employ linkers that are generally considered flexible or semiflexible are known. Many examples of such linkers exist; these include 1-(2-thiouracil-4-methylene)-3,6-diazahexane (**33**),[78] bis(4-pyridyl)methanes and -ethenes (**34a**,**b**),[59] bis(4-[2-(diphenylphosphino)ethyl]phenyl]ether (**35**),[85] 1,4-bis(methyl(4-pyridine)-2,3,5,6-terafluorobenzene (**36**) (giving water-soluble squares),[87] bipyridine phosphanes (**37**),[68] bis(β-diketone)-substituted benzene (**38**) and naphthalene,[75] certain amino acid substituted bis(phosphonates) (**39**),[71] and tetra(2-pyridyl)thiocarbazide (**40**)[77] (Chart 6). Molecular squares involving these ligands are typically stabilized by (i) conformational restraints inherent to the motif itself, (ii) steric or repulsive interactions to minimize crowding, (iii) attractive π-interactions, or (iv) the presence of bridging atoms/groups on the sides of squares. For example, the Co(II)-containing square formed by **40** is stabilized by bridging thiocarbazide S-atoms on each side;[77] as this molecule contains a large central cavity surrounded by a latticelike arrangement of ligands, it can also be considered a grid.

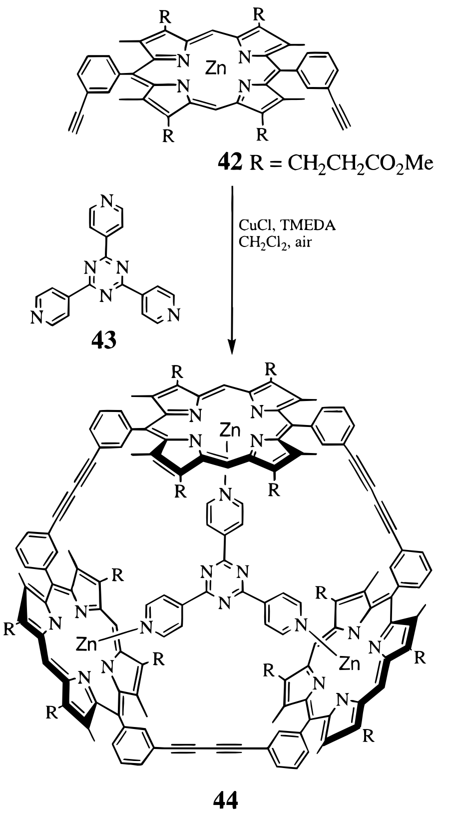
c. Rectangles. A series of luminescent molecular rectangles having rhenium ions on the corners have been reported.[88]

d. Hexagons. The reaction at room temperature of **34b** with *cis*-(en)Pd^{II} (**41**) in aqueous medium produced a mixture which included coordination oligomers/polymers (ca. 20%), the $A^2{}_2A^2{}_2$ square [(en)Pd(**34b**)]$_2{}^{4+}$ (53%), and the $A^2{}_3A^2{}_3$ hexagon [(en)Pd(**34b**)]$_3{}^{6+}$ (27%) shown in Figure 21.[59] The angle subtended by **34b** is 120° which is ideal for hexagon formation; however the binding angle of the square planar Pd(II) is 90° which is better suited to square formation. Since the dimeric square existed in greater proportion than the trimeric hexagon in solution, it appears that the stereochemical preferences of the metal complex dominated those of the ligand in this case. However, the relative proportion of the hexagon grew larger as the concentration of the mixture was increased, indicating that entropic effects can overcome the strain associated with distorted coordination. Conversely, the less-ordered square was progressively favored over the more-ordered hexagon as the temperature was raised. Thermal or entropic effects therefore strongly affected the equilibrium in this thermodynamic self-assembly reaction.

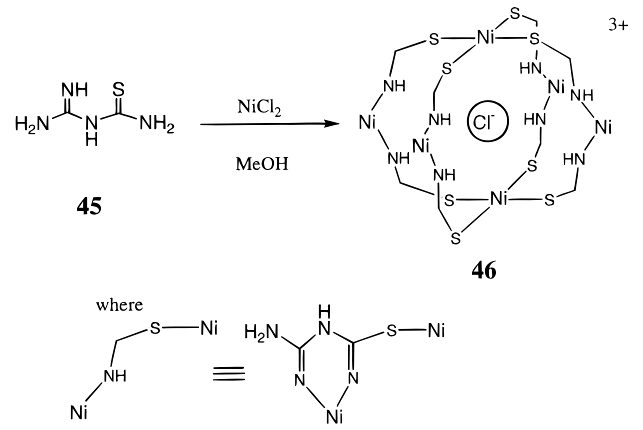
A series of interesting hexagons have been formed by irreversible, directed self-assembly involving the linkage of alkyne groups between three monomers containing zincated porphyrins.[89] For example, the hexagon **44** was obtained by a copper coupling reaction in dichloromethane of the substituted porphyrin **42** in the presence of tris(4-pyridyl)triazine (**43**) (Scheme 5). In coordinating solvents or in the absence of **43**, the hexagon did not form.[89e] In the presence of 4,4′-bipridine (**28**), the corresponding distorted square was instead formed. Thus, the coordination of the amines to the Zn(II) ions of the porphyrins templated the formation of the resulting motif. Once formed, these structures were also able to act as artificial receptors of guest complexes containing pyridines in a spatial arrangement suitable for the coordination of the porphyrin Zn(II) ions.[89d] Other molecular squares, hexagons, octagons, and linear coordination oligomers, formed in similar ways and incorporating zincated porphyrins, have also been reported by the same researchers.[89]

Molecular hexagons, including ones having the formulations $A^2{}_6$, $A^2{}_3L^2{}_3$, and $A^2{}_6L^2{}_6$, have been

Scheme 5



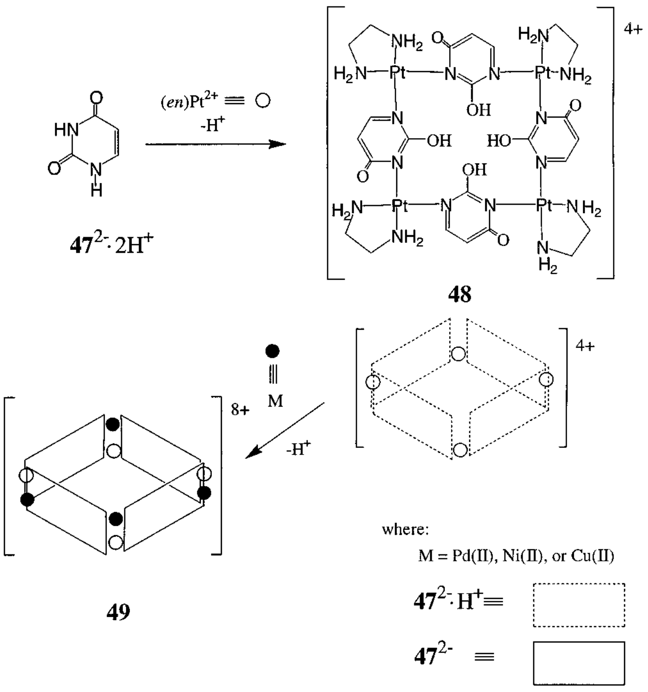
Scheme 6



reviewed elsewhere[3] and are not described here. pH-dependent hexagon formation has also been reported.[74a]

e. Other Metallocyclic Polygons. A vast range of nongeometric metallocycles are known. While simple metallocycles are not a subject of this review, the reader's attention is nevertheless drawn to several subclasses of such metallocycles in which repetitious inclusion of a small ligand within a single compound can lead to a distinctive, cyclic, geometric structure. For example, a recently prepared [16]-metallocrown-8 having Fe(III) corners and bearing a cesium guest in its central cavity can, quite correctly, also be considered an $A^6{}_8A^6{}_8$ molecular octagon,[90] while the [4]metallacalixarene **48** (Scheme 7) closely resembles an $A^2{}_4L^2{}_4$ molecular square.[91] Several of Pecoraro's metallacrown ethers also fall into this category.[92]

Scheme 7



f. Properties and Applications of Geometric Metallocyclic Polygons. Molecular squares are known to participate in hydrophobic–hydrophilic molecular recognition and to form host–guest complexes involving electron-rich or anionic guests.[46a,54b] One of the first squares reported, an $A^4{}_2A^4{}_2$ copper complex of **38**, was, for example, able to bind a variety of heteroaromatic guests within its central cavity, some with remarkable selectivity,[75] while other squares have been used for the transportation of salts over organic phases.[46a,66i] Squares are therefore potentially useful as artificial receptors. The properties of various artificial receptors, including some square complexes, have recently been reviewed.[45]

Redox-active squares displaying one or more reduction waves (depending on the metal–metal interactions permitted by the ligands) are well-known. In principle, a metallocyclophane host containing, for example, four reduced metal centers might be capable of delivering four electrons into a reducible, bound guest molecule.[44] Such a reaction may, additionally, lead to changes in the physical properties of the host–guest complex; electrochemical modification of the reactivity, magnetism, or optical properties of an inclusion compound involving such a host may thereby be possible.[44]

Luminescent rhenium–imine or –azine squares are of interest as visible light-addressable materials.[81] Induction of photoluminescence is particularly attractive in the context of eventual molecular sensing applications since this technique could be used as an alternative means of detecting guest inclusion. Indeed, guests which influence the excited state reactivity potentially constitute a field of study in themselves.[81]

The use of paramagnetic metal ions in the construction of a square not only provides access to paramagnetic host molecules but may also allow

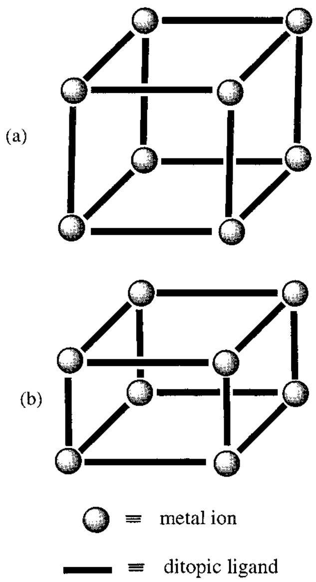


Figure 22. Square and rectangular boxes. Schematic illustration of the structural motif of (a) an $A^3_8L^2_{12}$ square box and (b) an $A^3_8L^2_8L^2_4$ rectangular box.

intramolecular interactions to be studied within molecular arrays.[44]

As molecular squares are relatively conformationally rigid, porphyrin-containing squares offer interesting systems with which to study the photochemical properties of linked porphyrin arrays similar to those in photosynthetic reaction centers and light-harvesting bacteria.[66i]

A frequently observed feature of square complexes is their tendency to stack uniformly within the solid state so that their internal cavities align to form a pore within the structure. This may be of value in solid-state catalysis where the dimensions of an absorbing channel are important.[46a]

4. Geometric Metallocyclic Polyhedra/Boxes

Numerous compounds having metallocyclic polyhedral secondary structures have been prepared using self-assembly processes. The variety and often elaborate geometry of these compounds can significantly complicate a description of their motif. While metallocyclic polyhedra are most comprehensively described using the analogy with Platonic and Archimedean solids developed by Atwood and MacGillivray,[3d] this nomenclature is not ideal as a descriptor of the self-assembly process involved in their formation. For this reason, the "common" nomenclature used by authors in this field has instead been employed below. This terminology classes polyhedra broadly, rather than narrowly, in terms of their similarity to simple geometric shapes (e.g. square or rectangular boxes, cylinders) or to well-known chemical compounds (e.g. adamantanoid boxes).

a. Square and Rectangular Boxes. Figure 22 illustrates the motif of an $A^3_8L^2_{12}$ square box (also described as a cube in equation L in Figure 13) and an $A^3_8L^2_8L^2_4$ rectangular box. While both of these boxes contain metal ions as angular units at the corners, other forms of these motifs are theoretically also possible. If suitable ligands were available, the metal ions could, for example, be bound between the corners on the edges of the cube, giving boxes of similar formulation in which the metal ions were the linear components and the ligands the corner, angular units.

Square and rectangular boxes have been extensively reviewed recently;[3] two representative examples are consequently discussed below.

The $A^2_4A^4_2A^2_8$ rectangular box **46** was spontaneously assembled in the reaction of $NiCl_2$ with amidinothiourea (**45**) (Scheme 6).[93] In the solid state this box was found to contain an encapsulated chloride ion, suggesting that the self-assembly process was directed by anion control. The fact that a similar box was not formed when nitrate, acetate, or perchlorate were used as anions supports this contention. The oligomeric products formed in those cases were spontaneously converted to the rectangular box depicted when potassium chloride was added.

Tetranuclear Pt(II) squares (or square boxes) **48**, resembling calix[4]arenes and having metal ions at alternating corners, have been prepared using nucleobases such as uracil (**47**$^{2-}$$\cdot$2H$^+$), 1-methylcytosin, or 2-aminopyridine as linking units.[94] These complexes also exhibit the solution dynamics and metal binding properties of calix[4]arenes. Thus, after deprotonation of the hydroxide groups, labile divalent cations such as Pd(II), Ni(II), and Cu(II) could be bound at the remaining vacant corners, giving the square boxes **49** of $A^2_4A^8_1$ formulation; the original metallacalixarene **48** is considered to be a kinetically stable A^8_1 fragment in this description. Each of the additional metal ions bound a uracil oxygen donor atom from two adjacent ligands in these boxes. The lability of these linkages was confirmed by the addition of cyanide; within minutes the original tetranuclear Pt(II) species **48** was re-formed.[94] It remained intact for extended periods of time, even in the presence of cyanide, confirming its kinetic stability. As the structure of the octanuclear square boxes **49** were largely due to the preorganization of the original metallacalixarene, the thermodynamic self-assembly which occurred in their formation was structurally trivial.

b. Hexagonal Boxes. Several hexagonally shaped boxes, also known as paddle-wheel complexes, have been obtained using Cu(I) ions. These, cuboctahedra-like structures may form with ligands incorporating bidentate NCS,[94,95] OCS,[96] or SCS[97] metal-binding domains. A common feature of these complexes is the formation of two parallel Cu_3S_3 six-membered rings, each of which usually adopt a slightly puckered chair form; the sulfur donors are a part of the bidentate donors and are bound to two Cu(I) ions as well as to the carbon atom of the ligand. Constable et al. have self-assembled several hexagonally shaped boxes, such as **51**, from Cu(I) and 4-alkyl-2(1H)pyridinethione ligands **50** (Figure 23).[98] Mass spectral data and NMR confirmed their hexanuclear structure in solution, while single-crystal X-ray structures displayed the paddle-wheel structures in the solid state.

Hexagonally shaped boxes of formulation $(E)_2M_4$(**52**)$_4$ were also obtained by the addition of mercaptothiazoline (**52**) (Chart 7) to Cu(I) or Ag(I) (M) in the presence of PPh_3, $AsPh_3$, or pyridine (E).[95] Several

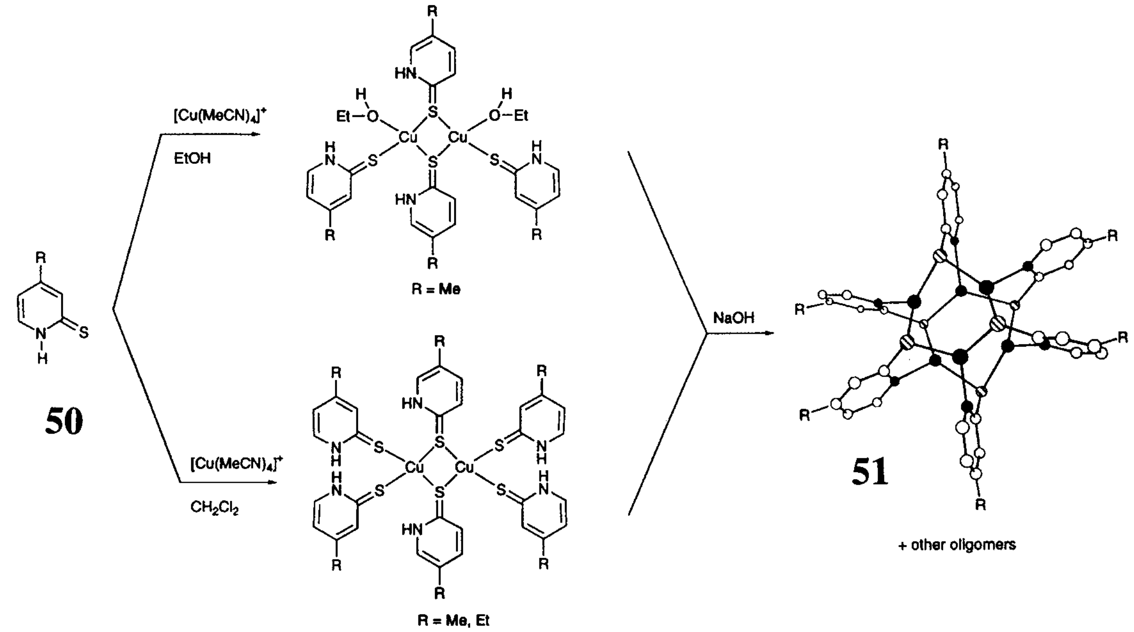
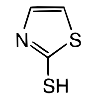


Figure 23. Hexagonal boxes. Synthesis and an ORTEP view of a hexagonally shaped, paddle-wheel complex (R = Me, Et). (Reproduced with permission; ref 98. Copyright 1996 Inorganica Chimica Acta.)

Chart 7



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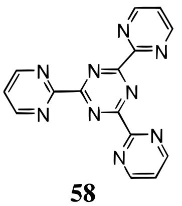
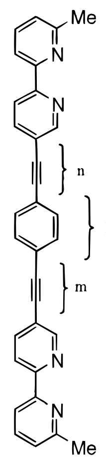
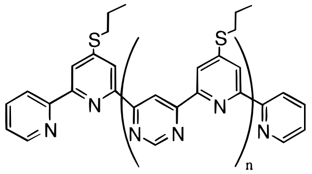


58



57a n = 1; l = 0; m = 0
57b n = 0; l = 1; m = 0
57c n = 0; l = 2; m = 0
57d n = 1; l = 1; m = 1
57e n = 1; l = 2; m = 1



59a n = 1
59b n = 2

of these complexes are fluxional and must therefore be assumed to be thermodynamic products which are structurally similar to butterfly clusters.

A hexagonal cyclophane box is also described in section V. B.4.d (Cyclophane Boxes) (Figure 30).

c. Cylinders. Figure 24a,b schematically illustrates the motif of some molecular cylinders. Cylinders are species which are self-assembled from appropriate metal ions with two different types of ligands, a planar, disklike polytopic ligand and a rigidly linear polytopic ligand. Triply connected, double-decker cylinders have the triangular prism secondary structure depicted in eq J in Figure 13.

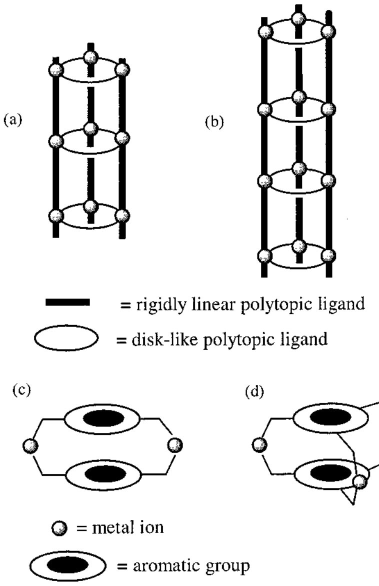


Figure 24. Cylinders and cyclophane boxes. Schematic depictions of a (a) triple-decker and (b) a quadruple-decker molecular cylinder, as well as a (c) bimetallic and (d) trimetallic cyclophane box. Each cylinder contains two different types of ligands, a disklike tritopic ligand and a rigidly linear polytopic ligand. Each cyclophane box is characterized by a central cavity stabilized by π-stacking interactions.

The $A^4{}_6L^4{}_3L^6{}_2$ cylinder **54** shown in Figure 25 was prepared by Lehn and co-workers.[99] It was characterized by mass spectrometry, and the association constants of the intermediate species were determined. This cylinder was thermodynamically self-assembled as an equilibrium product from the interaction of two cyclic hexaphenylhexaazatriphenylene ligands **53** and three linear bis(bipyridine) ligands **7a** with 6 equiv of $[Cu(CH_3CN)_4](BF_4)$. In the solid state, the cylinder was twisted about its central compartment (cavity), shortening its length along the cylindrical axis.[100] The reaction of the ligands with

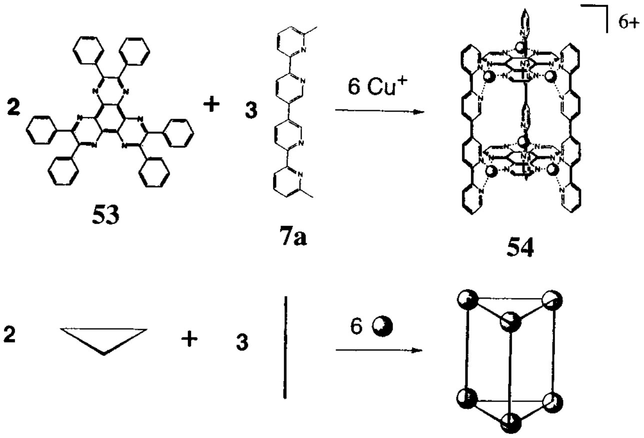


Figure 25. Cylinders. Formation of a molecular cylinder. (Reproduced with permission; ref 99. Copyright 1996 the American Chemical Society.)

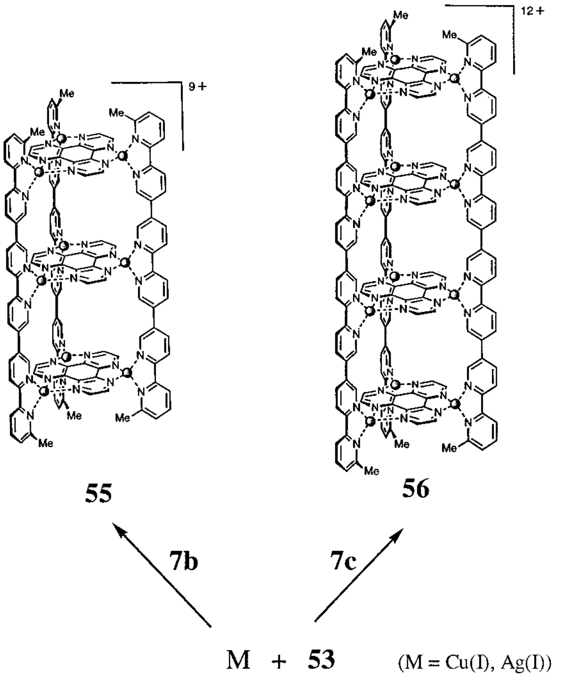


Figure 26. Cylinders. The formation of triple-decker and quadruple-decker cylinders. The shaded circles represent Cu(I) or Ag(I) ions. (Reproduced with permission; ref 102a. Copyright 1999 Wiley-VCH.)

Ag(OTf) produced an analogous cylinder which was not twisted in the solid state.[101] The presence of halogen or aromatic counterions in the reaction mixtures prevented the formation of cylinders, presumably because of competing bridging or aromatic-contact interactions.

Triple- and quadruple-decker analogue cylinders **55** and **56** have also been prepared by Lehn et al. using **53** and Cu(I) or Ag(I) ions with ligands **7b**,**c**, respectively (Figure 26).[102] In these cases, 15 (for the triple-decker) or 19 (for the quadruple-decker) units combined in a thermodynamic self-assembly to produce the bi- and tricompartmental cylinders having the formulations $A^4_9L^6_3L^6_3$ and $A^4_{12}L^8_3L^6_4$, respectively. Mass spectrometry indicated that these cylinders were stable to dissociation at concentrations as low as 10^{-4} mol dm^{-3}, while NMR studies indicated that the cylinders were highly symmetrical in solution. In the solid state they were twisted into triple-helical, cagelike structures. The X-ray crystal structures showed that the compartmental cavities within these cylinders contained anions; in the triple-decker compound, one cavity contained two PF_6^- anions with a water molecule, while the other contained one fully enclosed PF_6^- with a further partially enclosed PF_6^- and nitromethane molecule. The differing sizes of the compartments in both the triple- and quadruple-decker compounds were due to the non coplanarity of the "deck" ligands; these are slightly tilted toward or away from each other. Anion-exchange studies involving NMR measurements conclusively indicated that the cavities also contained anions in solution and that the anions were able to

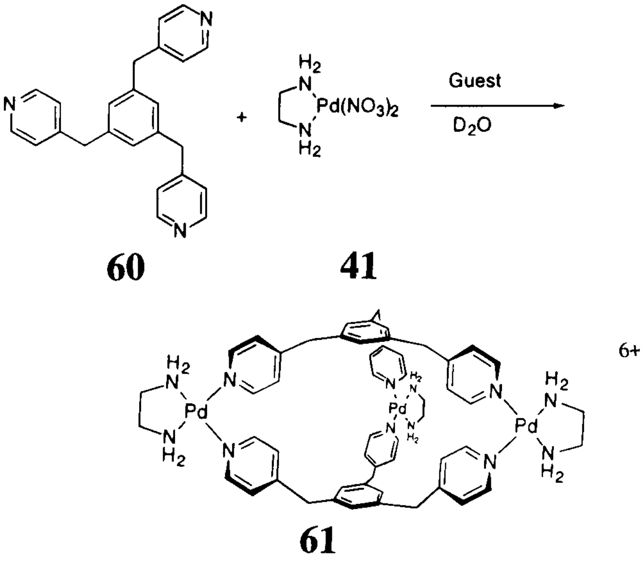


Figure 27. Cyclophane boxes. Self-assembly of an $A^3_2A^2_3$ cyclophane box under the influence of a guest. (Reproduced with permission; ref 45. Copyright 1997 American Chemical Society.)

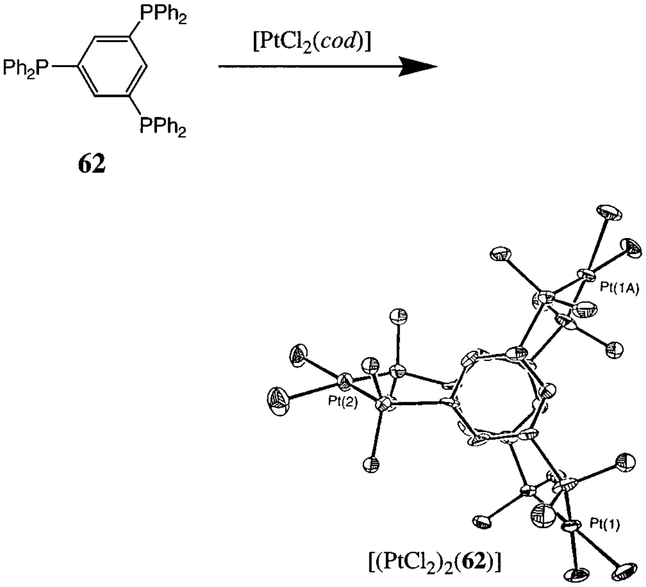


Figure 28. Cyclophane boxes. Formation and an ORTEP representation of the cyclophane box generated in the self-assembly of 1,3,5-tris(diphenylphosphino)benzene with Pt(II) (cod = cycloocta-1,5-diene). (Reproduced with permission; ref 105. Copyright 1996 The Royal Society of Chemistry.)

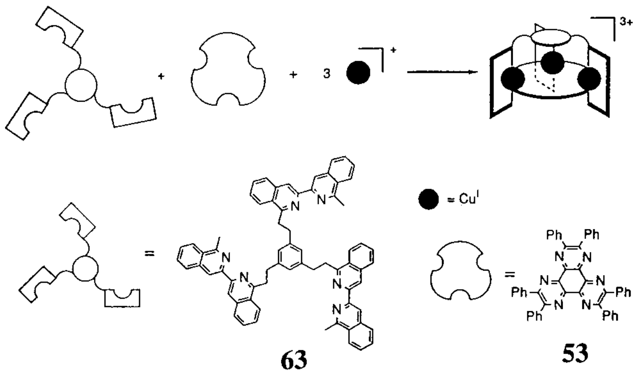


Figure 29. Cyclophane boxes. Self-assembly of a cyclophane box. (Reproduced with permission; ref 106. Copyright 1993 The Royal Society of Chemistry.)

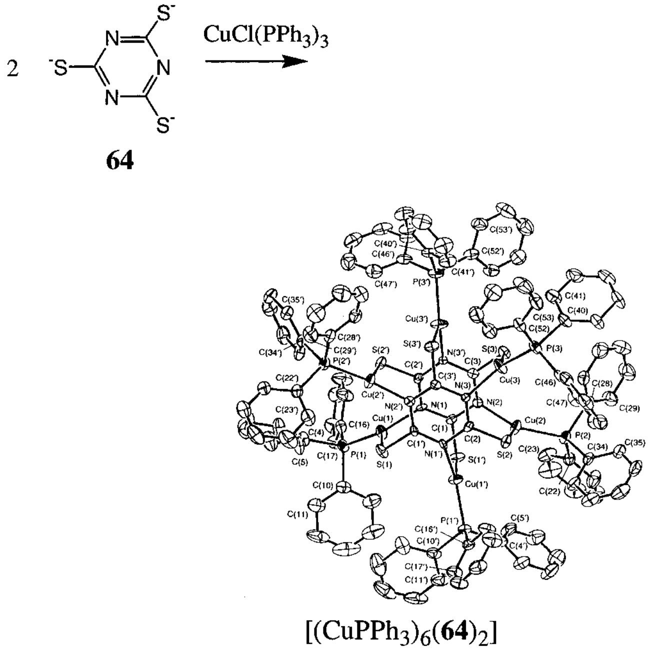


Figure 30. Cyclophane/hexagonal boxes. Formation and an ORTEP of a cyclophane/hexagonal box generated by the self-assembly of trithiocyanuric acid with CuCl(PPh$_3$)$_3$ in the presence of Et$_3$N. (Reproduced with permission; ref 107. Copyright 1996 The Royal Society of Chemistry.)

move in and out of the cavities at room temperature. Intramolecular “breathing” of the complexes by unwinding of the helix may result in opening up of the windows, thereby facilitating anion exchange in to and out of the cavities.

The size of the cavity of double-decker cylindrical complexes could be adjusted by the use of longer linkers between the binding sites of the axial ligands.[101] While the cylinder **54** shown in Figure 25 was 20 Å long, analogous cylinders of up to 33 Å in length were obtained by using the axial ligands **57a**−**e** (Chart 7), which include rigidly linear phenyl and acetylene linkers. The presence of acetylenic groups proved, however, to interfere with the self-assembly process, presumably because of their reactivity.

A remarkable testimony to the fidelity of thermodynamic self-assembly can be found in the reaction of the axial ligands **7a**, **57b**, and **57c** (in a 1:1:1 ratio) with the disklike ligand **53** and Cu(I).[102] After stirring of the sample for 72 h, ^{1}H NMR spectroscopy indicated the presence of only the three cylinder species which would have been obtained if each of the axial ligands had been used separately. Thus, the three cylinders were selectively formed as the thermodynamically most stable substances from a mixture containing four different ligands and Cu(I) ions.

While most cylinders have involved tetrahedral metal ions, in one case an octahedral ion has been employed.[103] The stoichiometric reaction of Pb(II) with a tris(2-pyrimidyl)triazine (**58**) and bis- or tris(terpyridine) ligands **59** (Chart 7) resulted in the formation of an $A^6{}_6L^6{}_3L^6{}_2$ double-decker and an $A^6{}_9L^9{}_3L^6{}_3$ triple-decker cylinder.

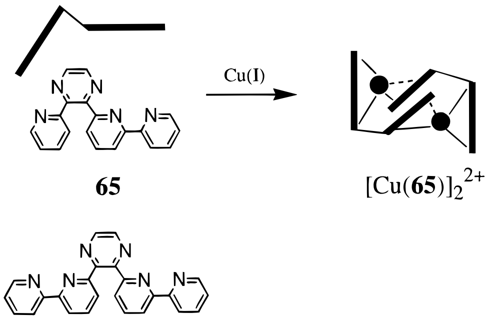
d. Cyclophane Boxes. Figure 24c,d depicts the general motif of cyclophane boxes. These species are characterized by the presence and stabilization of at least two coplanar aromatic groups on directly opposing faces of a box created by metal−ligand coordination. While cyclophane boxes do not describe one geometry exclusively but rather encompass a variety of structures having the characteristic central cavity, it is convenient to group such boxes into a single category because their cavity is usually ideally suited to accept π-interacting guests. In general, however, cyclophane boxes tend to be cylindrical about the central cavity.

A distinction has been made in this section between cylinders and cyclophane boxes on the basis of the driving force of box formation. Cyclophane boxes come about largely as a result of additional π-stacking interactions between the coplanar aromatic groupings prior to or during the self-assembly reaction. Cylinders on the other hand—or at least those reported thus far—result purely from the bonding and steric constraints associated with metal−ligand coordination.

The $A^3{}_2A^2{}_3$ cyclophane box **61** shown in Figure 27 has been prepared by Fujita et al.,[104] who combined the tridentate ligand 1,3,5-tris(4-pyridylmethyl)benzene (**60**) with (en)Pd^{II} (**41**). Interestingly, this species is only formed in the presence of an aromatic guest such as (4-methoxyphenyl)acetic acid, suggesting that a directed self-assembly process involving induced-fit molecular recognition occurs. In the absence of such a third-party molecule, poorly defined oligomeric complexes were instead obtained. The addition of a suitable guest to an oligomeric mixture of this type resulted in the selective conversion of the system back to the cyclophane box indicating that a reversible equilibrium must exist. It can therefore be concluded that the self-assembly process in this reaction was not only directed but also thermodynamic in nature.

Similar compounds have been obtained in the reaction of square planar Pt(II) or tetrahedral Cu(I) metal ions with ligands involving a benzene ring substituted in the 1-, 3-, and 5-positions with groups bearing diphenylphosphine (**62**; Figure 28)[105] or bis(isoquinoline) (**63**; Figure 29)[106] binding sites, respectively. The latter reaction appears to involve a thermodynamic self-assembly process, directed by π-stacking interactions between the coplanar rings.

Scheme 8



The luminescent $A^6{}_2A^3{}_6$ cyclophane box $[(CuPPh_3)_6(\mathbf{64})_2]$ in Figure 30 was obtained in 90% yield from the reaction of trithiocyanuric acid with 3 equiv of $CuCl(PPh_3)_3$ in the presence of triethylamine.[107] In this species, which can also be considered a hexagonal box, each Cu(I) ion has a distorted three-coordinate geometry and the parallel triazine rings are 3.07 Å apart. The complex shows room-temperature photoluminescence at 562 nm with a lifetime of 0.59 μs in the solid state. In dichloromethane, the complex luminesces at 580 nm, with a lifetime of 0.82 μs (298 K).

A racemic mixture of the chiral $A^4{}_2A^4{}_2$ cyclophane box $[Cu(\mathbf{65})]_2{}^{2+}$ has been prepared using Cu(I) and 2-(2,2′-bipyridyl)-3-(2-pyridyl)pyrazine (**65**) (Scheme 8).[108] The central cavity in this molecule has a height of 3.42−3.62 Å. The selective formation of the racemic diastereomer, rather than the meso compound previously obtained with **66**,[109] was believed to be due to favorable stacking interactions existing in both the solid state and solution.

Other cyclophane boxes have also been reported.[110]

e. Adamantanoid Boxes. One of the more interesting 3-D geometric motifs to have been described in recent years is that of the adamantanoid box. Molecules having secondary structural motifs of this type are characterized by a spatial arrangement of atoms resembling that seen in the well-known organic molecule, adamantane. A distinguishing feature of these complexes is that they may belong to the T symmetry point group, which has hitherto been rarely observed in coordination chemistry. The octahedron illustrated in eq K of Figure 13 depicts the general structure of an adamantanoid box.

When adamantanoid boxes are self-assembled, the metal ions may act as (i) the tritopic angular units which fill the four bridgehead positions as shown in Figure 31a or (ii) the ditopic angular units which fill the six positions on the connecting vertexes as shown in Figure 31b. In case i above, the four metal ions approximate a tetrahedral arrangement about the central cavity, so that such a structure can also be described as a tetrahedron[3a] or as a tetrahedral or tetranuclear adamantanoid box. Such compounds have the formulation $A^3{}_4A^2{}_6$, where the metal-containing building blocks, including any coligands, are the component A^3 and the ligands are the component A^2. In case ii above, the metal ions form an octahedral arrangement about the central cavity. Complexes of this type are therefore termed octahedra or octahedral or hexanuclear adamantanoid boxes and have the formulation $A^3{}_4A^2{}_6$, where the metal-containing building blocks, including coligands, are the angular component A^2 and the ligands are the component A^3.

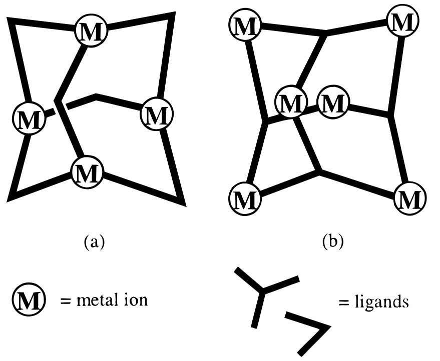


Figure 31. Adamantanoid boxes. Schematic illustration of (a) a tetranuclear adamantanoid box and (b) a hexanuclear adamantanoid box.

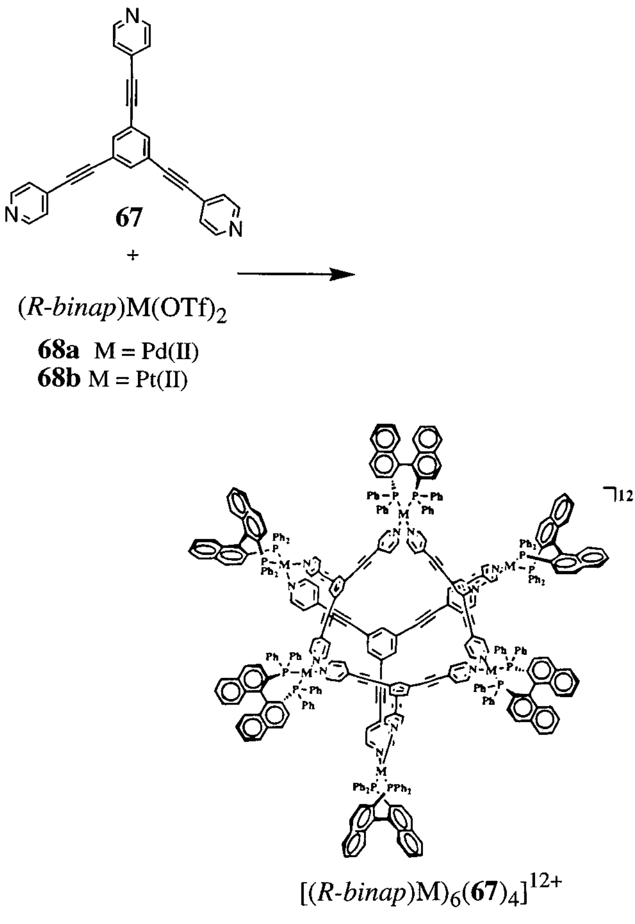
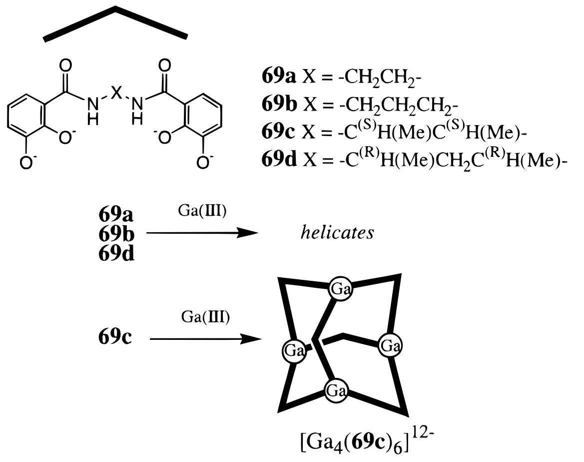


Figure 32. Adamantanoid boxes. Schematic depiction of the self-assembly of an octahedral adamantanoid box by the combination of $[(R\text{-binap})M]^{2+}$ with a 1,3,5-tris(ethynylpyridyl)benzene) ligand (M = Pd, Pt). (Reproduced with permission; ref 111. Copyright 1997 American Chemical Society.)

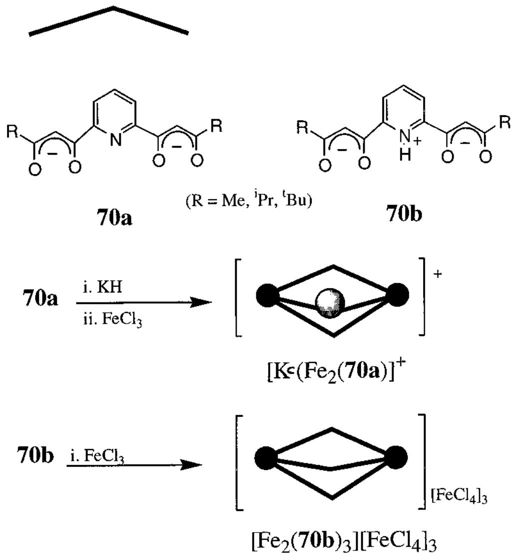
Adamantanoid boxes and their variations have recently been comprehensively reviewed.[3a−d] Representative examples are therefore described below.

Hexanuclear Adamantanoid Boxes. The chiral hexanuclear adamantanoid boxes $[((R\text{-binap})M)_6(\mathbf{67})_4]^{12+}$ (M = Pd(II), Pt(II)) illustrated in Figure 32 have been

Scheme 9



Scheme 10



self-assembled using Pd(II) or Pt(II) complexes of *R*-binap as shape-defining corner units and the benzene tri(ethynylpyridyl) ligand **67** as a connector.[111] The structure of these complexes, which are correctly termed "truncated tetrahedra" because of the planarity of the tritopic ligands,[3a−d] were inferred from mass spectrometry and molecular mechanics simulations; in solution they belong to the T-symmetry point group. An interesting observation regarding their self-assembly was that it was dependent on the order in which the reagents were combined. If a solution of the metal was added to a solution of the ligand, poorly soluble oligomers were obtained. However, when a solution of the ligand was added to a solution of the metal, the box was obtained.[111] This should not occur if all the interactions involved in its formation were reversible and kinetically rapid. The most likely explanation is that oligomers were favored and precipitated as kinetic products during the addition of the metal to the ligand when small quantities of the metal were present in a large excess of the ligand. The slow dissolution of the oligomers presumably then hindered formation of the box. When the ligand was added to the metal, however, a large excess of the metal initially existed so that the oligomers were not kinetically favored; the resulting mixture could therefore equilibrate rapidly. The formation of kinetic products in a system may consequently be highly pathway specific.

Hexanuclear adamantanoid boxes have also been prepared using a variety of other tridentate linking ligands.[112a,113,114] Certain of these molecules have proved able to selectively clathrate "C-shaped" molecules, such as *cis*-azobenzene and -stilbene, by the "ship-in-a-bottle" formation of stable hydrophobic dimers.[112b]

Tetranuclear Adamantanoid Boxes. A tetranuclear adamantanoid box has been reported in the reaction of the enantiopure (S,S)-bis(catecholamide) ligand **69c** with Ga(III) (Scheme 9).[115] In the resulting compound, each metal displayed a Λ-configuration, giving it an overall T point symmetry. When the racemic form of **69c** was used, a pair of mirror-image tetranuclear adamantanoid boxes were produced. The stereoselectivity of these reactions were remarkable; while analogous to that demonstrated in the formation of many helicates, they were statistically far less probable. The isomer obtained from the enantiopure ligand would, for example, comprise a mere $^{1}/_{16}$th of a truly statistical mixture, while the two isomers generated by the racemic mixture were selectively formed from 112 theoretically possible variants. The same reaction with the derivative ligands **69a**,**b**,**d** produced helicates.

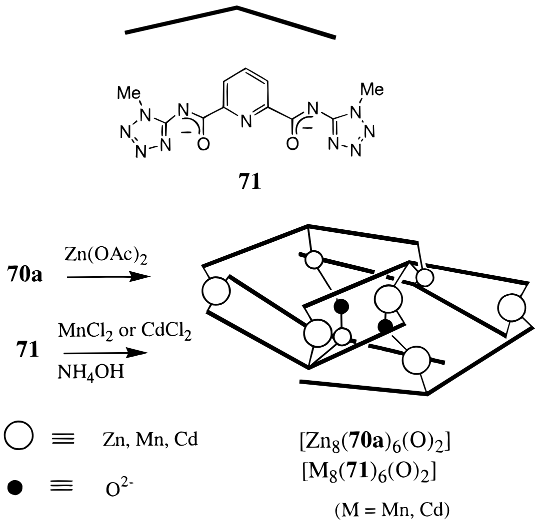
Tetranuclear adamantanoid boxes have also been reported by Saalfrank[116−120] and Raymond[47,121,122] and their co-workers. Certain of the boxes were able to selectively encapsulate small cationic guest within the central cavity in an entropy-driven process.[47,121,122]

f. Other Metallocyclic Boxes. *Binuclear Boxes.* While helicates have been specifically excluded from this work, it should be noted that many helicates and *meso*-helicates can be considered to be chiral and achiral binuclear boxes, respectively. This is especially true of triple-stranded helicates and *meso*-helicates involving rigid spacers, which commonly enclose a well-defined central cavity and exhibit many of the characteristics of molecular boxes. For example, Albrecht's *meso*-helicates[123] (comprising oligocatechol ligands with hard metal ions) may, like other of the boxes discussed here, be formed by directed self-assembly processes (involving induced-fit[124] or template-directed molecular recognition[125]), host small molecules in their internal cavities,[126,127] adopt cylinder-like motifs,[128,129] enclose nanometer-sized central cavities,[128] or simultaneously incorporate different metal ions.[129] A significant literature covering these aspects now exists for helicates.[1]

Beyond helicates, a series of conformationally rigid binuclear metallacryptates and -cryptands have been prepared.[130] Two examples are the {2}-metallacryptate $[K\subset(Fe_2(\mathbf{70a})]^+$ and the {2}-metallacryptand $[Fe_2(\mathbf{70b})_3][FeCl_4]_3$ prepared by Saalfrank and co-workers (Scheme 10).[130a] The former compound endohedrally encapsulates a K^+ ion; other cations, such as divalent alkaline earths or trivalent rare earths can also be encapsulated. The cavity in the latter compound is, however, free of cations.

Tetranuclear and Polynuclear Boxes. A wide variety of other molecular polyhedra are known. These

Scheme 11



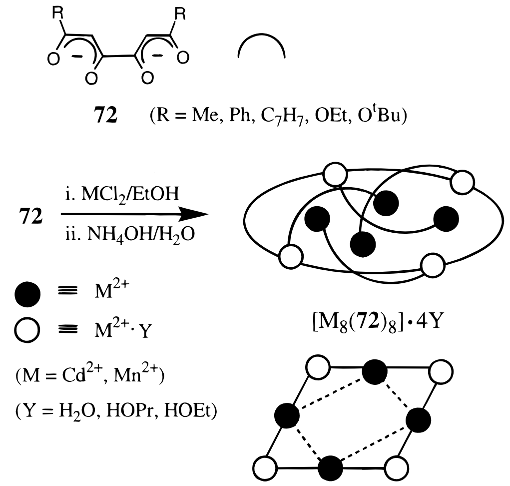
include tetranuclear $A^3_4L^2_6$ boxes[131] and $A^3_4A^3_4$ tetrahedra,[132] as well as polynuclear $A^3_8L^2_{12}$ cuboctahedra,[133a,b] $A^2_{18}A^3_6$ hexahedra,[133c] and self-assembled, discrete $A^2_6A^3_2A^3_2$ interpenetrating boxes.[133d] Recent reviews have comprehensively described these materials.[3]

Irregular Boxes. A series of unusual octanuclear bis(triple-helicate) boxes $[M_8(\mathbf{70a})_6(O)_2]$ and $[M_8(\mathbf{71})_6(O)_2]$ have been prepared (M = Cd(II), Mn(II), and Zn(II)) (Scheme 11).[134a] These species, which form in solution, were obtained from the reaction of 0.75 equiv of the diacid form of **70a** or **71** with 1 equiv of zinc acetate or cadmium/manganese dichloride in the presence of Et_3N. ^1H and ^{13}C NMR studies revealed that all six ligands were chemically identical in solution but that the two halves of each ligand were in a different magnetic environment.

Several examples of a previously unknown class of octanuclear box $[M_8(\mathbf{72})_8]\cdot 4Y$ ($M = Cd^{2+}$, Mn^{2+}) ($Y = H_2O$, HOPr, HOEt) have been formed in the reaction of the diacid of **72** with cadmium or manganese dichloride in methanol in the presence of aqueous ammonia.[134b] These boxes are characterized by the fact that each of the two differently complexed metal ions are arranged in tetranuclear squares of different sizes and rotated at 45° to each other but having a common center (Scheme 12). The ^1H and ^{13}C NMR spectra of the diamagnetic Cd(II) compounds indicate that four ligands in these complexes are identical and the two halves of each of these ligand are in different magnetic environments. This is consistent with the solid-state structures schematically depicted in $[M_8(\mathbf{72})_8]\cdot 4Y$. Deprotonation of the diacid of **72** (R = OEt) with MeLi/THF, followed by the addition of $MgCl_2$ and workup using NH_4Cl/H_2O, resulted in the formation of the corresponding tetranuclear adamantanoid box.[134b] Double deprotonation of the diacid of **72** in the presence of $CuCl_2\cdot 2H_2O$ and $NaBF_4$ led to a trinuclear copper−crown ether with an encapsulated Na^+ ion.[134c] A single-crystal X-ray structure of this material revealed a double- and triple-decker metallacoronate structure.

g. Properties and Applications of Geometric Metallocyclic Polyhedra/Boxes. The incorporation of electroactive metal centers into a box is significant; it makes possible the construction of a variety of molecular devices, such as tuneable sensors or multiple state switches. The host−guest chemistry of such boxes may influence these and other electron/energy transfer processes.[135]

Scheme 12



The formation of cylinders is analogous to the self-compartmentalization processes seen in biology in which, for example, multicompartmental proteases are spontaneously formed. Potential applications therefore exist in materials science and nanotechnology, where pathways leading to the controlled access of nanosized chemical entities is important.[102] The programmed formation of highly complex cylindrical architectures consequently represents a potential alternative to nanofabrication and manipulation. Cylinder formation is a highly convergent type of self-assembly, involving greater information content than other processes.[102]

A series of bowl-shaped molecular boxes based on hydroxyacids derived from L-serine and connected to each other with a xylenic linker have been self-assembled with metal ions;[136] these boxes proved effective in the transport of neutral, arene guests through an aqueous phase.

5. Circular Helicates

A circular helicate, also known as a wreath, is a double-helicate whose ends have been closed into a toroidal, doughnut structure. Circular helicates are described using the nomenclature $[n]^m\mathbf{cH}$, where n is the nuclearity and m the helicity ($m = 2$ for a double helix) of the torus.[7a]

Circular helicates are important motifs in coordination chemistry because, unlike most geometrically shaped polygonal and polyhedral motifs, their closed, cyclic nature is an element of tertiary rather than secondary structure. Primary structure in these molecules involves the covalent connectivity of the atoms in the ligands, while the multiply stranded helicity of the walls of circular helicates is a distinctive secondary structure. Tertiary structure exists in the overall toroidal shape of the molecule.[7a] The higher levels of structural complexity in these molecules is typically formed in a single thermodynamic

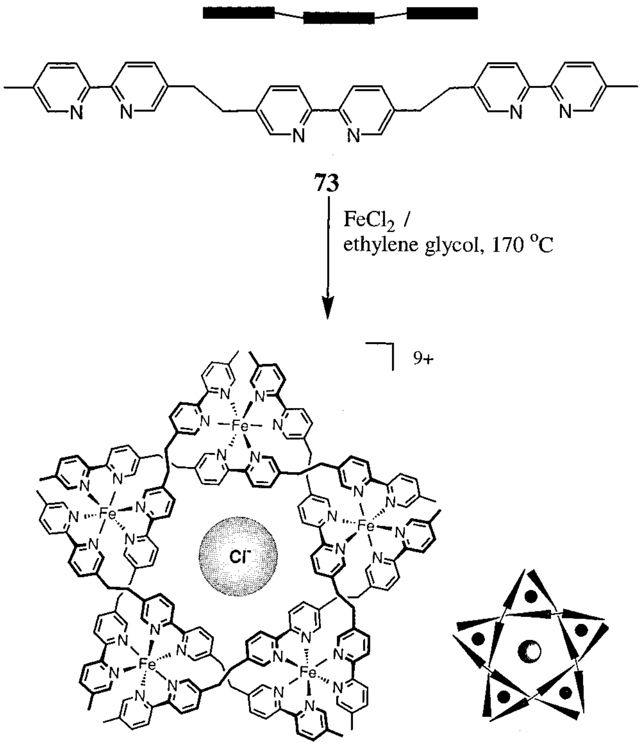


Figure 33. Circular helicates. Self-assembly of a pentanuclear circular helicate $[5]^2$**cH** from an ethyl-linked tris(bipyridine) ligand and Fe(II) in the presence of chloride anions. One chloride anion occupies the central cavity in the solid state. (Reproduced with permission; ref 7. Copyright 1997 American Chemical Society.)

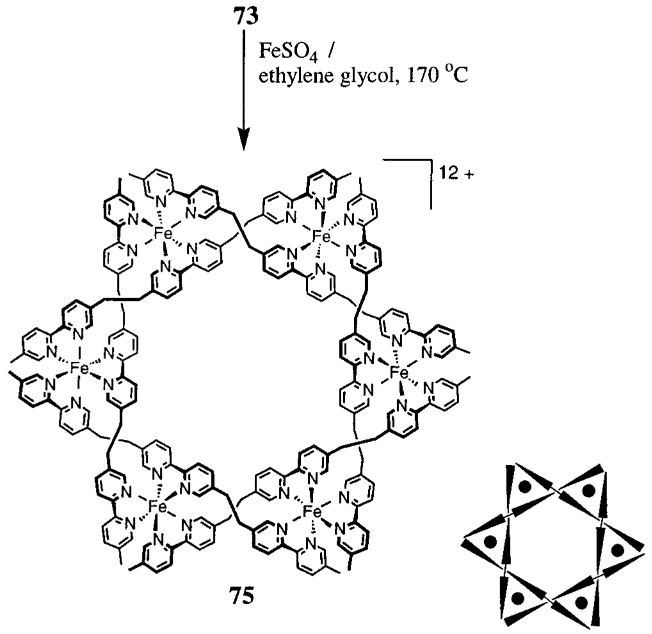


Figure 34. Circular helicates. Self-assembly of a hexanuclear circular helicate $[6]^2$**cH** from an ethyl-linked tris(bipyridine) ligand and Fe(II) in the presence of sulfate anions. The identical complex was obtained when FeSiF$_6$, Fe(BF$_4$)$_2$, or FeBr$_2$ was used as starting materials. (Reproduced with permission; ref 7. Copyright 1997 American Chemical Society.)

self-assembly process involving only metal–ligand coordination.

Several circular helicate coordination compounds have been prepared and characterized, primarily by Lehn and co-workers. The $[5]^2$**cH** (**74**) was obtained by the reaction of the semiflexible tris(bipyridine) ligand **73** with the chloride salt of octahedral Fe(II) (Figure 33).[7a,137] The pentanuclear nature of this complex was influenced by the presence of chloride anions since the use of FeSO$_4$, Fe(BF$_4$)$_2$, or FeSiF$_6$ as starting materials produced only the $[6]^2$**cH** (**75)** shown in Figure 34. The latter complex can accommodate a SO$_4^{2-}$ ion in its central cavity.[7a] The use of FeBr$_2$ led to a mixture of the $[5]^2$**cH** and $[6]^2$**cH** wreaths.

The selective formation of circular helicates of different size according to anion preference is an example of a directed self-assembly process utilizing induced-fit molecular recognition. This effect may be understood either in terms of a templating influence or as the self-assembly of a receptor according to the preferences of its substrate.[7a] It is possible that a library of oligomeric toroidal structures having a 1:1 metal–ligand stoichiometry is produced in solution and that the anions screen this collection for the most suitable receptor, which is then selectively stabilized. Alternatively, a particular number of ligands may simultaneously interact with each anion, resulting in the formation of a complex which would not otherwise occur. In the latter case the complex would be considered to be "templated", while in the former case it would be considered to be "expressed" in the same way that products are expressed in biology.[7a] Experiments showed that the $[6]^2$**cH** formed in the presence of SO$_4^{2-}$ could be quantitatively converted to its $[5]^2$**cH** analogue by exchanging the anion for chloride; the chloride ion therefore played a more significant role than simple templation.

The effect of a structural alteration in the ligand of this system has also been studied. The use of the longer and more flexible $-CH_2-O-CH_2-$ linkers between the bipyridine binding sites resulted in the stabilization and isolation of the smaller $[4]^2$**cH** (**76**) (Figure 35).[7a] Each of the $[4]^2$**cH**, $[5]^2$**cH**, and $[6]^2$**cH** circular helicates described above are unique; however, they all share the same secondary and tertiary structural elements.

The mechanism by which the $[5]^2$**cH** (**74**) was formed has been studied by Lehn using ES-MS and ^{1}H NMR spectroscopy.[138] This work indicated that the corresponding triple-stranded, trimetallic helicate $[3]^3$**H** was formed within 1 min as the first product of the reaction. The helicate was then transformed, over ca. 24 h, into the circular helicate. The rate of this transformation could be increased by heating or concentrating the reaction mixture. Further work indicated that the known Ni(II) triple-helicate $[Ni_2(\mathbf{73})_3]^{6+}$ could be partially transformed into an analogous circular helicate $[Ni_5(\mathbf{73})_5Cl]^{9+}$ by a similar manipulation of the reaction conditions; Ni(II) has the same coordination geometry as Fe(III).[138]

When complicated structures such as circular helicates self-assemble, the systems explore an energy hypersurface to find the thermodynamically most favored product. In this process they may be temporarily trapped in a local minima, from which escape

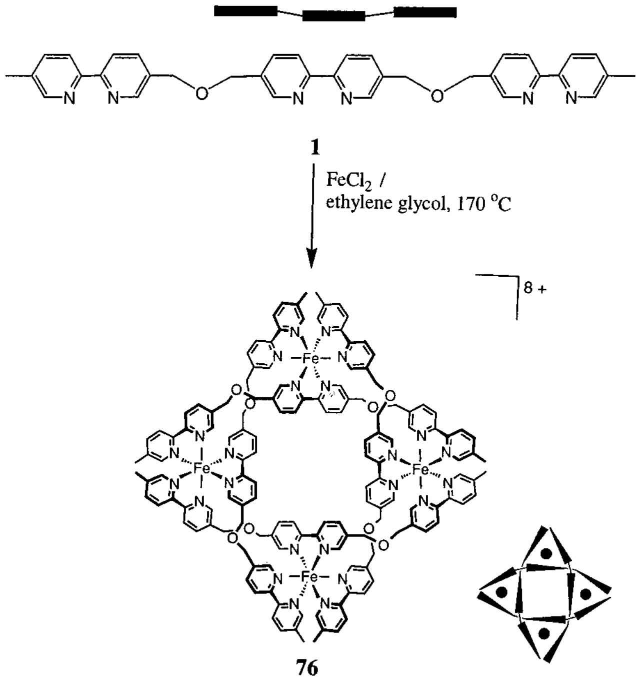


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Figure 35. Circular helicates. Self-assembly of a tetranuclear circular helicate [4]^2**cH** from $-CH_2OCH_2$-linked tris(bipyridine) ligands and Fe(II) in the presence of chloride anions. (Reproduced with permission; ref 7. Copyright 1997 American Chemical Society.)

to the global minima is slowed by a high activation barrier. In that case, the product corresponding to the local minima is a kinetic and not the thermodynamic product. This appears to have occurred in the formation of the circular helicates of Fe(II) described above, since they were formed very slowly from the corresponding helicates, which must have been kinetic products under the conditions of the self-assembly reaction.[138] As a product which is thermodynamically most-favored under one set of conditions may be only kinetic favored under another, it should not be concluded that the Fe(II) helicates are kinetic products under all reaction conditions.

An example in which helicates and circular helicates simultaneously existed in a mixture as apparent thermodynamic products was the reaction of Cu(I) with the 2,2′:2″,6″:6″,2‴-quaterpyridine ligand **77** in which an ethyl spacer was used to split the binding domain into two bipyridine binding sites (Scheme 13).[139] In the presence of acetonitrile-d$_3$, ES-MS revealed the existence of a library of compounds which included the [3]^2**cH** (**78**), as well as the [4]^2**cH** (**79**) and the [5]^2**cH** (**80**), in addition to the expected diastereomeric *P* and *M* double helicates. Concentration of the mixture resulted in an increase in the higher nuclearity species, suggesting that the formation of the circular helicates in the solution was strongly influenced by entropic factors. At concentrations below 10^{-4} M, only the binuclear helicates were present however. An X-ray crystal structure determination of **78**, which could be selectively isolated, revealed a diastereomeric pair of *P* and *M* circular helicate products.

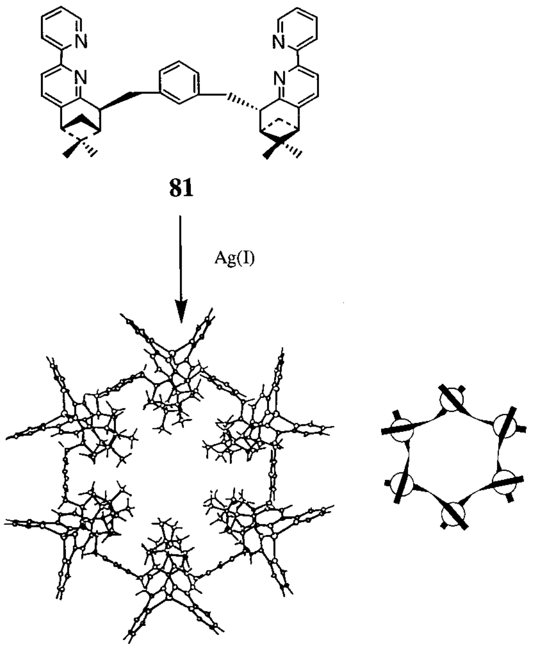

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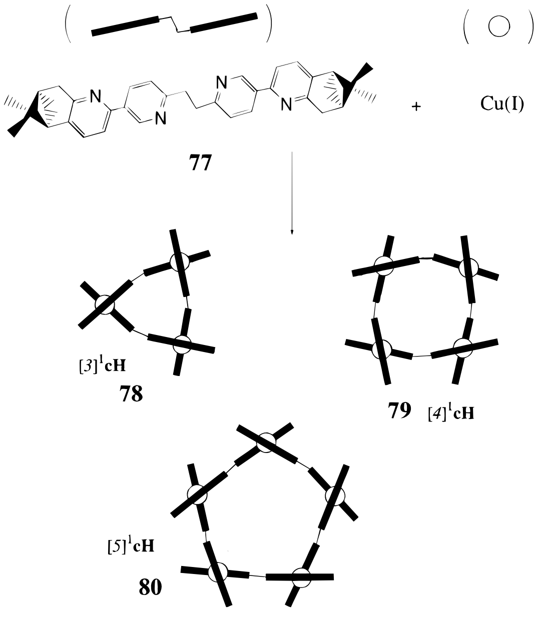
Figure 36. Circular helicates. Formation and an ORTEP of the single-stranded circular helicate [6]^1**cH** formed in the stereoselective reaction of Ag(I) with a bis(2,2′-bipyridyl) ligand having a spacer incorporating two chiral pinene groups. (Reproduced with permission; ref 140. Copyright 1998 Wiley-VCH.)

Scheme 13



Several other self-assembled circular helicates have been reported. Von Zelewsky and co-workers have prepared the single-stranded [6]^1**cH** (**82**) (Figure 36).[140] This circular helicate was obtained by the completely stereoselective reaction of Ag(I) with the bis(2,2′-bipyridyl) ligand **81** having a spacer incorporating two chiral pinene groups. In the reaction with the ligand prepared from (−)-α-pinene, a circular helicate of *P*-handedness was obtained. The corresponding reaction with the ligand prepared from (+)-α-pinene delivered the *M* analogue.

The reaction of (*R*,*R*)-bis(phenyloxazolinyl)pyridine (**83**) (Chart 8) with Ag(I) also produced a single-stranded [3]^1**cH**.[141] By virtue of the configuration of the ligand, only the *P* circular helicate was obtained.

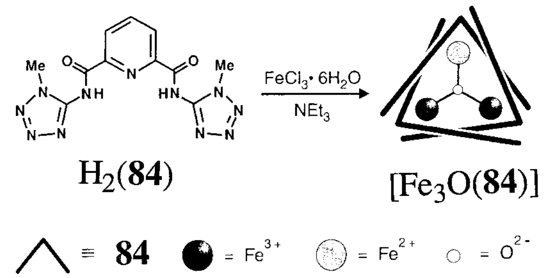
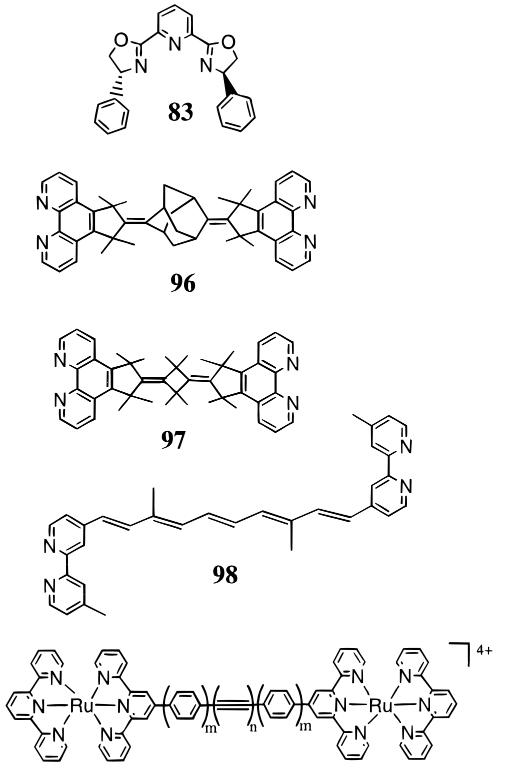


Figure 37. Schematic depiction of the formation of a mixed valence $[3]^2$**cH**-like toroid in which the metal ions (Fe^{II}, Fe^{III}) are also bound to a central μ_3-O ligand. (Reproduced with permission; ref 143. Copyright 1996 Wiley-VCH.)

Chart 8



99 n = 1,2; m = 0,1

In this case the formation of the circular helicate was assisted by π-stacking interactions between the strands. In solution, an equilibrium appeared to exist between the helicate $[2]^2$**H** and the circular helicate $[3]^1$**cH**.

Self-assembled circular helicates have also been observed using mass spectrometry within mixtures involving Ni(II) and various imidazolate ligands.[142]

An interesting case of a toroidal species which has all of the characteristics of a circular helicate is that of the trinuclear, $[3]^2$**cH**-like [Fe_3O(**84**)] (Figure 37).[143] In this compound, each ligand is bound to two Fe(III) ions and one Fe(II) ion in a double-helical arrangement having D_3 symmetry. The iron centers—which are homochiral—are also coordinated to a μ_3-O ligand at the center of the toroid. The structure of this complex in solution was verified by mass spectrometry and ^{1}H and ^{13}C NMR spectroscopy, while a single-crystal X-ray determination confirmed the solid-state structure. The mixed-valence character of the structure was verified by Mössbauer spectroscopy.

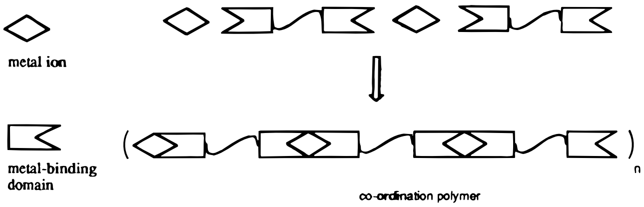


Figure 38. Coordination oligomers. Schematic depiction of the spontaneous formation of a coordination oligomer/polymer. (Reproduced with permission; ref 144a. Copyright 1995 IUPAC.)

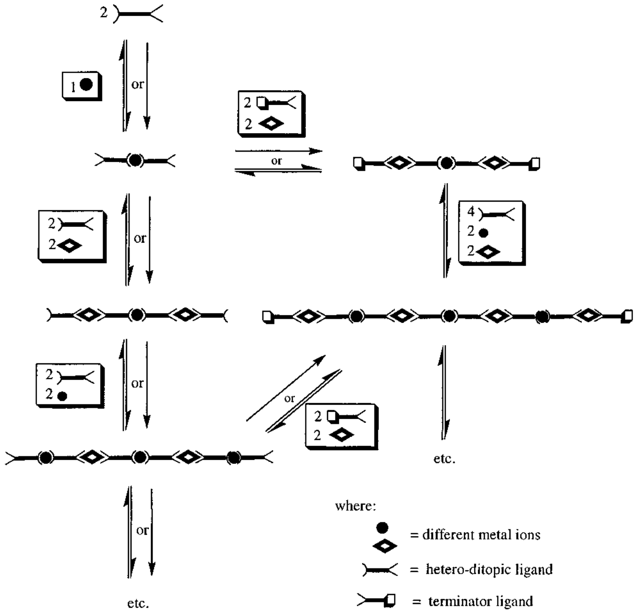


Figure 39. Rods. Schematic depiction of the stepwise (single-headed arrows) or reversible (double-headed arrows) formation of rod coordination oligomers by the use of a heteroditopic ligand with binding sites selective for two different metal ions. If all interactions are labile (double-headed arrows), the steps may be carried out simultaneously in a one-pot thermodynamic self-assembly reaction involving a cumulative combinination of suitable proportions of the reagents.

C. Filamentous Motifs

Several filamentous structural motifs have been obtained by the self-assembly of metal ions with ligand strands bearing donor sites at their ends. The resulting compounds are collectively known as 1-D, 2-D, or 3-D linear coordination oligomers. Two of the most common coordination oligomers are rods and metallodendrimers. Figure 38 schematically illustrates the formation of coordination oligomers in general,[144a,c] while Figures 39 and 40 depict routes for the formation of rod and metallodendrimer coordination oligomers, respectively.[144b,146] It should be noted that the term "linear coordination" is generalized in this section to mean "filamentous coordination": i.e. the formation of a complex in which a series of metals and ligands are sequentially and alternately coordinated down the length of one or more molecular strands. The linking ligands in such oligomers therefore need not subtend a strict 180° binding angle about the metal center; they may also be branched.

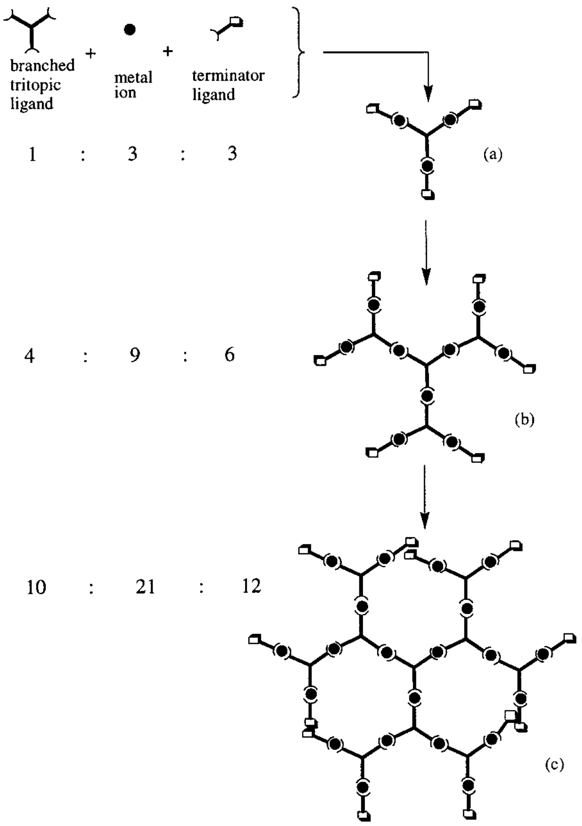


Figure 40. Metallodendrimers. Schematic depiction of a theoretically feasible means of divergently forming metallodendrimers by thermodynamic self-assembly. Combining the starting materials in the proportions shown favors the formation of the (a) zeroth generation, (b) first generation, and (c) second generation metallodendrimers. Because of increasing congestion at the outer surface, steric effects rapidly dominate growth in going from lower to higher order divergent dendrimers; the usefulness of this technique should decline concomitantly.

Rods, metallodendrimers, and other linear coordination oligomers have the following features in common: (i) They are strandlike macromolecules which contain metal ions separated by coordinated bridging ligands having binding sites at each end. (ii) They cannot be coordinatively saturated unless a terminator species, which is capable of binding or deactivating the remaining reactive sites at each end of these macromolecules, is used.[144c] Alternatively, photo-, redox-, or pH-dependent reactive sites may be employed to act as termination sites when activated.[144c] (iii) Except for rods, the spacers between the binding sites of the ligands in complexes belonging to these motifs need not be rigidly straight.

The motifs differ as follows: rods are conformationally inflexible linear coordination oligomers in which the entire molecule, including the metal centers and ligand spacers, lie on or about a single, straight axis. Metallodendrimers are highly branched coordination oligomers which are produced by the use of branched spacers or the presence of a branched polydentate starburst progenitor ligand at their center. The branches in metallodendrimers terminate in the same way that other linear coordination oligomers do: by the coordination of a terminator species or by the activation of a termination site.

The potential influence of the terminator species in the preparation of complexes bearing these motifs is of some interest. The primary driving force in a self-assembly reaction in coordination chemistry is the enthalpic formation of the largest possible number of metal—ligand coordination bonds. Because the terminator is the only species able to halt enthalpy-driven polymerization, its relative proportion in a thermodynamically self-assembling mixture will determine the length of the coordination oligomer generated. For example, a 1:1 mixture of a ditopic ligand and a two-coordinate metal ion will undergo polymerization until the number of metal ions at the termini of the polymers has decreased to equal the amount of any terminator ligand present. When the terminator ligands bind these metal ions, no further coordination bonds can be formed and the enthalpic demands of the system will be met; the thermodynamically most-stable oligomer will then have been generated. Thus, an increase in the proportion of the terminator ligand present should see a decrease in the average length of the coordination oligomers produced and vice versa. This argument assumes, of course, that a perfect thermodynamic equilibrium exists at all stages in the reaction and that other influences, such as steric congestion and solvent interactions, inter alia, do not affect the self-assembly reaction.

A means therefore exists—at least in theory—to selectively self-assemble a rod, metallodendrimer, or other linear coordination oligomer containing a particular number of constituent metals and ligands in solution and to vary this by simply altering the relative proportion of the terminator present. This sort of control has largely remained unachieved to date. Instead all of the above motifs are dominated by structurally trivial thermodynamic or irreversible self-assembly processes.

1. Rods

A substantial number of molecular rods have been reported in the chemical literature, primarily with the aim of studying the photophysical properties of these entities when they contain one or more photoactive metal units. Several recent reviews of rod complexes addressing this specific topic are available.[145,146]

A divergent synthetic strategy has generally been employed in the preparation of molecular rods. In this approach, a bidentate initiator ligand containing a rigid spacer to separate the binding domains is progressively elongated into a rigidly linear complex by the attachment of further bi- or monodentate ligands using metal ligand coordination.[147,148] A variety of multinuclear rod complexes and linear coordination oligomers are accessible in this way. Figure 41 depicts an example of such a process, as used by Constable in the stepwise formation of coordination oligomers using bis(tpy) ligands.[148] Figure 39 schematically illustrates a similar process employing heteroditopic ligands in which the two ligand binding sites are selective for different metal ions;[146] heteropolymetallic rods or other linear coordination oligomers result.

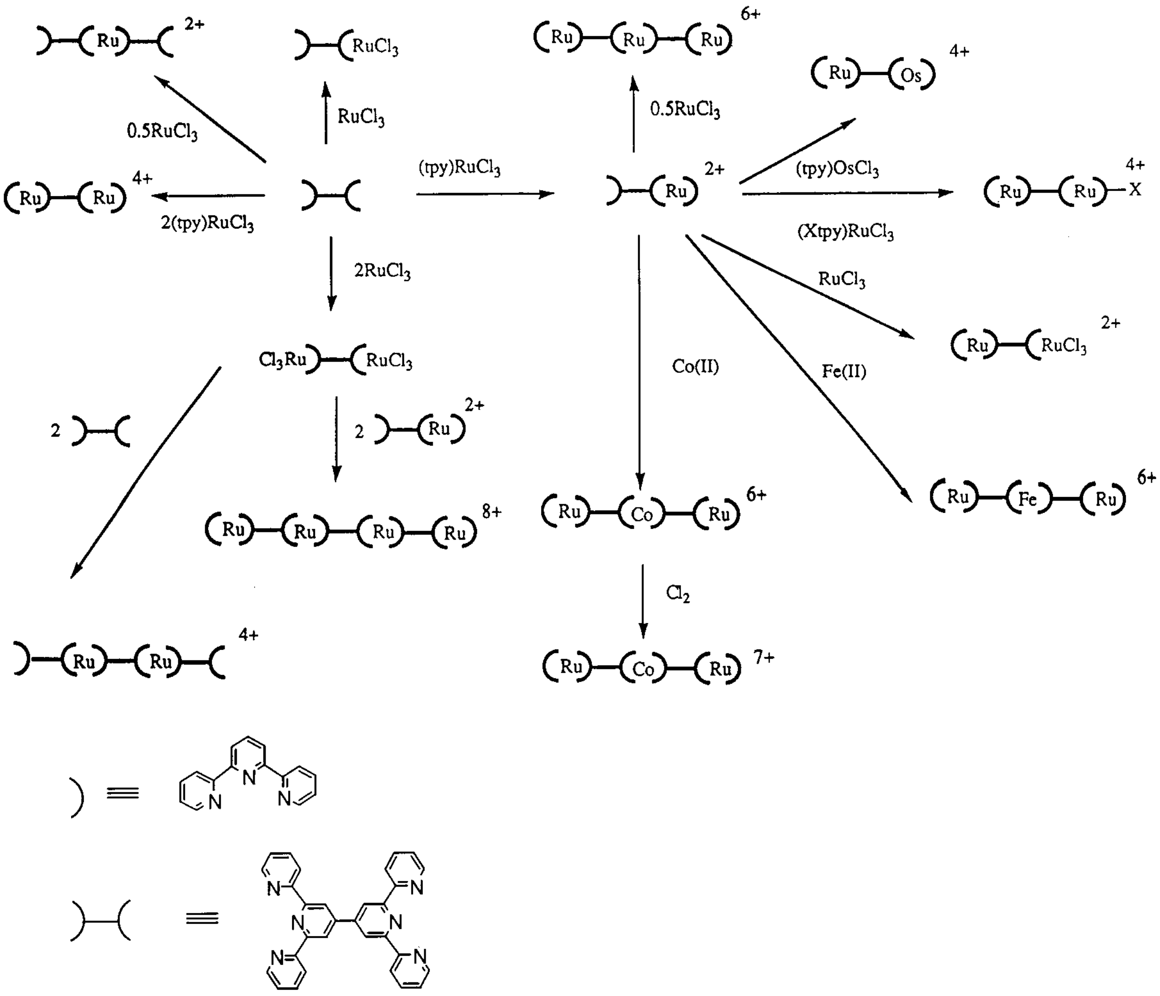


Figure 41. Rods. Routes to the stepwise formation of rod and other linear coordination oligomers incorporating tpy binding sites (X = Cl; tpy = 2,2′:6′6″-terpyridine). (Reproduced with permission; ref 148. Copyright 1994 Wiley-VCH.)

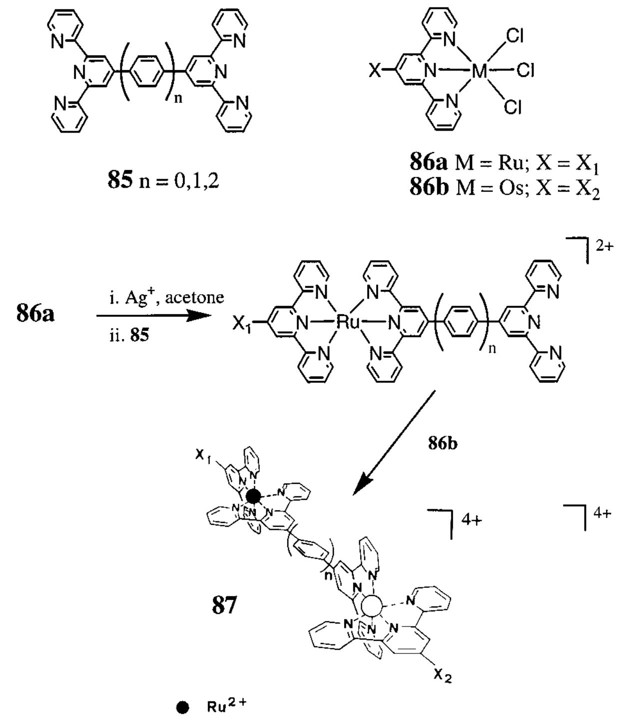
Both of the processes depicted in Figures 39 and 40 are independent of the kinetics of each step. Thus, the steps can be made to occur sequentially (using kinetically stable complexes in a stepwise synthesis) or simultaneously in situ (using a kinetically rapid thermodynamic equilibrium in a one-pot self-assembly). While terminator species are not necessary when kinetically stable complexes are produced, they are required to control the degree of polymerization in a thermodynamic self-assembling situation.

Using this approach, or variations on this theme, a significant number of complexes displaying rod secondary structures have been obtained. For example, binuclear ruthenium–ruthenium[146,147] and ruthenium–osmium[146,149,150] rod complexes in which two M(tpy)$_2$ (M = metal) groups are separated by multiple phenylene or phenylene-containing spacers of various lengths (of the type illustrated in Figure 42)[150] have been prepared from **85** and **86**. During luminescence, the materials **87** exhibit electron transfer from the Ru(II) to the Os(II) center by a Dexter (two electron transfer) exchange mechanism.[150]

Multinuclear rods of this type have also been prepared. For example, the self-assembly of the ligating Ru(II) complex **88** shown in Figure 43[151] with Fe(II) or Co(II) allowed the quantitative formation of the trinuclear rods **89**.[151] Oxidation of the Co(II) complexes produced their kinetically inert Co(III) analogues. Triruthenium rods of similar type have also been reported.[151]

Several other ligand types have been employed in molecular rods. For example, the binuclear ruthenium rods **91** employing bis((dimethylamino)methyl) aryl-based ligands have been synthesized by Cu(II)-mediated oxidative coupling (Scheme 14).[152] Chelating bidentate, bipyridyl- and phenanthroline-type ligands have also been used.[153,154] The chirality of the metal centers in these cases has generally been controlled by the use of an enantiomerically pure starting material. Thus, the π-conjugated molecular rod (*M*,*M*)-**93** was obtained from the enantiomer (*M*)-**92** (Figure 44).[153] The octahedral Ru(II) centers in **93** were 35 Å apart. ^{1}H NMR studies of this molecule indicated that extensive ligand exchange took place when an excess of the synthons were present; the complex is consequently reversibly self-assembled. The rods (*M*,*M*)-**94** (Scheme 15) were similarly obtained.[154]

A vast array of spacers have been employed to separate the metal ions in rod formation; these include, by way of example only, linkers containing bicyclo[2.2.2]octane (e.g. in **95**; Scheme 14),[155] adamantane (e.g. **96**; Chart 8),[156] tetramethylcyclobutane (e.g. **97**; Chart 8),[157] polyene (e.g. **98**; Chart 8),[158] and



● Ru^{2+}
○ Os^{2+}
1 X_1 = X_2 = phMe, n = 0
2 X_1 = X_2 = phMe, n = 1
3 X_1 = X_2 = phMe, n = 2
4 X_1 = SO_2Me, X_2 = H, n = 0
5 X_1 = SO_2Me, X_2 = H, n = 1
6 X_1 = SO_2Me, X_2 = phMe, n = 2

Figure 42. Rods. Formation of a series of luminescent heterobinuclear rods containing Ru(II) and Os(II). (Adapted and reproduced with permission; ref 150. Copyright 1994 American Chemical Society.)

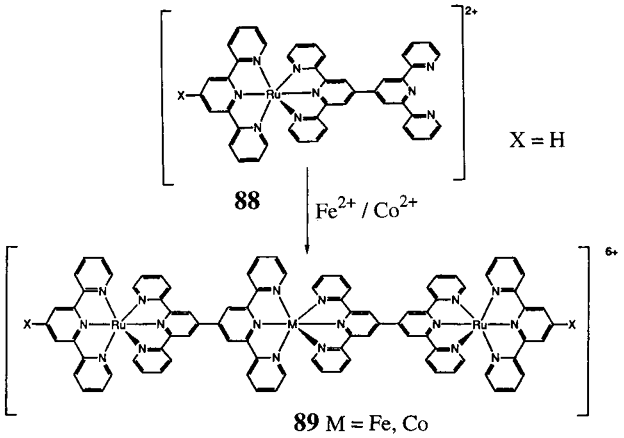


Figure 43. Rods. Self-assembly of molecular rods by the reaction of two ligating Ru(II) complexes with labile metal ions. (Reproduced with permission; ref 151. Copyright 1995 Royal Society of Chemistry.)

poly(ethyne) (e.g. **99**; Chart 8)[159] groups. Significant separations can be achieved; for example, compound **95** displays an intermetallic distance of 24 Å. This compound also exhibits temperature and solvent independent energy transfer.[155]

Rod complexes of formulation Ru(tpy)$_2$, where the tpy ligands are differently substituted with metalated or protonated porphyrins (e.g. **100** (Chart 9)),[160c] have also been prepared in a stepwise manner with the aim of studying interporphyrin electron transfer.[160]

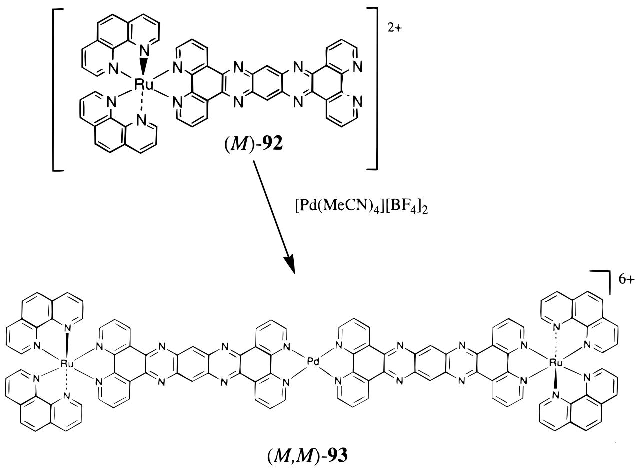
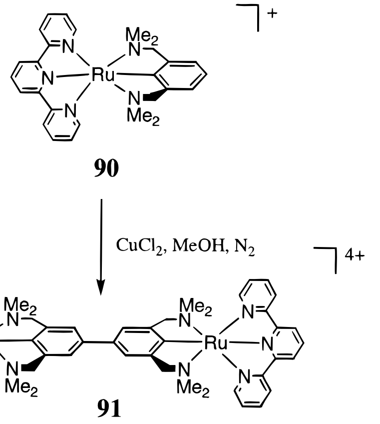
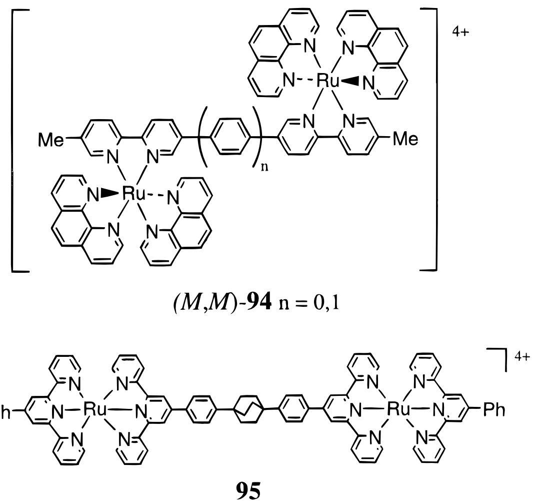


Figure 44. Rods. Self-assembly of a nanometer-scale Ru^{II}-Pd^{II}Ru^{II} π-conjugated molecular rod of (*M*,*M*)-stereochemistry. (Reproduced with permission; ref 153. Copyright 1996 Royal Society of Chemistry.)

Scheme 14

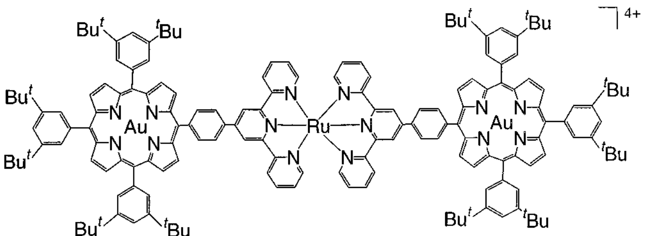


Scheme 15

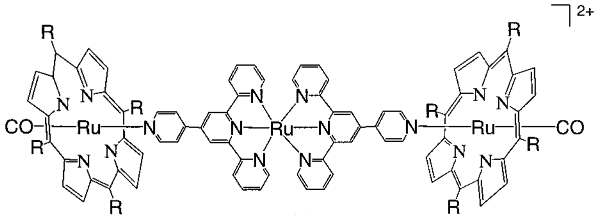


The role of the Ru(II) ion in these complexes is 2-fold: (i) to gather and rigidly orientate the porphyrins at a fixed distance from each other; (ii) to participate in electron transfer as a relay (albeit a rather poor one). Similar compounds involving axially coordinated porphyrins (e.g. **101**) or porphyrins incorporated in a conjugated backbone (e.g. **102**) have also been described.[161]

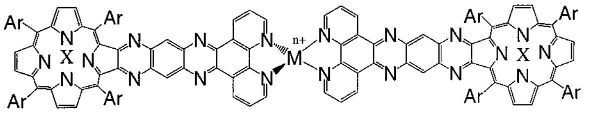
Chart 9



100



101 R = PhMe



102a $X = 2H^+$; M = Zn; n = 2
102b $X = 2H^+$; M = Cu; n = 1
102c X = Zn; M = Zn; n = 2

2. Metallodendrimers and Branched Coordination Oligomers

Figure 40 schematically illustrates a divergent, thermodynamic, self-assembly process for the formation of zeroth-, first-, and second-generation metallodendrimers by manipulation of the proportions in which the reagents are combined. Such a reaction is theoretically possible when a branched and sterically unhindered tritopic ligand, a labile metal ion, and a monotopic terminator ligand are combined. When mixed in the molar ratio 10:21:12 (i.e. 1.4:3:1.7), respectively, the second-generation metallodendrimer is the only species which can satisfy the bonding requirements of all the ligands and metals present. When mixed in the ratio 4:9:6 (i.e. 1.3:3:2), the corresponding first-generation metallodendrimer should be similarly assembled. While this approach is hypothetically feasible, other factors may also play a role. For example, steric congestion at the surface of divergently prepared dendrimers rapidly increases with each succeeding generation, so that steric effects and not reagent proportions can be expected to ultimately control and terminate growth. It is perhaps for this reason that a metallodendrimer which has been divergently self-assembled along these lines has, to the best of our knowledge, not yet been reported.

Heteropolymetallic metallodendrimers could, theoretically, also be self-assembled by adapting the technique illustrated in Figure 39 to dendrimer formation. In that case branched, heteropolytopic ligands would be used rather than the linear ditopic ones shown.

While a large number of dendrimers containing metal ions are known,[162] significantly fewer have been prepared using metal−ligand coordination as a primary means of their assembly and still fewer have involved nontrivial self-assembly steps in their formation.

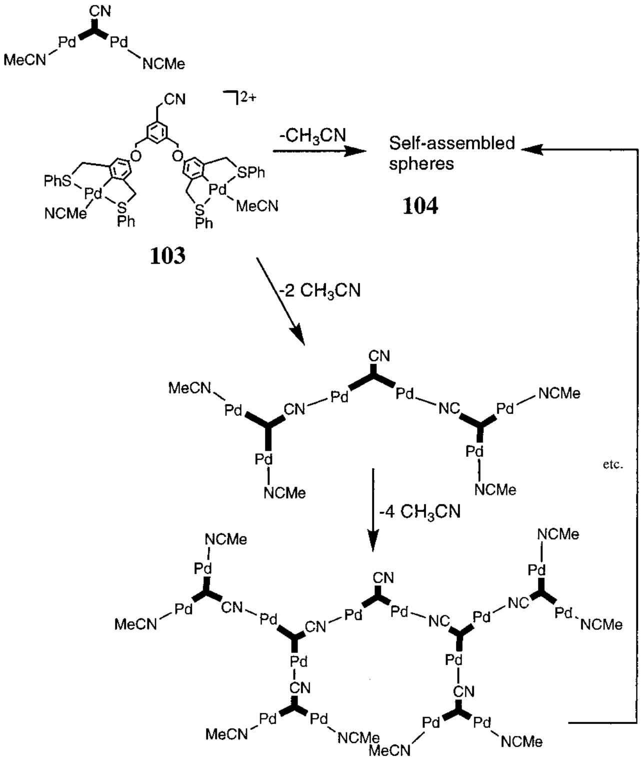


Figure 45. Self-assembling metallodendrimers. On evaporation, the acetonitrile molecules coordinated to **103** are substituted by the benzylic cyano groups on other complexes. Dendritic wedges **104** having a pendant cyano group result. The addition of acetonitrile to **104** spontaneously regenerates **103**.

Several reviews of metallodendrimers are available.[144a,b,162−166]

a. Thermodynamically Self-Assembled Metallodendrimers. The AB$_2$ monomer **103** depicted in Figure 45 is the basis of the only truly self-assembling metallodendrimer known, although the products are more correctly considered dendritic wedges rather than higher generation metallodendrimers.[167] When a solution of monomer **103** was heated under vacuum, dendritic aggregates **104** were convergently formed by the replacement of the labile acetonitrile coligands with the pendant cyanomethyl group as illustrated in Figure 45; the process could be monitored by FTIR spectroscopy. The addition of acetonitrile reversed the assembly, resulting in the selective re-formation of **103**. Thus, acetonitrile molecules served as the terminator species in this reaction; a decrease in their concentration led to an increase in the size of the metallodendrimer aggregates. When all of the solvent had been removed, narrowly uniform aggregates of 200 nm diameter (±30 nm) were obtained.[167] Similar treatment of an unbranched analogue complex did not result in globular structures of the type observed.

A later study showed that an increase in the size of the thioether groups or the counterions in this system resulted in the formation of smaller metallodendrimers.[168] Thus, the self-assembly of **103** into **104** upon removal of acetonitrile was ultimately

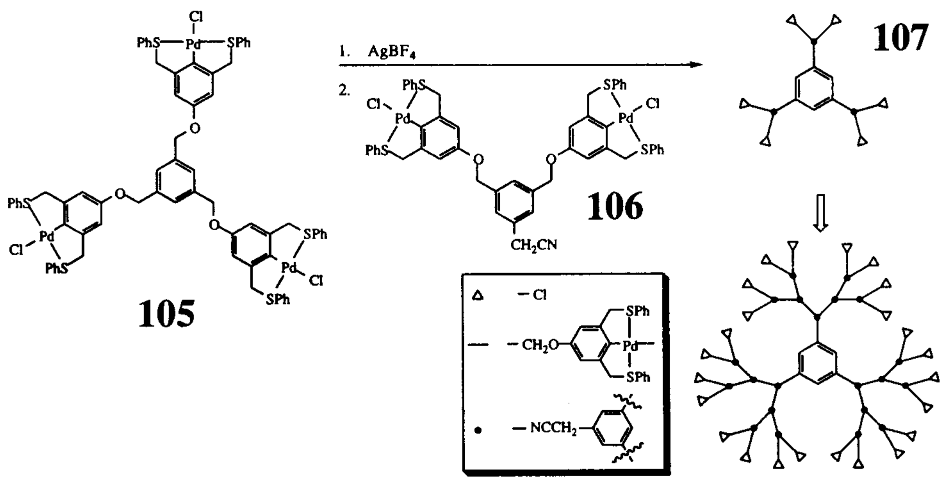


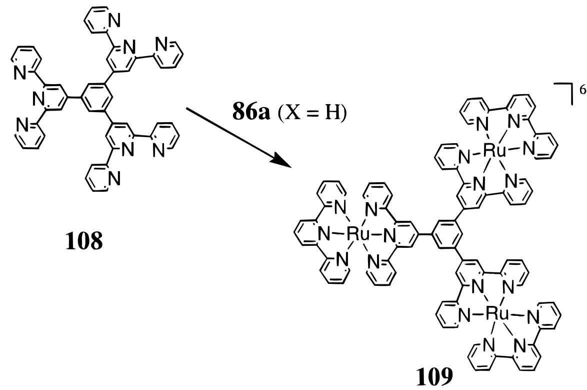
Figure 46. Stepwise assembly of metallodendrimers. Treatment of **105** with Ag(I) produces a reactive solvento complex which readily coordinates the benzylic cyano groups in **106**, giving the first-generation metallodendrimer **107**. A repetition of this reaction sequence on **107** produces the second-generation product. (Reproduced with permission; ref 163. Copyright 1998 Elsevier Scientific.)

terminated by factors involving steric hindrance and charge compensation; when the anions in the sphere could no longer compensate for the accumulating charges, they started to occupy the surface, hindering further growth. Interestingly, when more bulky nitrile solvents were added to the metallodendrimer assemblies, the monomer was re-formed but significantly more slowly than with acetonitrile. This suggests that these solvents did not penetrate the outer shell as easily, a phenomenon in accordance with the characteristic of a closely packed surface in dendrimer architecture.

The system above has also been employed to divergently prepare true higher-order metallodendrimers of controlled size by the sequential addition of a chloride-protected AB_2 monomer **106**, preceded by $AgBF_4$, to a tripalladium(II) core molecule **105** (Figure 46).[169] The Ag(I) removes the protecting chloride ions on **105**, allowing formation of a Pd(II)−cyanomethyl bond and generating the first-generation metallodendrimer **107**. The addition of further $AgBF_4$, followed by monomer, gives, in similar fashion, the second generation dendrimer, and so on. This procedure has also been modified to allow the assembly of dendritic wedges, which were prepared in an analogous manner using a barbituric acid core;[170] hydrogen-bonding interactions mediated the process in that case.

Among the numerous other metallodendrimers known, extensive use has been made of substituted 2,2′:6′,2″-terpyridine-based ligands (tpy) to construct ruthenium-based metallodendrimers.[144a] Figure 41 illustrates the general principle if a starburst progenitor ligand or if multiply branched polytopic ligands are used instead of the ditopic ligands illustrated. For example, the tris(tpy) ligand **108** yields the first generation triruthenium complex **109** when heated with [Ru(tpy)Cl_3] (Scheme 16).[171] When more labile metal ions, such as Fe(II) were employed, however, insoluble polymers and oligomers resulted.[165]

Scheme 16

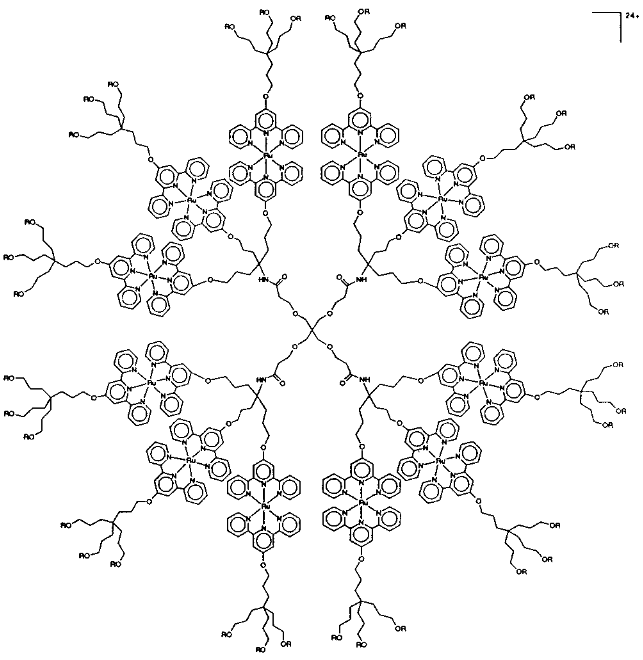


Using this approach, a large variety of metallodendrimers,[163] including **110** (Figure 47),[172] have been obtained. The central quadruply branched pentaerythritol derivative, $C(CH_2O-)_4$, employed in **110**, has proved to be particularly versatile as a central core or as a branched spacer ligand in the formation of other metallodendrimers.[17]

When sterically hindered ligands are used, divergent strategies are risky, even for low generation products. For example, the ruthenium complex **111** depicted in Figure 54[174] could not be completely coordinated on all six unbound tpy ligands to form the desired heptanuclear species **112** due to steric hindrance. Instead a mixture of incompletely reacted products was obtained.

An alternative approach has been to convergently coordinate ligand strands about a metallocentric core. For example, the metallodendrimer **114** containing 1,4-phenylene linkers illustrated in Figure 49[174] could be obtained by coordination to Co(II) or Fe(II) of the unbound 4,4′-bipyridyl units within the ligand strands **113**, which incorporate terminal bis(tpy)Ru(II) units. Hyperbranched structures containing extremely bulky groups may also be prepared using this technique.[175] For example, metallodendrimers with tethered fullerenes have been similarly obtained,[176] as have dendritic networks in which cascade macromolecules have been tethered to each other by metal−ligand complexation.[177]

Finally, a “complexes as metals/complexes as ligands” strategy involving both divergent and con-



110

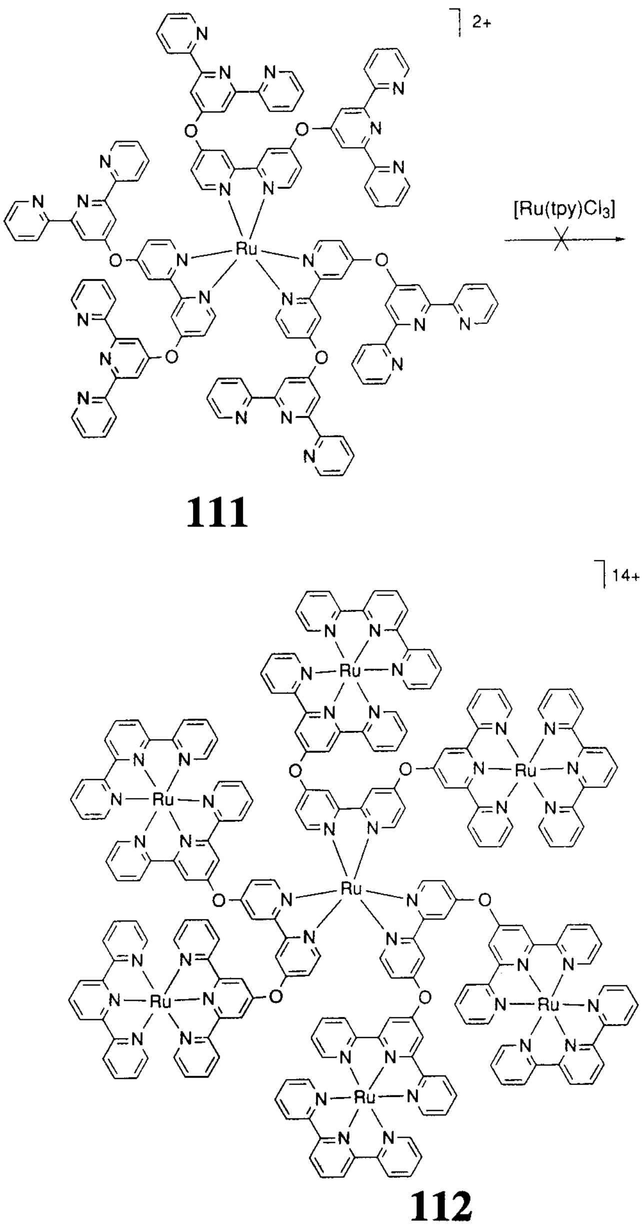
Figure 47. Metallodendrimers. A first-generation metallodendrimer which was self-assembled from a 1:12:12 ratio, respectively, of the central core ligand (containing the 12 inner tpy groups), $RuCl_3$, and the external tpy-containing alkoxide ligands. (Reproduced with permission; ref 172. Copyright 1993 Royal Society of Chemistry.)

vergent growth steps has been developed. In this method, angular binucleating ligands, such as 2,3-bis(2-pyridyl)pyrazine (**115**) or 2,5-bis(2-pyridyl)pyrazine (**116**) act as bridging species, while simple 2,2′-bipyridines (bipy) or the methylated species **117**, in which the chelation site is blocked by the presence of the methyl group, are used as terminator species.[178] From these simple materials a multitude of metallodendrimers incorporating Ru(II) and Os(II) have been prepared.[178] Figure 50 illustrates the general principle for convergent synthesis of this class of dendrimer: monomeric **118** is able to chelate a metal ion through the vacant binding site on the 2,3-bis(2-pyridyl)pyrazine ligand. Treatment of **118** with $RuCl_3$ and $AgNO_3$ therefore generates the trimeric complex **119**. This species can, however, coordinate a ligand after removal of the chloride ions. The addition of 2 equiv of $AgNO_3$ followed by **116**, therefore, produces the hexanuclear species **120**.[179]

Alternatively, metallodendrimers of this type may be formed using a purely divergent approach.[180a] Here a monomer, such as **121** (Scheme 17) is typically treated with 3 equiv of the terminator complex **122** which had been activated by the removal of chloride ions. The first-generation metallodendrimer **123** results. Removal of the N-methyl groups in this compound activates the terminal chelation sites and allows preparation of the second-generation, decanuclear metallodendrimer by further treatment with **122**/Ag(I), and so on.

Heterodecanuclear[181] and tridecanuclear[182] metallodendrimers have been prepared in similar fashion.

b. Irreversibly Assembled Metallodendrimers. A substantial number of metallodendrimers have been prepared using irreversible conventional organic reactions in the final step (self-assembly with post-modification).[162] Several of these were obtained by exploiting changes in the reactivity of ligand substituents upon metal coordination. For example, 4-halopyridines are weakly electrophilic, but their electrophilicity is drastically enhanced by coordination to a transition-metal ion.[144b,165] This allows their use in the synthesis of a variety of coordination oligomers, including metallodendrimers. For example, the species **111** in Figure 48 was prepared by the reaction of **124** with **125** (Scheme 18).



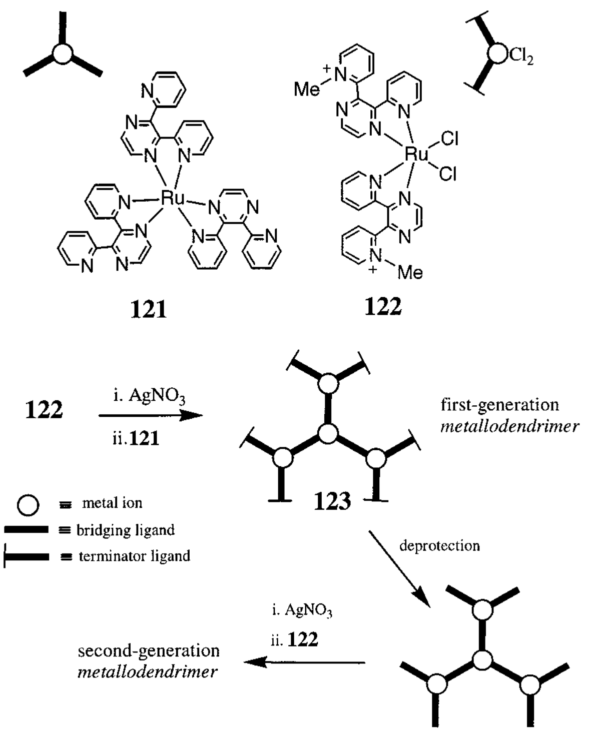
111

112

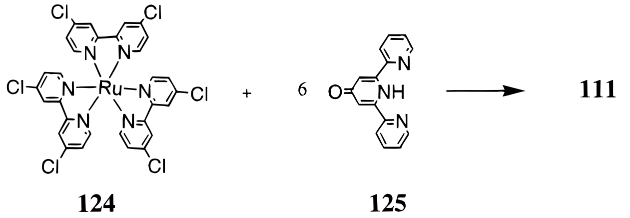
Figure 48. Metallodendrimers. An unsuccessful attempt at the divergent synthesis of a first-generation metallodendrimer. Steric hindrance leaves unreacted tpy sites on the central ligand after reaction. (Reproduced with permission; ref 144b. Copyright 1997 Royal Society of Chemistry.)

Other organic reactions have also been employed. The octadecanuclear species **128** was, for example, prepared by the reaction of hexakis(bromomethyl)-benzene (**126**) with the coordination oligomer **127** (Figure 51).[183] Related materials have been obtained by the reaction of various other benzyl methyl halides

Scheme 17



Scheme 18



with ruthenium–tpy coordination oligomers bearing a reactive hydroxyl functional group.[184,185]

3. Other Coordination Oligomers

a. Thermodynamically Self-Assembled and Other Linear Coordination Oligomers. Several linear coordination oligomers have been self-assembled using starting materials already described. For example, the tapelike trimeric 1-D linear coordination oligomer **131** was produced in 62% yield when the porphyrin derivatives **129** (2 equiv) and **130** (1 equiv) were mixed with **12** (2 equiv) (Scheme 19).[40] The corresponding dimer **132** and trimer **133** were also obtained in 23% and 15% yields, respectively.

A 2-D tape has been prepared along similar lines. The reaction of the zincated porphyrins **9** and **11** (1 equiv each; R = Me, ^{t}Bu) with 3 equiv of *cis*-[PdCl$_2$(NCPh)$_2$] (**134**) resulted in the formation of the 2-D linear coordination oligomer **135** after 4 d at 40 °C (Scheme 20).[40] The trimer **136** and pentamer **137** accompanied its formation in a ratio of 4:2:1 (**135**:**136**:**137**).

Trimetallic coordination oligomers **139** having a 90° turn in their center and ethynyl linkages in the ligand backbones (Figure 52)[186] have been self-assembled by the coordination of tetrahedral Cu(I) with the preformed Ru(II) complexes **138**.

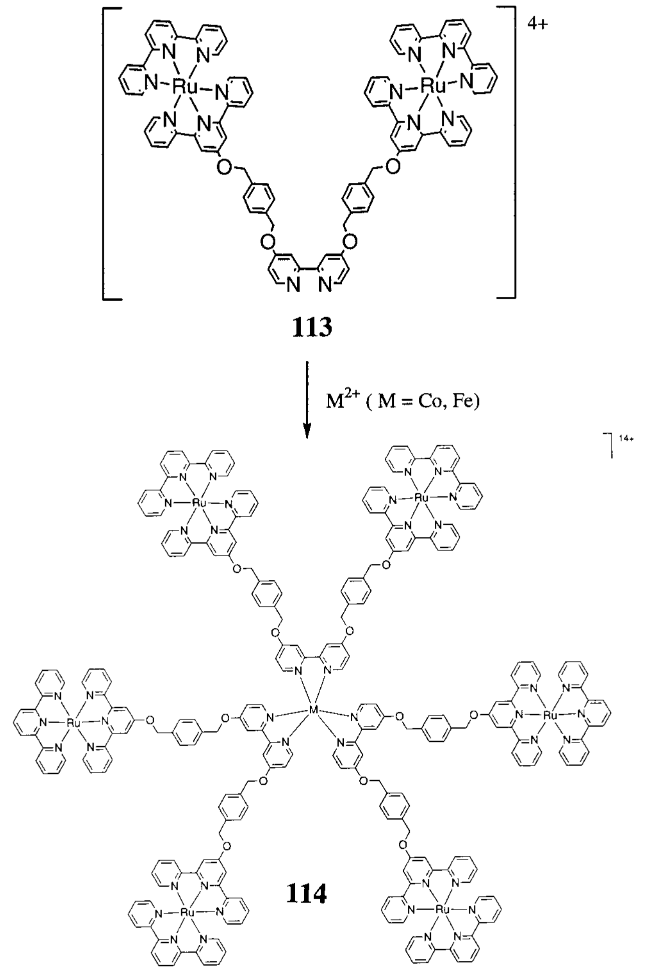
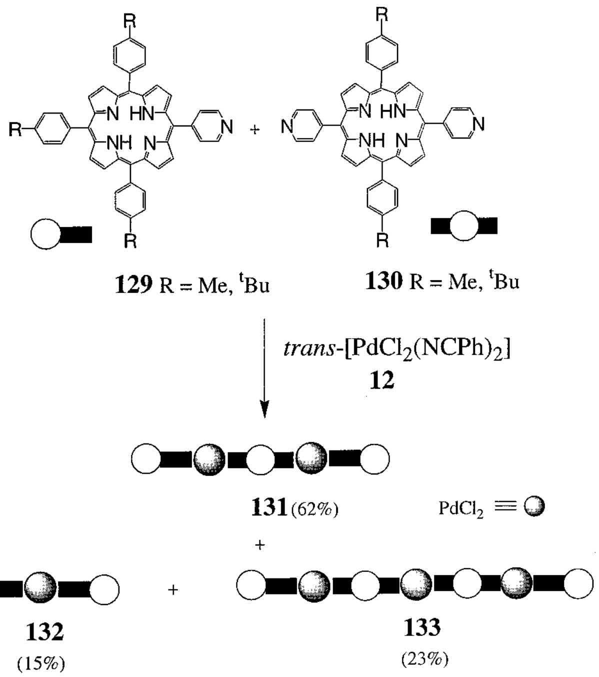
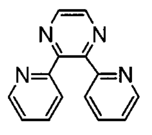


Figure 49. Metallodendrimers. Schematic depicting the successful convergent self-assembly of a metallodendrimer. (Reproduced with permission; ref 144b. Copyright 1997 Royal Society of Chemistry.)

Scheme 19



A series of interesting coordination oligomers involving tpy-based ligands have been prepared in a



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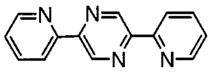

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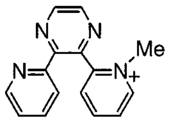

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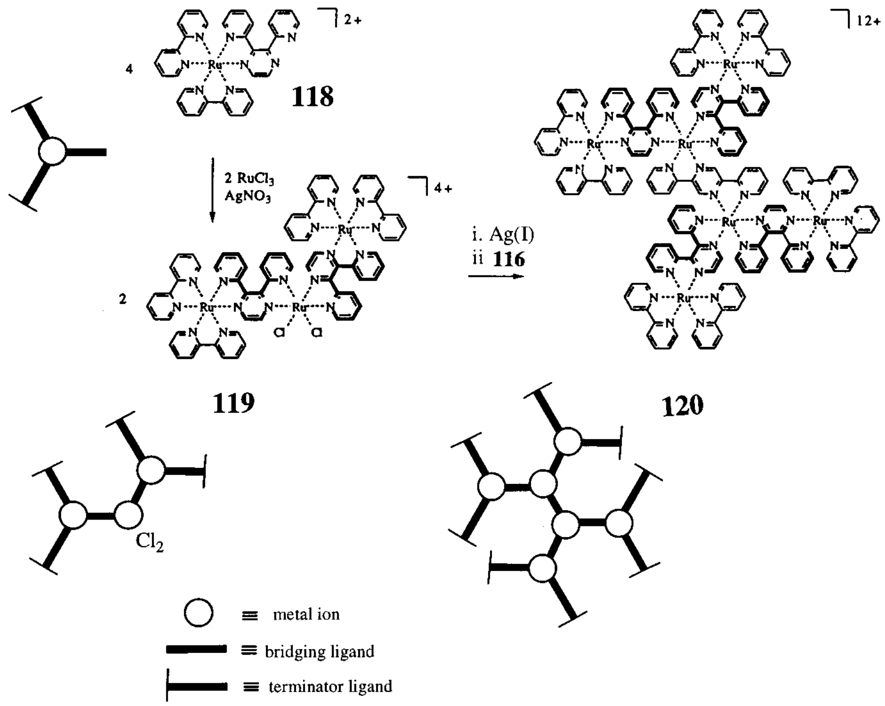
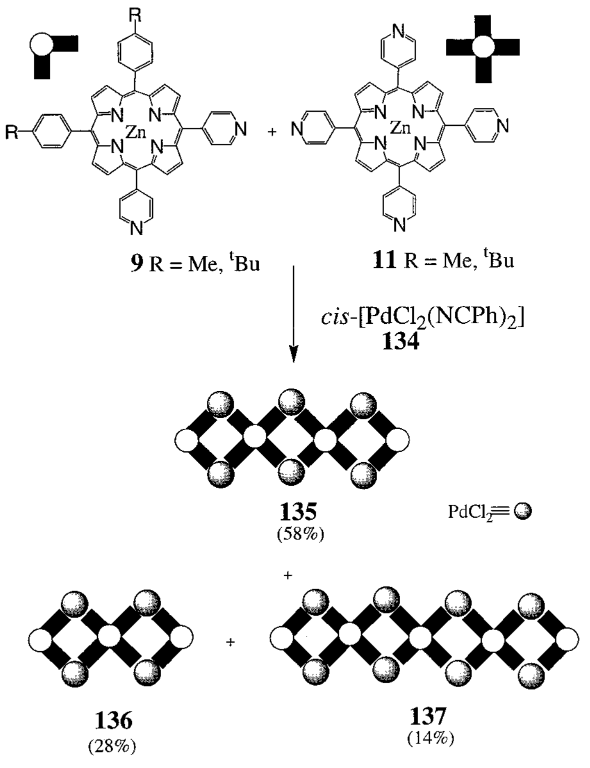


Figure 50. Metallodendrimers. An example of a convergent “complexes as metals/complexes as ligands” strategy to metallodendrimer formation. (Reproduced and adapted with permission; ref 163. Copyright 1998 Elsevier Science.)

Scheme 20



stepwise manner by Constable and co-workers. In this work, convergent and divergent synthetic strategies involving either metal–ligand coordination or irreversible organic reactions were employed to link a variety of Ru(II)–tpy complexes into linear coordination oligomers. For example, the trinuclear linear coordination oligomer **143** could be obtained in a convergent, metallocentric reaction by the treatment of **142** with $RuCl_3$ (Figure 53)[144b,185] or in a divergent process by the reaction of **145** with $[Ru(tpy)Cl_3]$.[185] The hexanuclear linear coordination oligomer **147** was formed by the convergent but not metallocentric reaction of **146** with 1,4-bis(bromomethyl)benzene (Figure 54).[144b,187] While **143** is self-assembled by metal–ligand coordination for both of the preparative routes described, **147** is formed by an irreversible organic reaction in a self-assembly with post-modification. Other bridging ligands have recently been employed in similar vein[188a] and cyclized coordination oligomers of this type have also been reported by strict, directed, and self-assembly with post-modification.[188b]

b. Network Coordination Oligomers/Polymers. A major obstacle in many attempts to self-assemble discrete coordination complexes is the uncontrolled formation of infinite coordination oligomers/polymers. While this review is limited to discrete coordination compounds, the reader’s attention is nevertheless drawn to the fact that extended 1-D, 2-D, or 3-D network coordination polymers are themselves of fundamental interest.[4,189,190] As may be expected, this field bears many similarities to the topic of this review.[4,191] For example, like the discrete

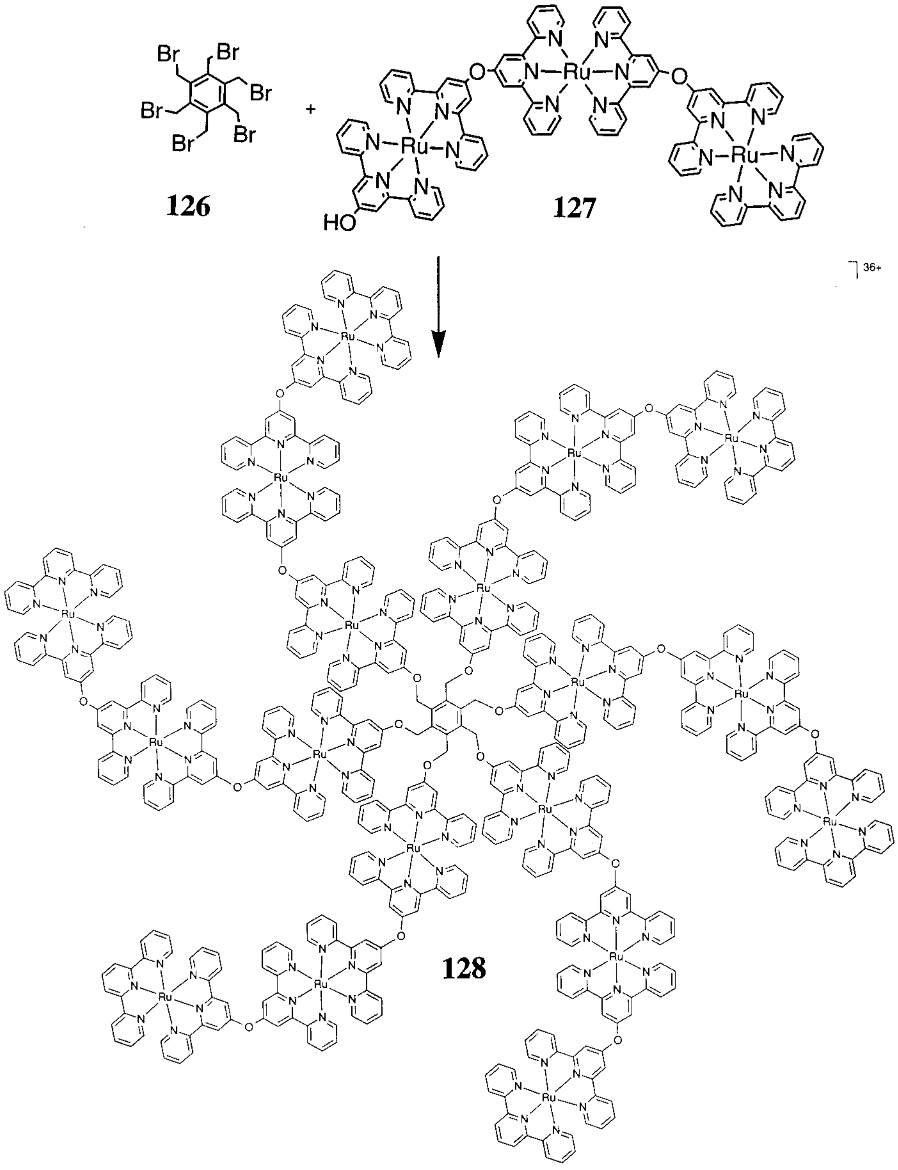


Figure 51. Metallodendrimers by post-modification of self-assembled coordination oligomers. (Reproduced with permission of ref 144b. Copyright 1997 Royal Society of Chemistry.)

complexes, infinite networks have been prepared in a variety of structural motifs including, inter alia, diamondoid, honeycomb, square grid, ladder, “brick wall”, or octahedral motifs, sometimes as two or more motifs interpenetrating one another within a single crystal.[4] The synthetic approach for preparing such polymers is also similar to that used for the discrete complexes described in this review; a metal having a propensity for a certain stereochemistry is typically combined in a particular stoichiometric ratio with a polydentate ligand which is unable to fulfill the coordination requirements of the metal ions except by forming a certain motif. As with the discrete complexes, variations in the metal or ligand employed alters the resulting motif in novel ways. Unlike most of the discrete complexes, however, the majority (but not all) infinite networks are formed by self-assembly at the crystal surface rather than in solution itself. Enthalpic factors driving the formation of metal−ligand coordination bonds in solution typically make such crystallization favorable.

4. Properties and Applications of Linear and Branched Coordination Oligomers

a. Rods. Rods have been widely used as conformationally rigid materials useful in the study of energy and/or electron-transfer processes between selected metal−ligand assemblies.[192] Studies of this type may lead to applications in fields such as light-harvesting/solar energy conversion, photochemical molecular devices, molecular electronics, and information storage devices. For example, spectroscopic and electrochemical studies of the adamantyl-bridged rods $[(bipy)_2Ru(\mathbf{96})Os(bipy)_2]^{4+}$ (Chart 8) indicated that the two metal-based units were electronically coupled, albeit weakly.[156] Both metal centers had luminescence bands that were well separated. After irradiation into the MLCT band of the Ru(II) unit, a strongly quenched emission with a corresponding sensitization of the Os(II)-based luminescence was observed indicating that an intercomponent energy transfer took place. Selective oxidation of the Os(II) center converted the emissive osmium unit into a

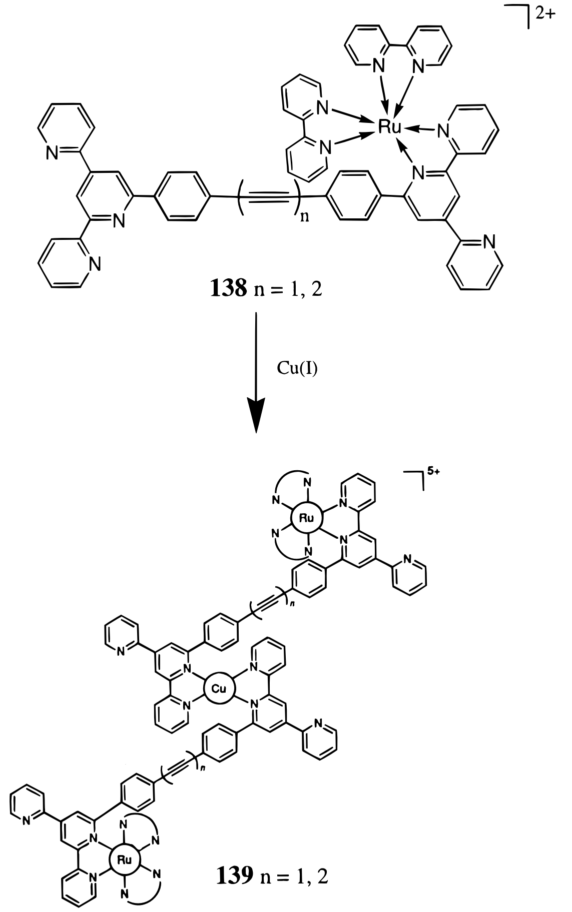


Figure 52. Coordination oligomers. Schematic depiction of the assembly of a trinuclear Ru(II)–Cu(I) coordination oligomer having ethynyl or diethynyl bridges (n = 1, 2). (Reproduced and adapted with permission; ref 189. Copyright 1993 Royal Society of Chemistry.)

nonemissive one. The overall luminescence properties of such a molecule are consequently electrochemically switchable. The Os(III) unit acts as a quencher for the Ru(II)-based excited state. The quenching process leads to a $Ru^{III}Os^{II}$ intervalence transfer product which decays to the ground-state $Ru^{II}Os^{III}$ isomer.

b. Metallodendrimers. Dendritic systems containing metal ions are of considerable interest as novel magnetic, electronic, photooptical, catalytic, sensor, receptor, or encapsulant materials. A complete discussion of all of these facets is well beyond the scope of this review. However, other reviews which discuss them in detail are available.[162–163,180]

An interesting recent practical development has been the discovery that complexes of the type **128** adsorb onto silica–titania surfaces.[193] Optical waveguide lightmode spectroscopy indicates that monolayers are formed, with the deposition mode strongly dependent on the bulk concentration of the metallodendrimer in the coating solutions. Metal oxide supported dendrimeric complexes of this type may be conveniently employed in one of the applications mentioned above.

D. Interlaced Motifs

Coordination complexes having interlaced motifs are characterized by a metal ion-directed threading of one ligand through or about itself or another ligand. Figure 55a–c schematically illustrates the structural motifs of coordination complexes exhibiting rotaxane, pseudorotaxane, and catenane motifs, respectively, while Figure 56 and Figure 57 illustrate various knot motifs. Several reviews of metal complexes displaying interlaced motifs are available.[14–16,43,194,195]

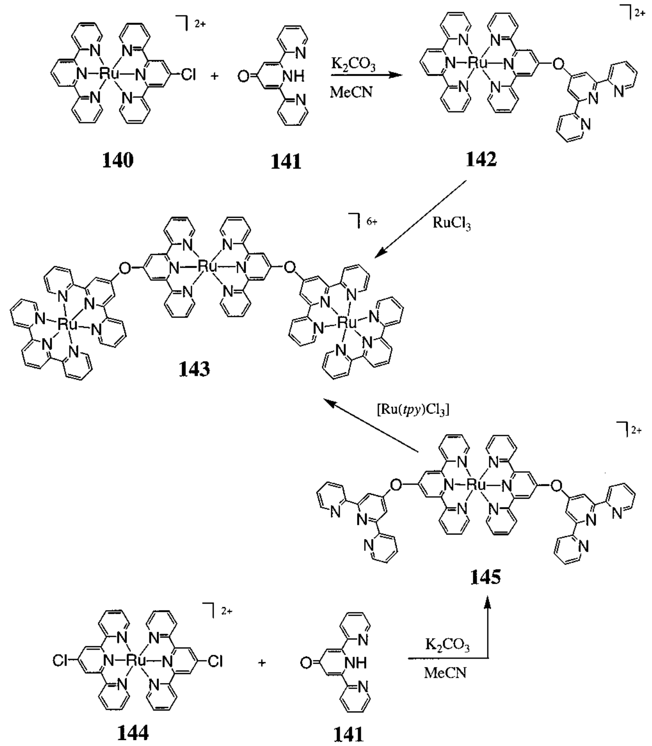


Figure 53. Metal-mediated assembly of coordination oligomers. A triruthenium(II) coordination oligomer convergently assembled (upper) or divergently assembled (lower) from suitably substituted $Ru(tpy)_2$ units.

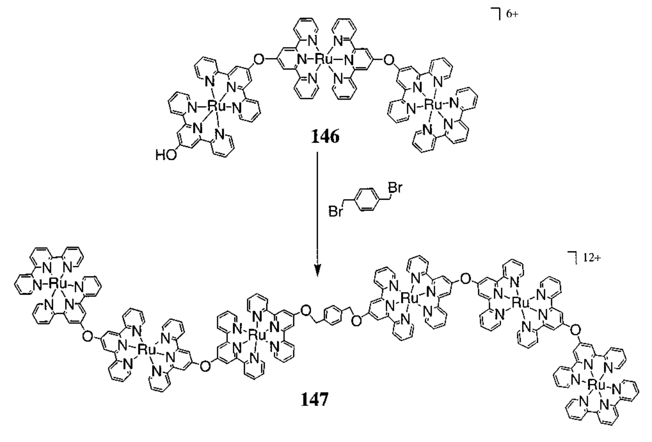


Figure 54. Coordination oligomers by post-modification of self-assembled precursors.

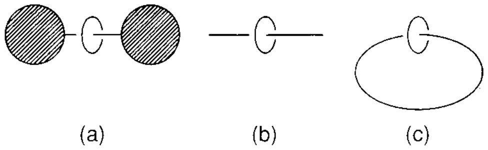


Figure 55. Rotaxanes and catenanes. Schematic illustration of the structural motif of (a) a rotaxane, (b) a pseudorotaxane, and (c) a catenane. (Reproduced with permission; ref 208. Copyright 1993 American Chemical Society.)

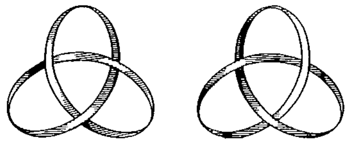


Figure 56. Knots. Schematic depiction of *M*- and *P*-trefoil knots. (Reproduced with permission of ref 15. Copyright 1990 American Chemical Society.)

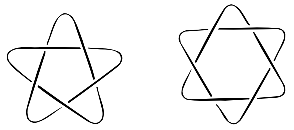


Figure 57. Knots. Schematic illustration of a hexafoil (right) and a pentafoil (left) knot. (Reproduced with permission; ref 15. Copyright 1990 American Chemical Society.)

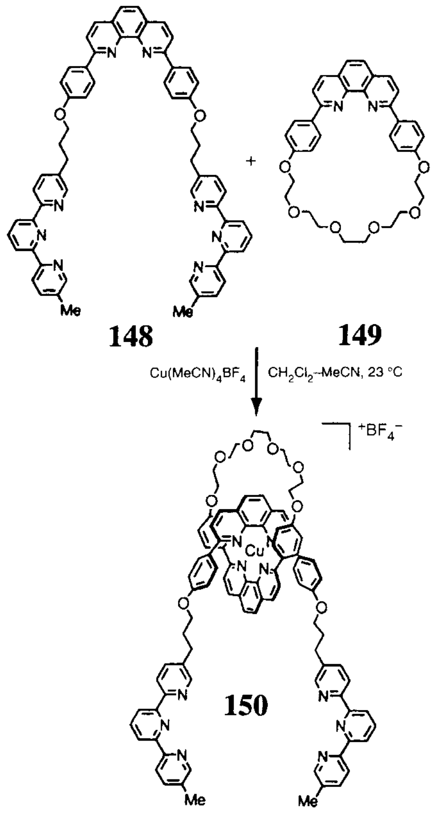


Figure 58. Pseudorotaxanes. A self-assembled pseudorotaxane having free tridentate binding sites at each end of the threaded ligand. (Reproduced with permission; ref 202. Copyright 1996 Royal Society of Chemistry.)

1. Rotaxanes and Pseudorotaxanes

A rotaxane is an interlaced moiety in which a filamentous species, stoppered at each end, is threaded through a cyclic one (Figure 55a). Pseudorotaxanes are not sterically trapped in their interlaced state by the presence of bulky stoppers on the termini of the filamentous species (Figure 55b).[196] Thus, while pseudorotaxanes are physically able to "dethread" to their separate components, the components of rotaxanes are sterically locked and considered to be topologically bound. The nomenclature [*n*]rotaxanes and [*n*]pseudorotaxanes is used, where n indicates the nuclearity of the complex.

The treatment of a tetrahedrally disposed metal ion with a mixture of a linear bidentate ligand strand and a stoichiometric amount of a macrocyclic bidentate ligand in which the coordination site lies on the inside of the cycle may lead to a mixed-ligand complex having a pseudorotaxane structure. As illustrated in Figure 58, simple [1]pseudorotaxanes such as **150** can be readily self-assembled by treating Cu(I) with linear (**148**) and cyclic (**149**) derivatives of 2,9-diphenyl-1,10-phenanthroline; thermodynamically stable, singly threaded pseudotetrahedral complexes result.[197,198]

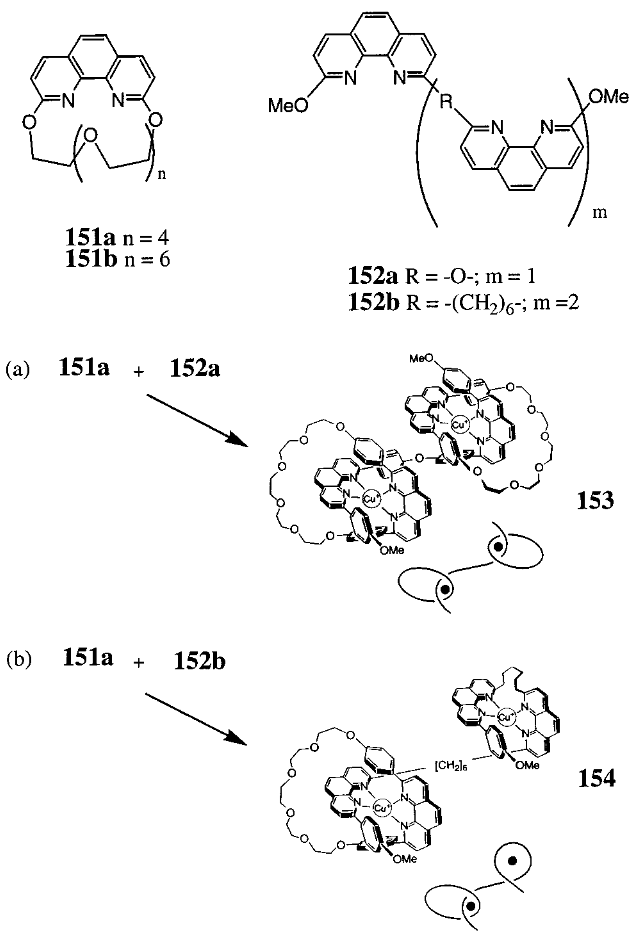


Figure 59. Self-assembling pseudorotaxanes. Formation of (a) a [2]pseudorotaxane and (b) a half-stoppered [1]-pseudorotaxane. (Reproduced with permission; ref 199. Copyright 1993 Royal Society of Chemistry.)

The use of filamentous ligands containing several coordination sites along their length makes reactions of this type more complex and the products less predictable. However, as with helicates, a rigid or semiflexible spacer between the binding sites prevents the filamentous ligand from multiple chelation to a single Cu(I) ion and thereby forces the formation of polynuclear pseudorotaxanes. This "rings and strings" approach has been used effectively by Sauvage and co-workers to self-assemble the [2]pseudorotaxanes **153** (Figure 59a)[199] and **155** (Figure 60)[200] with Cu(I). The presence of the more flexible $-(CH_2)_6-$ spacers in **152b** led to the "half-stoppered" [1]pseudorotaxane **154** (Figure 59b)[199] instead of the [3]pseudorotaxane which may have been anticipated. Interestingly, kinetic experiments indicated that lengthening the spacers in the filamentous ligands within such compounds significantly slowed the rate

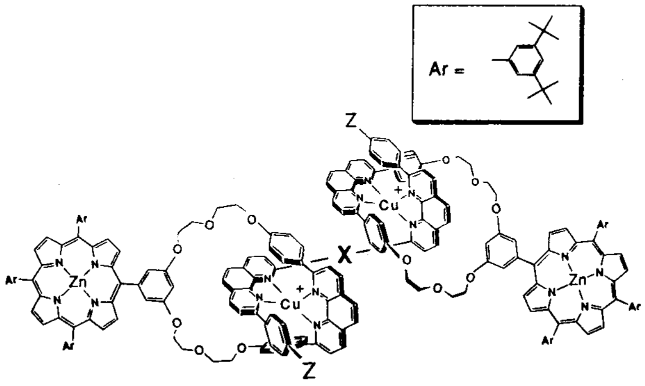


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Figure 60. Pseudorotaxanes. A self-assembled [2]pseudorotaxane obtained using a molecular "rings and strings" approach (X = $-(CH_2)_3-$, *m*-benzyl; Z = OMe). (Reproduced and adapted with permission of ref 200. Copyright 1996 American Chemical Society.)

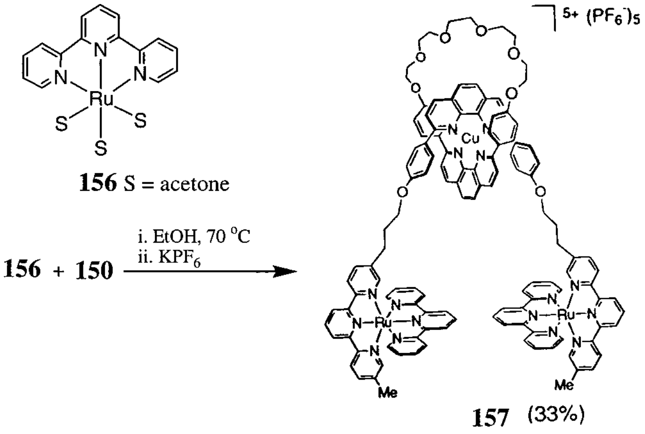


Figure 61. Rotaxanes. Formation of a rotaxane stoppered with $Ru(tpy)_2$ complexes. (Reproduced and adapted with permission of ref 202. Copyright 1996 Royal Society of Chemistry.)

of dethreading when cyanide was added as a decomplexation reagent.[201]

The preference of Cu(I) for tetrahedral coordination was exploited in the self-assembly of the [1]pseudorotaxane **150**.[202,203] Treatment of complex **150** with $[Ru(tpy)(Me_2CO)_3][BF_4]$ (**156**) produced the corresponding rotaxane **157** having two $Ru(tpy)_2$ groups as stoppers (Figure 61).[203]

Polymeric pseudorotaxanes containing a conjugated backbone have been prepared by the electrochemical polymerization of self-assembled [1]pseudorotaxanes containing thiophene groups on the ends of the threaded ligand.[204] The presence of lithium ions during decomplexation of the Cu(I) ions, maintained the scaffold of the structure, so that it could later be remetalated without the loss of structure using a directed self-assembly process.

a. Properties and Applications of Rotaxanes and Pseudorotaxanes. Rotaxanes offer useful frameworks for examining through-bond and through-space electron transfer in molecules.[194c,205] A series of self-assembled [1]–[5]pseudorotaxanes[205–209] have been employed as precursors in the irreversible preparation of rotaxanes containing metalated porphyrin stoppers at the termini or within the backbone of the threaded filamentous ligand.[205–209] Figure 62 schematically illustrates the formation of such species. Photoinduced electron transfer between chemically nonconnected chromophores may occur in these materials and has been studied as a model of the electronic processes in photosynthesis.[210–213] A rotaxane stoppered with fullerenes has been prepared and studied in similar fashion.[214,215] All of these compounds were formed by self-assembly processes involving post-modification.

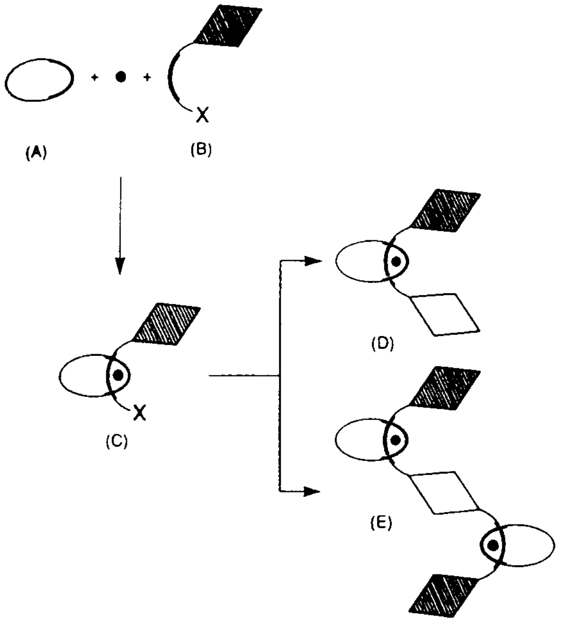


Figure 62. Rotaxanes containing porphyrins. A macrocycle (A) incorporating a coordinating fragment (thick line) interacts with a metal center (black circle) and an asymmetric, open chain chelate (B) bearing one porphyrin (shaded parallelogram) and a precursor functional group X which is small enough to pass through the ring. After the threaded intermediate (C) is assembled, an additional porphyrin ring (unshaded parallelogram) is attached at site X, giving the rotaxanes (D and E). (Reproduced with permission; ref 208. Copyright 1993 American Chemical Society.)

Inducing controlled molecular motion in rotaxanes and pseudorotaxanes has recently become a subject of considerable interest. Compounds in which this can be achieved are seen as precursors to molecular nanomachines and motors employing similar principles.[194b,c,269] A self-assembled [1]pseudorotaxane has been reported in which the filamentous ligand could be electrochemically induced to translate through the cyclic one in a controlled fashion. As schematically illustrated in Figure 63,[216] the [1]pseudorotaxane **158** initially contains a Cu(I) ion bound to a bidentate phen binding site (phen = 1,10-phenanthroline) on a filamentous ligand which also contains a free tridentate tpy site. Cu(I) ions favor tetrahedral binding, while Cu(II) ions favor a coordination number of 5 or 6. Thus, oxidation of the Cu(I) to Cu(II) in the pseudorotaxane caused the metal ion to dissociate from the bidentate phen site and to coordinate the tridentate tpy site (giving **159**). Subsequent reduction of the Cu(II) back to Cu(I) reversed the process.

In earlier work a similar ligand was self-assembled with Cu(I) to give a [1]pseudorotaxane which could be electrochemically induced into motion only after

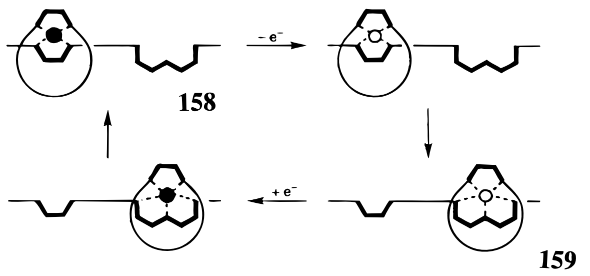


Figure 63. Induced translational motion in a pseudorotaxane. The principle of electrochemically induced molecular motion in a Cu(I) pseudorotaxane: the stable four-coordinate univalent complex **158** undergoes a rearrangement to the pentacoordinate divalent species **159** upon oxidation (black circle = Cu(I); unshaded circle = Cu(II)). Reduction induces the reverse motion. (Reproduced with permission; ref 216. Copyright 1996 Royal Society of Chemistry.)

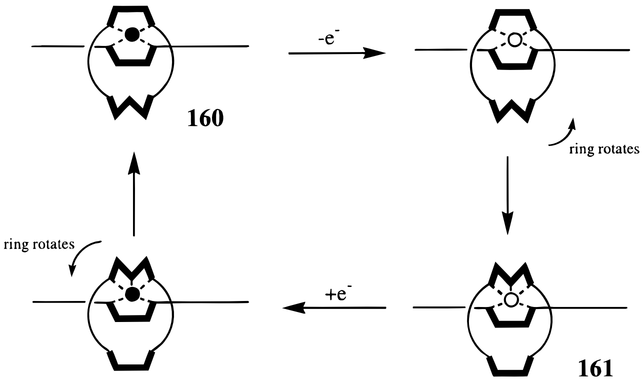


Figure 64. Induced gliding motion in a pseudorataxane. The stable four-coordinate complex **160** becomes unstable when the central Cu(I) (shaded circle) is oxidized to Cu(II) (unshaded circle). The cycle rotates to allow formation of the five-coordinate complex **161**. Reduction of **161** reverses the process.

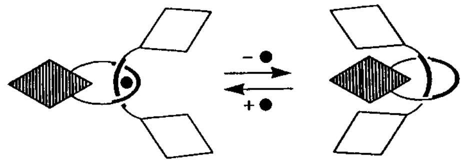
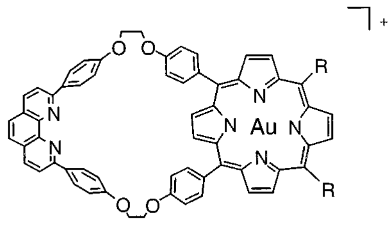


Figure 65. Controlled molecular motion in the rotaxane [Cu(**162**)(**163**)]$^{2+}$. The metalated porphyrins (unshaded parallelograms) of **163** are oriented away from the porphyrin (shaded parallelogram) of **162** when the rings are joined by coordination to Cu(I) (shaded circle). Upon selective removal of the Cu(I), the three groups rearrange to eclipse one another. (Reproduced with permission; ref 220. Copyright 1998 Royal Society of Chemistry.)

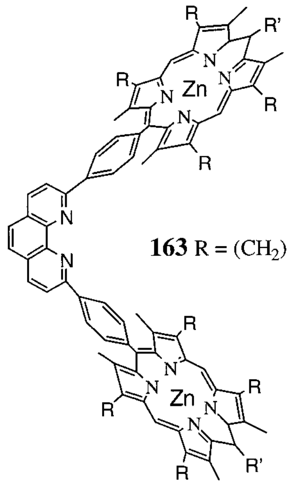
stoppering of the filamentous ligand.[217,218] A gliding motion in which the cyclic ligand of a pseudorotaxane was induced to rotate in a controlled fashion about the filamentous ligand (**160** to **161**) has also been achieved using the same principle (Figure 64).[219]

The Cu(I)-linked [1]rotaxane [Cu(**162**)(**163**)]$^{2+}$ in which a Au(III) porphyrin forms part of the ring ligand **162** (Chart 10) and the filamentous ligand **163** is stoppered with zincated porphyrins has also been used to trigger rotation.[220] When linked by Cu(I), the terminal porphyrins of **163** are oriented away from the porphyrin of **162** (Figure 65). However, selective removal of the Cu(I) ion induces the porphyrins of **163** to swing around and eclipse the Au(III) porphyrin of **162**. Attractive interactions between the [Au−porphyrin]$^+$ (electron acceptor) and the [Zn−porphyrin] (electron donor) bring about this change.

Chart 10



162 R = 3,5-(^{t}Bu)$_2$Ph



163 R = (CH$_2$)$_5$Me; R' = 3,5-(^{t}Bu)$_2$Ph

Most recently, controlled threading and dethreading of pseudorotaxanes by a photoinduced electron-transfer process has been attempted.[221] In this experiment, a photosensitizer (typically a Ru(bipy)$_3^{2+}$ or Ru(tpy)$_2^{2+}$ complex; bipy = 2,2′-bipyridyl) was covalently attached to a π-electron-deficient unit (a 4,4′-bipyridium or 2,7-diazapyrenium), which also acted as a single electron acceptor. As illustrated in Figure 66, the latter unit spontaneously self-assembles (via aromatic donor−acceptor interactions) with a π-electron-rich cyclic moiety (such as a crown ether containing two hydroquinone or dioxynaphthalene units) to form a pseudorotaxane. Light excitation of the photosensitizer in the presence of a sacrificial electron donor (e.g. triethanolamine) should then cause single electron transfer to the electron-acceptor unit, eliminating the donor−acceptor interactions and dethreading the pseudorotaxane. In the presence of oxygen, the reduced acceptor unit would then reoxidize, restoring the donor−acceptor interaction and allowing the pseudorotaxane to again self-assemble. In practice however, incompatibilities between the various components of the system complicated this process.[221]

2. Catenanes

Catenane motifs involve the interlocking of two cyclic structures as shown in Figure 55c. If two such cycles are simultaneously bound to a single metal ion, the resulting motif can also be termed a catenate.

The nomenclature [*n*] is used for simple catenanes, where *n* indicates the number of interlocked rings. In addition; catenanes may also differ with respect

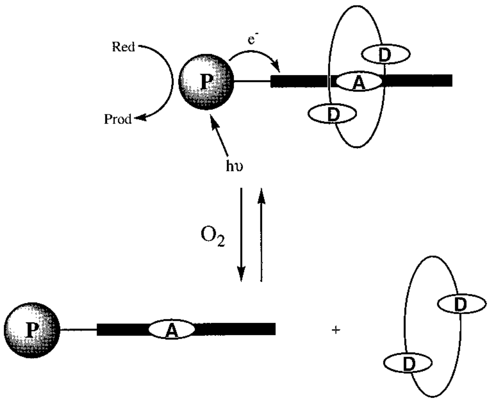


Figure 66. Light-induced threading and dethreading of a pseudorotaxane. When irradiated in the presence of a sacrificial reductant, Red, the photosensitizer P (an excited-state electron donor) donates an electron to the attached π-deficient, electron-acceptor unit (A). In so doing, the aromatic donor (D)−acceptor (A) stacking interactions stabilizing the pseudorotaxane structure are lost, causing dethreading. Oxygen (O_2) reverses the process by reoxidizing the reduced acceptor unit, thereby restoring the donor−acceptor interaction and allowing self-assembly of the pseudorotaxane. Prod are species originating from the oxidation of Red.

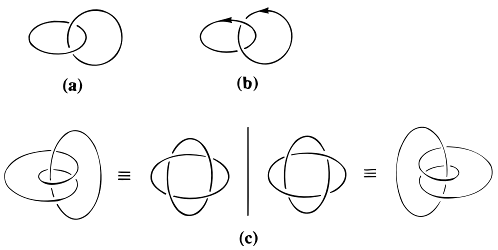


Figure 67. Catenanes and knots. Schematic depiction of the structural motifs for (a) a singly interlocked [2]-catenane, (b) a singly interlocked [2]catenane made chiral by directionality in the rings, and (c) mirror-image enantiomers of a doubly interlocked 4-crossing-[2]catenane. (Reproduced with permission; ref 222. Copyright 1996 Royal Society of Chemistry.)

to the number of times one ring is interlinked with another; i.e. the number of times one ring “crosses” another in one traversement of its length. Most catenane coordination complexes are singly interlocked; however, multiply interlocked complexes are known. Singly interlocked species (such as that in Figure 67a[222]) are termed 2-crossing catenanes. Doubly interlocked species are known as 4-crossing-catenanes (e.g. Figure 67c[222]); the absence of a prefix specifying the extent of interlocking in a catenane normally implies a singly interlocked structure. Figure 67b depicts a 2-crossing catenane in which the interlocking rings have directionality. Such species are chiral and therefore exist as two mirror image enantiomers (not shown in the figure). The 4-crossing-[2]catenane illustrated in Figure 67c is also chiral; its two mirror-image enantiomers are depicted. Multiring catenanes are molecules in which several small rings are threaded onto a single large ring. Such compounds have recently been termed molecular necklaces[223] and described using the nomenclature [*n*]MN, where *n* refers to the number of cycles present. Figure 68[224] schematically illustrates [4]-, [5]-, [6]-, and [7]MN. The smaller necklaces [2]-MN and [3]MN are identical to [2]- and [3]catenanes, respectively.

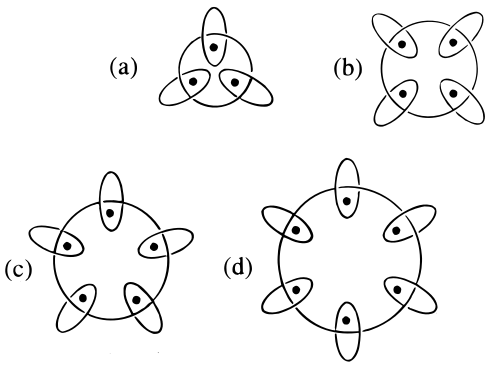


Figure 68. Molecular necklaces. Schematic illustrations of (a) [4]MN, (b) [5]MN, (c) [6]MN, and (d) [7]MN. (Reproduced with permission of ref 224. Copyright 1991 American Chemical Society.)

Metallocatenanes are species exhibiting interlocked-ring motifs in which one or more of the rings have been closed by metal ion coordination.[195] This typically requires the self-assembly of two interlinked metallocycles. Alternatively, a pseudorotaxane having free chelating sites at the termini of the threaded, filamentous ligand (such as compound **150** in Figure 58) may undergo ring-closure by coordination to a single metal ion, giving a complex which is then correctly termed a metallocatenate. Since individual metallocycles are distinct structural entities brought about by self-assembly, they constitute secondary structural motifs. The interlinked nature of two metallocycles in a metallocatenane can therefore be regarded as a tertiary structural motif.

a. Self-Assembled Catenanes. For a catenane to be self-assembled from ligands and metals, its constituent cycles need to be both spontaneously formed and interlocked during the reaction. Such an event is statistically unlikely, so that catenanes of this type are somewhat rare. However, in principle there is no reason that enthalpic driving forces associated with metal−ligand coordination cannot be harnessed for the cyclization step and entropic or other influences for the interlocking step. Fujita et al. have used exactly this approach in the self-assembly of several [2]metallocatenanes.[195,225]

In Fujita’s Pd(II) system illustrated in Figure 69,[225,226] the free metallocycle **164** (M = Pd) was formed because of the enthalpy of formation of the Pd−N bonds. However, the lability of these bonds allowed a rapid equilibrium to exist between the free metallocycle and its interlocked catenane **165**. Thus, when a solution of this type is concentrated from 2 to 50 mM, π-aromatic donor−acceptor interactions between the phenyl groups on the interlocking species and hydrophobic interactions, assisted by entropic influences, caused the equilibrium to shift in favor of **165**. The use of D_2O as solvent instead of water enhanced the hydrophobic interactions also resulting in an increased proportion of the catenane. Attempts to replicate catenane formation using the analogous ligand **36** proved fruitless; while the corresponding metallocycles were formed, the catenane was not.[195] This suggested that the influence of

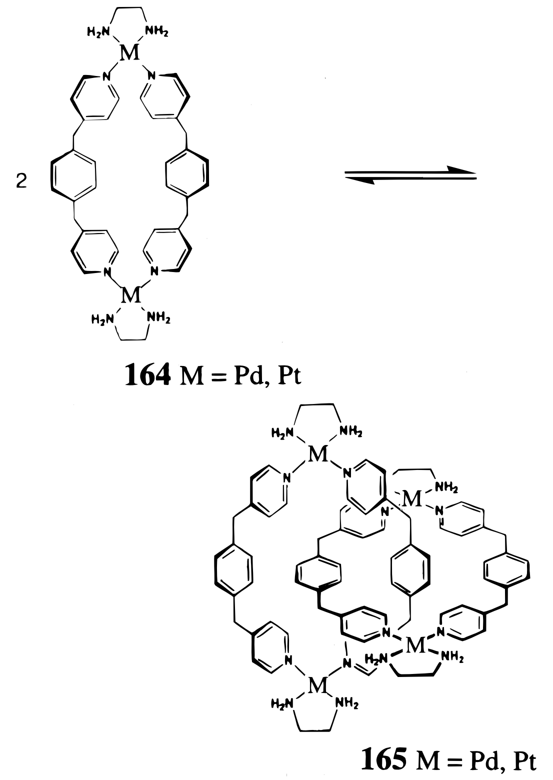


Figure 69. Self-assembling metallocatenanes. While the Pd(II) species **164** spontaneously forms the metallocatenane **165** upon concentration of the reaction solution, the lack of kinetic lability in the Pt(II) system necessitates the addition of $NaNO_3$ at high temperature to labilize the Pt−pyridine bonds. (Reproduced and adapted with permission; ref 43a. Copyright 1996 Chemical Society of Japan.)

atractive edge-to-face or CH−π interactions were significant. The role of the noncoordinative interactions in this process was crucial; they were estimated to double the free energy change of the process, making the metallocatenane stable enough to be essentially quantitatively self-assembled at high concentrations.[195] This reaction can therefore be seen as a double-molecular recognition process in which the two interlocking molecules bind each other in their cavities;[195] the metallocyclic secondary structure is generated by metal-directed self-assembly, while the π- and hydrophobic interactions and the entropic effect generate the interlocked catenane tertiary structure. A "Möbius strip" mechanism has been proposed for the formation of **165**.[227]

A range of similar self-assembled [2]metallocatenanes have also been prepared by Fujita.[195,228] The complexes **167** and **169** depicted in Figure 70[195,225] and compounds **171** and **174** in Figure 71[195] were obtained as two- or three-species−eight component systems. Interestingly, since the metallorectangles comprising the rings in these complexes have directionality, the resulting metallocatenanes are topologically chiral; i.e. the second ring may be interlocked into the first ring in either a clockwise or anticlockwise manner.[229] The complexes **167** and **169** were shown, using ^1H NMR, to exhibit topological chirality, proving that the catenated structures existed in solution.[195,228] However the three-species−eight component systems **171** and **174** were obtained in only one topological form, both in solution and in the solid state. Metallocatenane formation of this type was unsuccessful when more flexible ligands were employed.

In the Pt(II) system depicted in Figure 69,[226] the coordination bonds are inert under normal conditions, so that the Pt−N bond can be considered "locked". However, in a highly polar medium at high temperature, these bonds are labilized and consequently "released". Thus, the "locked" diplatinum(II) monocycles **164** (M = Pt), which were the product of the initial reaction, could be "released" by the addition of $NaNO_3$ and then interlocked into a catenane structure by concentrating the mixture at 100 °C. The resulting catenane was then trapped by removal of the salt and cooling, thereby "locking" the coordination bonds again. Figure 72 illustrates the sequence

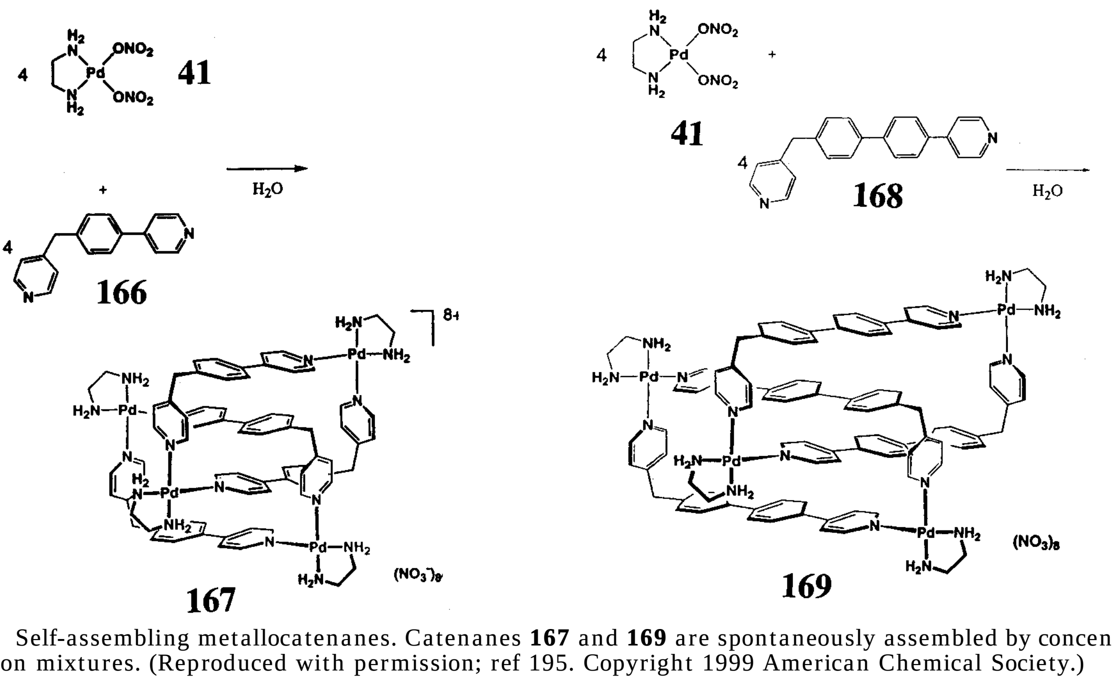


Figure 70. Self-assembling metallocatenanes. Catenanes **167** and **169** are spontaneously assembled by concentration of their reaction mixtures. (Reproduced with permission; ref 195. Copyright 1999 American Chemical Society.)

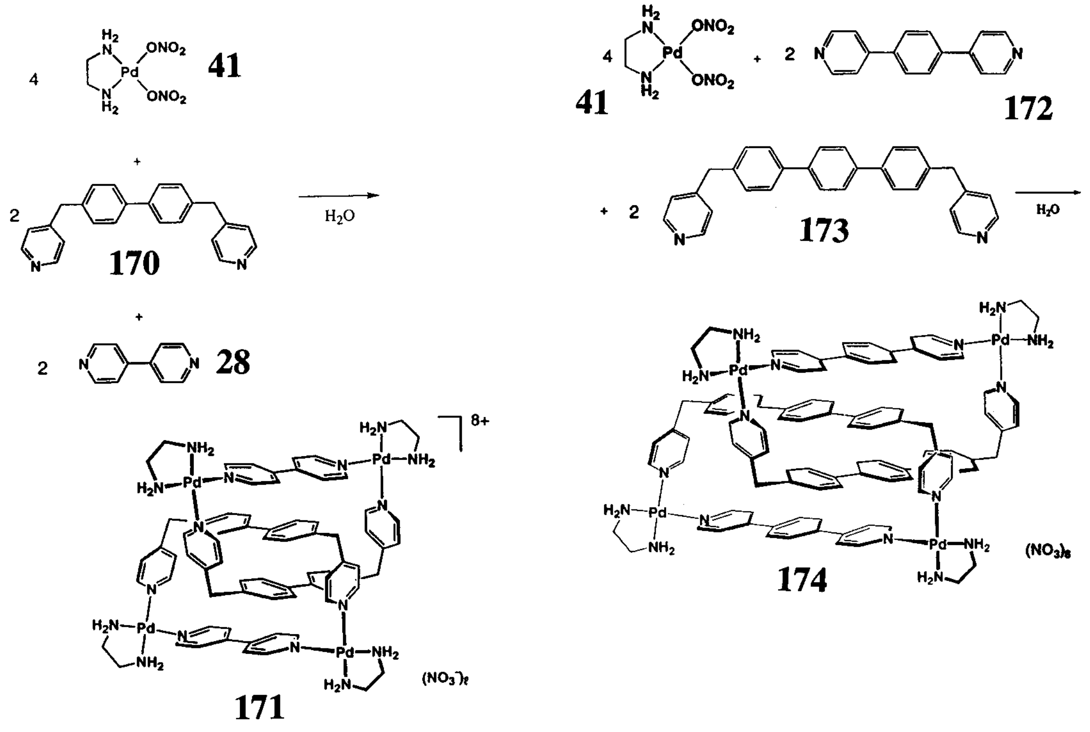


Figure 71. Self-assembling metallocatenanes. Catenanes **171** and **174** are spontaneously assembled by concentration of their reaction mixtures. (Reproduced with permission; ref 195. Copyright 1999 American Chemical Society.)

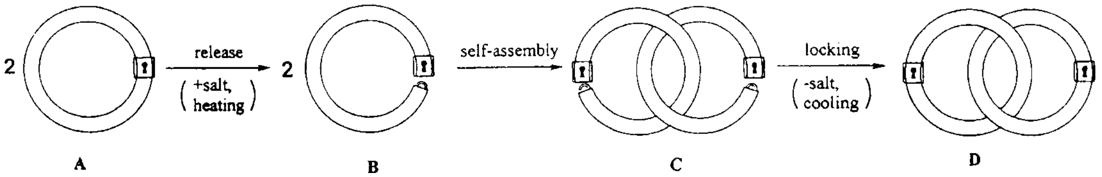


Figure 72. Metallocatenane molecular locks. Schematic depiction of the principle of a "molecular lock". The coordination bonds in the metallocycle **164** (M = Pt) are kinetically inert (A). Upon addition of $NaNO_3$ and heating to 100 °C, these bonds are labilized (B). Concentrating the solution leads to the self-assembly of the metallocatenate **165** (M = Pt) (C). Removal of the salt and cooling of the solution restores the normal lack of kinetic lability in the Pt–N bonds (D). (Reproduced with permission of ref 43a. Copyright 1996 Chemical Society of Japan.)

of events in this "molecular lock", which serves as an elegant mimic—on the smallest possible level—of the interlocking rings trick used by conjurers and magicians.

Isomeric [2]metallocatenanes have also been obtained by another route involving a one-step, self-assembly reaction.[230] The segmented ligand strand **175** contains a central tridentate binding site with bidentate binding sites at each terminus. When added to stoichiometric quantities of Ag(I) and Fe(II), **175** was found to self-assemble the complex $[FeAg_2(\mathbf{175})_2]^{4+}$ having the [2]metallocatenate structures III and IV shown in Figure 73.[230] This complex contains two tetrahedral Ag(I) units selectively bound to the outer, bidentate sites (each producing metallocyclic secondary structures) and an octahedral Fe(II) unit selectively coordinated to the central binding sites of the two ligand strands (generating the catenane tertiary structure). As each of the interlocked rings constitute a helical domain,[1a] *M* or *P* stereoisomers are possible. In this reaction both the *meso*-(*P*,*M*)-[2]metallocatenate and a racemic mixture of the (*M*,*M*)- and (*P*,*P*)-[2]metallocatenate enantiomers were obtained. The helicate and side-by-side structures I and II in Figure 73 were not observed.

Metallocatenates of similar type may be prepared using a stepwise methodology; treatment of the self-assembled [1]pseudorotaxane **150** shown in Figure 58 with $[Ru(DMSO)_4Cl_2]$ resulted in the formation of the kinetically stable [2]metallocatenate **177** shown in Figure 74.[203] In this case, only *M* or *P* diastereomers at ruthenium were possible. Heterotri- and bimetallic [2]metallocatenates of similar type have also been obtained;[231] selective removal of the labile central Cu(I) ions in these complexes delivered the corresponding kinetically inert [2]metallocatenanes.

b. Catenanes Generated by Self-Assembly with Post-modification. Most other catenane coordination compounds have been obtained by the cyclization of self-assembled pseudorotaxanes using conventional organic reactions employing appropriate linkers (usually polyethers). Figure 75 illustrates the formation of a [2]catenate by this means;[194a] similar strategies have also been used in the syntheses of a series of [2]–[7]catenates.[194a,232] As the rings in such complexes involve purely covalent linkages, they have a cyclic primary structure which generates the catenane motif as a secondary structure. Multiringed catenates involving a tricyclic core have been pre-

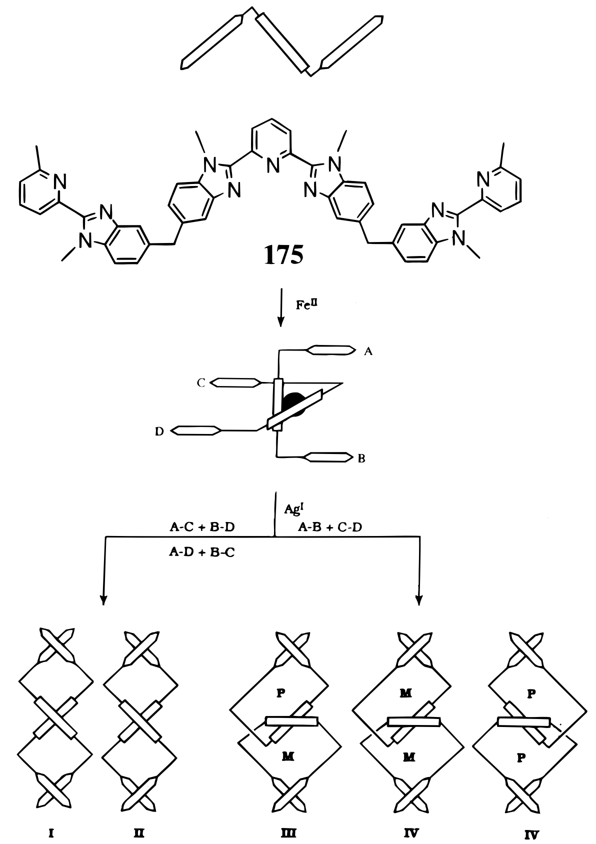


Figure 73. Self-assembling metallocatenates. Schematic depiction of the self-assembly of a heterotrinuclear [3]-metallocatenate using Fe(II) and Ag(I). The central chelating site in the ligand is a tridentate unit (illustrated as a square wedge), while the outer two are bidentate (illustrated as pointed wedges). The inner sites selectively coordinate Fe(II). The outer sites coordinate Ag(I). While compounds **I**−**IV** may be anticipated, in practice only structures **III** and **IV** were obtained. Structure **I** is a helical, D_2-symmetric structure, **II** a D_2-symmetric, side-by-side structure, **III** a S_4-symmetric (*P*,*M*)-[2]metallocatenate, and **IV** a D_2-symmetric (*M*,*M*)- and (*P*,*P*)-[2]-metallocatenates. (Reproduced with permission; ref 230. Copyright 1995 Wiley-VCH.)

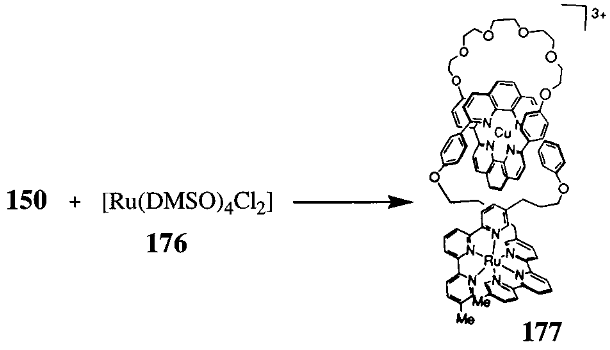


Figure 74. Metallocatenates. Formation of a [2]metallocatenate by the reaction of a self-assembled pseudorotaxane **150** with $Ru(DMSO)_4Cl_2$. The (*M*)-form of the catenate is depicted here, although both diastereomers are possible. (Reproduced and adapted with permission; ref 203. Copyright 1997 American Chemical Society.)

pared by analogous means,[233] as have several catenates containing porphyrin moieties.[234−236]

Ring-closing metathesis reactions, involving Grubb's ruthenium benzylidene catalyst, have also proved useful in such cyclizations.[237] Self-assembled [1]-pseudorotaxanes bearing terminal vinyl groups on the threaded, linear ligand have been converted to [2]catenates in high-yield using this technique.

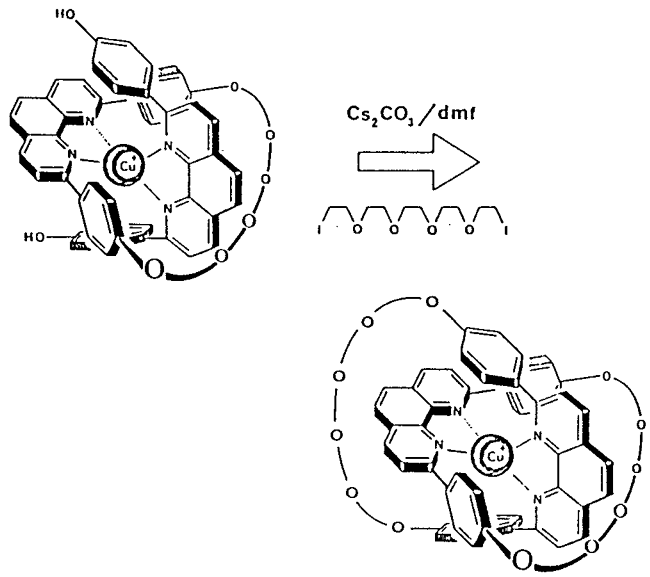
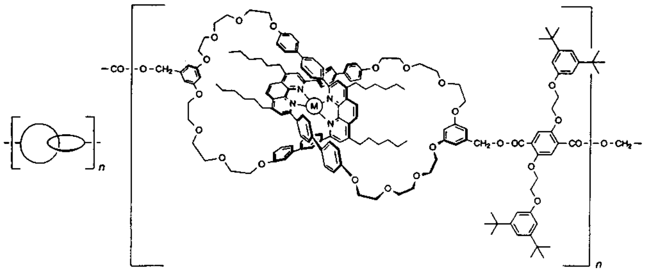


Figure 75. Catenates formed by post-modification of a self-assembled precursor. The cyclization is shown of a self-assembled pseudorotaxane using a polyether diiodide. (Reproduced with permission; ref 194a. Copyright 1992 ESME/Gauthier-Villars, 23, rue Linois, 75724 Paris cedex 15.)



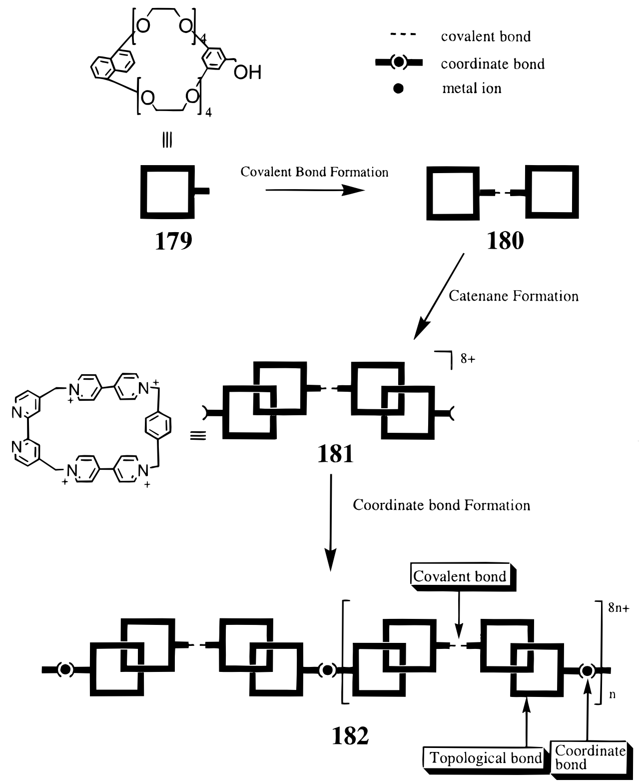
178

Figure 76. Polycatenates formed by post-modification of a self-assembled precursor. The formation of a poly[2]-catenate (M = Cu) is shown. (Reproduced with permission; ref 238. Copyright 1996 Royal Society of Chemistry.)

A recent development has seen the preparation of poly[2]catenates like **178** (Figure 76) in which the interlocked rings in a catenane are covalently linked to similar rings on adjacent catenanes.[238] Polymeric chains containing alternating topological and covalent bonds in their backbone are thereby obtained. In this molecule, irreversible modification of the self-assembled precursor generates secondary structure in the form of the individual catenane motifs but also tertiary structure in their linear arrangement relative to each other.

A poly[2]catenane, schematically illustrated as **182** in Scheme 21, which exhibits alternating topological, covalent, and coordination bonds down its backbone has also been prepared.[239] This compound was formed by covalently tethering two cycles **179** via pendant alcohol functionalities, followed by formation of the dicatenane **181** using aromatic π-donor−acceptor interactions. The new rings on **181** each contain a 2,2′-bipyridyl group, so that the addition of Ag(I) results in the formation of coordinate bonds, giving

Scheme 21



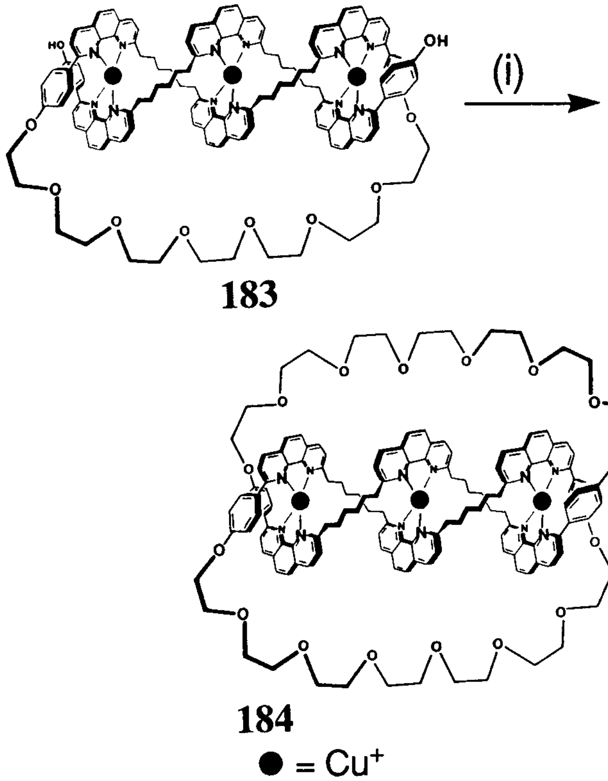


Figure 77. 4-Crossing-catenanes. Schematic depiction of the synthesis of a doubly interlocked 4-crossing-[2]catenane by post-modification of the self-assembled helicate precursor **183**. Reaction conditions: (i) $ICH_2(CH_2OCH_2)_6CH_2I/Cs_2CO_3$/DMF/60−62 °C. (Reproduced with permission; ref 240. Copyright 1994 American Chemical Society.)

the polymer **182**. The compound **181** contains catenane secondary structures arranged in a linearly tethered tertiary structure, all of which have been self-assembled by favorable π-interactions. The formation of the coordination bonds in **182** serve to generate a molecule displaying a nondiscrete polymeric quaternary structure.

c. Multiple-Crossing Catenanes. Just as cyclization reactions on pseudorotaxanes may lead to singly interlocked catenates, so cyclizations of helicates can lead to doubly intertwined catenate or knot structures. 4-Crossing-catenates are obtained when a cyclization reaction connects the two ends of each ligand in a self-assembled, double-stranded, trinuclear helicate. Figure 77 illustrates the formation of the doubly intertwined 4-crossing-[2]catenate **184** from the helicate **183** according to this method.[222,240] Demetalation of **184** produces the corresponding 4-crossing-[2]catenand. Both **184** and its catenand are topologically chiral, as are all doubly intertwined moieties.[229] This chirality arises from, and is dependent upon, the chirality of the helicate from which they were derived.

d. Molecular Necklaces. The first self-assembled molecular necklace has recently been reported by Kim and co-workers.[223] Figure 78 illustrates this [4]-MN molecule, which was prepared from nine species, including three molecular "beads", three "strings", and three "angle connectors". Refluxing a 1:1:1 mixture of cucurbituril (**185**) ("bead"), N,N′-bis(4-pyridylmethyl)-1,4-diaminobutane dihydronitrate (**186**) ("string"), and $Pt(en)(NO_3)_2$ (**41**) ("angle connector"; en = ethylenediamine) in water for 24 h, followed by the addition of ethanol, produced the necklace **187** in 90% yield. The structure of the product was confirmed by X-ray crystallography in the solid state and by ES-MS and ^1H NMR in solution. While the three cucurbituril-based catenane secondary motifs are self-assembled by weak, noncoordinative interactions, the formation of the coordination bonds in compound **187** generates the overall metallocyclic tertiary structure of the molecule. While Pt(II) is normally too kinetically inert to participate in self-assembly processes, it typically becomes more labile at high temperature, permitting formation of the thermodynamic product.

Several molecular necklaces have been previously prepared using conventional organic reactions.[224,241]

e. Properties and Applications of Catenanes. The electron-transfer properties[242−246] and behavior in controlled molecular motion[194b] of catenanes have been extensively studied.

[2]Catenanes, in which one of the cycles incorporates a bidentate phen and a tridentate tpy binding site, can be induced to undergo "swinging" by electrochemical or photochemical conversion of the templating Cu(I) to Cu(II).[247−249] Figure 79 illustrates the general principle: since the binding preference of Cu(II) is for the tridentate tpy site rather than the bidentate phen site (which is favored by Cu(I)), oxidation of the Cu(I) catenane **188** causes dissociation and re-formation of the metal−ligand bond giving the Cu(II) catenane **189**, with a resulting movement in the rings.

A switchable [2]catenane **190** has also been prepared by combining the techniques of Sauvage and Stoddart (Scheme 22); here metal−ligand and π-elec-

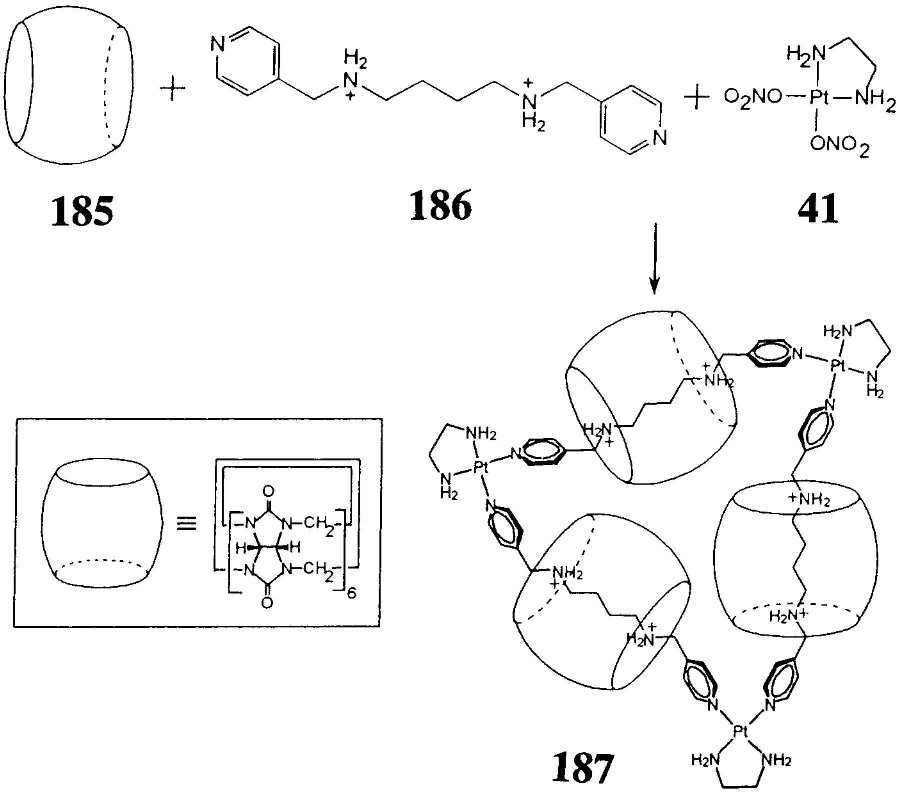


Figure 78. Molecular necklaces. Self-assembly of a [4]MN: weak attractive interactions drive the self-assembly of the three catenane secondary structural units, while coordinate bond formation drives the metallocycle assembly; the latter constitutes tertiary structure. (Reproduced with permission; ref 223. Copyright 1998 American Chemical Society.)

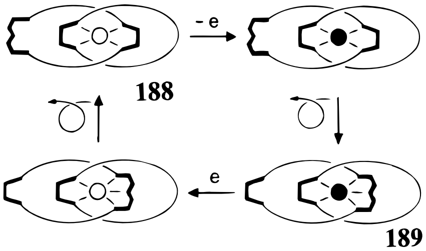


Figure 79. Induced swinging motion in a catenane. The stable four-coordinate complex **188** becomes unstable when the central Cu(I) (unshaded circle) is oxidized to Cu(II) (black circle). The cycle then rotates to allow formation of the five-coordinate complex **189**. Reduction of **189** reverses the process. (Reproduced with permission; ref 247. Copyright 1994 American Chemical Society.)

tron interactions compete to control the topographical structure of the catenane.[250] Upon removal of the coordinating Cu(I) in **190**, the rings of the catenane swing to the structure **191** which is stabilized by interactions between π-donors (**D**) on one ring and π-acceptors (**A**) on the other.

3. Knots

Knots are species in which a single strand alternately passes over and under itself several times in a continuous loop. Knot motifs are named according to the number of times the strand crosses itself. Figure 56 schematically illustrates the two mirror-image enantiomers of a trefoil knot, in which the strand crosses itself three times. Figure 57[15] illustrates pentafoil and hexafoil knots, in which the strand crosses itself five and six times, respectively. Knots having a single structural motif, such as the trefoil knot, are known as prime knots, while those with more than one knotted motif are called composite knots.

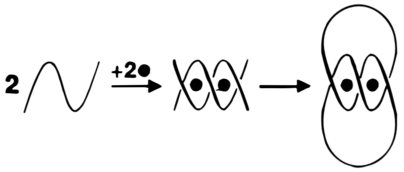
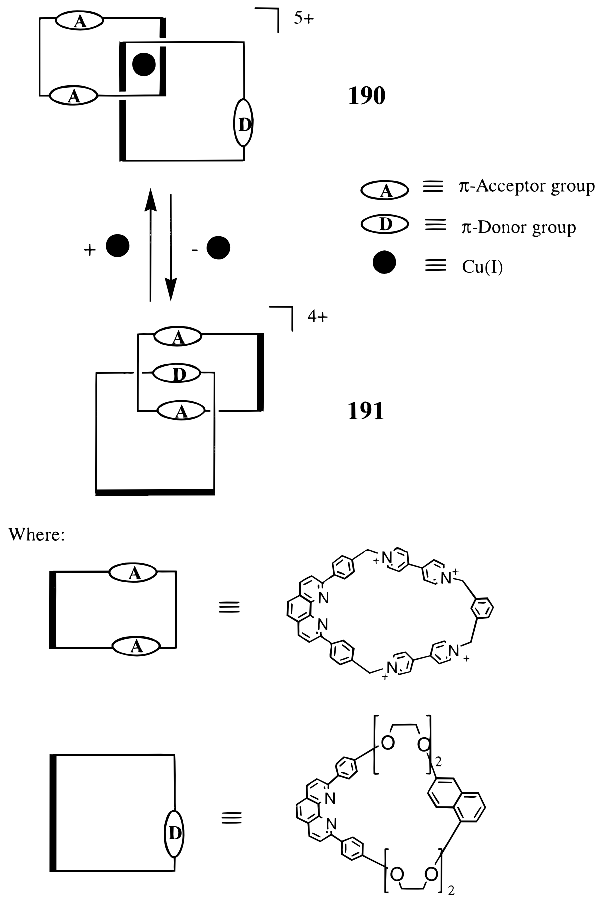


Figure 80. Knots. Strategy for the synthesis of a dimetallic trefoil knot: in the first step two metal ions (●) self-assemble with two semiflexible ligands (~) to give a helicate, whose *P*-form is shown only. In the next step the opposing ends of each ligand are connected with an appropriate linker to give the knot complex, of similar chirality. The knot complex contains a single ligand strand. (Reproduced with permission; ref 254. Copyright 1993 American Chemical Society.)

In coordination chemistry, knots are typically obtained by connecting opposite ends of the two ligands in a double-stranded helicate to form a single, continuous, intertwined ligand strand about the metal ions. Figure 80 illustrates the formation of a trefoil knot by this means. In all cases known, this cyclization involves an irreversible organic reaction so that a knot coordination complex has, to the best of our knowledge, not yet been prepared in a one-step self-assembly process. Instead, all known knots involve self-assembly processes with post-modification.

The starting helicate provides the twisting of the unconnected ligand strands which is essential to the formation of a multiply intertwined knot structure. In general, the number of metal ions and the pitch

Scheme 22



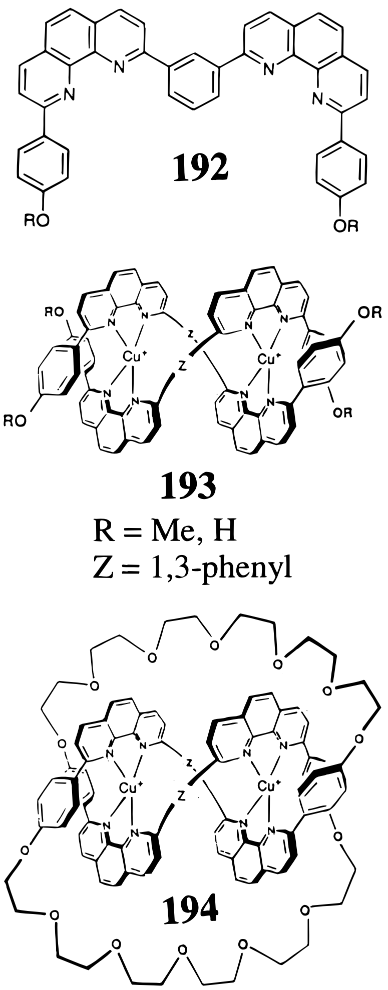
190

191

of the initial helicate govern the type of knot obtained when cyclization occurs in the correct manner. Thus, cyclization of a double-stranded, binuclear helicate which undergoes a half-turn of the helix about each metal ion will produce a trefoil knot motif when correctly cyclized (Figure 80),[15] while tetranuclear and pentanuclear helicates of similar pitch will produce pentafoil and hexafoil knots, respectively, under the same conditions.[15]

The trefoil knot, which has three crossing points, is the simplest nontrivial prime knot known. Several coordination complexes having trefoil knot structures have been prepared from self-assembled helicates.[251−254] For example, the knot **194** has been prepared from the helicate **193**, which incorporates the ligand **192** (Figure 81). Since helicates may have *M*- or *P*-helicity, the knots from which they are prepared must incorporate the chirality of their precursor complexes. While having the same overall motif, for example, the two trefoil knots illustrated in Figure 56[194a] are not interconvertable by continuous transformation, being instead mirror images of each other. Knotted coordination complexes prepared from racemic mixtures of helicates are therefore obtained as racemic mixtures of the relevant topological enantiomers. Such mixtures can be resolved by diastereoselective crystallization or by HPLC on a chiral stationary phase.[229,255]

Because the cyclization reaction required to form knots is typically of low statistical probability, yields of knot complexes can be low (<10%), with coordination oligomers and polymers constituting the major products.[254] Laborious separations of the resulting mixtures are generally necessary to isolate the knots, although higher-yielding (>30%) synthetic routes have been reported recently.[256,257]



192

193

R = Me, H
Z = 1,3-phenyl

194

Figure 81. Trefoil knots. Preparation of a trefoil knot: the reaction of ligand **192** with Cu(I) generates helicate **193** by a thermodynamic self-assembly process. When this is treated, in turn, with $ICH_2(CH_2OCH_2)_5CH_2I$ ($CsCO_3$, DMF, 60 °C), the knot **194** is obtained in 30% yield. (Reproduced and adapted with permission of ref 256. Copyright 1994 Royal Society of Chemistry.)

Knotted complexes can generally be demetalated by treatment with cyanide, leaving only the multiply crossed knotted ligand strand. The entanglement of the ligands about the metals in the complex usually causes demetalation to occur significantly more slowly than in similar complexes having open faces.[258,259] Demetalation reactions also typically involve a different mechanism because of a rearrangement of the knotted structure after the loss of one metal ion.[259]

Composite knots contain more than one knotted motif. The composite knot **198**, incorporating two trefoil knot motifs, is illustrated in Figure 82. It was prepared, along with other, macrocyclic and mixed species, by a coupling reaction joining two helicates **196** into one continuous ligand strand.[260] The helicate was obtained in a 1:2.3 mixture (**196**:**197**) from the reaction of **195** with Cu(I). Since each prime knot in a composite knot may display *M*- or *P*-helicity, composite knots are typically obtained as mixtures

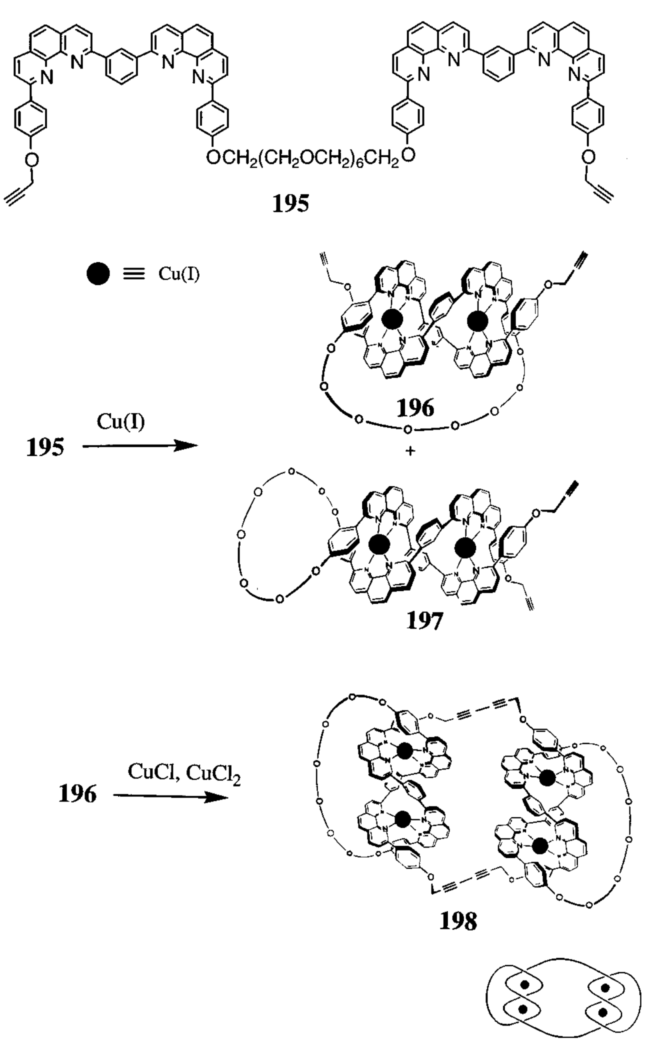


Figure 82. Composite knots. Formation of composite knot **198**: while only the *M*,*M* isomer is illustrated here, the *P*,*P* and *M*,*P* forms are also produced. (Reproduced with permission; ref 260. Copyright 1996 American Chemical Society.)

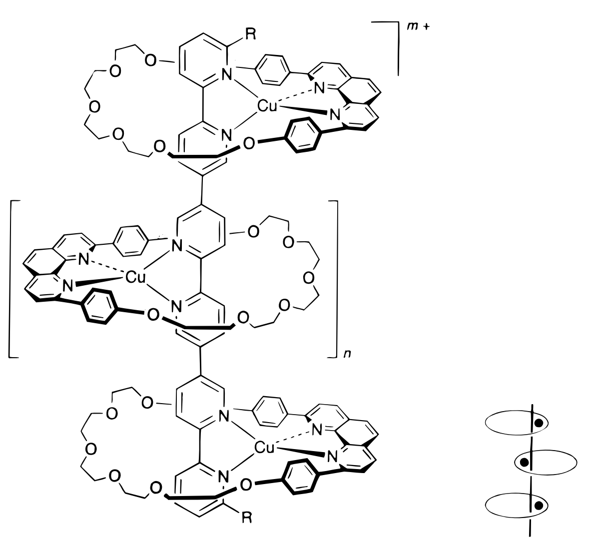
of topological diastereomers.[260] Knot **198** in Figure 82 is illustrated as the *M*,*M*-isomer, although the *P*,*P*-isomer and the *M*,*P*-diastereomer were also produced.

a. Recent Developments. In the field of knotted coordination complexes these include the use of heterodinuclear helicates to form heterodinuclear knotted complexes involving Cu(I) and Ag(I)/Zn(II)[261] and the application of ring-closing metathesis to form a trefoil knot containing Fe(II) in high yield.[266]

E. Metal-Directed Mixed-Motif Complexes

A range of compounds are known in which two or more different secondary motifs have been formed by metal-ion coordination only. These “mixed-motif” complexes typically also display tertiary structure since more than one arrangement of the secondary structural motifs is usually possible.

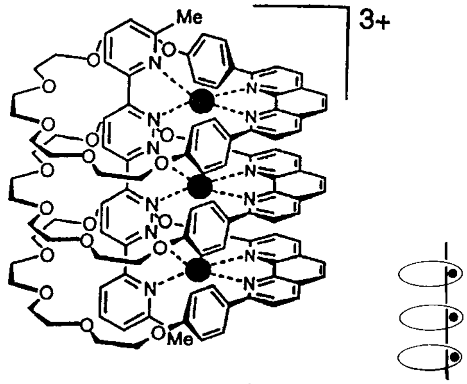
Some examples of mixed-motif complexes are the self-assembled [2]- and [3]pseudorotaxanes $[Cu_2(\mathbf{149})_2(\mathbf{6})]^{2+}$, $[Cu_3(\mathbf{149})_3(\mathbf{7b})]^{3+}$, and $[Cu_3(\mathbf{149})_3(\mathbf{2a})]^{3+}$ depicted in Figures 83 and 84, which also exhibit a [2]R and [3]R rack motif since the threaded, filamentous ligand is rigid.[262,263] Other complexes of this type have also been reported.[263−265] Like rack complexes in general, these species may adopt trans or syn conformations in which the metal ions are situated on alternating sides of the threaded ligand (e.g. in $[Cu_2(\mathbf{149})_2(\mathbf{6})]^{2+}$ and $[Cu_3(\mathbf{149})_3(\mathbf{7b})]^{3+}$) or only on one side (e.g. in $[Cu_3(\mathbf{149})_3(\mathbf{2a})]^{3+}$), respectively. The stability of the syn complex in the latter case was noted to stem in part from the large number of noncovalent interactions present, such as $\pi-\pi$ stacking and aromatic edge-to-face interactions.[263]



$[Cu_2(\mathbf{149})_2(\mathbf{6})]^{2+}$ n = 0, R = Me, m = 2

$[Cu_3(\mathbf{149})_3(\mathbf{7b})]^{3+}$ n = 1, R = Ph, m = 3

Figure 83. Mixed-motifs. Rigid-rack [2]- and [3]pseudorotaxanes displaying trans-organization of the metal ions about the central, threaded ligand. (Reproduced with permission of ref 262. Copyright 1995 Royal Society of Chemistry.)



$[Cu_3(\mathbf{149})_3(\mathbf{2a})]^{3+}$

Figure 84. Mixed-motifs. A rigid-rack [3]pseudorotaxane displaying syn-organization of the Cu(I) ions (indicated as shaded circles). (Reproduced with permission; ref 263. Copyright 1997 Wiley-VCH.)

Tertiary structure is evident in these complexes although it is trivial; the rigid multilayered, double- or triple-decker arrangement of the pseudorotaxane units can only occur when they are combined with a rack motif.

A more interesting and complicated mixed-motif compound resulted from the reaction of tetrahedral Cu(I) with the ligand **199** (Figure 85).[266] As described earlier, treatment of tetrahedral Cu(I) with a rigidly

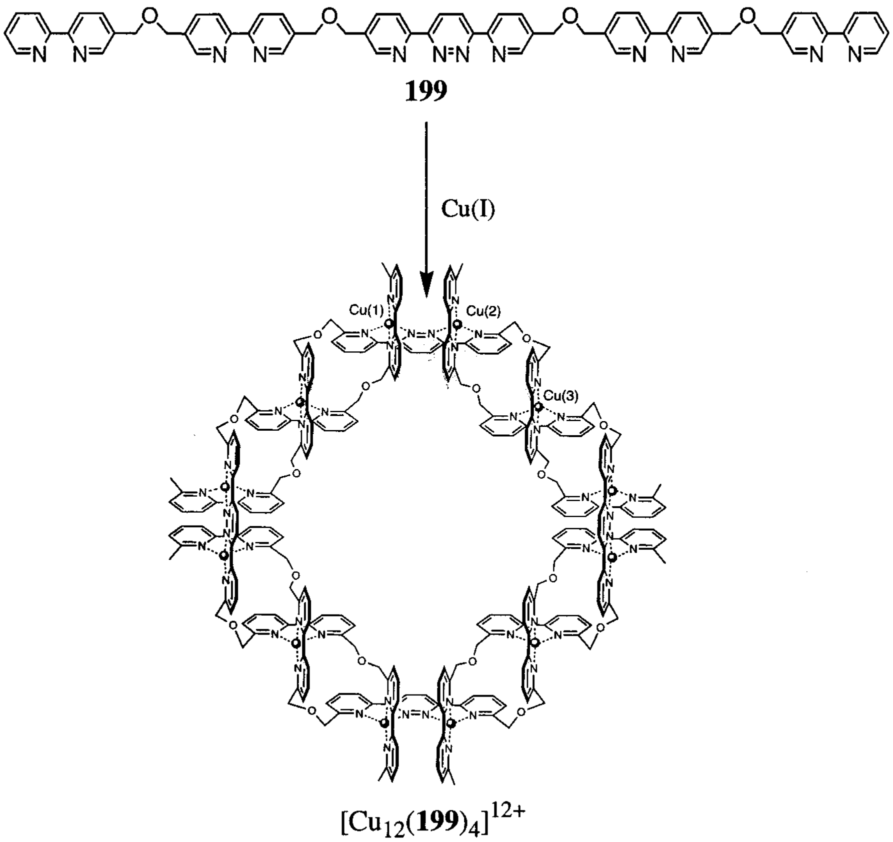


Figure 85. Mixed-motifs. The multiple subroutine self-assembly of $[Cu_{12}(\mathbf{199})_4]^{12+}$, a compound containing both helicate and grid secondary structural elements and having a cyclic, perpendicularly braided tertiary structure. (Reproduced and adapted with permission; ref 266. Copyright 1997 Wiley-VCH.)

linear poly(bis(pyridyl)pyridazine) ligand typically results in the formation of complexes displaying a grid motif, because the rigid planarity of the ligand's binding sites prevents the formation of any other structure. However, a similar reaction employing a poly(bipyridine) ligand with semiflexible spacers between the binding sites typically leads to a helicate complex. Thus, the reaction of Cu(I) with a hybrid ligand strand, such as **199**, employing both a bis(pyridyl)pyridazine and two bis(bipyridyl) binding sites connected by a semiflexible linker should lead to a complex containing both a grid and a helicate motif. Lehn and co-workers have prepared **199** and studied its reaction with Cu(I) as an example of a multiple subroutine self-assembly reaction.[266] The product of the reaction was found to be the complex $[Cu_{12}(\mathbf{199})_4]^{12+}$, which exhibited a cyclic, perpendicularly braided tertiary structure (Figure 85). This compound displays four grid and four helicate domains. While the helicate domains are individually chiral, the cyclic tertiary structure results in a molecule which is achiral overall. Figure 86 illustrates two tertiary structures which are theoretically possible for this molecule. Structure B was selectively formed in practice, presumably because of differences in the binding affinities of the two chelating sites.[266]

VI. Conclusion

Self-assembly in coordination chemistry has generated many new molecular architectures, often in one-step, in-situ processes. This has been achieved thanks to new insights into the role of the structural, stereochemical, kinetic, and other relationships required for sucessful self-assembly. The structural complexity possible in coordination compounds has been drastically enhanced in this process; today complexes displaying levels of organization upon other levels, going down to the individual constituent atoms, are well-known. Further advances may be anticipated, however. The most significant of these will involve the development of new self-assembly methodologies. As is currently the case, these are likely to arise from a biomimetic or bioinspired[267] approach.

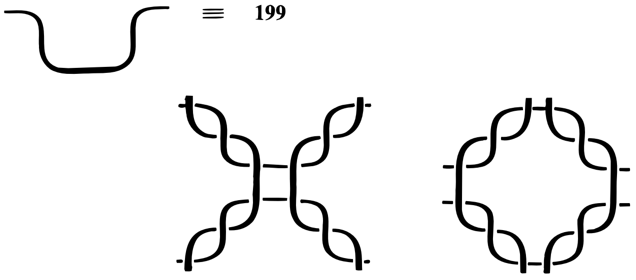


Figure 86. Mixed-motifs. Schematic depiction of two theoretically possible tertiary structures, A and B, for $[Cu_{12}(\mathbf{199})_4]^{12+}$. (Reproduced with permission; ref 266. Copyright 1997 Wiley-VCH.)

In coordination chemistry, the bio-inspired route can be broadly considered to seek novel and complicated higher structure using new metal-directed self-assembly processes. Such techniques can be expected to deliver innovative combinations of new ligands and metals for the generation of higher architecture by metal-directed self-assembly. Self-assembling metallodendrimers and more complicated boxes, among others, are likely to result.

The biomimetic direction can be considered to focus more on the self-assembly process and particularly on a closer imitation of the complexities of biological self-assembly. Thus, biomimetic methodologies would typically employ both strong (coordinate bond formation) and weak noncovalent interactions (e.g. π donor−acceptor or hydrogen-bonding interactions) in a single in-situ process; a similar hierarchy of stronger to weaker interactions is thought to sequentially drive the formation of local structures in biology before the final product architecture is settled upon.[268] Techniques of this type have already elegantly yielded entities displaying tertiary structure, such as some of the catenanes, boxes, and circular helicates described in this review. Further developments in this vein can be anticipated with new intermolecular forces being employed. This approach additionally offers interesting and undeveloped possibilities for switchable systems, host−guest based sensors, and molecular machines.[269]

VII. Abbreviations

binap	*o*,*o*′-(1,1′-binaphthyl-2,2′-diyl)bis(diphenylphosphine)
bipy	2,2′-bipyridyl
dppp	1,2-bis(diphenylphosphino)propane
cod	cycloocta-1,5-diene
cyclen	1,4,7,10-tetraazacyclododecane
diop	2,3-*o*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane
en	ethylenediamine
ES-MS	electrospray mass spectrometry
MLCT	metal−ligand charge transfer
NMR	nuclear magnetic resonance
OAc$^-$	acetate
OTf $^-$	triflate
tpy	2,2′:6′6″-terpyridine
triphos	1,1,1-tris(diphenylphosphinomethane)ethane

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IX. Additional Note: Developments Since the Submission of This Review

a. Grids. Several new coordination grids were reported in late 1999−early 2000. These include the following: (i) a magnetically coupled, alkoxide-bridged [3 × 3]G involving nine Mn(II) ions and six of a heptadentate ligand;[270] (ii) [2 × 2], [3 × 3], and [4 × 4] grids involving octahedral Pb(II) with ligands qualitatively similar to **4a**,**d**,**e**, respectively;[271] (iii) tetranuclear Zn(II)- and Co(II)-based [2 × 2]G with **4e** (R^1 = Ph or $C_6H_4N(CH_3)_2$);[272] (iv) the first grid assembly secured only by hydrogen bonds.[273]

b. Hexagons. A new example of an $A^2{}_3A^2{}_3$ hexagon has been reported by the complementary binding of **34c** and a bis(platinum(II) triflate) bis(benzyl)methyl ketone complex.[274] Each building block subtends an angle of 120°, facilitating hexagon formation.

c. Cylinders. A new class of $A^6{}_6A^6{}_6$ molecular box has been reported by Saalfrank and Raymond.[275] The reaction of a C_3-symmetric tris-bidentate pyrazolone-based ligand (L) with Ga(III) produces a D_3-symmetric $[Ga_6(L)_6]$ box in which the metal ions are octahedrally disposed about a central cavity with the ligands occupying six of the eight faces of the octahedron. As the unoccupied faces are directly opposite each other, a cylindrical void extends through the center of the cluster. The authors therefore describe the structure as a new class of molecular cylinder. This cylinder differs from previous ones in that it does not involve a triangular prismatic or related metal-ion geometry (eq J in Figure 13). Rather it is equivalent to an incompletely filled octahedron or a more completely filled hexanuclear adamantanoid box.

d. Cyclophane Boxes. A series of novel and rather stable cyclophane boxes have been self-assembled by the reaction of a tris(Zn^{2+}−cyclen)(Zn_3L^1) complex (L^1 = 1,3,5-tris(1,4,7,10-tetraazacyclododecan-1-ylmethyl)benzene) with di- or trideprotonated cyanuric acid (cyclen = 1,4,7,10-tetraazacyclododecane).[276]

d. Adamantanoid Boxes. Several new examples of adamantanoid boxes have been reported. These include (i) a new tetranuclear adamantanoid box[277] and (ii) a remarkable and unique octahedral adamantanoid box in which each bridgehead position is filled by a $Mo_2{}^{4+}$ unit.[278]

e. Dodecahedra. Stang has recently reported the first self-assembly of molecular dodecahedra.[279] The correct stoichiometric combination of tris(4′-pyridyl)-methanol (directing angles 108°) with a linear bidentate unit, such as bis[4,4′-*trans*-$Pt(PEt_3)_2OTf$]benzene (directing angle 180°), produced the corresponding molecular dodecahedron in quantitative yield. Rigid building blocks were necessary to correctly transmit the directing effects over long distances; the use of flexible linkers resulted in oligomers because of the formation of defects which could not self-correct. Each of the dodecahedra were spontaneously generated by the in-situ formation of 60 coordination bonds, involving 50 individual molecules in solution. The molecules produced had outer diameters of 5−8 nm; they were imaged by TEM micrography.

f. Linear Coordination Oligomers. A new class of linear coordination oligomer has recently been described.[280] In these molecules chirally twisted iron-(III) porphyrin dimers were self-assembled via axial intermolecular μ-oxo bridging to form high molecular weight polynuclear chains. To the best of our knowledge, this is the first example of such a process.

g. Catenanes. A very interesting recent development has seen the partial harnessing of intermetallic Au−Au bonds for the spontaneous self-assembly of gold metallocatenanes.[281] The reaction of alkylbridged diphosphine ligands $Ph_2P(CH_2)_nPPh_2$ ($n = 1-5$) with the gold diacetylide complexes $[(AuC{\equiv}C-R-C{\equiv}CAu)_x]$ (R = linear spacer groups such as C_6H_4) produces the corresponding gold metallocycles when $n = 2-3$ but the interlocked metallocatenanes when $n = 3-5$. While attractive inter-aryl forces and a lack of steric hindrance appear to be the more important factors in the spontaneous formation of the catenanes, aurophilic attractions (which have the approximate strength of hydrogen bonds) may have enhanced their formation.

X. References

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