



Review Article

## Multiple-Interaction Self-Assembly in Coordination Chemistry

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### Abstract

This work briefly reviews self-assembly reactions which involve multiple interactions in coordination chemistry. Two classes of such reactions are recognised: (i) uni-mediated processes in which several different coordinate interactions cooperate or compete with each other, and (ii) multi-mediated processes in which coordinate interactions are accompanied by one or more non-coordinate interactions. In both cases the result is often the same: the generation of considerable and hierarchical structural complexity in the product.

### Introduction

The term ‘self-assembly’ is generally agreed to involve the spontaneous aggregation of molecules into stable, non-covalently joined ensembles displaying 3-D order [1–3]. The driving force for such processes typically involves the formation of non-covalent inter- or intramolecular interactions, which may range in strength from the very weak (e.g., van der Waals attractions; bond energy *ca.* 1–5 kJ mol<sup>-1</sup>) [4] to the relatively strong (e.g., coordinate bond formation; bond energy *ca.* 40–120 kJ mol<sup>-1</sup>) [5]. Most of the interactions involved in biological self-assembly are toward the weak end of this scale; this includes the van der Waals forces mentioned above, ion-pairing interactions (bond energy *ca.* 12–20 kJ mol<sup>-1</sup>) [4], hydrophobic/hydrophilic interactions (*ca.* 12–15 kJ mol<sup>-1</sup>) [6], and hydrogen bonding (bond energy *ca.* 10–20 kJ mol<sup>-1</sup>) [4]. In artificial, non-biological self-assembly [7, 8],  $\pi$  donor-acceptor interactions (free energy of complexation *ca.* 7–20 kJ mol<sup>-1</sup>) [9], hydrogen-bonding, and coordinate bonding are widely used.

While non-covalent in nature, coordinate bonds are nevertheless highly directional and stronger than other interactions employed in self-assembly. Indeed, their effect can be considered to lie between that of 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 structures using a self-assembly process [10]. However, this rigidity and strength also limits the variety of architectural forms which may be obtained.

Self-assembly in coordination chemistry has until recently focused almost entirely on processes involving the formation of only one type of coordination bond between building blocks: so-called single-code or single-interaction self-assembly [11]. However, in the last few years reactions involving several different interactions – some of which may be non-coordinate in nature – have become increasingly common: so-called multiple-code or multiple-interaction self-assembly. This work overviews multiple-interaction self-assembly with special reference to the hierarchies of structure that can be generated. The ongoing development of this field into two main strands of investigation is also described. While examples of multiple-interaction self-assembly in coordination chemistry have appeared in several reviews [5, 10–12, 14] none of these has sought to broadly illuminate this increasingly important field.

### Single- and multiple-mediation in coordinative self-assembly

As depicted in Figure 1, self-assembly processes may be driven by the formation of linkages arising from a single type of interaction between the component parts or from multiple interactions between the component parts. Figure 1(a) depicts a single-interaction process involving the formation of one type of coordinate bond only. Figure 1(b) illustrates a multiple-interaction process involving the formation of two different types of coordinate bonds. Figure 1(c) depicts a multiple-interaction process involving the formation of one type of coordinate bond and one type of hydrogen bond. Processes of the type depicted in Figure 1(b) involve mediation by metal-ligand coordination only. They are therefore referred to as *uni-mediated multiple interaction* self-assemblies in this work. Processes like that depicted in

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Figure 1(c) involve mediation by two different classes of interaction; they are therefore referred to as *multi-mediated, multiple interaction* self-assemblies in this work. These divisions and sub-divisions are illustrated above (a)–(c) in Figure 1 for self-assembly in general.

While the three processes illustrated in Figure 1(a)–(c) may appear outwardly similar, they have very different capacities to generate complicated structural architecture. The formation of only one type of coordinate bond between assembling components severely limits the range of product architectures which may be obtained because of its inherent directionality and specificity. For example, if a tetrahedrally disposed metal ion is used in such an assembly, only structures having bond angles of *ca.* 109.5° are possible. The formation of two different coordinate bonds during a self-assembly increases the variety of possible architectures because two different types of coordinate bonds are now present. The formation of both a coordinate and a non-coordinate linkage still further increases the architectural possibilities because not only are two different interactions present, but each has drastically different physical properties. Thus, for example, while the coordinate bond is relatively strong and rigidly directed, the non-coordinate interaction is weak and more flexibly directed.

Increasing the range of product architectures available in such reactions is important because it increases the probability of obtaining a novel structure – possibly one having novel physical properties. More significantly, it implies that a small change to the system may create a large change in the product architecture. An enhanced capacity for control or manipulation of the self-assembly process therefore exists. Because such a change may be reproducible under invariant conditions, the self-assembly process can be considered a form of encoding in which the product architecture – and any unusual physical properties it may possess – indicates the conditions under which it was formed. In the case of reversible self-assembly, it additionally becomes conceivable for the product to “switch” between two different architectures upon a change in the conditions or by the deliberate application of an external stimulus (e.g., an electrochemical potential). From a practical point of view, this raises the possibility of, for example, a “smart” catalyst, whose mode of operation differs with different substrates, or a molecular information storage, encryption, or computational system in which the physical properties associated with the different product architectures reveal the switch setting.

For reasons such as these, the field of coordinative self-assembly is seeing an increased interest in multiple-interaction processes. Similar multi-disciplinary developments can, incidentally, be discerned in the study of  $\pi$ -based and hydrogen-bonding based self-assembly. Uni- and multi-mediated approaches therefore constitute two distinct and developing strands of investigation along which the study of artificial self-assembly is advancing. As briefly noted previously [10], these two directions are essentially bio-inspired (uni-mediated) or bio-mimetic (multi-mediated) in nature.

The field of uni-mediated, multiple-interaction self-assembly in coordination chemistry has largely been de-

veloped by Lehn and co-workers [11]. These researchers have described several reactions in which different metal ions are induced to interact selectively with different binding sites on a single, hybrid ligand. Because each interaction in such processes can be considered to execute a set of instructions encoded into the structure of the ligand and the stereochemistry of the metal – like the routine of a computer program – they have termed such processes *multiple sub-routine self-assembly* [13]. Several examples of multiple sub-routine self-assembly are described below.

The field of multi-mediated, multiple-interaction self-assembly in coordination chemistry is exemplified by the work of Fujita and co-workers [14]. These researchers have developed a range of reactions in which coordinative self-assembly is accompanied *in situ* by weaker interactions such as  $\pi$  donor-acceptor and hydrophobic/hydrophilic interactions. They have termed such procedures *multiple-molecular recognition processes* [14]. Reactions of this type can be considered the artificial equivalent of most self-assembly in biology because a hierarchy of stronger to weaker interactions drive the formation of local structure before the final product architecture is settled upon [15].

Despite their different names and contexts, the two concepts – *multiple sub-routine self-assembly* and *multiple molecular recognition processes* – are very similar, differing only in the nature of the interactions involved (i.e., uni- vs. multi-mediated).

### Multi-mediated processes

Because of their strength relative to other types of interactions, coordinate bond formation is the primary driver of all multi-mediated, multiple-interaction self-assemblies in coordination chemistry. The non-coordinate interactions involved in such processes generally fulfil a supplementary function in which they play one of the following roles:

- (a) *multi-mediated thermodynamic self-assembly*: in a self-assembly leading to the formation of the thermodynamically most-favoured product [2], the non-coordinate interactions provide a thermodynamic impetus for further processes which substantially alter the product architecture.
- (b) *multi-mediated assisted or directed self-assembly* [2]: the non-coordinate interactions assist or direct the self-assembly by weakly ‘pre-assembling’ or templating an ensemble before coordinate bond formation occurs. Alternatively, they selectively stabilise one particular product architecture out of a variety of available structures.
- (c) *multi-mediated self-assembly with precursor modification* [2]: the non-coordinate interactions bring about a physical change in one or more of the reagents which allows them to self-assemble properly.
- (d) *multi-mediated switchable self-assembly*: when activated, non-coordinate interactions switch the self-assembled product from one architecture to another. When deactivated, the product switches back to its original architecture.

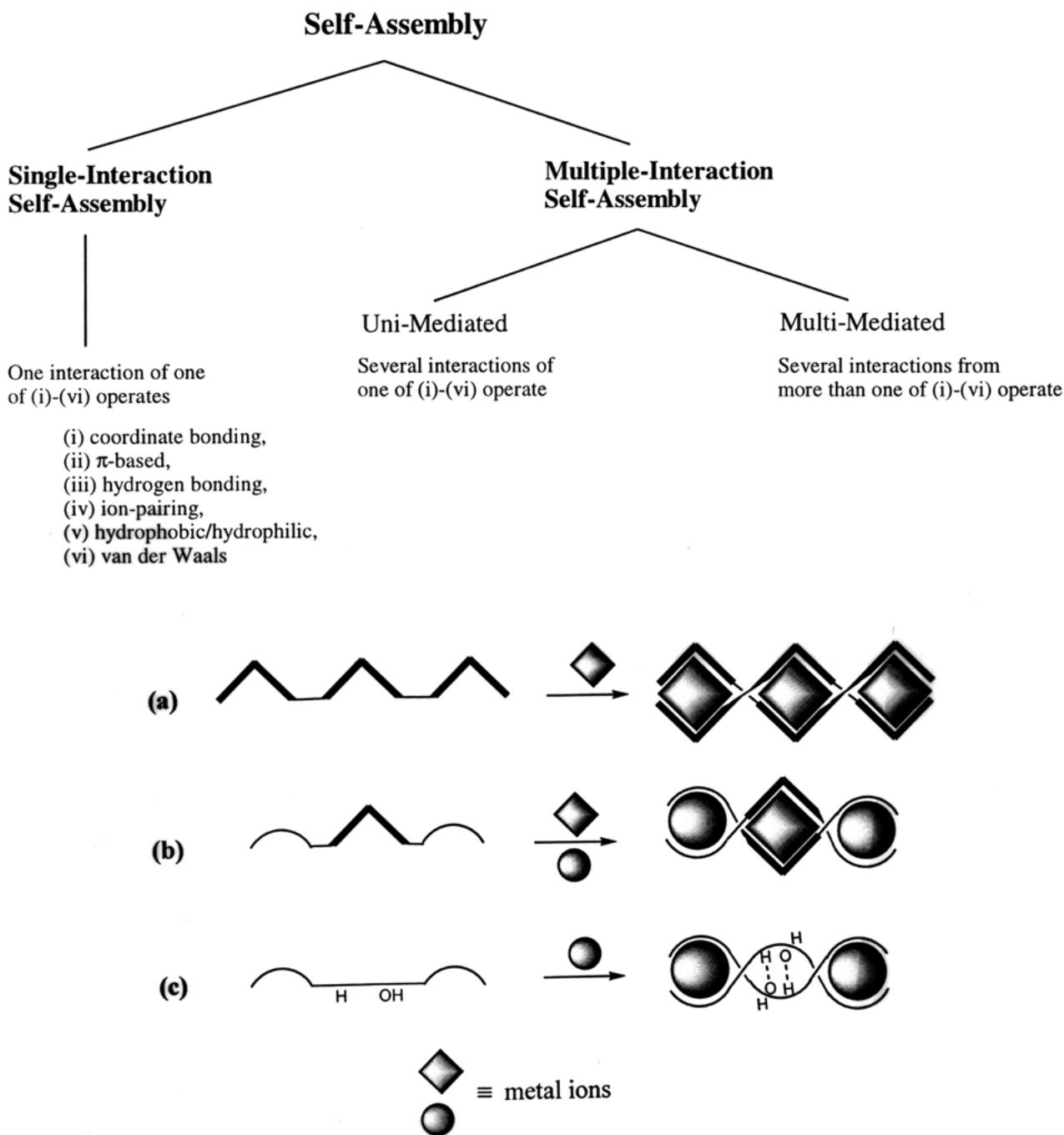


Figure 1. Classes of self-assembly. Schematics depicting the formation of double-helical complexes by coordinative self-assembly involving: (a) a *single-interaction* process, (b) a *uni-mediated, multiple-interaction* process, (c) a *multi-mediated, multiple-interaction* process (also involving hydrogen-bond formation).

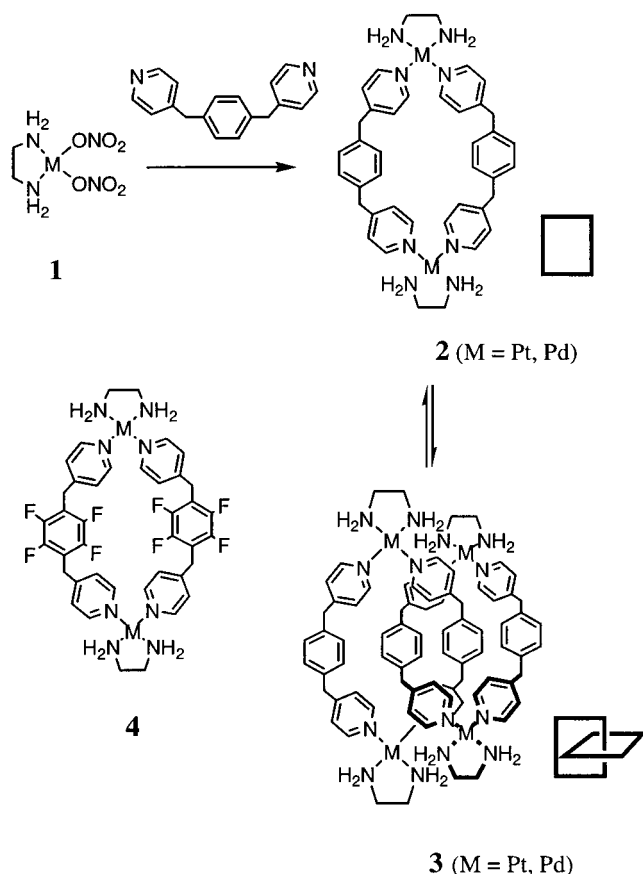
Examples illustrating (a)–(d) are discussed below.

#### *Multi-mediated thermodynamic self-assembly*

*Catenanes* are species in which two rings are interlocked within each other. Their synthesis using classical organic chemistry is typically formidable since a ring closure reaction is required in which two rings are also interlocked; this is statistically a highly unlikely possibility. However *catenanes* can be readily formed if two self-assembly processes can be simultaneously established – one for ring closure and the other for ring-interlocking. Fujita *et al.* have used this ap-

proach in the self-assembly of several [2]*metallocatenanes* [14, 16].

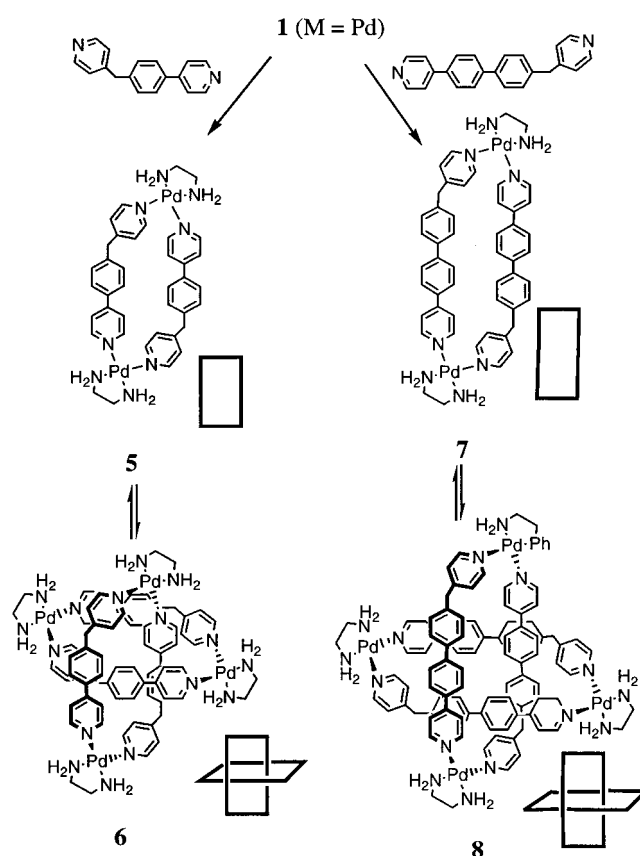
In the Pd(II) system illustrated in Scheme 1 [17], the formation of the free metallocycle **2** (M = Pd) was driven by the enthalpy of formation of the Pd–N bonds, which dominated all other non-covalent interactions. Once this process was complete however, the lability of the coordination bonds permitted the *in-situ* formation of the interlocked *catenane* **3** (M = Pd). An investigation of this process revealed that when concentrating a solution of **2** (M = Pd) from 2 mM to 50 mM, the equilibrium shown in Scheme 1 shifted to



Scheme 1.

favour **3** (M = Pd), indicating that entropic effects played a role. The use of D<sub>2</sub>O as solvent, instead of water, also increased the proportion of the *catenane*, suggesting the involvement of hydrophobic interactions (since D<sub>2</sub>O is more polar than water). Use of the analogous ligand **4** (Scheme 1) did not result in formation of the *catenane* [14], indicating that attractive edge-to-face or CH- $\pi$  interactions were also significant. In essence therefore, **3** (M = Pd) formed spontaneously because two molecules of **2** (M = Pd) bound each other in their cavities. This was driven by: (i) hydrophobic interactions to minimise the contact of their cavities with the water solvent, (ii) the formation of  $\pi$ -stacking interactions between two such rings, and (iii) an entropic effect due to a decline in the number of species present in solution after interlocking. The role of the non-coordinate interactions in this process was crucial; they were estimated to double the free energy change, making the *metallocatenane* stable enough to be quantitatively self-assembled at high concentrations [14]. A ‘Möbius strip’ mechanism has been proposed for the formation of **3** [18].

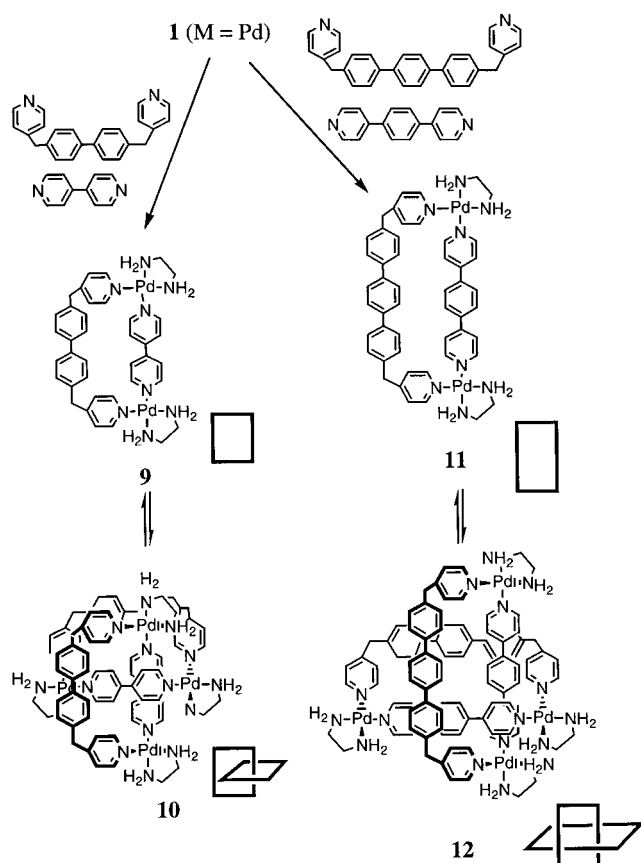
Fujita has prepared several [2]*metallocatenanes* involving interlocked rectangular boxes [14, 19]. The complexes **6**, **8**, **10**, and **12** (Schemes 2 and 3) were obtained in high yield as two- and three-species-eight component systems, respectively. In these cases the corresponding *metallorectangles* **5**, **7**, **9**, and **11** were not observed, indicating that the equilibria in Schemes 2 and 3 strongly favoured the catenated products. This remained the case even in highly dilute solution (1 mM) or in a less polar



Scheme 2.

medium (50% methanol-d<sub>4</sub>). Very efficient  $\pi$ - $\pi$  stacking of the four aromatic systems within their respective central cavities appeared to play the most significant role. A van der Waals separation of 3.5 Å between the planar rings in a cycle seem to be ideal to promote catenation of this type. As the component *metallorectangles* in these molecules have directionality, the resulting *metallocatenanes* are topologically chiral. This arises because the rings may be interlocked in either a clockwise or anti-clockwise manner [20]. Using <sup>1</sup>H NMR, the complexes **6** and **8** were shown to be topological chiral, proving that the catenated structures existed in solution. However the three-species-eight component systems **10** and **12** were selectively obtained in only one topological form, both in solution and in the solid state.

A similar principle has been employed for the self-assembly of discrete interlocked cages [21]. By retrosynthetic analysis of a target framework, a cage complex was designed in which the interplanar surface-to-surface distance between the ‘floor’ and ‘ceiling’ of the central cavity was 3.5 Å; this being the ideal distance for inclusion of an aromatic ring. The reaction of **1**, **13** and **14** in a ratio of 3 : 1 : 1 respectively, initially produced a kinetic distribution of oligomers (Scheme 4). However, this was gradually converted to the desired thermodynamic product **15** (M = Pt) during heating of the solution over 3 d at 100 °C. The elevated temperature was necessary to labilise the Pt(II)-pyridine bonds. The structure was confirmed by X-ray crystallographic analysis which showed that quadrupole stacking of the central aromatic rings had occurred; this stacking strongly stabilises the

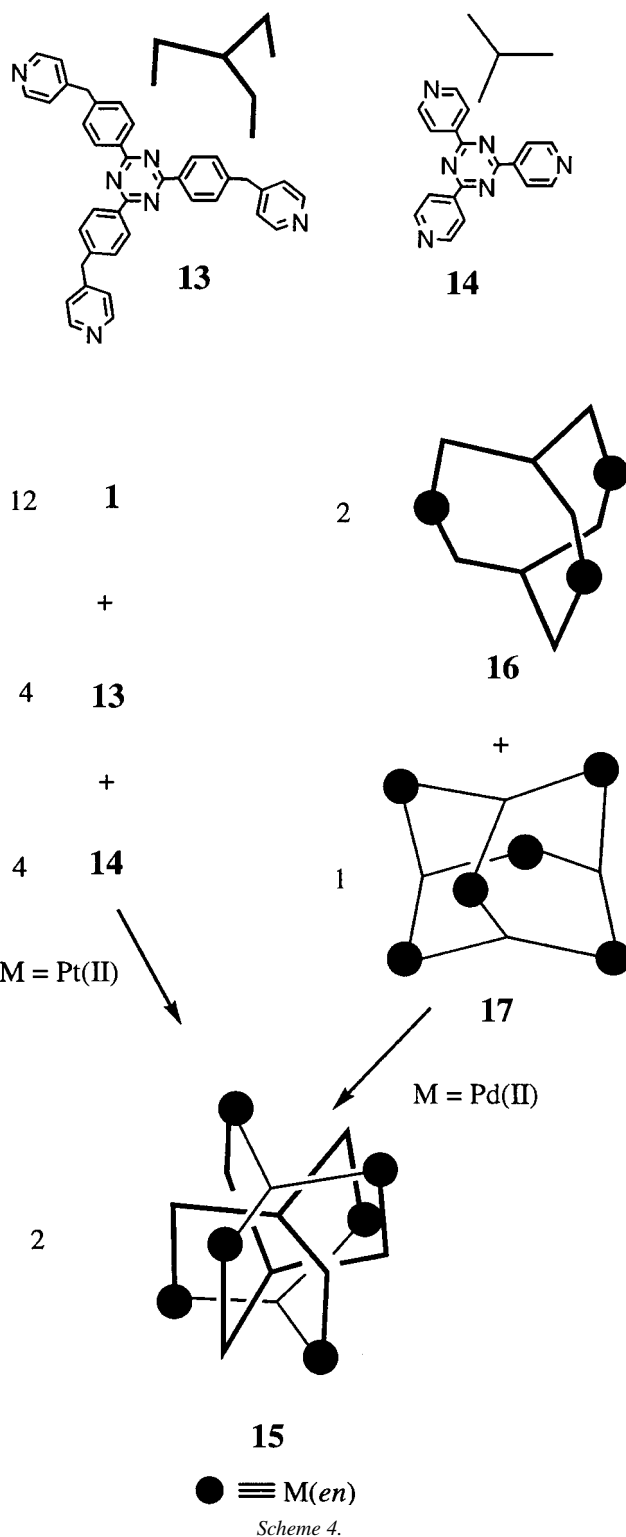


Scheme 3.

assembly, so that the corresponding non-interlocked cycles were not observed. The analogous palladium complex **15** ( $M = \text{Pd}$ ) was prepared by combining the two preformed cages **16** and **17** in a reaction which serves as a remarkable illustration of the specificity of thermodynamically-driven self-assembly.

Since individual metalocycles or cages are structurally distinct entities which are readily viewed only at a more macroscopic level, it can be argued (along the lines proposed by Lehn [22, 23]) that their cyclic, closed architecture constitutes a higher level of structural organisation: *viz.* secondary structure. Because the interlinked nature of two metalocycles or cages in such an assembly can only be described using a still further hierarchy of structure, the *catenane* motif represents a tertiary structure in such molecules.

Another example illustrating the generation of hierarchical structural complexity using multiple-interaction self-assembly of this type can be found in the spontaneous formation of *multi-ring catenanes*. Such molecules have several smaller rings threaded onto a single larger ring and have recently been termed *molecular necklaces* [24]. The first self-assembled *molecular necklace* was reported by Kim and co-workers who obtained it using a multi-mediated process [24]. A 1 : 1 : 1 mixture of cucurbituril **18** ('bead' molecule), *N,N'*-bis(4-pyridylmethyl)-1,4-diaminobutane dihydronitrate **19** ('string' molecule), and **1** ( $M = \text{Pt}$ ) ('angle connector molecule') (Figure 2) was re-



Scheme 4.

fluxed in water for 24 h, followed by the addition of ethanol. The molecular necklace **20** was obtained from this mixture in 90% yield. While the three cucurbituril-based *catenane* structures are self-assembled by hydrogen bonding interactions, it is the formation of the coordination bonds which generates the overall metalocyclic structure of the molecule. As noted above, while Pt(II) is normally too kinetically inert to participate in self-assembly processes, it typically becomes more labile at high temperature, permitting formation

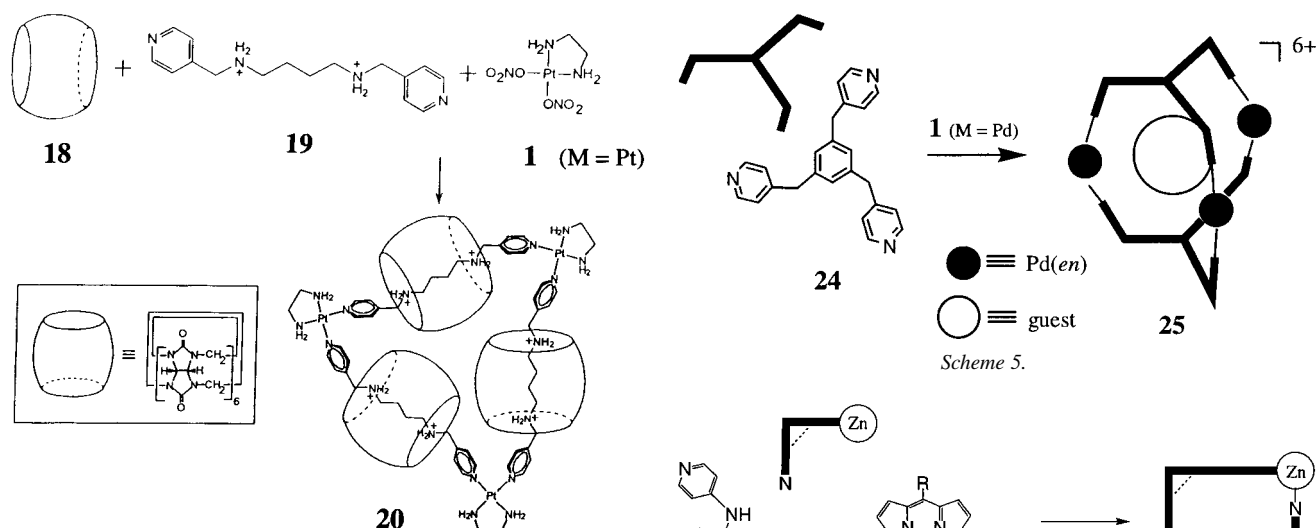


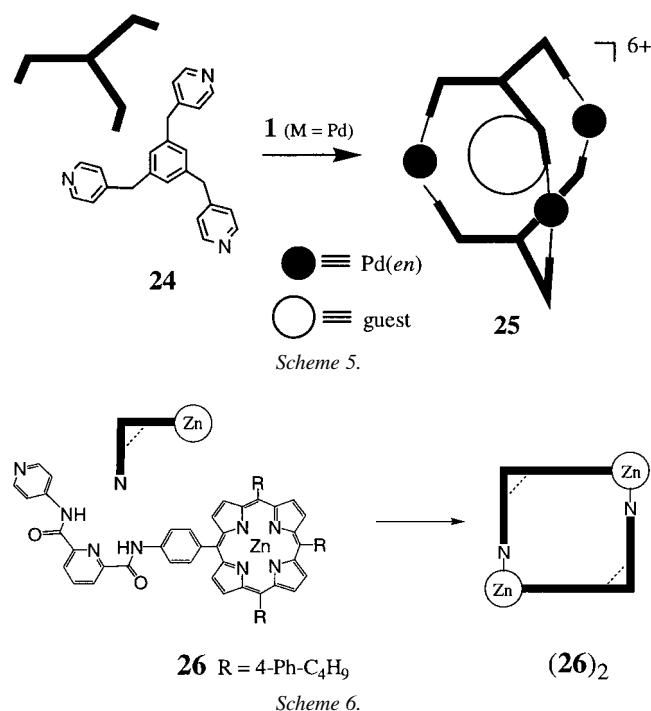
Figure 2. Self-assembly of a Molecular Necklace. Reproduced with permission of Ref. 24; Copyright 1998 American Chemical Society.

of the thermodynamic product. The three *catenane* motifs encompass one hierarchy of structure above the covalent interconnections present; they therefore constitute a secondary structure in this molecule. The metallocyclic arrangement involves a still higher hierarchy and consequently comprises a tertiary structure.

#### Multi-mediated assisted or directed self-assembly

Many elegant coordinative self-assembly processes involving induced-fit molecular recognition are multi-mediated. One example of such a process is Lehn and co-workers's selective formation of *circular helicates* of different size according to anion preference. The pentanuclear *circular helicate*  $[5]^2\text{cH}$  **22** was exclusively generated from **21** only when the chloride salt of octahedral Fe(II) was used (Figure 3) [22, 25]. When  $\text{FeSO}_4$ ,  $\text{Fe}(\text{BF}_4)_2$ , or  $\text{FeSiF}_6$  were used as starting materials, the hexanuclear  $[6]^2\text{cH}$  **23** was obtained instead; this complex can accommodate a  $\text{SO}_4^{2-}$  ion in its central cavity [22]. The use of  $\text{FeBr}_2$  led to a mixture of the  $[5]^2\text{cH}$  and  $[6]^2\text{cH}$  species. In all cases, the corresponding *helicates* were formed as intermediates in the reaction [26]. As **23** could be spontaneously converted to **22** by the addition of chloride ions, it appears that the transformation of the *helicates* into the *circular helicates* occurred via the self-assembly of a receptor according to the preferences of its substrate [22]. This means that a library [27] of oligomeric toroidal structures having a 1 : 1 metal : ligand stoichiometry was most likely present in solution and that the chloride screened this collection for the most suitable receptor, which was then selectively stabilized. A product formed in such a way is expressed in the same way that products are expressed in biology.

As pointed out by the authors [22], the closed, cyclic nature of *circular helicates* constitutes a tertiary structure in these molecules. The comparable primary structure involves the covalent connectivity of the atoms in the ligands, while the multiple-stranded helicity of the walls of *circular helicates* is the equivalent of a secondary structure. All



three levels of structural organisation are formed in a single thermodynamic self-assembly process.

Another example involving a product which is expressed as a result of multi-mediated, multiple-interaction self-assembly is the formation of the cyclophane box **25** depicted in Scheme 5 [28]. This species was spontaneously formed when an aqueous solution of the tridentate ligand and 1,3,5-tris(4-pyridylmethyl)benzene **24** was mixed with  $(en)\text{Pd}(\text{NO}_3)_2$  **1** (*en* = ethylenediamine) in the presence of an aromatic guest, such as (4-methoxyphenyl)acetic acid. Without the guest, poorly defined oligomeric complexes were obtained. However when the guest was added to the oligomers, the system spontaneously converted to **25**. Thus, a thermodynamically-driven self-assembly process which was directed and mediated by both coordinate interactions and hydrophobic-hydrophilic interactions, took place.

#### Multi-mediated self-assembly with precursor modification

Non-coordinate interactions have also pre-organised molecules, enabling them to participate in coordinative self-assembly. Such interactions also stabilise the resulting ensembles. For example, the zincated porphyrin **26** spontaneously forms the very stable molecular square  $(\mathbf{26})_2$  (Scheme 6) because intramolecular hydrogen bonding in its side-chains reduces the angle subtended by the linkers from the  $120^\circ$  expected for *meta*-substituted pyridyls to  $96^\circ$ . Intermolecular Zn–N coordination, generating  $(\mathbf{26})_2$  is therefore able to occur at low concentrations ( $10^{-7}$ – $10^{-2}$  M in chloroform at room temperature) [29].

A similar example exists in the spontaneous assembly of the square  $[(\mathbf{27})(\mathbf{28})]$  (Scheme 7) [30]. Intramolecular hydrogen-bonding in its side-chains – like that in  $(\mathbf{26})_2$  – is thought to assist in the formation of this discrete 1 : 1 complex, secured by Zn–N coordinate bonds.

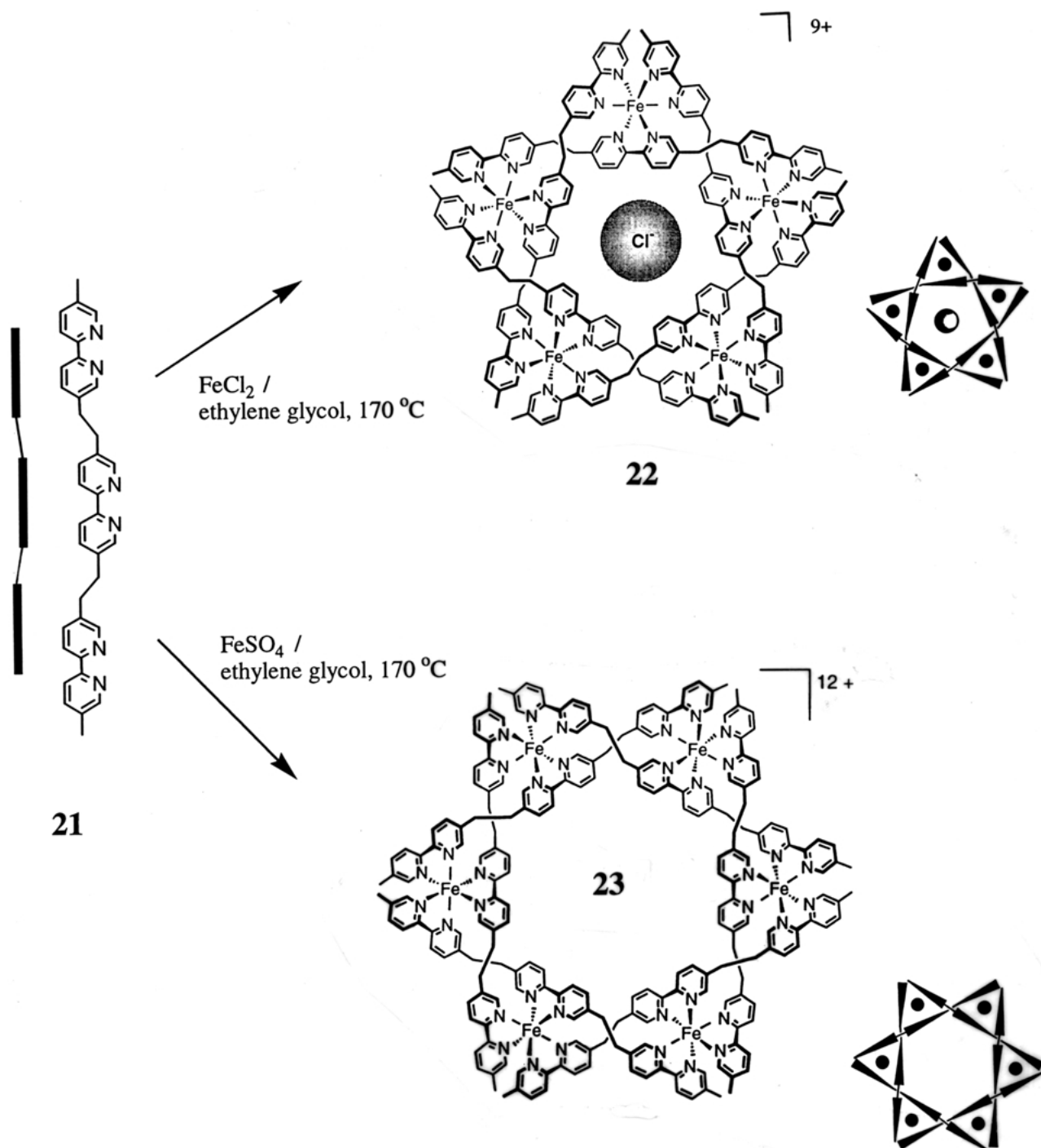


Figure 3. Self-assembly of Circular Helicates. Reproduced with permission of Ref. 22; Copyright 1997 American Chemical Society.

#### Multi-mediated switchable self-assembly

Several examples of multi-mediated self-assembly processes, in which one or more of the individual steps can be controlled in a switchable way, are known. One such system is depicted in Scheme 1 when  $M = \text{Pt}$  [17]. The Pt-N coordination bonds in **2** ( $M = \text{Pt}$ ) are normally inert and therefore 'locked'. However, when the solvent medium is made more polar and the temperature is elevated, these bonds become labilized and are therefore 'released'. The addition of  $\text{NaNO}_3$  followed by concentration of the mixture at  $100\text{ }^\circ\text{C}$  consequently led to the *catenane* **3** ( $M = \text{Pt}$ ).

This species could then be trapped by removal of the salt and cooling, to re-'lock' the coordination bonds. Figure 4 illustrates the sequence of events in this 'molecular lock'.

Another example is the switchable [2]*catenane* **29** prepared by Sauvage and co-workers (Scheme 8). Here coordinate metal-ligand- and  $\pi$  donor-acceptor interactions compete to control the topographical structure of the *catenane* [31]. Upon removal of the coordinating Cu(I) in **29**, the rings of the *catenane* swing to the structure **30** which is stabilized by interactions between  $\pi$ -donors (**D**) on one ring and  $\pi$ -acceptors (**A**) on the other.

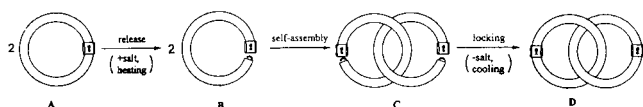
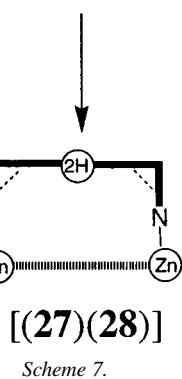
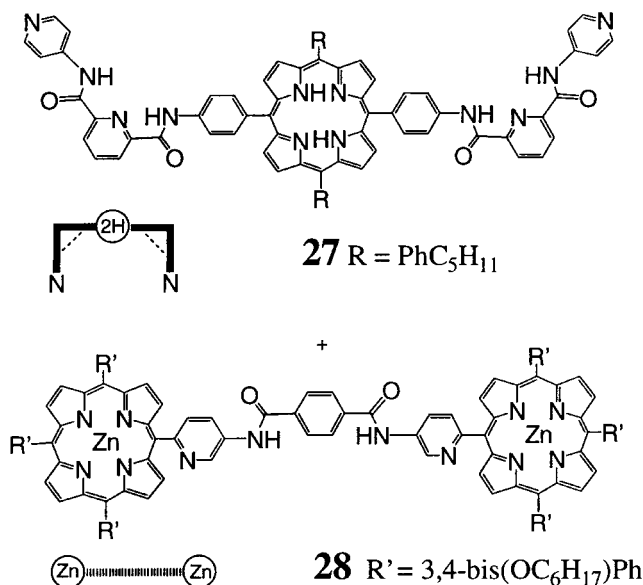
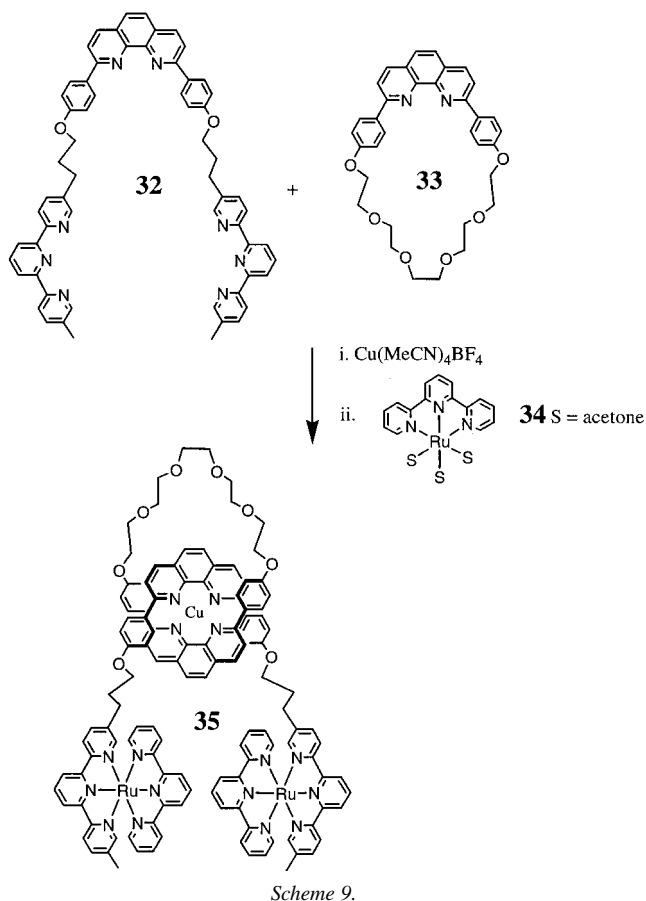
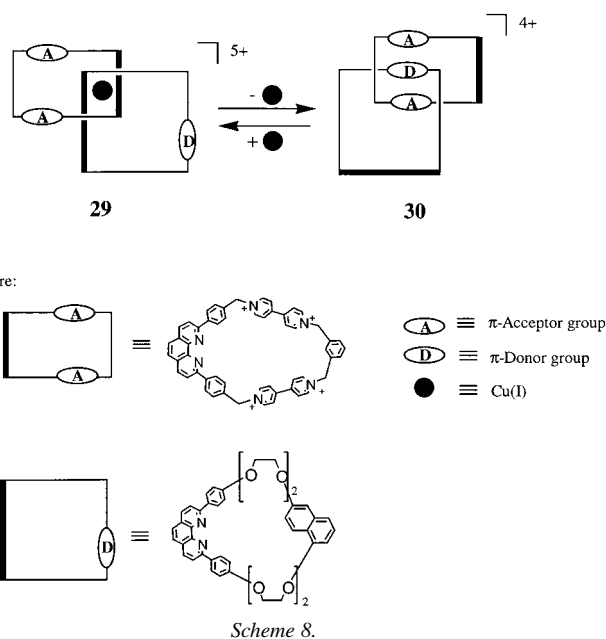


Figure 4. Principle of switchable *catenane* formation. The coordination bonds in the metalocycle **1** ( $M = \text{Pt}$ ) are kinetically inert (A). Upon addition of  $\text{NaNO}_3$  and heating to  $100\text{ }^\circ\text{C}$ , these bonds are labilized (B). Concentrating the solution leads to the self-assembly of the metalocatenate **2** ( $M = \text{Pt}$ ) (C). Removal of the salt and cooling of the solution restores the normal lack of kinetic lability in the  $\text{Pt-N}$  bonds (D). (Reproduced with permission of Ref. 39. Copyright 1996 Chemical Society of Japan).

A system which undergoes switchable rotation has also been developed in a  $\text{Cu(I)}$ -linked  $[2]$ rotaxane containing a  $\text{Au(III)}$  porphyrin as part of the ring ligand and  $\text{Zn(II)}$  porphyrins as the stoppers in the filamentous ligand [32]. Removal of the  $\text{Cu(I)}$  induces the filamentous porphyrins to swing around and eclipse the  $\text{Au(III)}$  porphyrin. Attractive interactions between the  $[\text{Au-porphyrin}]^+$  (electron acceptor) and the  $[\text{Zn-porphyrin}]^+$  (electron donor) bring about this change.

### Uni-mediated processes

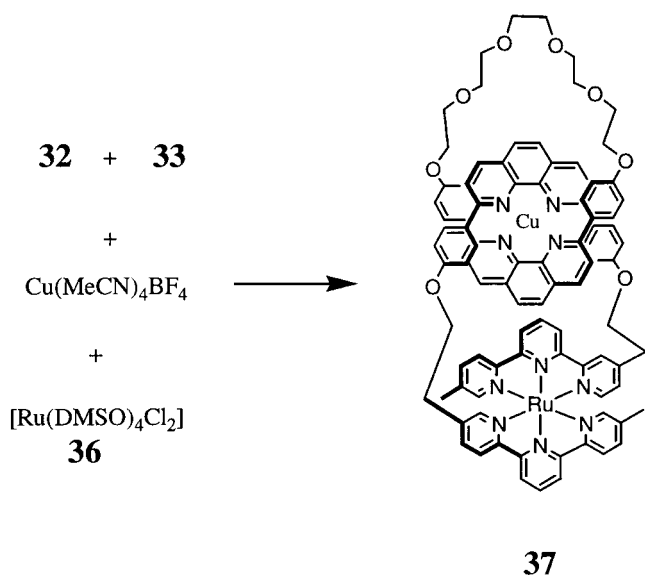
Several examples of uni-mediated, multiple-interaction self-assemblies are known in coordination chemistry. Such pro-



cedures have proved particularly useful in the one-step formation of interlocked structures.

The tri-segmented ligand strand **31** (Figure 5) contains bidentate binding sites at its termini with a central tridentate binding site. When added to  $\text{Ag(I)}$  and  $\text{Fe(II)}$  in the correct stoichiometry, **31** self-assembles into the complex  $[\text{FeAg}_2(\mathbf{31})_2]^{4+}$  having the  $[2]$ metalocatenate structures III and IV shown in Figure 5 [33]. The complex forms be-





Scheme 10.

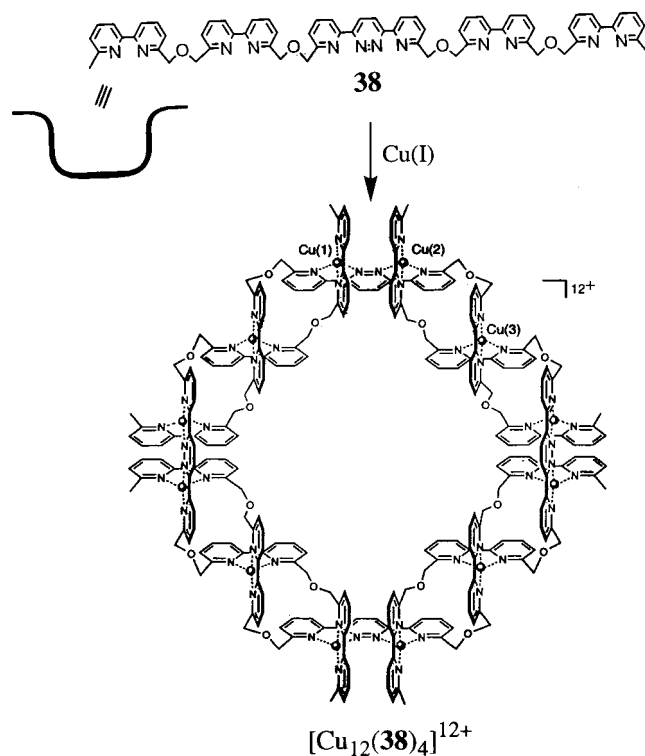


Figure 6. Schematic depiction of the uni-, metal-mediated self-assembly of the perpendicularly-braided complex,  $[\text{Cu}_{12}(\mathbf{38})_4]^{12+}$  (structure B below), containing *helicate* and *grid* structural domains. While theoretically possible, the structure A was not observed. (Reproduced with permission of Ref. 23. Copyright 1997 Wiley-VCH).

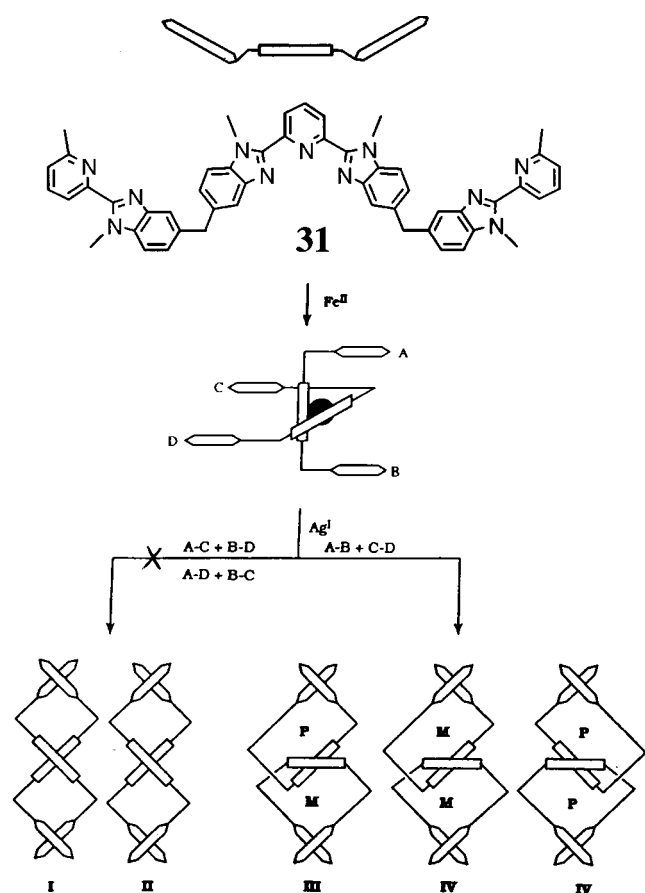


Figure 5. Uni-, metal-mediated assembly of a heterotrimeric [3]metallocatenate using  $\text{Fe}(\text{II})$  and  $\text{Ag}(\text{I})$ . (Reproduced with permission of Ref. 33. Copyright 1995 Wiley-VCH).

cause the tetrahedral  $\text{Ag}(\text{I})$  units selectively bind the outer, bidentate sites, while the octahedral  $\text{Fe}(\text{II})$  ions selectively coordinate the central binding sites of the two ligand strands. Coordinate bond formation occurs entirely selectively, with neither metal interfering with the binding site preferred by the other. As each interlocked ring constitutes its own helical domain [12], each may have *M* or *P* stereochemistry. The *meso* (*P,M*)- and the *racemic* diastereomer (which consists of the (*M,M*)- and (*P,P*)-enantiomers) were obtained in the statistically expected ratio of 1:1. The individual metallocycles (of *M*- or *P*-helicity) consequently represent a secondary structure in this molecule, while the catenated motif ((*M,M*)-, (*P,P*)-, or (*M,P*)-helicity) displays a tertiary structure. The *helicate* products I and II in Figure 5 were not observed.

The reaction of ligands **32** and **33** with  $\text{Cu}(\text{MeCN})_4\text{BF}_4$  and then  $[\text{Ru}(\text{tpy})(\text{Me}_2\text{CO})_3][\text{BF}_4]$  **34** resulted in the spontaneous formation of the rotaxane **35** having two  $\text{Ru}(\text{tpy})_2$  groups as stoppers (Scheme 9) (*tpy* = 2,2':6'6''-terpyridine) [34, 35]. *Catenanes* have been prepared in similar fashion;



A and B in Figure 6 are hypothetically possible. Structure B was selectively formed in practice, presumably because of differences in the binding affinities of the two chelating sites.

The concept of multiple sub-routine self-assembly has been further elaborated using ligand **39** (Figure 7) [37]. This material generates either of the tertiary structures A or B (also depicted in Figure 6), depending on the stoichiometry of the metal ions with which it is combined. Treatment with 8 equiv. of Cu(I) and 4 equiv. of Cu(II) delivers the 'linear combination' complex shown on the left of Figure 7, which has the tertiary structure A. However, treatment with 4 equiv. Cu(I) and 8 equiv. Cu(II) generates the 'crossover' complex shown on the right of Figure 7, which has the tertiary structure B. A four-electron electrochemical reduction of the crossover complex causes a switch in the product architecture to that of the linear combination architecture. A four-electron oxidation reverses this change.

Thus, by varying the stoichiometry of the metal ions, different output architectures were obtained. These architectures could, moreover, be electrochemically switched from one to another. The same molecular information can therefore produce different output structures depending on how it is processed. This multiprocessing capacity has important implications for the study of 'programmed' chemical systems and also for molecular information storage, encryption, and computation [38].

## Conclusion

The studies described in this work indicate that multiple-interaction self-assembly in coordination chemistry offers an extraordinarily useful route to complex molecular structure, particularly that of intertwined species such as *catenanes* and *rotaxanes*. Such compounds are, additionally, obtained in a one-step process because several interactions operate simultaneously. Indeed, it is largely thanks to such procedures that coordination chemistry can now legitimately claim to produce discrete complexes whose structural complexity approaches that common in biology. The dramatic impact that this new field has had to date suggests that it offers outstanding potential for the development of novel, highly organised compounds in the future. Unusual physical properties and novel opportunities in materials chemistry will almost certainly accompany such advances.

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