Metal Based Self-Assembly

L. F. Lindoy

University of Sydney

Reference:

Self-Assembly in Supramolecular Systems
L. F. Lindoy and I. M. Atkinson,
Royal Society of Chemistry, 2000,
Cambridge UK

A Monograph in the series: Supramolecular Chemistry,
Ed. J. F. Stoddart

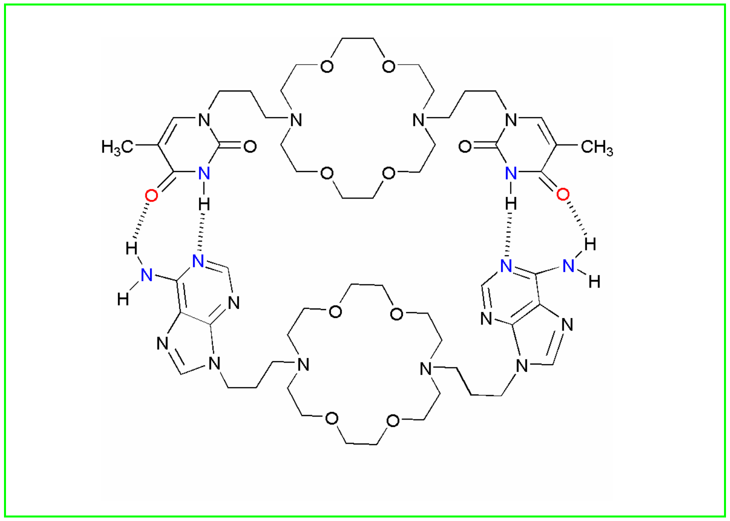
http://www.rsc.org/is/books/selfassembly.htm

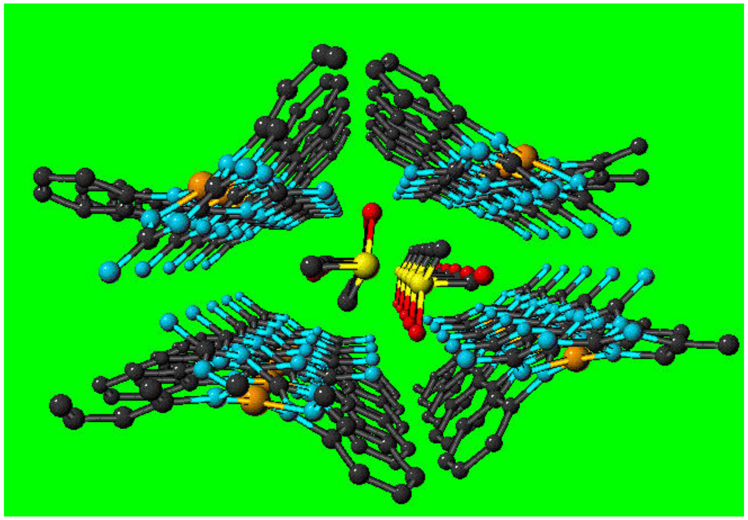
1987 Nobel Prize to Donald J. Cram Jean-Marie Lehn Charles J. Pedersen

For their development of the field of supramolecular chemistry

Supramolecular Chemistry- Focus on Discrete Assemblies

Crystal Engineering- Focus on Non-Discrete Assemblies





Supramolecular systems are still simple relative to DNA, viruses etc. They do not yet match biological systems in subtlety or function – therein lies the challenge!

Tobacco mosaic virus: 2130 protein units self-assemble around a RNA strand via non-covalent interactions

Supramolecular Chemistry

The designed chemistry of the intermolecular bond'

J.-M. Lehn

- Interdisciplinary
- Weaker non-covalent interactions including hydrogen bonding – same forces as nature employs
- Can also include M-donor bonds (to give metallo-supramolecular chemistry)

- Now many systems, size range: ~ 1 – 1000 nanometres

‘

- Mimics Nature’s way of doing things – but does not necessarily copy nature

- Complementarity, recognition, self-assembly, preorganisation and (even) self-replication are part of the language

- Self assembly – convergent synthesis – reversible → thermodynamic product but sometimes combined with traditional covalent synthesis

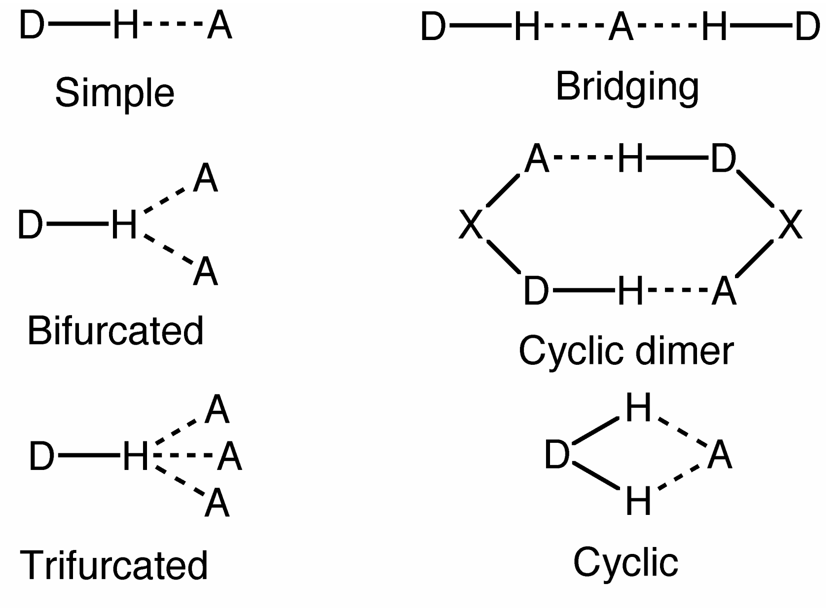
Some Preliminaries

Non-Covalent Interactions

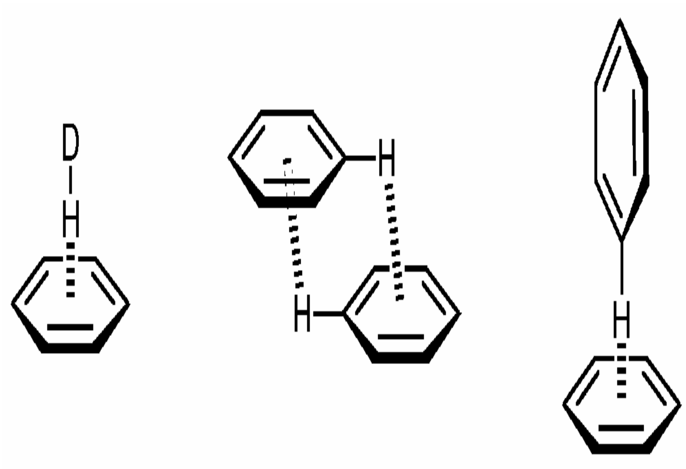
- Hydrogen bonding
- π-π Stacking interactions
- Electrostatic interactions (ion-ion, ion-dipole and dipole-dipole)
- Dispersion and induction forces (van der Waals forces)
- Hydrophobic/solvatophobic interactions

Hydrogen Bonding

- Hydrogen bonding is the most directional of all the intermolecular interactions and is also the most widely used interaction in forming supramolecular structures.
- Hydrogen bond formation covers a wide variety of interaction types.



Classical hydrogen bonds



π-Facial interactions

Hydrogen Bonding

An X–H···A interaction is called a 'hydrogen bond', if (i) it constitutes a local bond, and (ii) X-H acts as proton donor to A. (Due to Steiner)

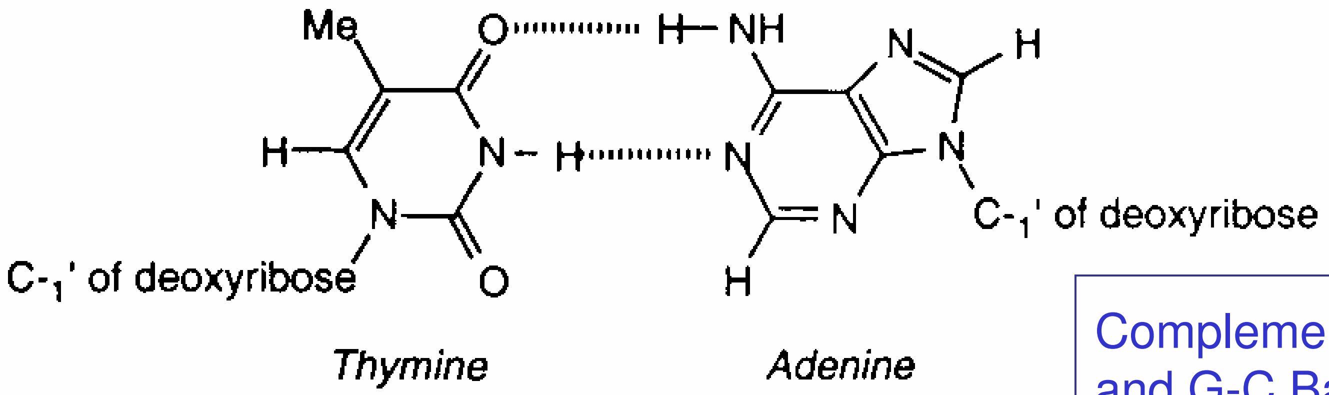
Some common hydrogen bond donor groups are C-H, N-H, O-H, S-H, P-H, F-H, Cl-H, Br-H and I-H while acceptor groups include N, O, P, S, F, Cl, Br and I as well as a range of unsaturated aliphatic and aromatic compounds.

The degree of directionality in the resulting hydrogen bond is quite dependent on the polarity of the donor.

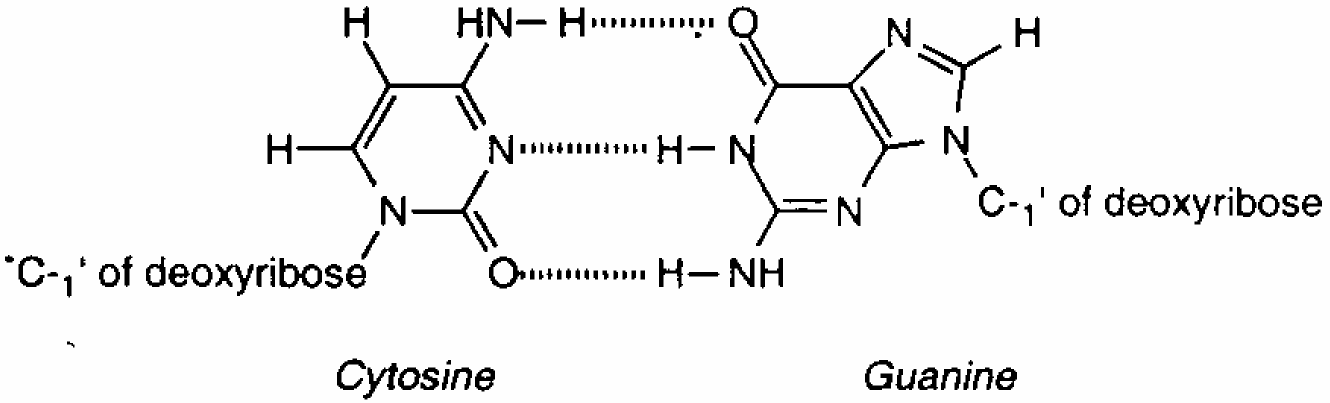
The strength of such bonds can range from very weak to substantial, typically falling in the approximate range of 3 - 40 kcal mol^{-1}.

Additivity of Weak Interactions such as H-Bonds

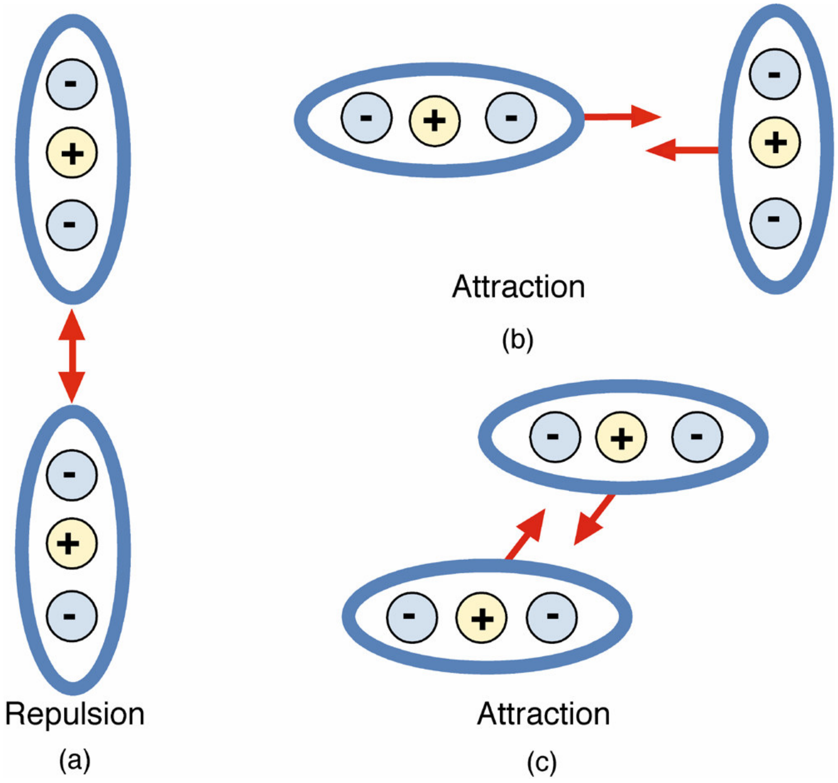
- A number of hydrogen bonds may act in unison resulting in, overall, strong forces operating between the individual molecular components



Complementary A-T and G-C Base Pairs in DNA



π-π Stacking



Bonding model based on the concept of an idealised π-system that consists of a positively charged σ framework (+ le) sandwiched between two regions of π-electron density (2 x -½e).

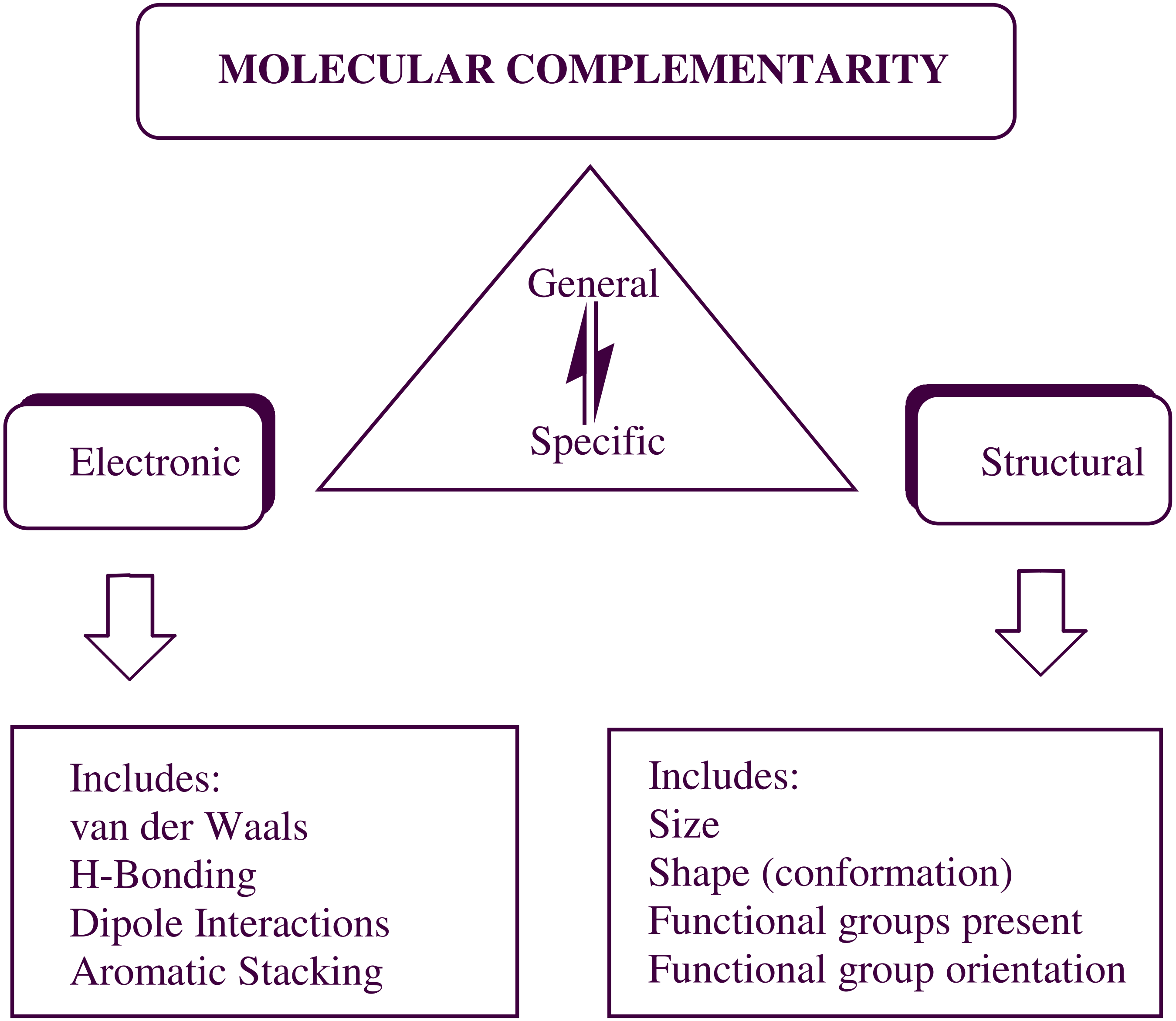
Although van der Waals forces also contribute to the interaction energy, it is the electrostatic π-σ interactions that dictate the preferred geometry to be adopted.

C.A. Hunter and J.K.M. Sanders, *J. Am. Chem. Soc.,* 1990, **112**, 5525

Complementarity

- Increased appreciation of the latent steric and electronic information inherent in the wide diversity of molecular building blocks that are either already available or that are capable of being synthesized.

- The self-assembly process requires that molecular recognition between the assembling components initially occurs and this in turn implies that such components be designed such that steric and electronic complementarity occurs between their respective binding sites.



MOLECULAR COMPLEMENTARITY

General

Specific

Electronic

Structural

Includes:
van der Waals
H-Bonding
Dipole Interactions
Aromatic Stacking

Includes:
Size
Shape (conformation)
Functional groups present
Functional group orientation

Molecular Recognition

- Steric and electronic complementarity
- Allosteric behaviour possible – *i.e.* cooperativity
- Chirality a ‘second order’ source of stored information – recognition based on ‘handedness’

Molecular and ionic self-assembly is ubiquitous

Controlled **molecular and ionic assembly is not**

Self-Assembly

- Self-assembly processes involving weak non-covalent interactions have now been reported to generate an impressive range of different supramolecular architectures.

- Examples include simple (1:1) host-guest systems, molecular tweezers, zippers, boxes, tubes, grids, capsules, rotaxanes, catenanes, helices, knots and large cyclic assemblies.

Properties of Supramolecular Assemblies

- Supramolecular assemblies have been constructed that exhibit novel properties which include unusual redox and/or electron transfer properties, photoactivity, conductivity as well as non-linear optical behaviour.

- Interest in such behaviour for application in new supramolecular 'devices' continues to remained a further motivation for the interest in the synthesis of new assemblies of the above type.

Capacity for Error Correction

- An important outcome of employing weak non-covalent interactions/metal donor bonds for the construction of supramolecular assemblies is that their formation is often readily ***reversible***, since the final assembly remains in thermodynamic equilibrium with its components.

- As a consequence, supramolecular systems of this type have an inherent capacity for assembly ***'error correction'*** that is not normally available to systems that are fully covalently bound.

Preorganisation Effect

- This concept, first proposed by Donald Cram, can help rationalize the strength of binding between the components in particular supramolecular systems.

- In essence, Cram proposed that the more closely the binding sites of a host molecule are structurally preorganized for binding to a guest, the greater will be the binding strength between host and guest in the resulting assembled species.

- Preorganisation results in a minimum change in degrees of conformational freedom – entropic advantage

predisposes ***promotes***

Preorganisation ——————>recognition ————>self assembly

Entropic Considerations

Entropic Considerations: Predicts tendency to form *discrete* over polymeric systems

Less favourable: 100 components → 1 polymer

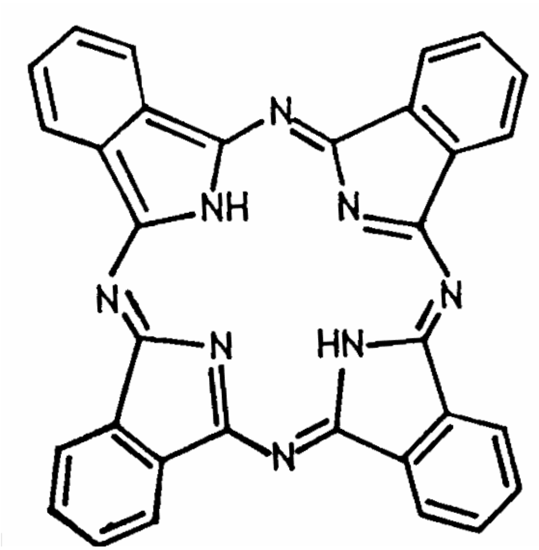
More favourable: 3 components → 1 supramolecular assembly

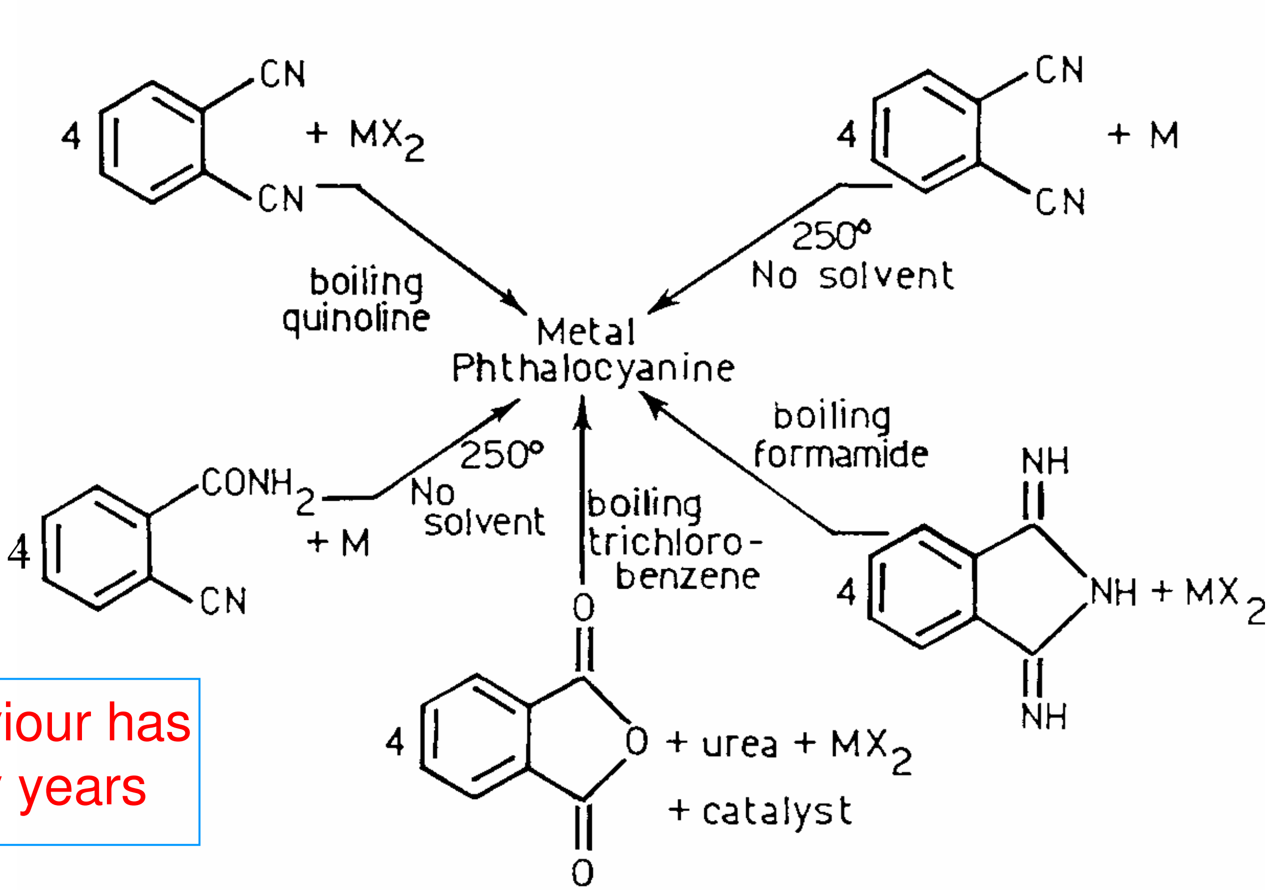
Less loss of disorder occurs in the latter case on forming the product. However, it is stressed that this is only one of several contributions that will operate for a given system.

Metal Directed Self-Assembly

Metal Template Effect

Metal Phthalocyanine Synthesis



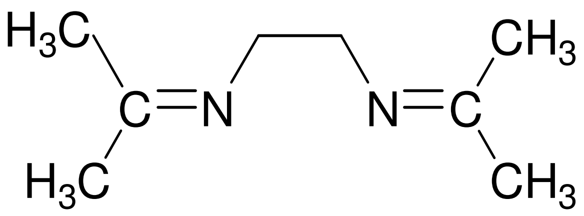


Metal template behaviour has been known for many years

Pre-1960 Synthetic macrocyclic chemistry mainly that of phthalocyanine and derivatives. Synthesized via metal template procedures.

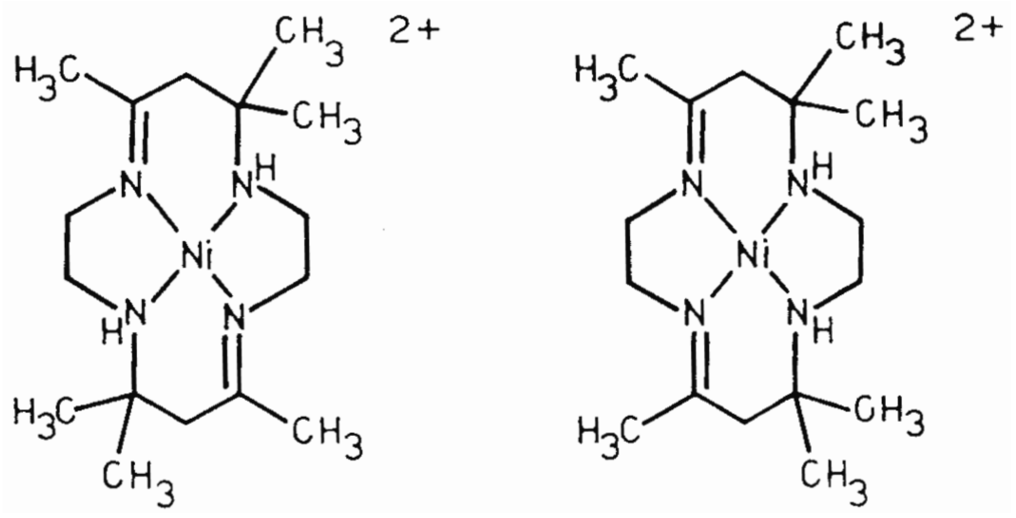
THE CURTIS MACROCYCLES (1960)

- Curtis investigated the reaction between dry acetone and $[\mathrm{Ni(ethylenediamine)}_3]^{2+}$. Obtained a yellow crystalline product. Initially formulated as the Schiff base Ni(II) complex of



of type $[\mathrm{NiL}_2]^{2+}$.

- Extreme stability did not fit this formulation.
- Correct formulation is a mixture of the isomeric complexes:



THE CLASSICAL MACROCYCLES – TYPICAL SYNTHESES

Macrocycle Synthesis

/ \

Direct	In situ
Conventional Organic reactions - NOT dependent on metal ion	Reaction in presence of metal ion which acts as a template

Direct Syntheses

- Frequently performed under high dilution – favours self-condensation over linear polymerization.
- Special procedures developed for such reactions – slow addition of reagents to large reaction volumes using motor-driven burettes.

THE CLASSICAL MACROCYCLES – TYPICAL SYNTHESES (Cont'd).

Template Syntheses:

- Large number in macrocyclic literature
- Reactions often complicated multistep procedures – difficult to define precise role of metal.
- Very little research into specific reactions – much '*witchcraft*'!

An aim of both template and direct syntheses is to maximize yields by choosing strategies which inhibit the formation of competing linear polymerization reactions.

THERMODYNAMIC AND KINETIC TEMPLATE EFFECTS

Two template effects have been delineated (Busch):

The thermodynamic template effect

The metal ion sequesters the cyclic product from an equilibrium mixture (for example, between products and reactants). Formation of the macrocycle is promoted as its metal complex.

The kinetic template effect

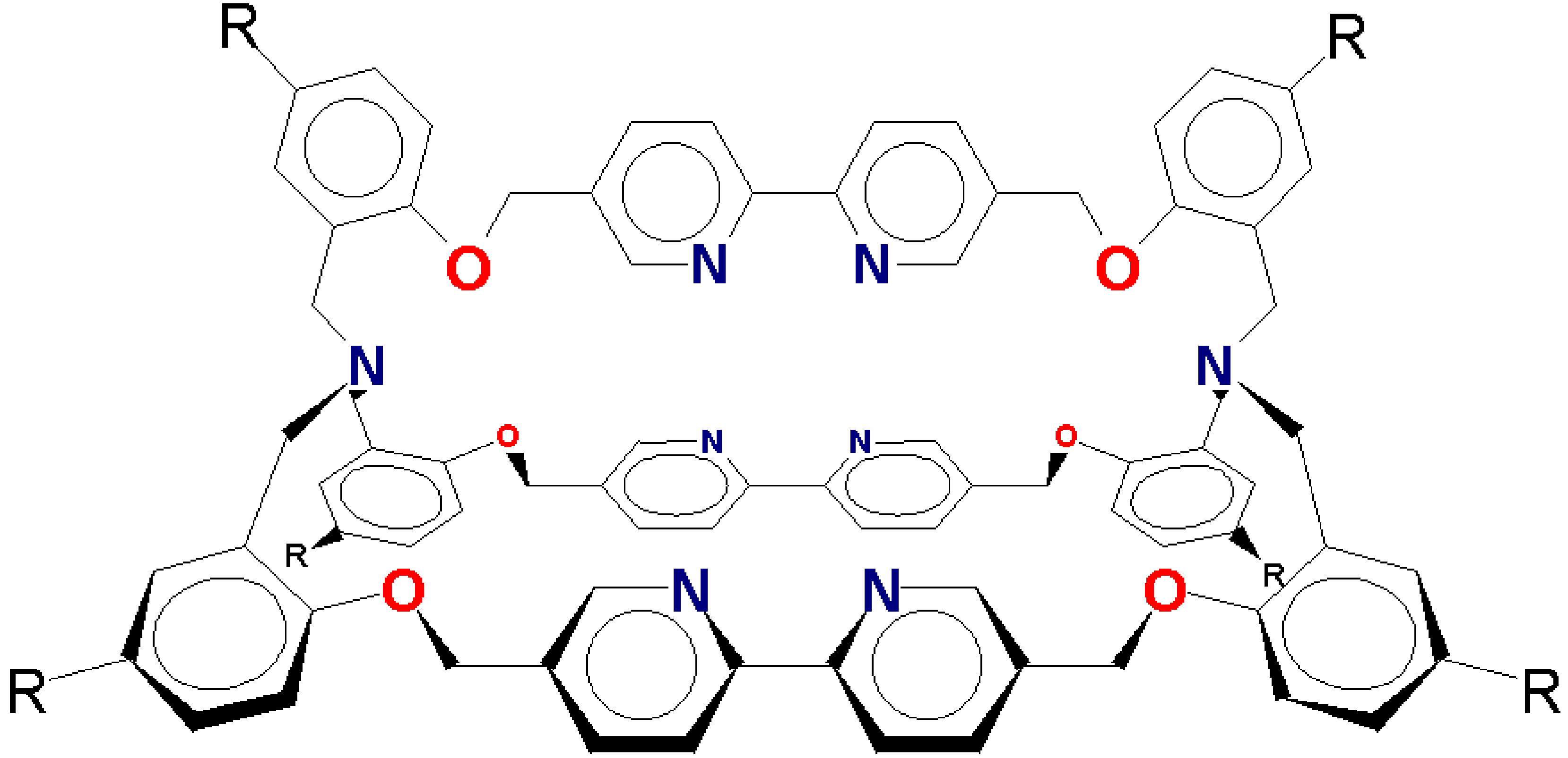
The metal ion directs the steric course of a condensation such that formation of the required cyclic product is facilitated.

A Recent Template Synthesis of a Molecular Cage

Reference:

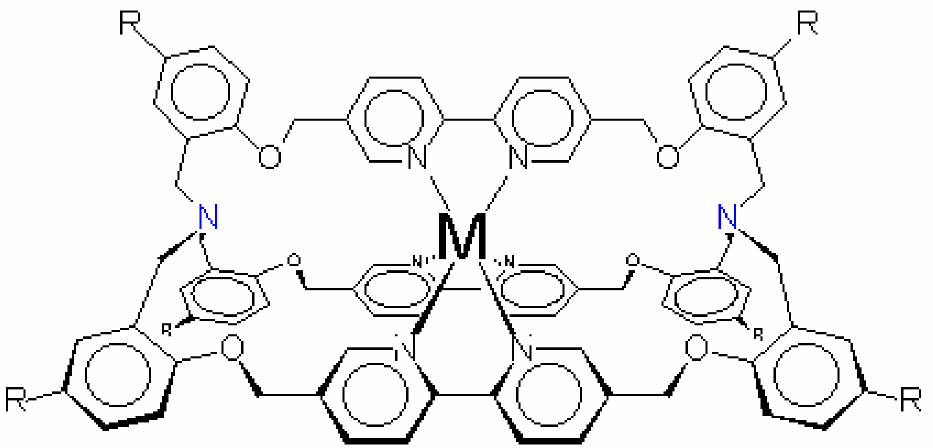
Inherent helicity in an extended tris-bipyridyl molecular cage.

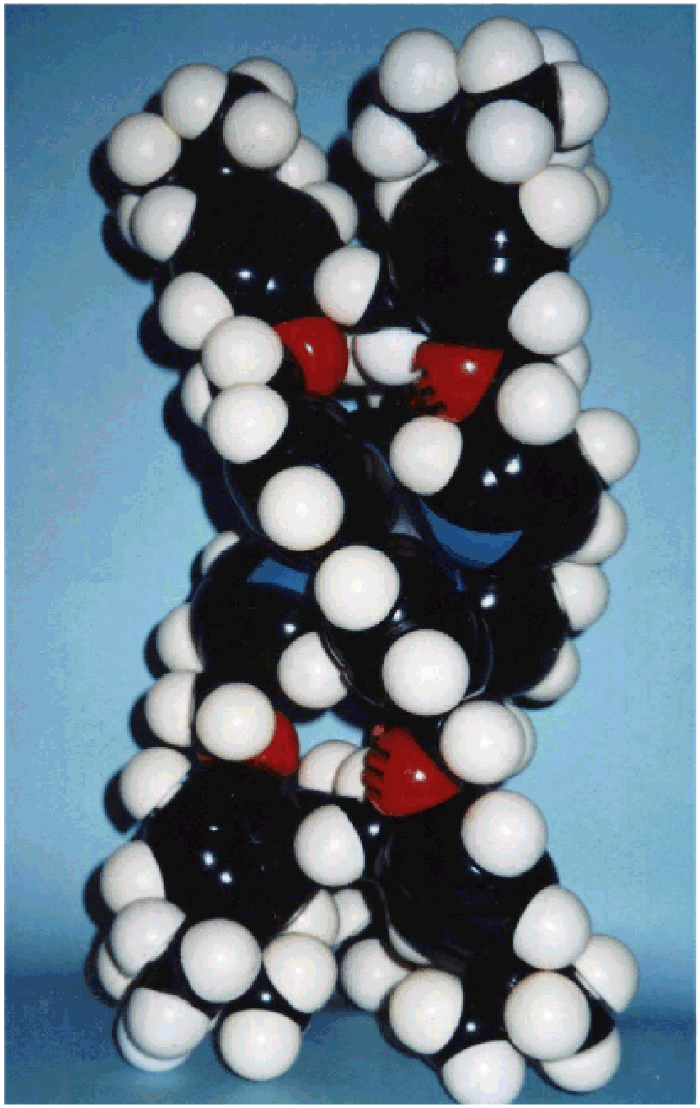
D. F. Perkins, L. F. Lindoy, G. V. Meehan, P. Turner, *Chem. Commun.*, 2004, 152.



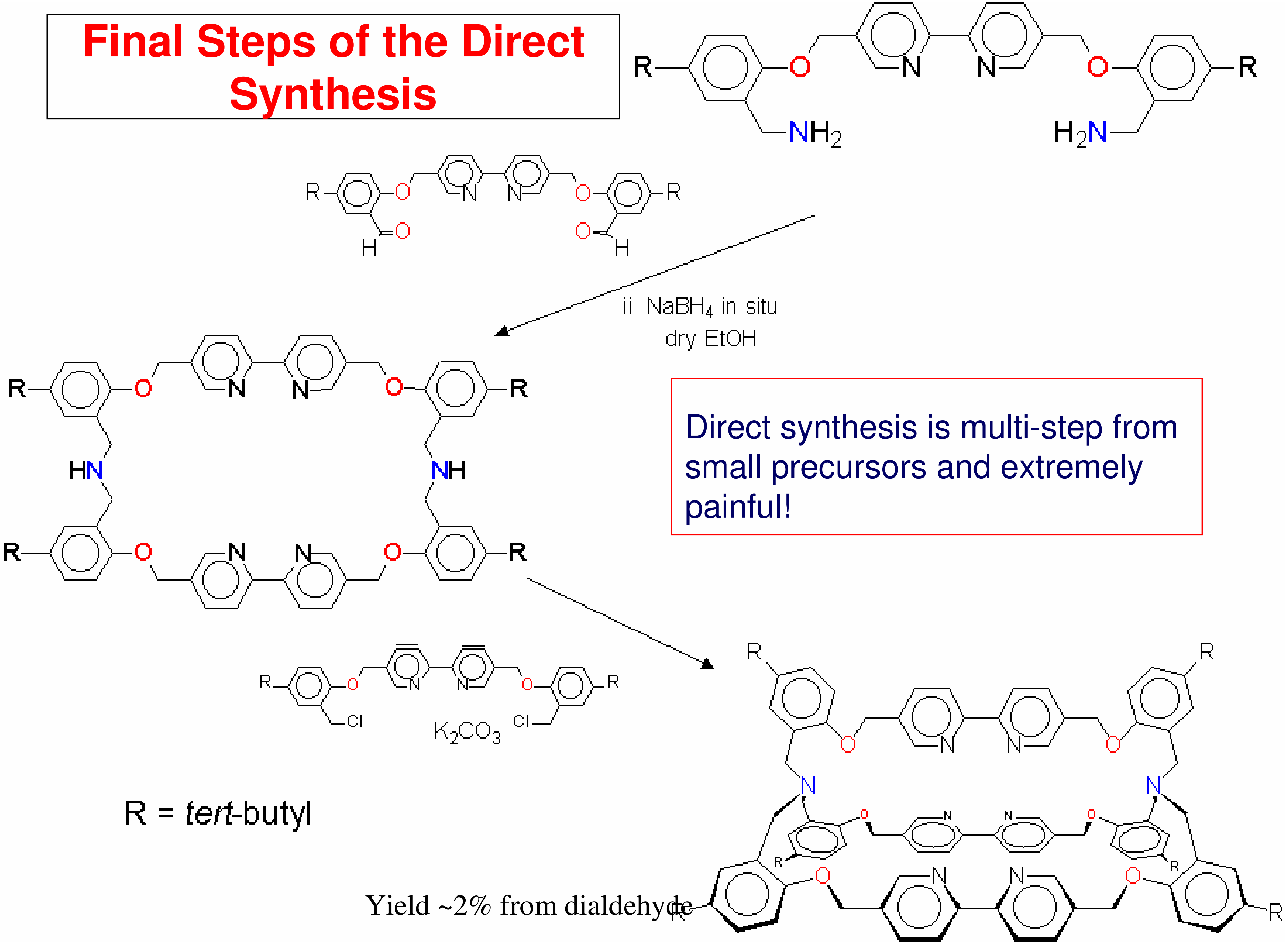
R = *tert*-Butyl

CPK Model of the Tripyridyl Cage Coordinated to an Octahedral Metal





Final Steps of the Direct Synthesis

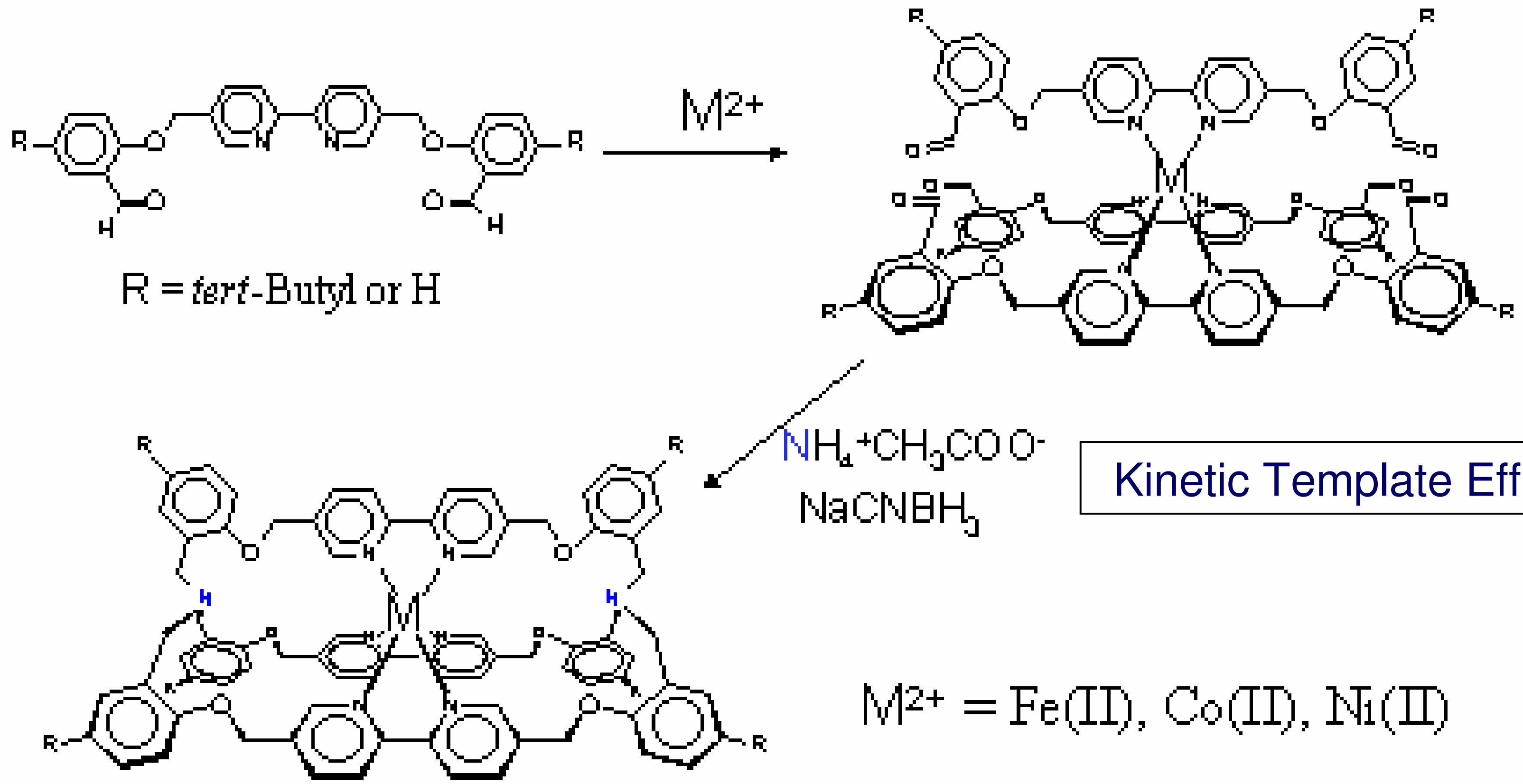


Direct synthesis is multi-step from small precursors and extremely painful!

R = *tert*-butyl

Yield ~2% from dialdehyde

Alternative metal template synthesis of the cage



Kinetic Template Effect

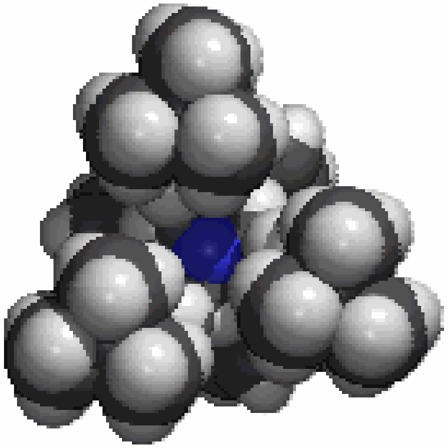
M^{2+} = Fe(II), Co(II), Ni(II)

For M = Fe; yield = 70%

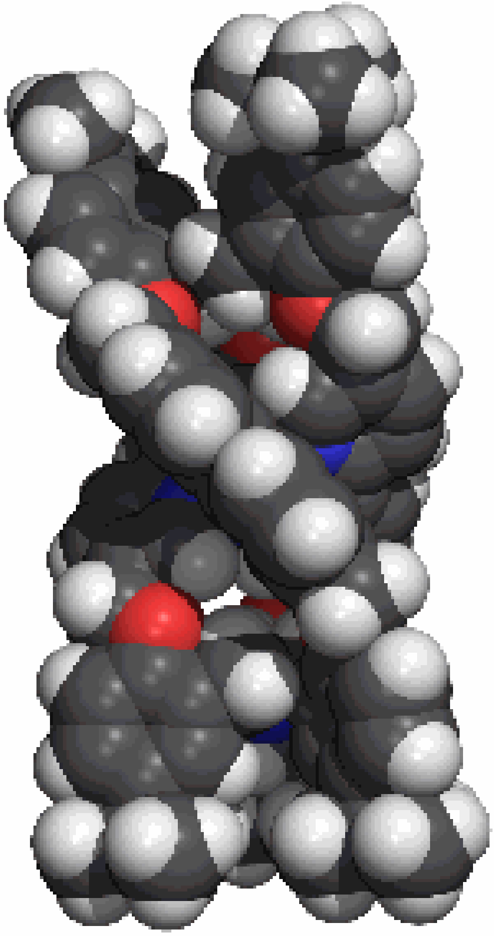
Initial synthesis involving Fe(II) based on the well known stability of the classical low-spin (d^6) complex $[Fe(bipy)_3]^{2+}$

Space filling view of the $[Ni(cage)]^{2+}$ X-ray structure

The single central metal directs a triple helical twist that extends ~ 22 Å along the axial length of the system



Space filling view of the $[Ni(cage)]^{2+}$ X-ray crystal structure down N-N axis Lone-pair (exo)



Cu cage has a similar structure

(An Aside)

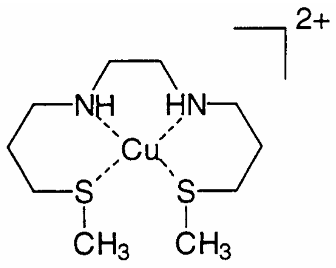
The Macrocyclic Effect

The Macrocyclic Effect

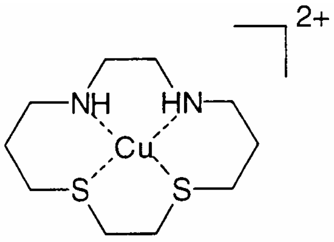
- Frequently macrocyclic ligands give rise to metal complexes that are more kinetically and thermodynamically stable that their open-chain analogues.
- Known as the macrocyclic effect.

  Kinetic stability refers to the rate at which demetallation of the complex occurs.
- Additional stability of the macrocyclic system is usually considerably greater than would occur for the presence of an additional chelate ring.
- The origins of the effect have engendered much debate for individual systems. Not helped by the observation that the effect is very variable from system to system.

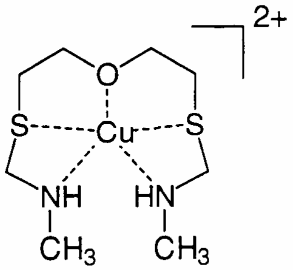
Stability Constants for Cu(II) Complexes



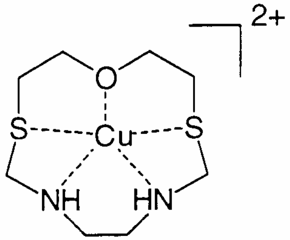
log K_{ML} = 11.4



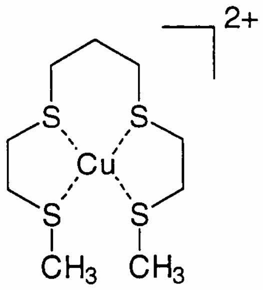
log K_{ML} = 16.0



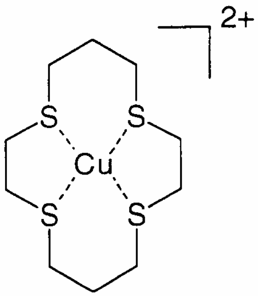
log K_{ML} = 9.2



log K_{ML} = 13.3



log K_{ML} = 9.2



log K_{ML} = 13.3

Macrocyclic effect is reflected by a favourable entropic term (TΔS = 17.6 kJ/mol) as well as by a lessor contribution from the enthalpic term (-ΔH = 8.4 kJ/mol)

Values are for water at 25°

Micheloni *et al.*, *Dalton Trans.*, 1983, 1189.

The Macrocyclic Effect (cont.)

Origins of the effect:

- In the **simpliest** situation, one may compare the formation of an open-chain ligand complex and its cyclic analogue: $\mathrm{M} + \mathrm{L} \rightarrow \mathrm{ML}\ (k_f)$
- For both ligand types, the above process should be facile, although formation of the cyclic complex is expected to be somewhat slower.
- However, the dissociation of the metal from the macrocyclic complex (consider to be first order) is likely to be much slower than for the open-chain analogue which can unrap one bond at a time, for example, in a series of $\mathrm{S_N1}$ steps:

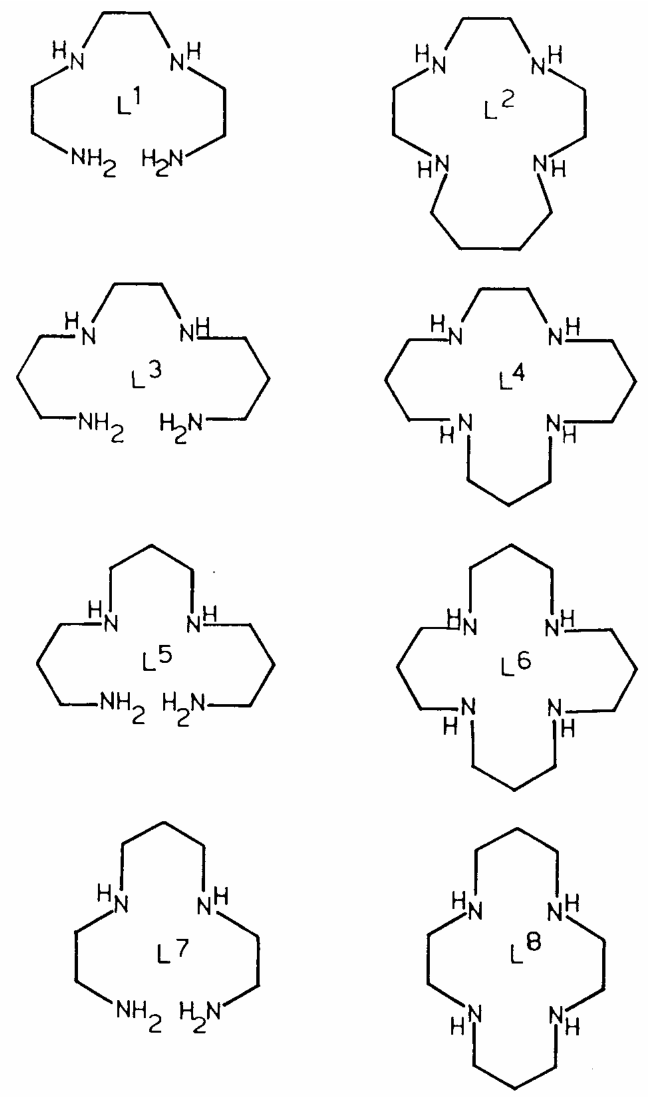
$$\mathrm{ML} \rightarrow \mathrm{M} + \mathrm{L}\ (k_d)$$

Macrocyclic Effect (cont.)

At equilibrium: $$\mathrm{M} + \mathrm{L} \underset{k_d}{\overset{k_f}{\rightleftharpoons}} \mathrm{ML} \qquad K = k_f / k_d$$

Hence for the macrocyclic complex case k_d will be smaller and K will be enhanced.

Comparative Thermodynamic Parameters



$$[NiL_{oc}]^{2+} + L_{mac}{}^{2+} \rightleftharpoons [NiL_{mac}]^{2+} + L_{oc}$$

where oc = open chain; mac = macrocylic.

L_{oc}/L_{mac}	$\frac{-\Delta G}{\text{kJ mol}^{-1}}$	$\frac{\Delta H}{\text{kJ mol}^{-1}}$	$\frac{T\Delta S}{\text{kJ mol}^{-1}}$
L^1/L^2	2.43	5.1	7.4
L^3/L^4	21.05	5.3	26.4
L^5/L^6	15.69	3.5	19.2
L^7/L^8	33.67	−20.5	13.2

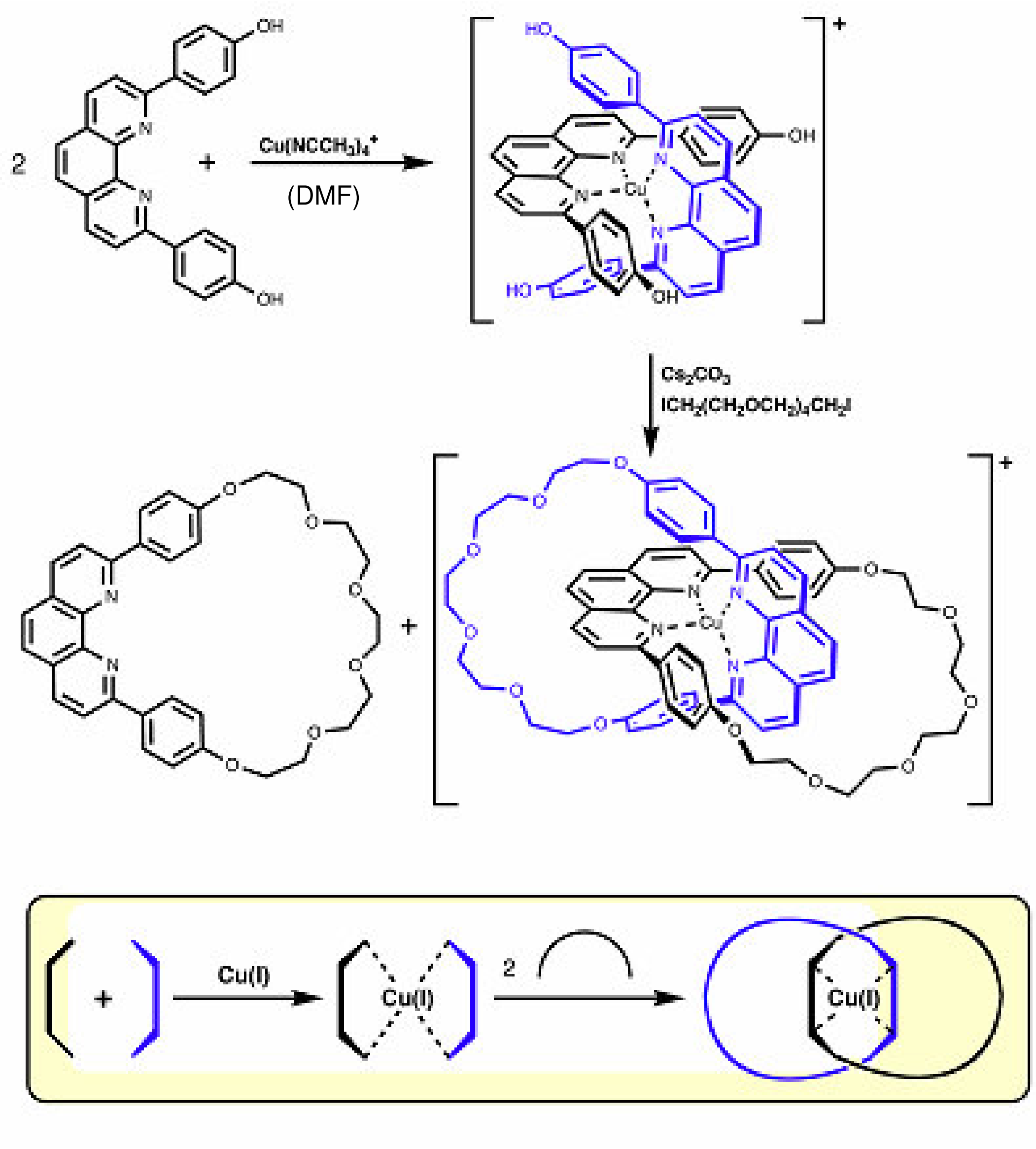
The entropy term associated with the macrocyclic effect tends to be favourable while the enthalpy term can be quite variable (and either favourable or unfavourable).

Micheloni *et al.*, D*alton* Trans,1983, 1189.

Metallo-Catenanes

Metal-ion directed formation of mechanical bonds

Synthesis of a [2]-catenane incorporating 2,9-substituted 1,10-phenanthroline ring derivatives coordinated to Cu(I)



- Product is deep red.
- Cu(I) acts as a template.
- High dilution, 27% yield.
- Need CN$^-$ to remove Cu(I) – slow kinetics – shows a substantial macrocyclic effect.
- Can then add NI(II); Ni(I) is stabilized on reduction as prefers tetrahedral coordination
- Reaction is a marriage of metal template and conventional synthetic procedures

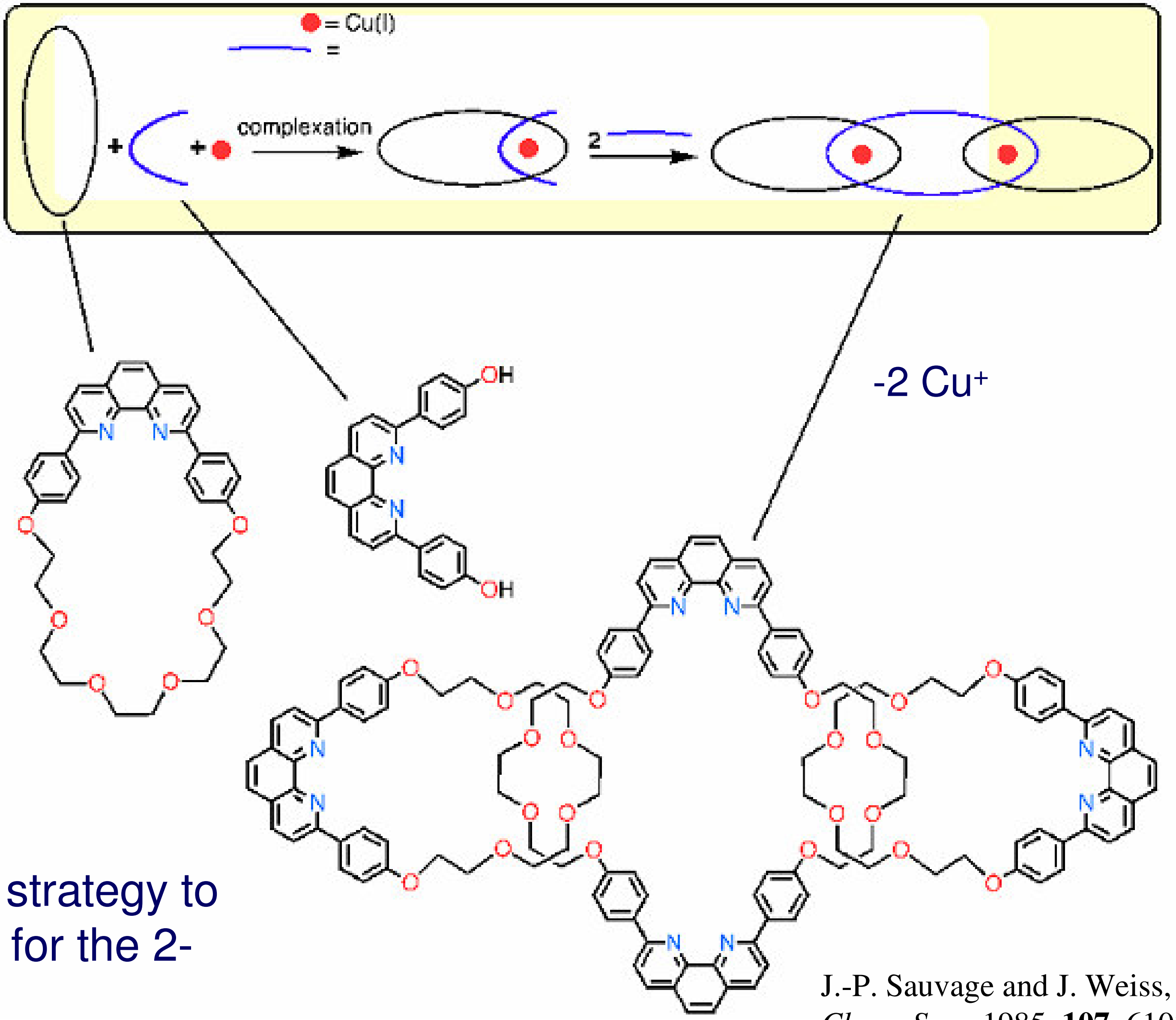
C.O. Dietrich-Buchecker, J.-P. Sauvage and J.-M. Kern, *J. Am. Chem. Soc.*, 1984, **106**, 3043.

Why chose copper(I)?

- Copper(I) has a d^{10} electronic configuration - no inherent steric dictates.
- Univalent – favours 4-coordinate (tetrahedral) coordination over higher coordination numbers.
- No crystal field effects – relatively kinetically labile - error correction and metal removal/exchange from final product both possible (despite a significant macrocyclic effect).
- Diamagnetic – can readily follow assembly processes by ^1H NMR.
- $[Cu(phen)_2]^+$ is a ‘classical’ complex known since 1933 – its coordination chemistry well documented.
- It is a redox active - Cu(I)/Cu(II)/Cu(III) all commonly generated electrochemically. Adds potential further functionality to the initial catenane product.

Creativity in Action! Structurally elaborating the system

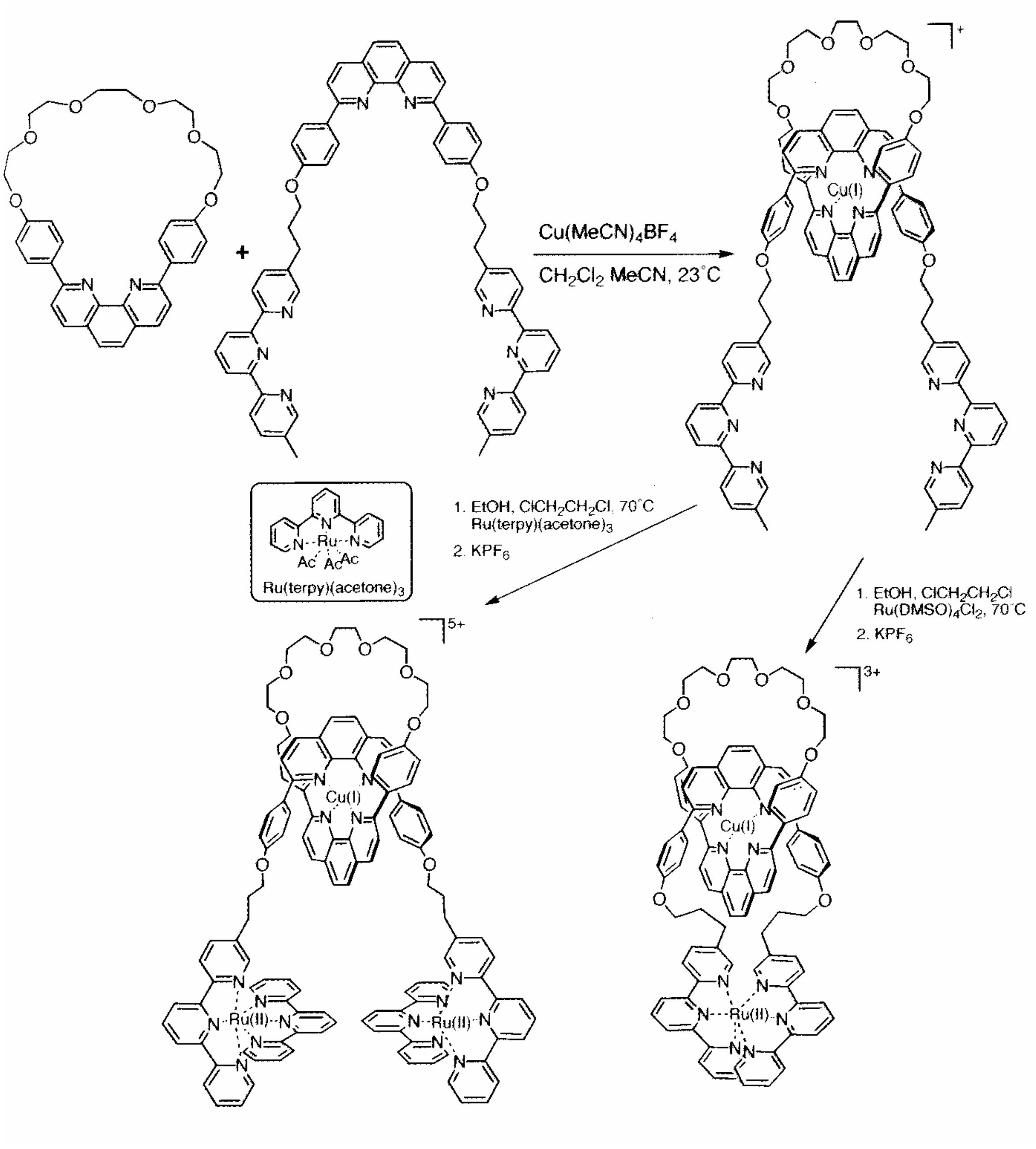
Formation of a [3]-catenane



A related strategy to that used for the 2-catenane

J.-P. Sauvage and J. Weiss, *J. Am. Chem. Soc.*, 1985, **107**, 6108.

Synthesis of a mixed Cu(I)/Ru(II) rotaxane and catenane



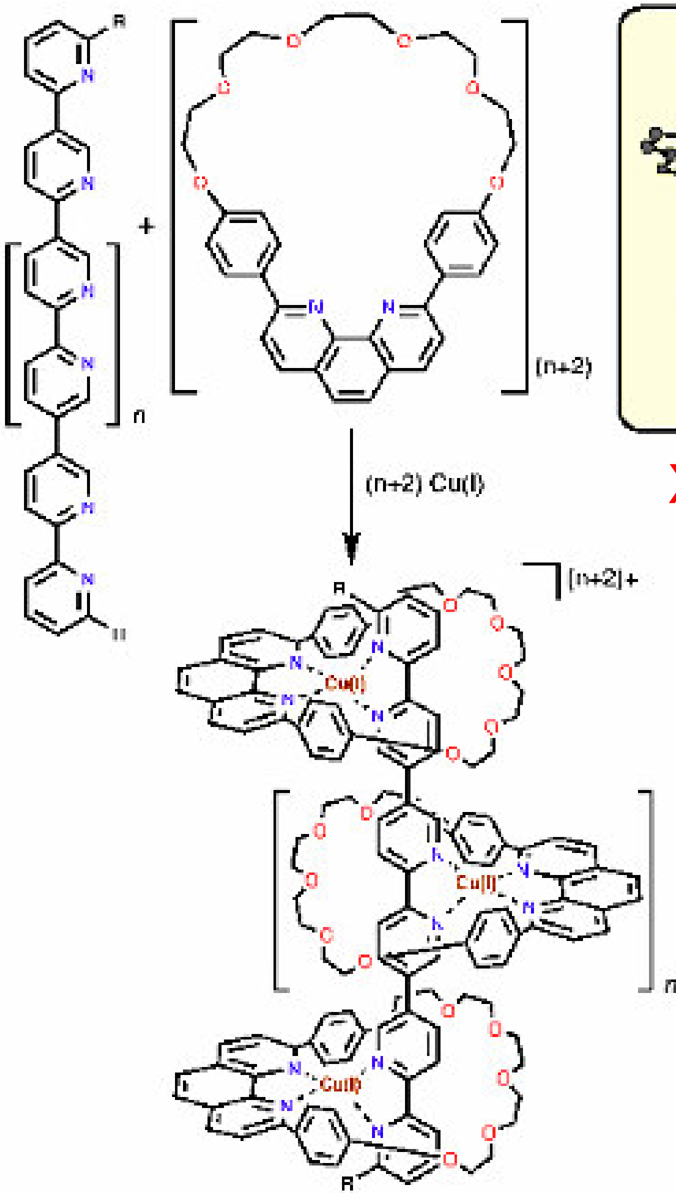
- Cu(I) prefers 2 x phen while Ru(II) prefers 2 x terpy.
- Cu(I) added first then Ru(II).
- Can remove Cu(I) with CN$^-$ (MeOH/Water), Ru(II) remains intact.

D. J. Cardenas, P. Gavina and J.-P. Sauvage, *J. Am. Chem. Soc.*, 1997, **119**, 2656.

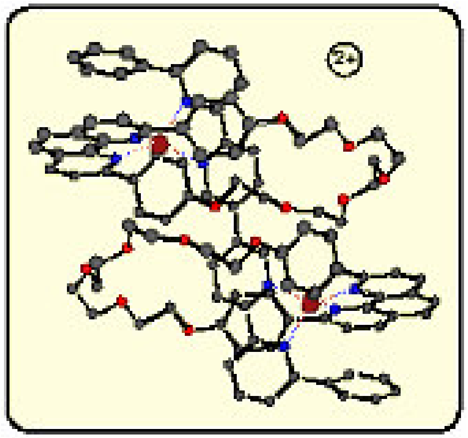
Why chose bis(terpyridine)Ruthenium(II) groups for the ‘stoppers’?

- $[Ru(terpy)_2]^{2+}$ is sufficiently bulky to inhibit macrocycle loss.
- Ruthenium(II) has a low spin d^6 electronic configuration in $[Ru(terpy)_2]^{2+}$(diamagnetic).
- Ruthenium favours 6-coordinate (octahedral) coordination.
- Large crystal field stabilisation and crystal field activation energies – low spin complexes thermodynamically stable and kinetically inert.
- $[Ru(terpy)_2]^{2+}$ - coordination chemistry is well documented; for example, this group is photoactive.

Formation of Polyrotaxanes



n = 0, R=Ph
n = 0, R=Me
n = 1, R=Me



X-ray structure

Insert shows the structure of the dinuclear Cu(I) species for the system with n = O, R = Ph

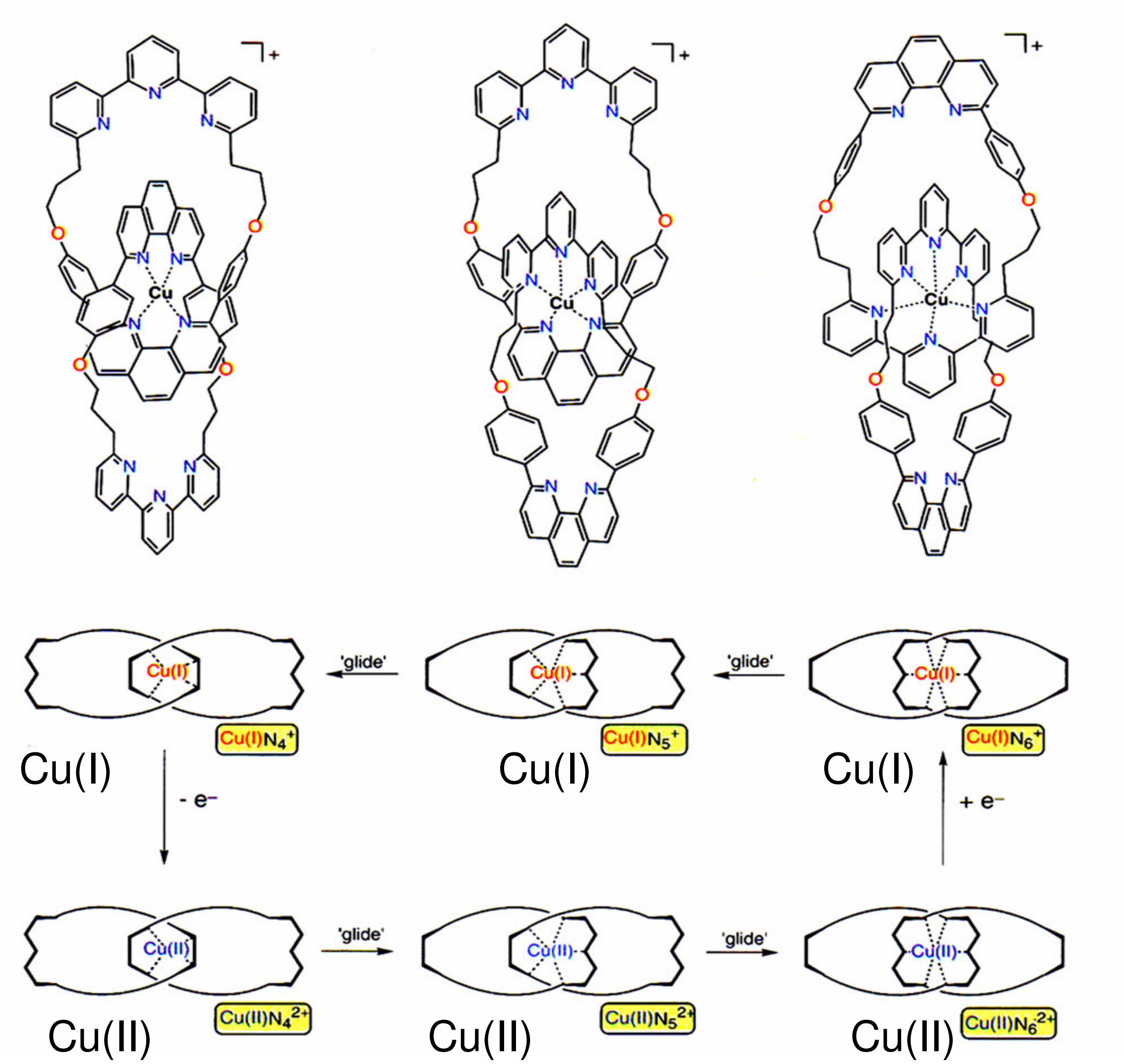
Note alternating orientation of phenanthroline fragments

Self-assembled, rigid- rack di- and tri-rotaxanes.

H. Sleiman, P. Baxter, J.-M. Lehn and K. Rissanen, *J. Chem. Soc., Chem. Commun.*, 1995, 715.

Increasing the functionality - Exploiting the redox properties of copper

Redox-Controlled Ring 'Gliding' in a Cu(I)-Containing [2]-Catenane



- Each step gives a different coordination number
- Three different coordination geometries
- Mechanical motion will be slow in terms of molecular electronics

D. J. Cardenas, A. Livoreil and J.-P. Sauvage, *J. Am. Chem. Soc.*, 1996, **118**, 11980.

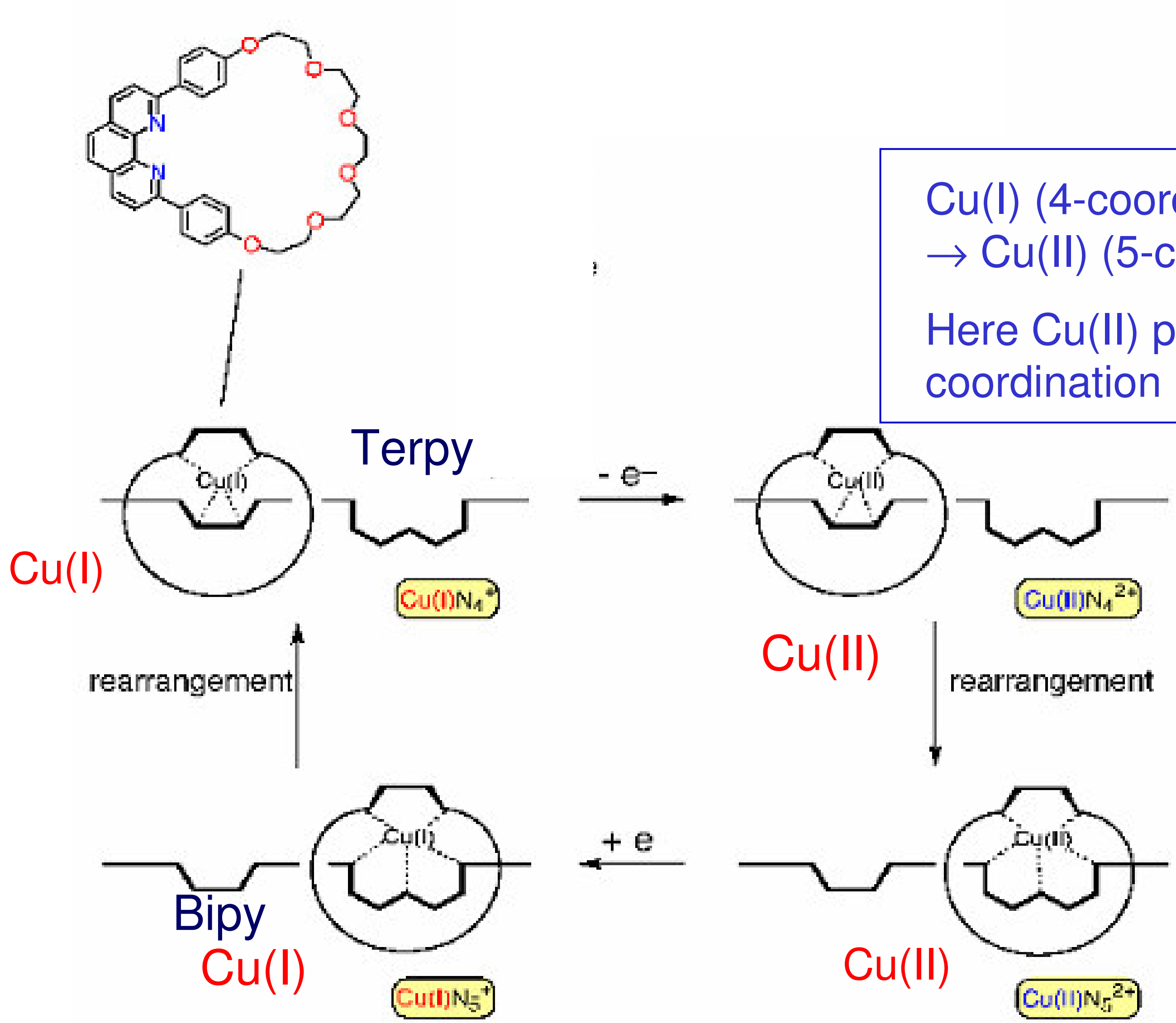
Why does this work?

Cu(I) ($d^{10)}$ likes tetrahedral coordination

Cu(II) (d^9) likes octahedral coordination

- Rings contain bipy (bidentate) and terpy (tridentate) sites
- Redox control of ring gliding employed through 3 different geometries
- Each step a different coordination no.
- Mechanical motion – switch

A Pseudo-Rotaxane Capable of Switching Between Two Arrangements Under Redox Control



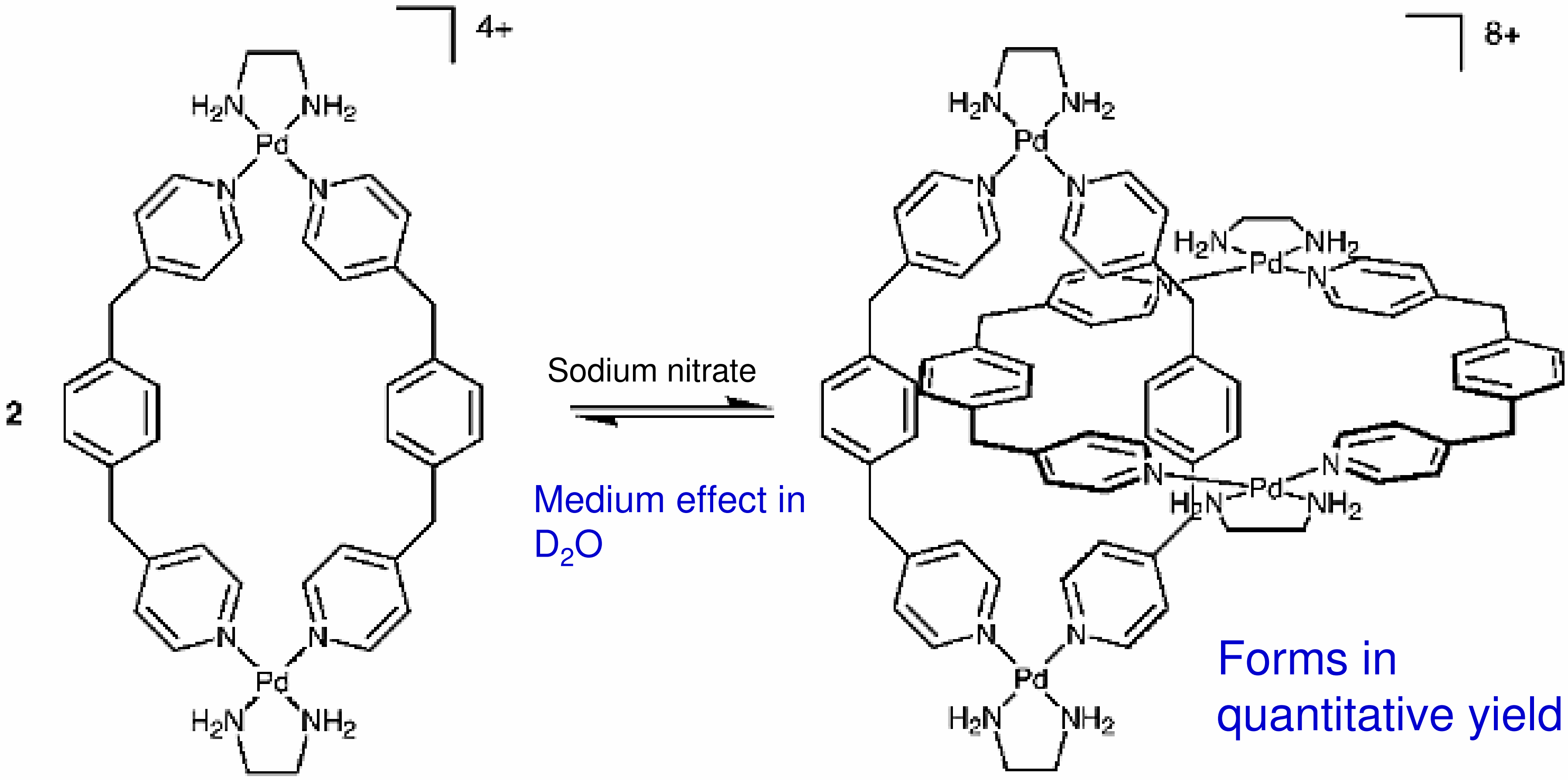
Cu(I) (4-coordinate) - e$^-$ → Cu(II) (5-coordinate)

Here Cu(II) prefers 5-coordination

J.-P. Collin, P. Gavina and J.-P. Sauvage, *Chem. Commun.*, 1996, 2005.

A ‘Lock and Key’ System

Formation of a palladium-containing [2]-catenane promoted by a high salt (sodium nitrate) concentration



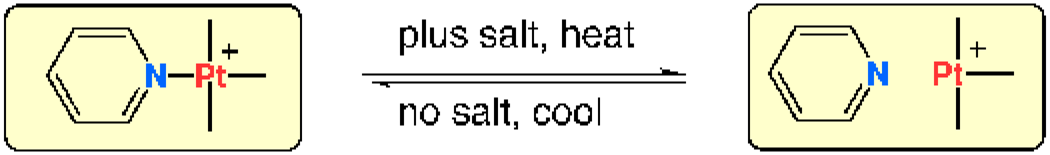
Medium effect in D_2O

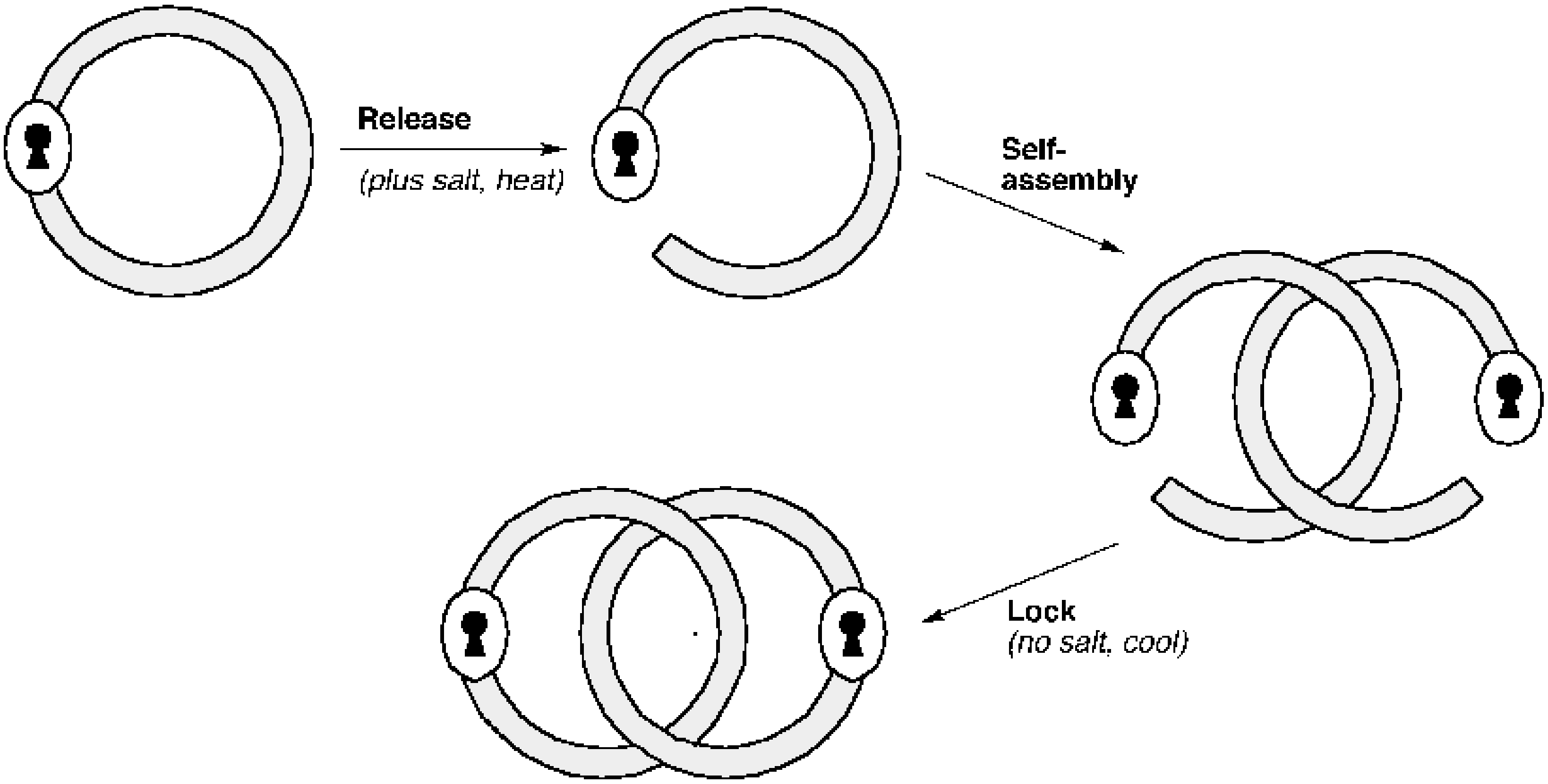
Forms in quantitative yield

Cavity is hydrophobic

M. Fujita, F. Ibukuro, H. Hagihara and K. Ogura, *Nature*, 1994, **367**, 720.

Operation of a Molecular ‘Lock’





M. Fujita, F. Ibukuro, H. Hagihara and K. Ogura, *Nature*, 1994, **367**, 720.

What is important here?

- Remarkable medium effect (Fujita) - polar D_2O solution containing sodium nitrate pushes equilibrium towards catenane → 99%! (even at reasonably low $NaNO_3$ concentrations)

- Presumably interlinks to gain lipophilic environment when polarity is increased.

- Nitrate promotes ligand exchange on platinum.

- Can freeze as catenane by cooling solution

The Building Block Approach

Molecular Building Blocks for Forming 2D and 3D Molecular structures

Molecular Components:

Corner units, common angles exhibited: 60°, 90°, 109.5°, 120°, 180°

Combine with linear and other shaped components

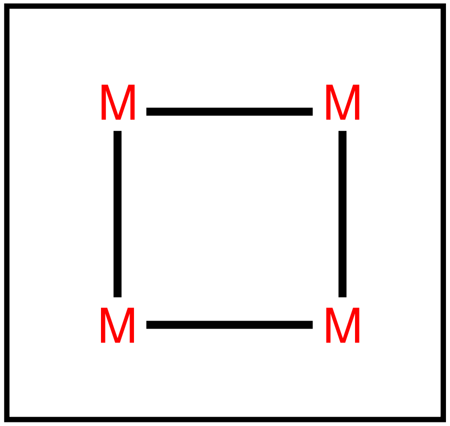
Combinations can be used to build both simple and more complex structures – limited only by the imagination of the practitioner!

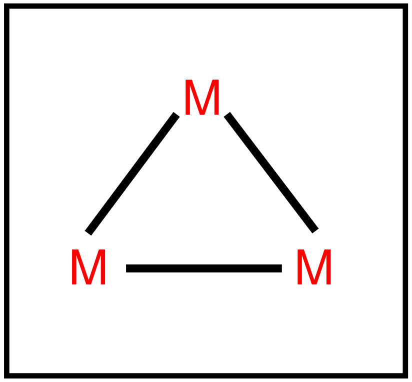
Common Shapes:

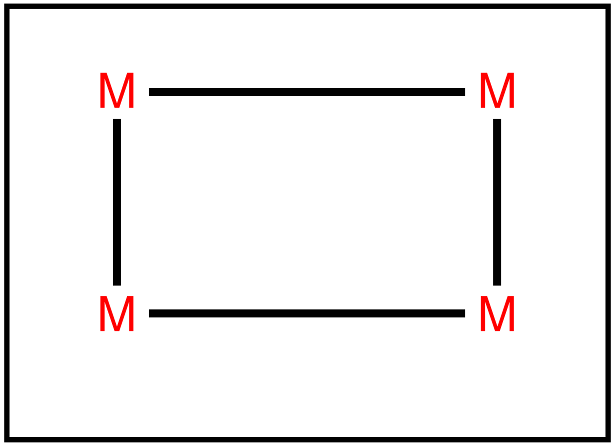
Triangles, squares, polygons, tetrahedra, octahedra, cubes, higher polyhedra

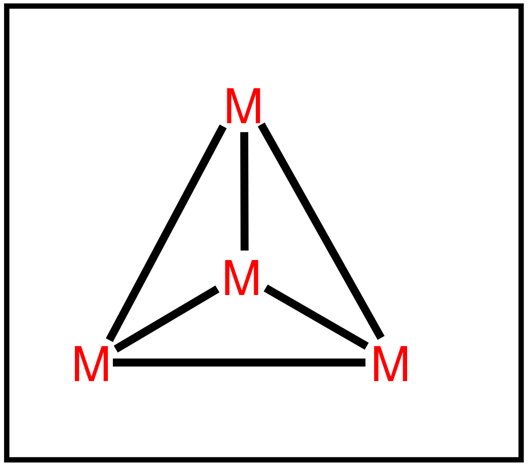
See, for example: S. Leininger, B. Olenyuk and P.J. Stang, *Chem. Rev.*, 2000, **100**, 853

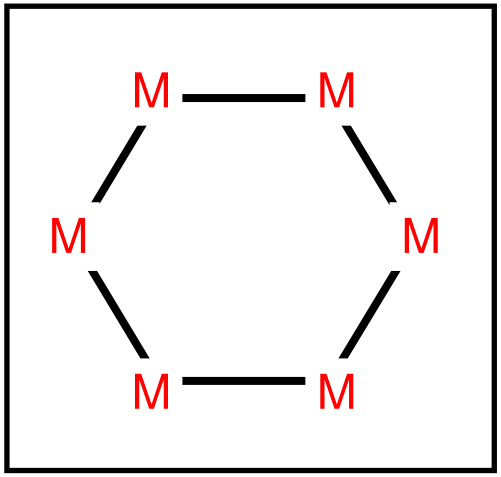
Some Simple Metallo-Supramolecular Architectures
(Metals at Corners)





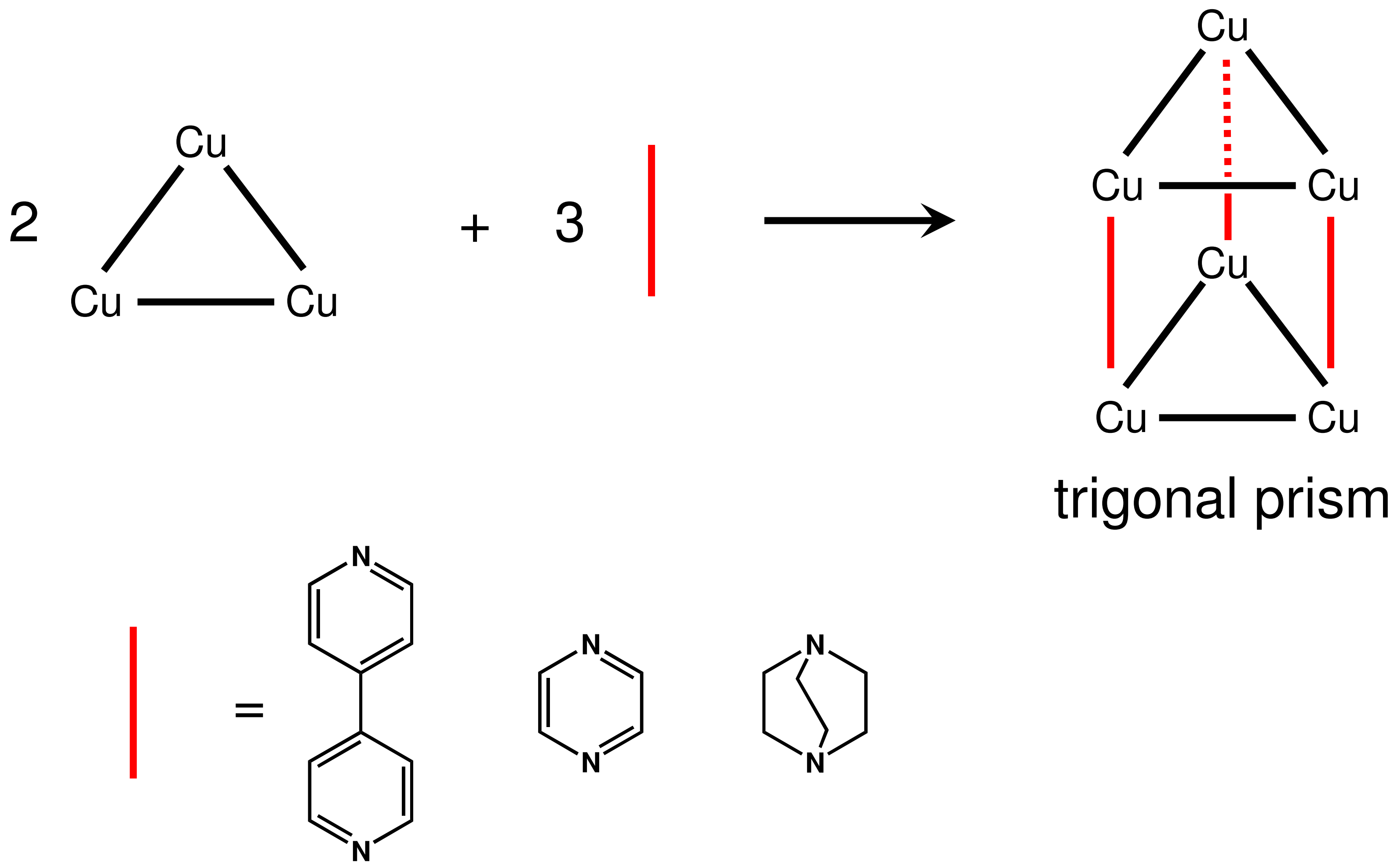






Christou – Fujita – Raymond – Saalfrank – Soldatov – Stang

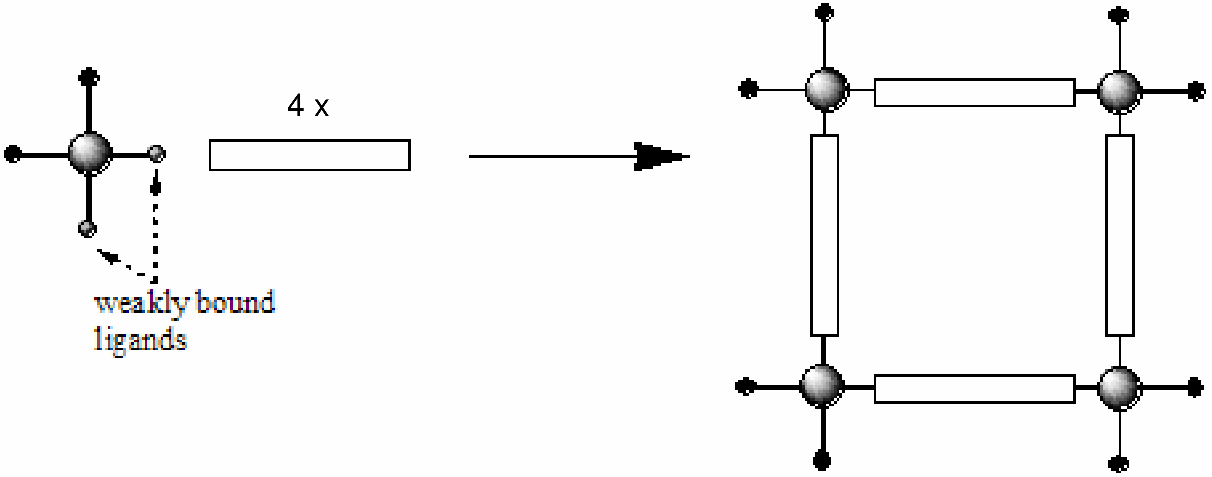
A typical example - construction of a larger metallo-supramolecular architecture

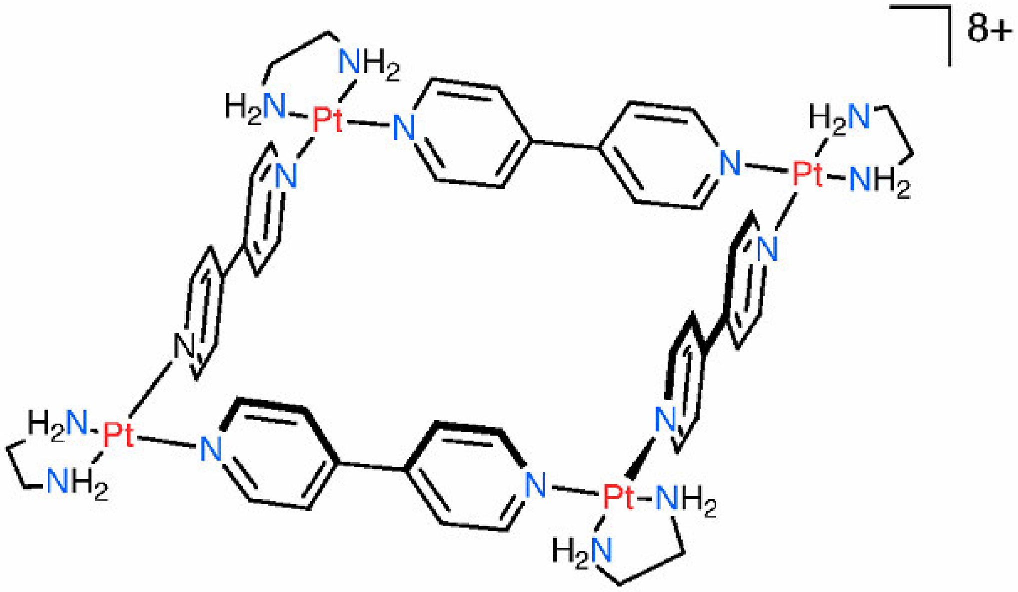


trigonal prism

A Metallo-Square

A Molecular Square Derived from Pt[1,2-diaminoethane)$(NO_3)_2$]

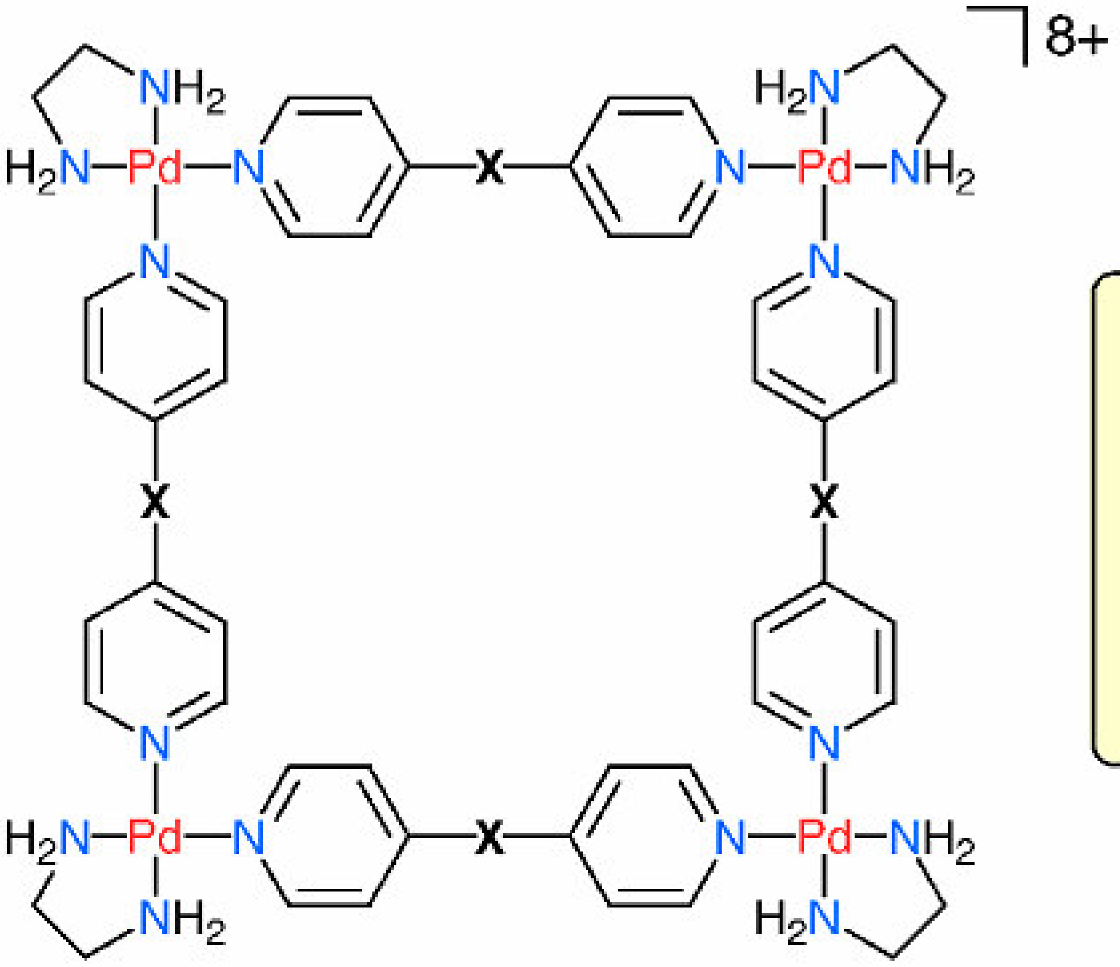




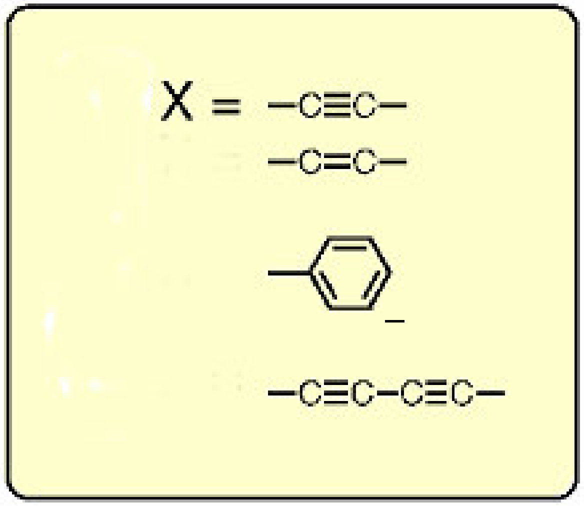
M. Fujita, *et al.*, *Chem. Commun.*, 1996, 1535.

- Rigid sides and corner units
- Pt(II) complex took one month to equilibrate
- Pd(II) analog also synthesised – more labile (90% yield)
- Formed from di-nitro substituted metal complex. Nitro ligands are labile
- Some cyclic trimer also formed

Extended Molecular Squares



Fully-conjugated spacers



Some are perfect squares, some have rhomboidal distortion

Some examples shown to bind electron-rich aromatic guests and anions

M. Fujita and K. Ogura, *Coord. Chem. Rev.*, 1996, **148**, 249; M. Fujita, *et al.*, *Chem. Commun.*, 1996, 1535; S.B. Lee, *et al.* *Tetrahedron Lett.*, 1998, **38** 873.

Design considerations

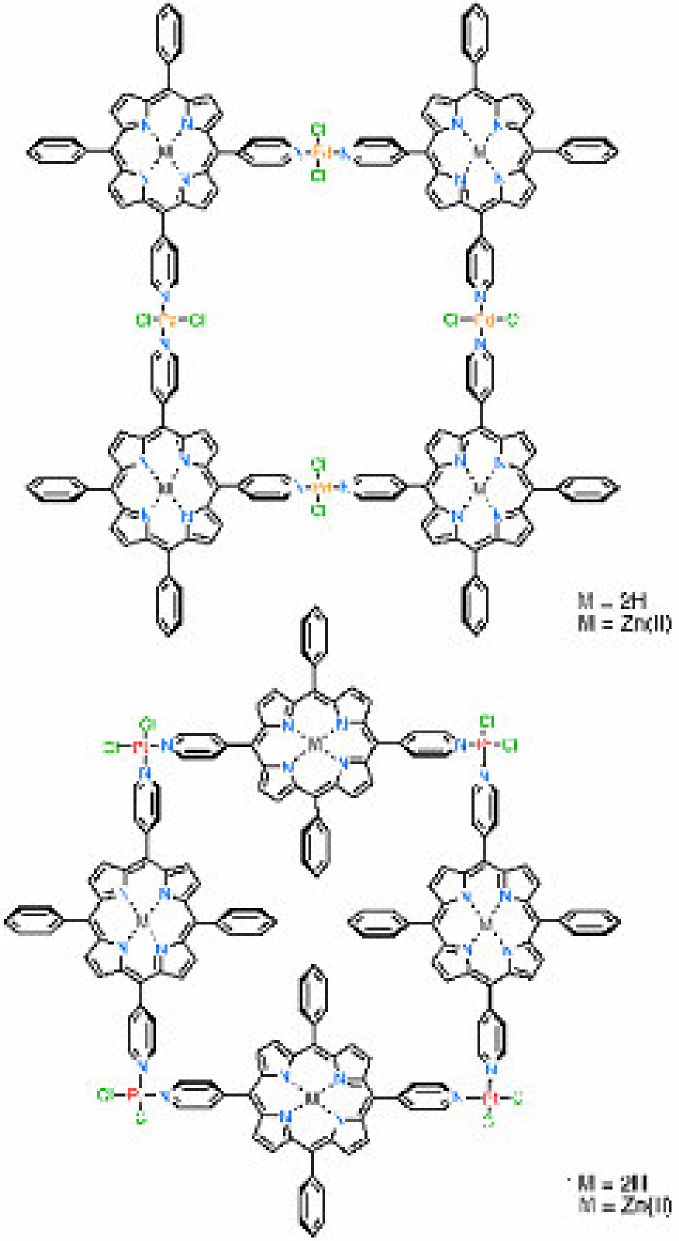
- Pd(II) and Pt(II) are square-planar d^8 and kinetically inert (especially platinum)

- Diamagnetic - can follow by proton NMR – may take weeks to reach equilibrium for platinum

- As side unit becomes more flexible, tendency to for corresponding triangle or even an ellipse to form (entropy driven)

- Flexibility means that 90° may be approximately maintained at the palladium or platinum corner units when triangle (or ellipse) generated

Porphyrin-containing Molecular Squares

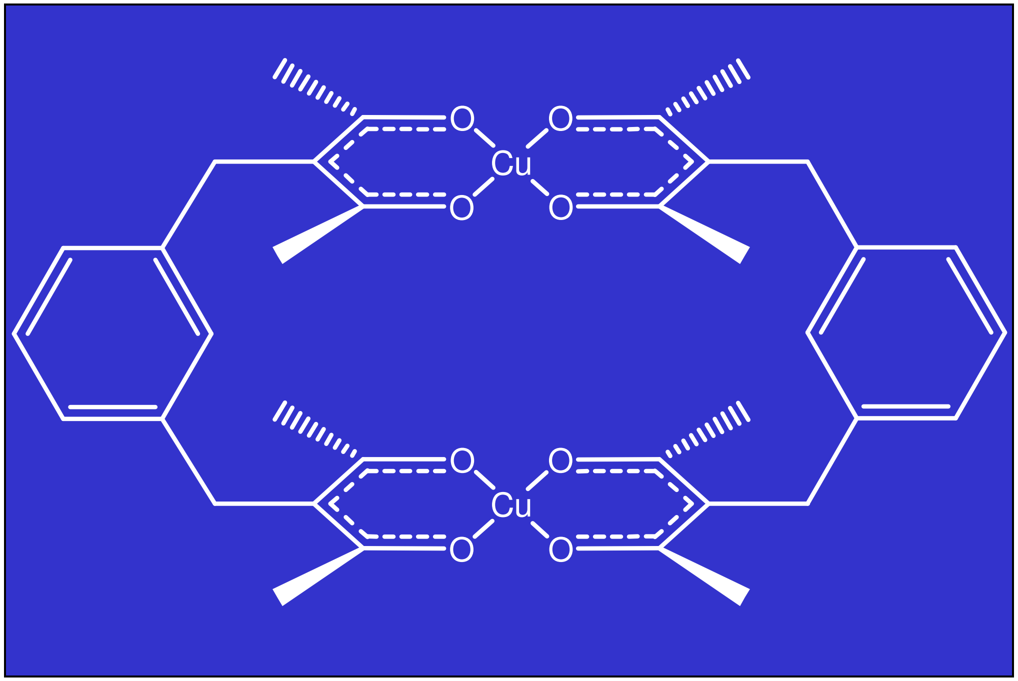


C.M. Drain and J.-M. Lehn, *J. Chem. Soc., Chem. Commun.*, 1994, 2313.

Case study:

Designing self-assembled metallo-structures based on bis-β-diketonato ligands

Use a flexible linker – get simple dinuclear metallocycle with square planar copper(II)

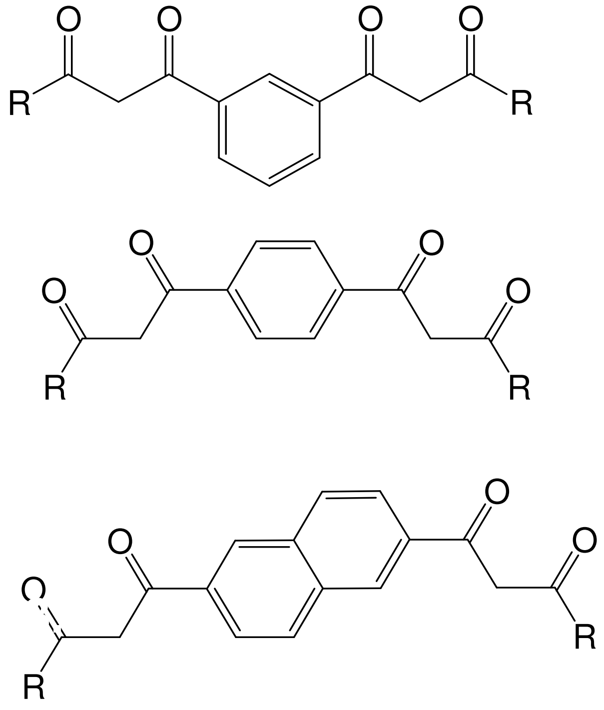


What if the linker is not flexible?

Maverick, A.W. and Klavetter, F.E. *Inorg. Chem*. (1984) 4130.

Ligand Geometry Affects Supramolecular Architecture

Because of the *sp*^{2} hybridisation there is a significant difference in the shape of the *meta* substituted ligand (**1**) compared with the *para*.



Parallel donors

Donors 120º apart

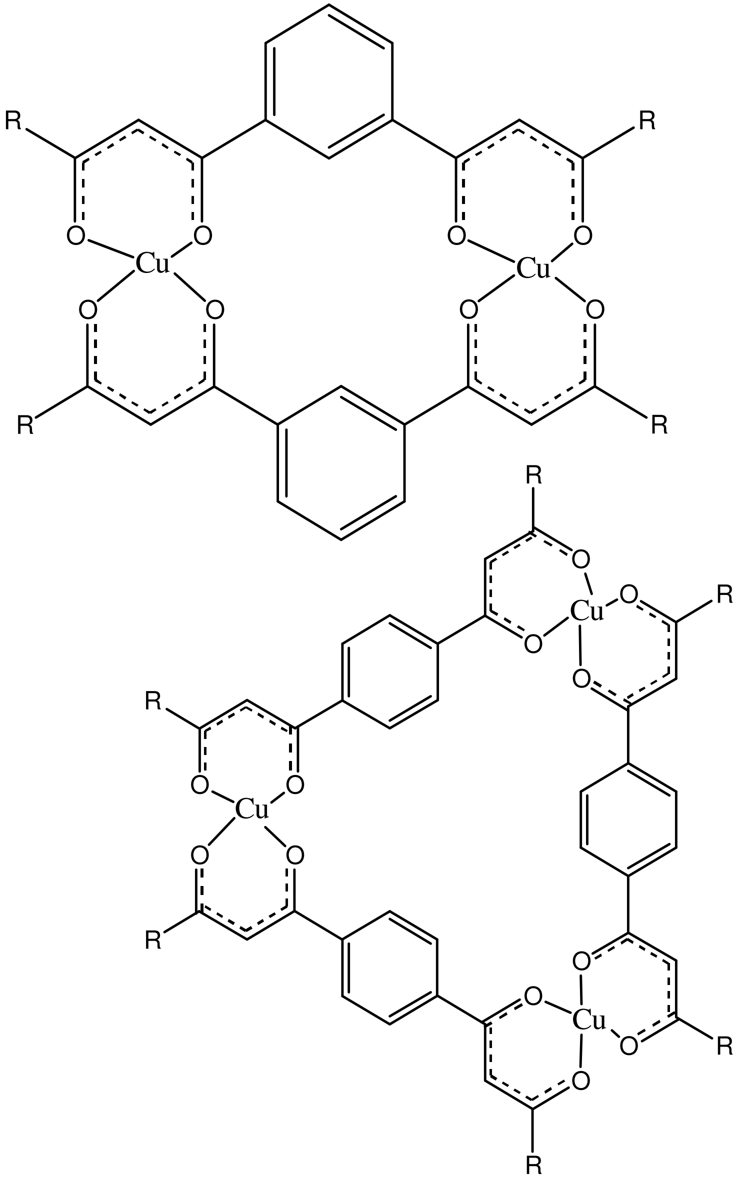
Christou – Lindoy - Ripmeester

Complex Design: *Meta* vs *Para Ligands Interacting with a Square-Planar Divalent Metal*

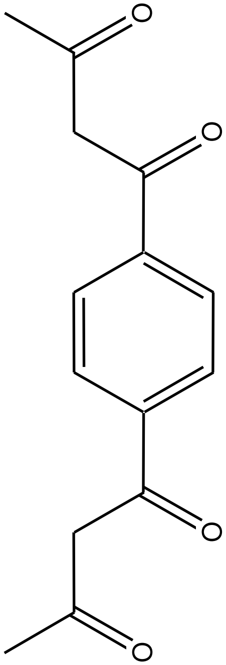
Comparing the geometries of 1:1 square planar copper complexes:

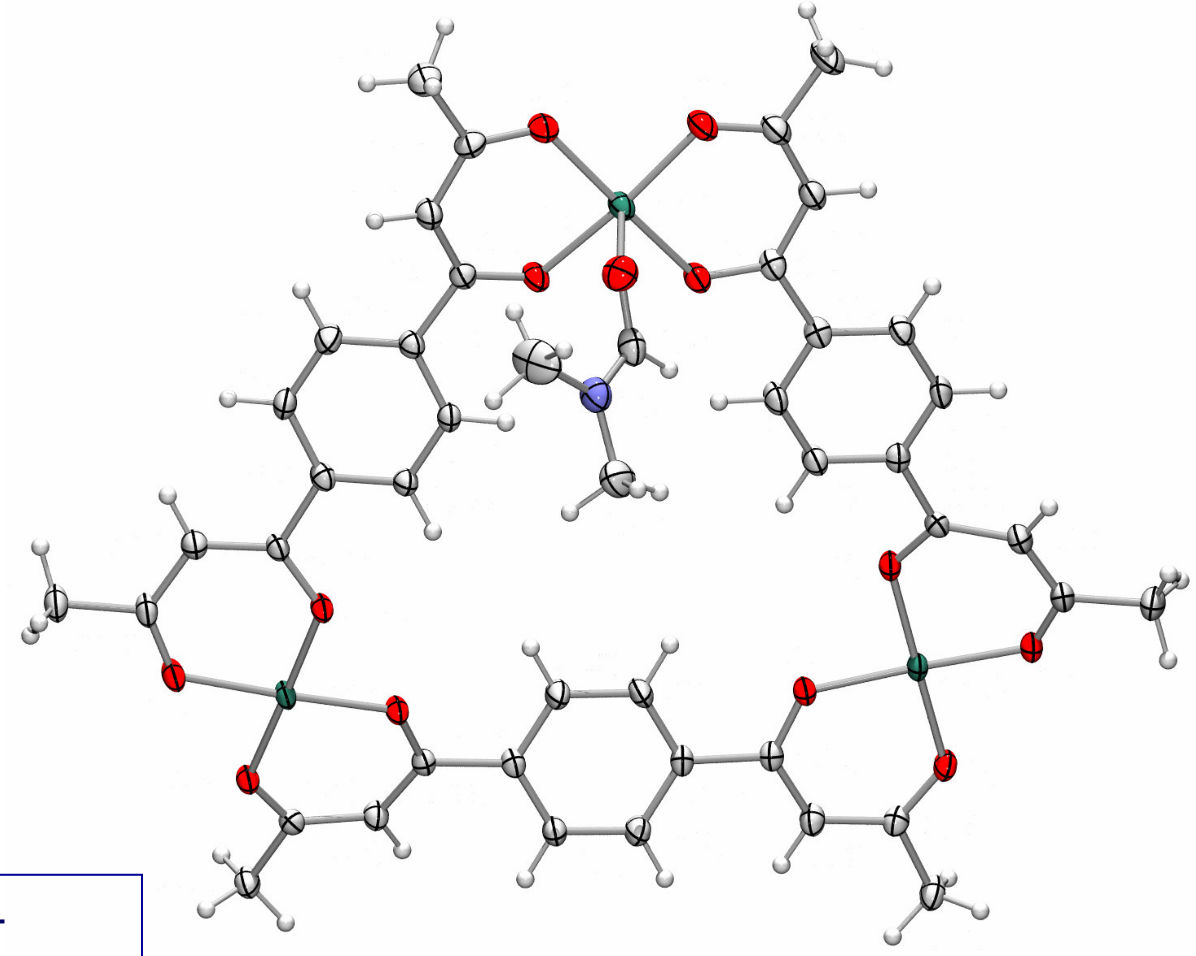
meta → aligned

para → triangular



$[Cu_3(L\text{-}H_2)_3(DMF)]$

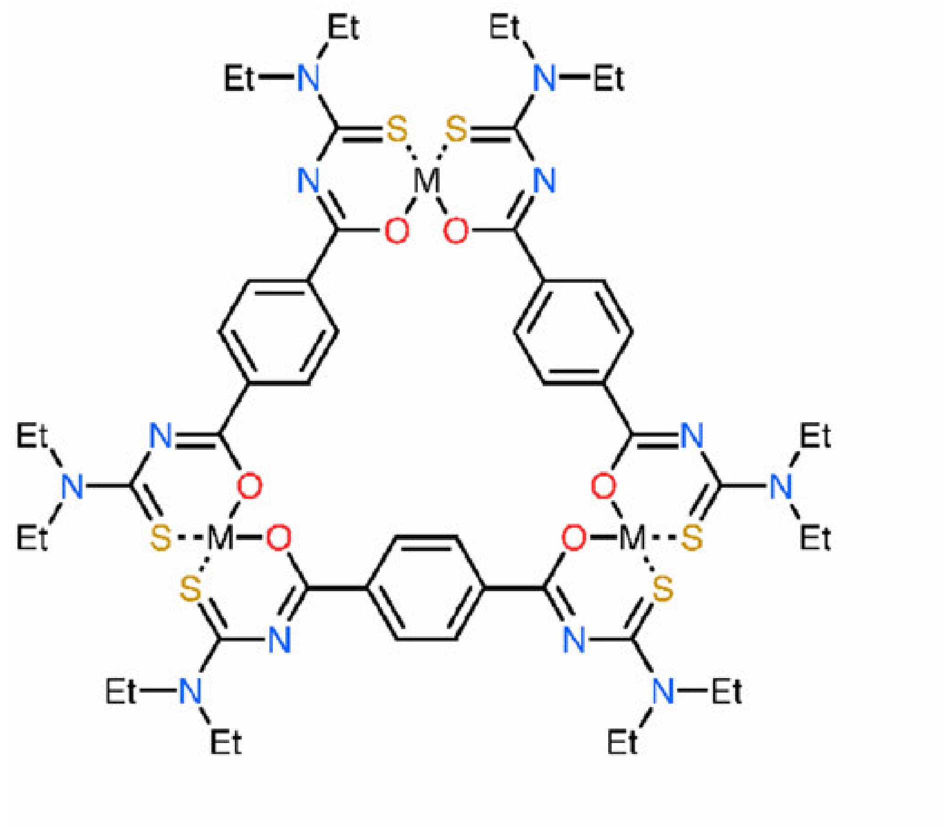




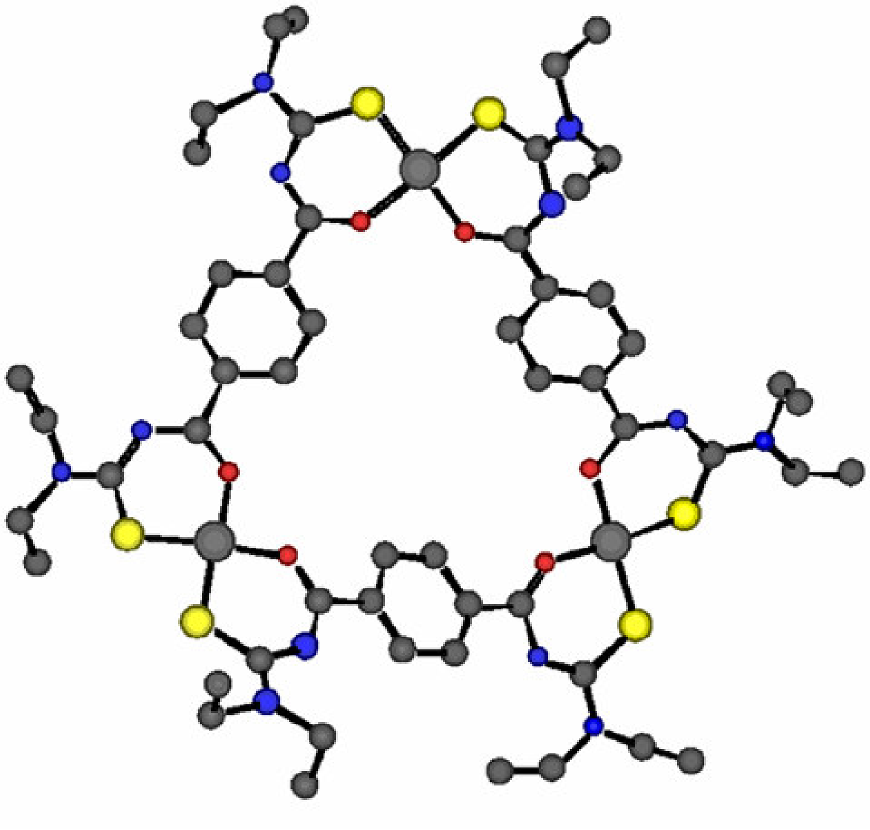
One Cu(II) center is 5-coordinate in the solid state

Clegg et al., *Dalton Trans,* 2004, in press

The Triangular Structures of the Ni(II) (low-spin) and Cu(II) Complexes Shown



Para-substitution and sp^2 hybridisation favours triangle with square-planar metal ion

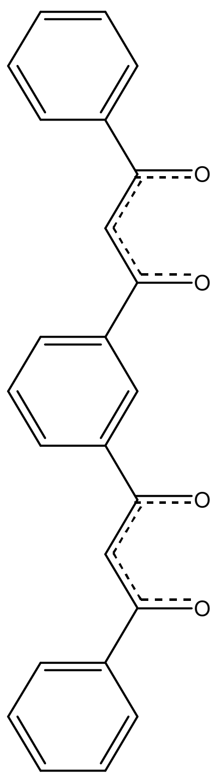


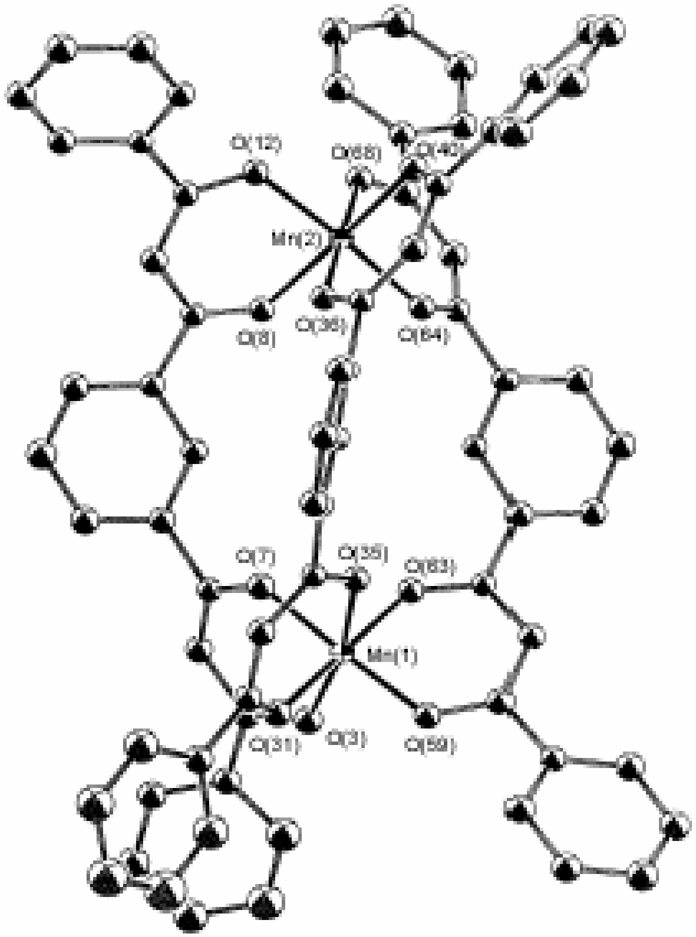
X-ray structure

R. Köhler *et al.*, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 119.

What will happen with an Octahedral metal ion ?

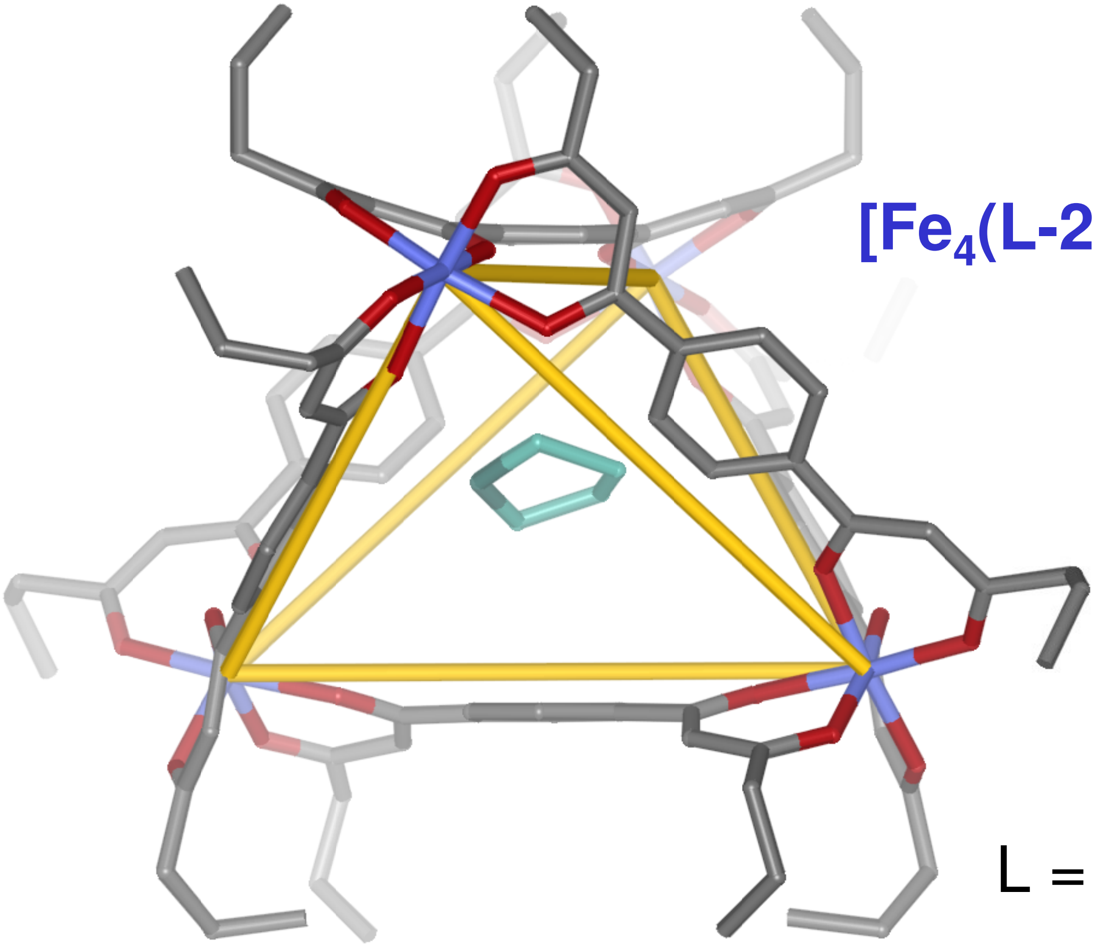
1,3-Aromatic linker gives triple helicate structure with an octahedral Metal [Mn(III)]





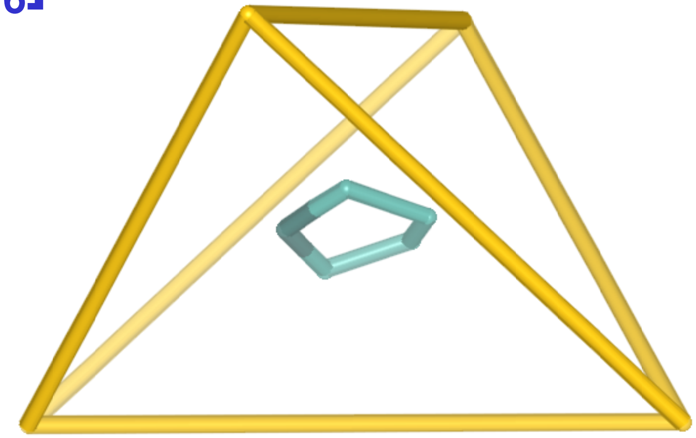
Grillo, E. J. Seddon, C. M. Grant, G. Arom´ý, J. C. Bollinger, K. Folting and G. Christou, *Chem. Comm.,* **1997,** 1561.

For 1,4-benzo derivative a tetrahedron is generated with an octahedral metal

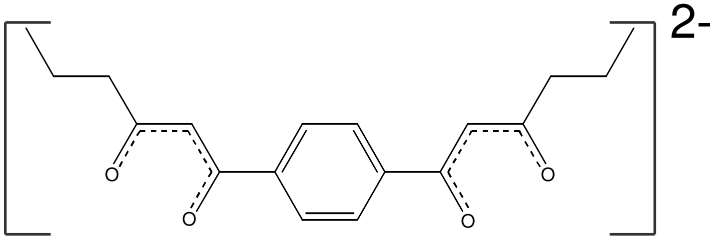


$[Fe_4(L\text{-}2H)_6].THF$

Estimated (vdW) cavity size ca. 25 Å^3



L =

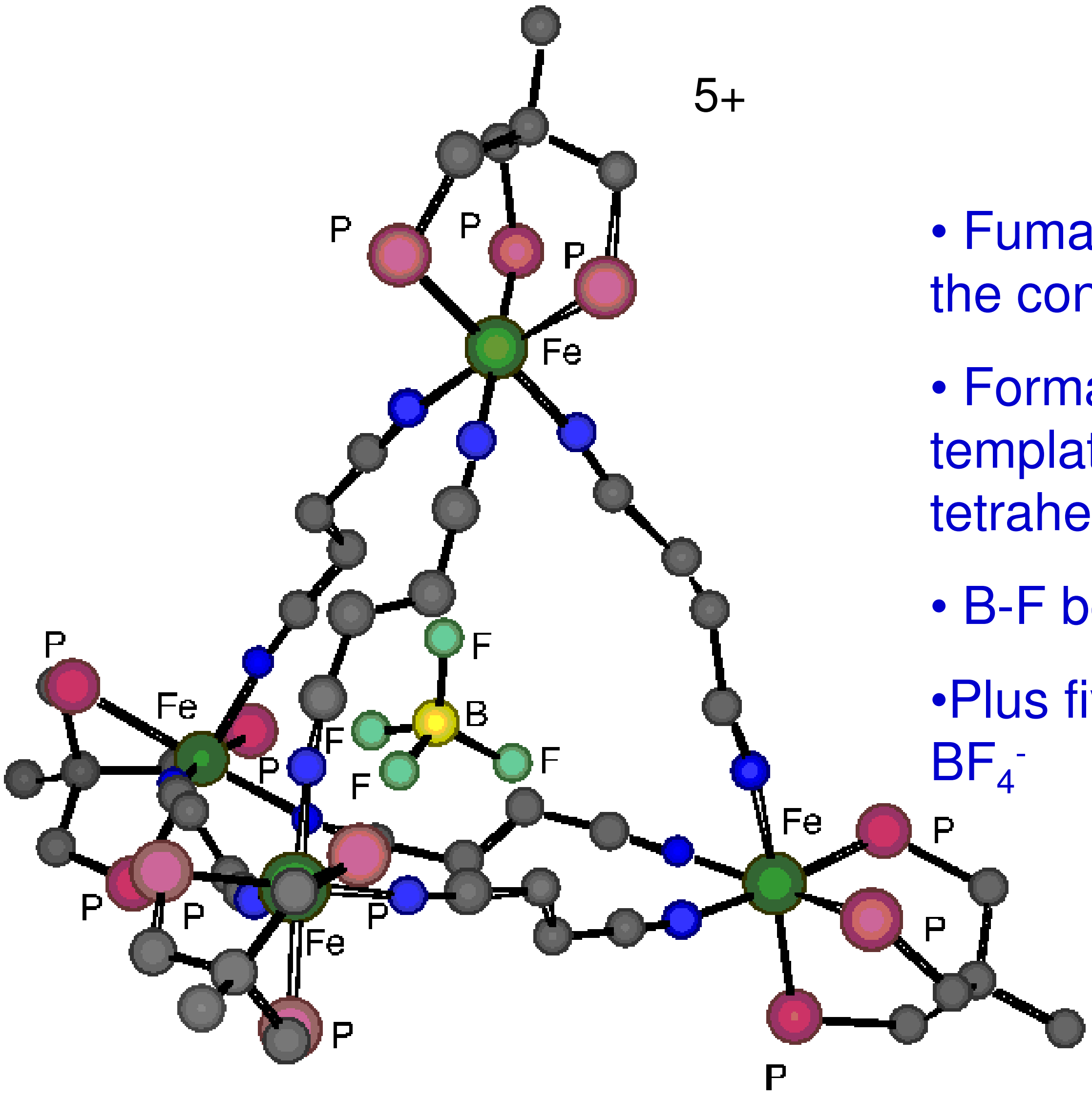


Key: ● =Fe(III) ● =C ● =O ● =C_{thf} ● =O_{thf}

Clegg et al., *Dalton Trans,* 2004, in press

Two Further Cage-Like Assemblies Based on Octahedral Metals

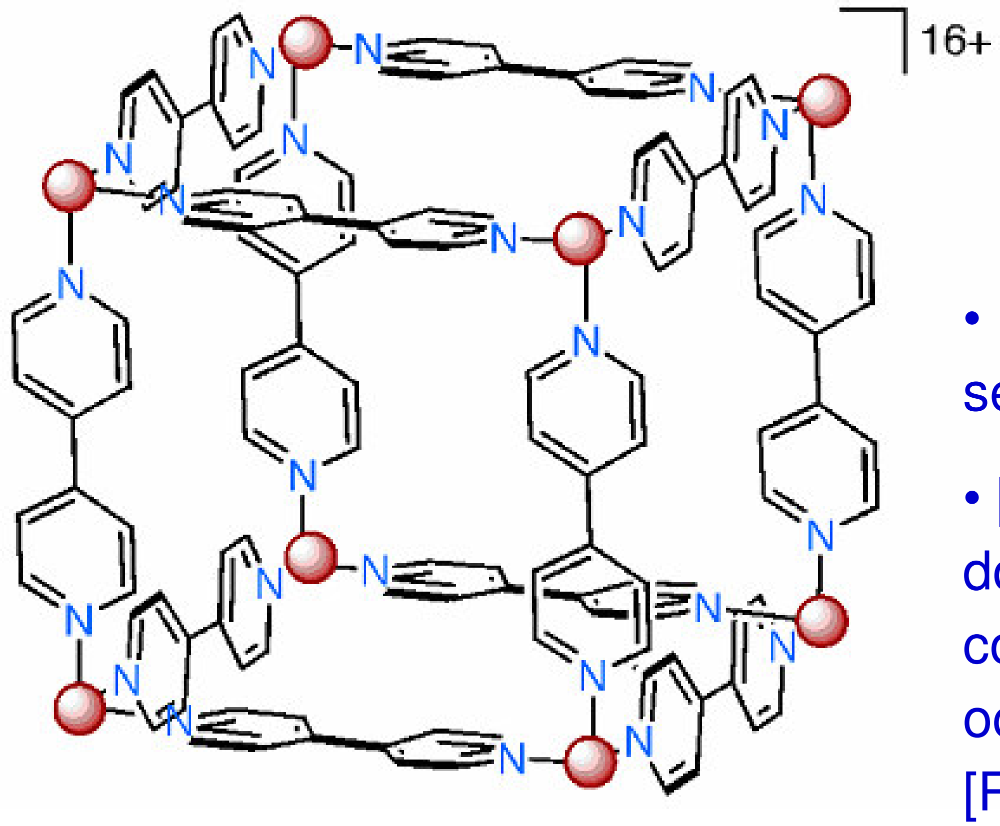
X-Ray Structure of a Tetrahedral Metallo-Cage Including a Tetrafluoroborate Guest



- Fumaronitrile ($NCCH_2CH_2CN$) is the connecting ligand
- Formation suggested to be templated by the presence of the tetrahedral BF_4^- ion
- B-F bonds point at Fe(II) ions
- Plus five charge aids inclusion of BF_4^-

S. Mann, G. Hunttner, L. Zsolnai and K. Heinze, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2808.

Assembly of a Supramolecular Cube



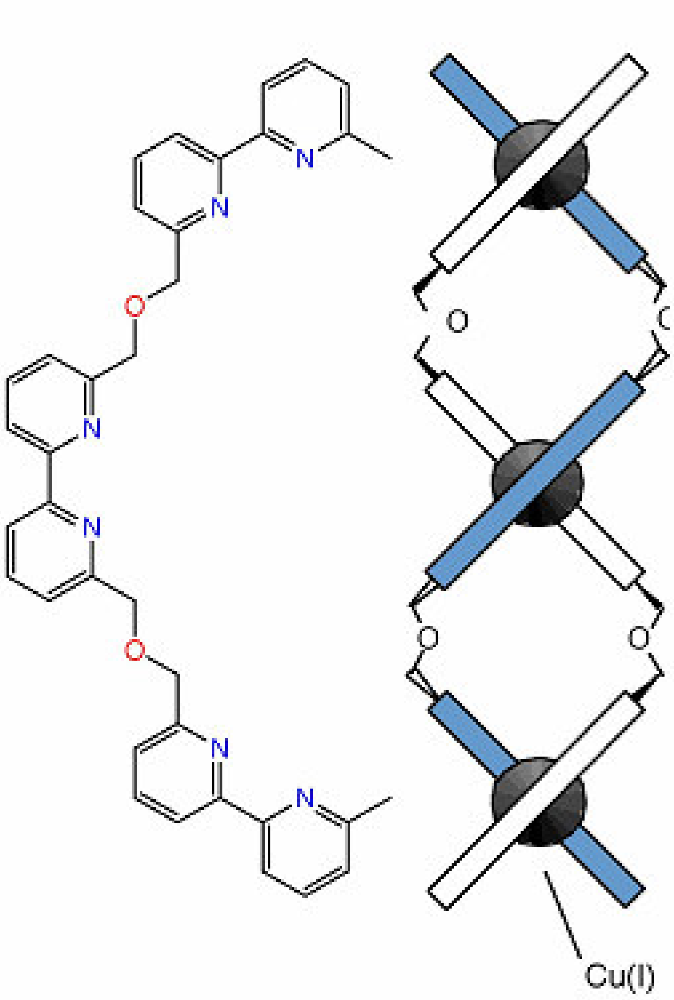
● = [([*9*]-aneS$_3$)Ru]

- Forms from 20 components by self-assembly over 1 month
- [*9*]-ane is the 9-membered 3S-donor macrocycle (L) that coordinates around one octahedral face of precursor [RuL(DMSO)Cl$_2$]

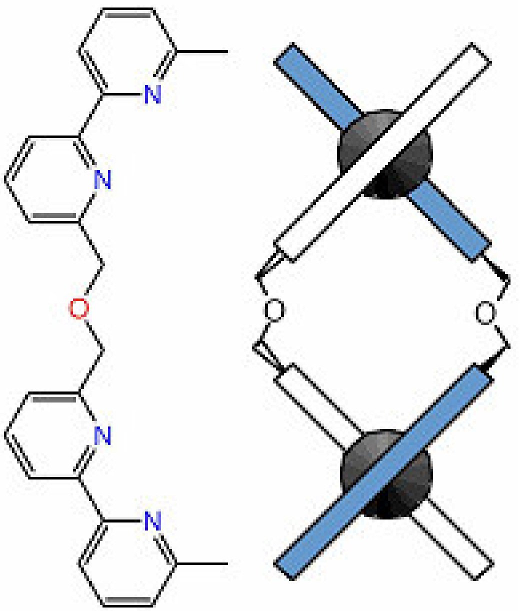
S. Roche, *et al.*, *Chem. Commun.*, 1998, 1681.

HELICIES

Double Helicies – Use of a Tetrahedral Metal Ion



Cu(I) and Ag(I) are favoured ions

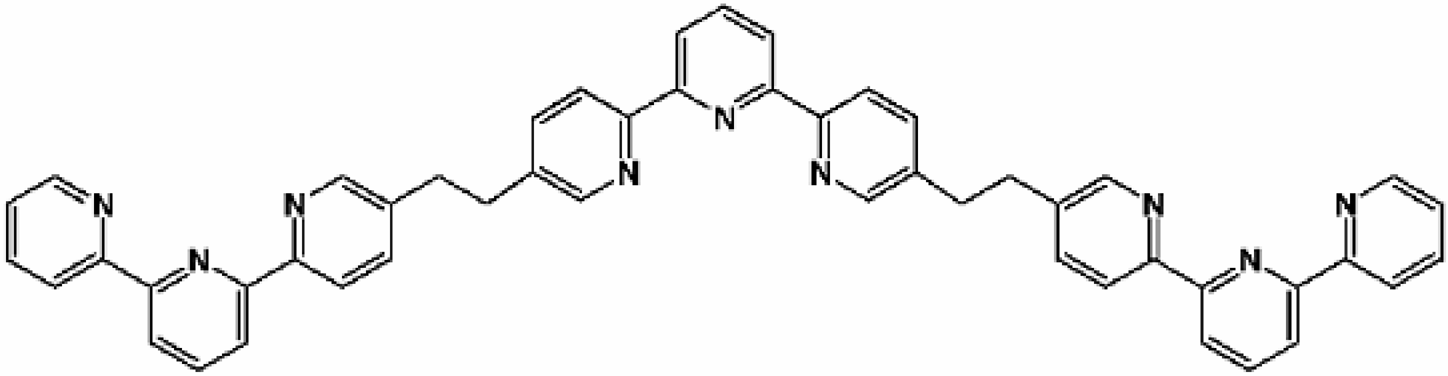


Cooperative binding shown to occur ($K_2 > K_1$)

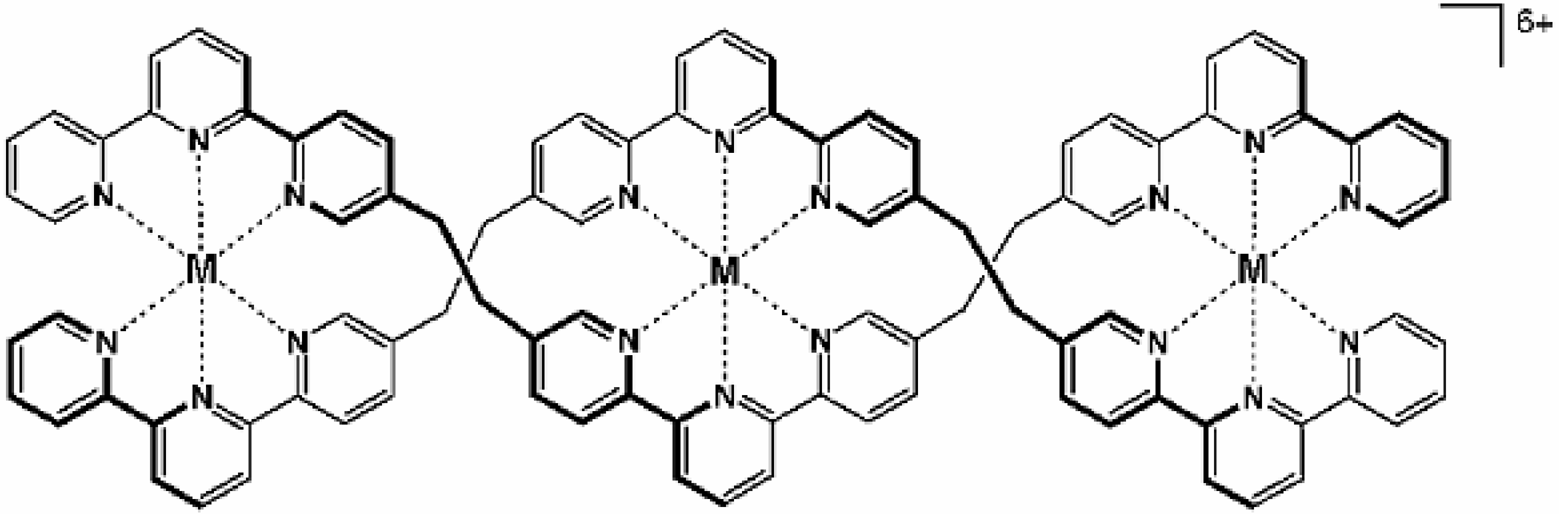
Helical arrangements– once again stereochemical preferences of both the metal and ligand are important

J.-.M. Lehn *et al.*, *Proc. Natl. Acad. Sci. USA*, 1987, **84**, 2565.

Double-Helical Structures of Complexes of Type $[M_3L_2]$



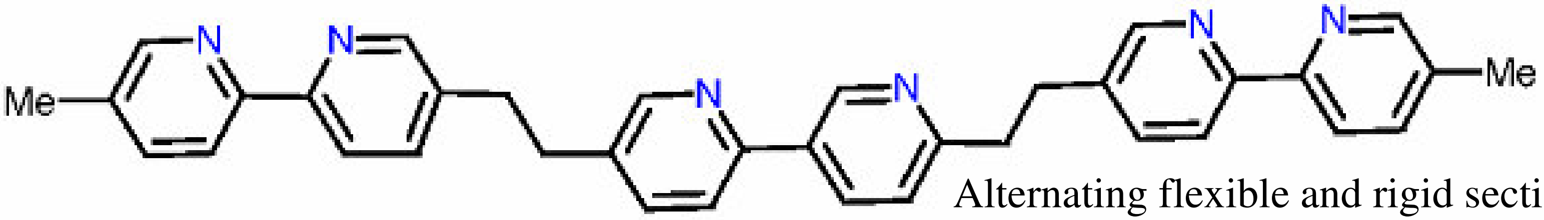
Use of two tris-tridentate strands plus an octahedral metal ion



M = Fe(II)
M = Ni(II)

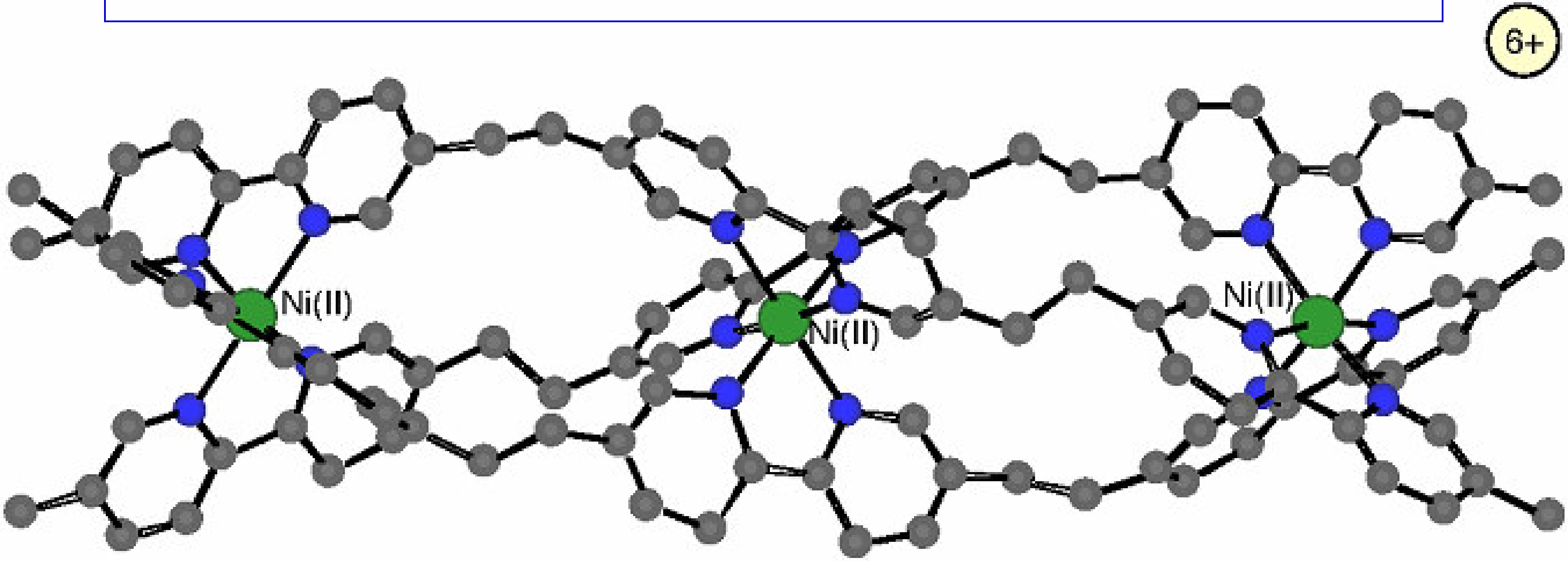
B. Hasenknopf and J.-M. Lehn,
Helv. Chim. Acta, 1996, **79**, 1643.

Alternatively an Octahedral Metal can generate a Triple Helix



Alternating flexible and rigid sections

Structure of a triple-helical complex of high-spin Ni(II)

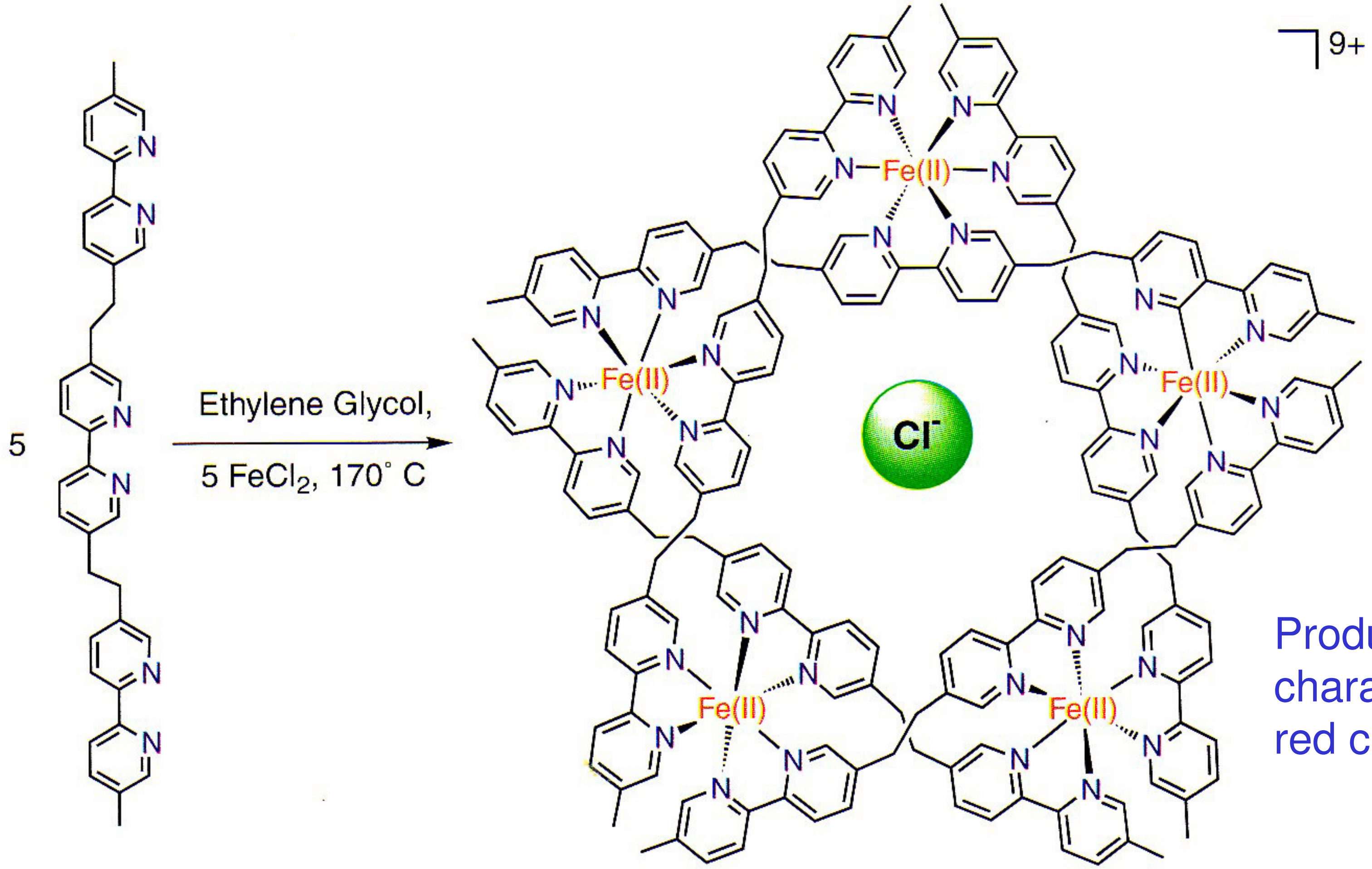


This uses a high-spin (d^8) ion that will not give kinetically inert complexes - aids error correction

R. Kramer, J.-M. Lehn, A. De Cian and J. Fischer, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 703.

The unexpected can still happen!

A cyclic triple-helical system incorporating Fe(II)



Product has characteristic red colour

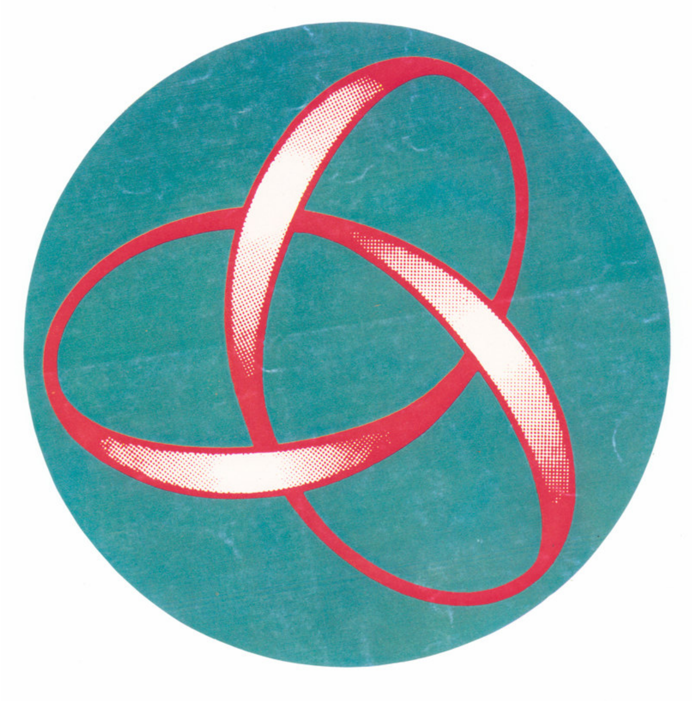
Cyclic assembly may be templated by the presence of chloride ion – strongly bound: present in mass spectrum of compound

B. Hasenknopf, J.-M. Lehn, *et al.*, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1838.

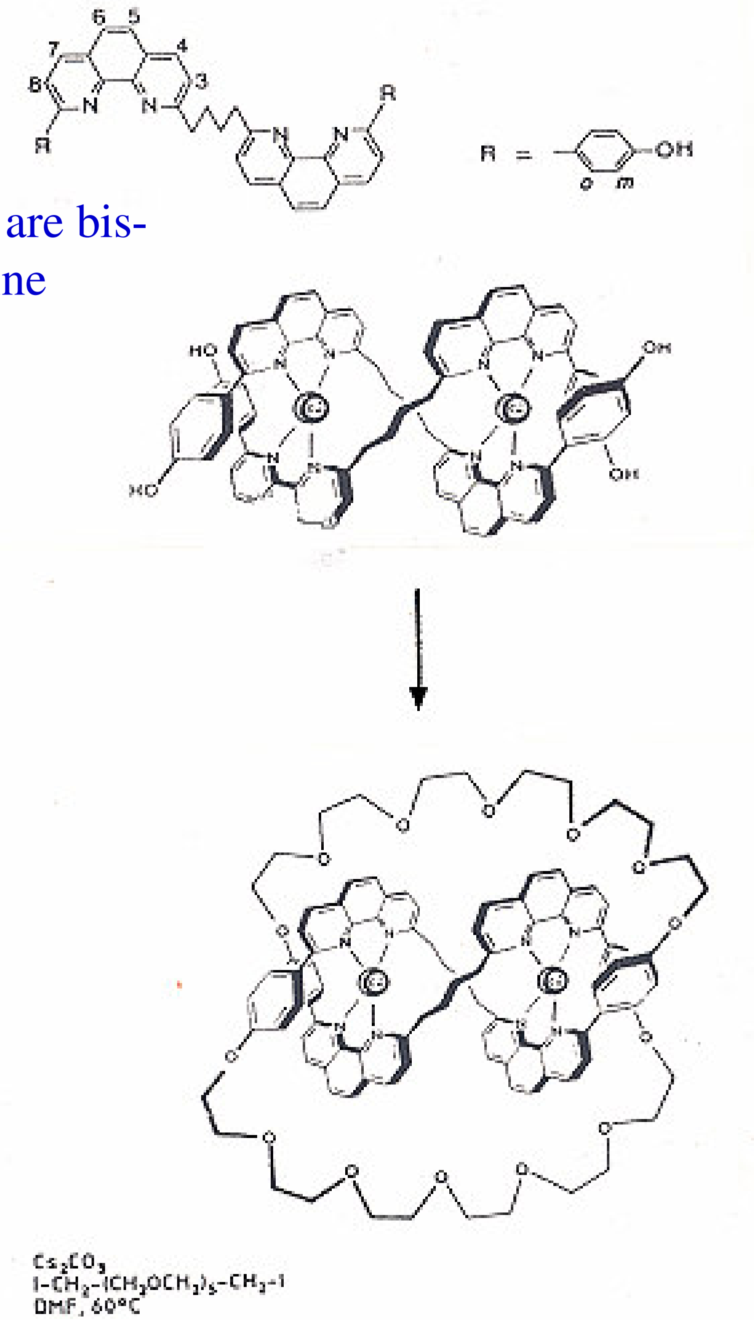
KNOTS

Formation of a Trefoil Knot

Precursor ligands are bis-1,10-phenanthroline derivatives



Simpliest ‘three-crossing’ knot

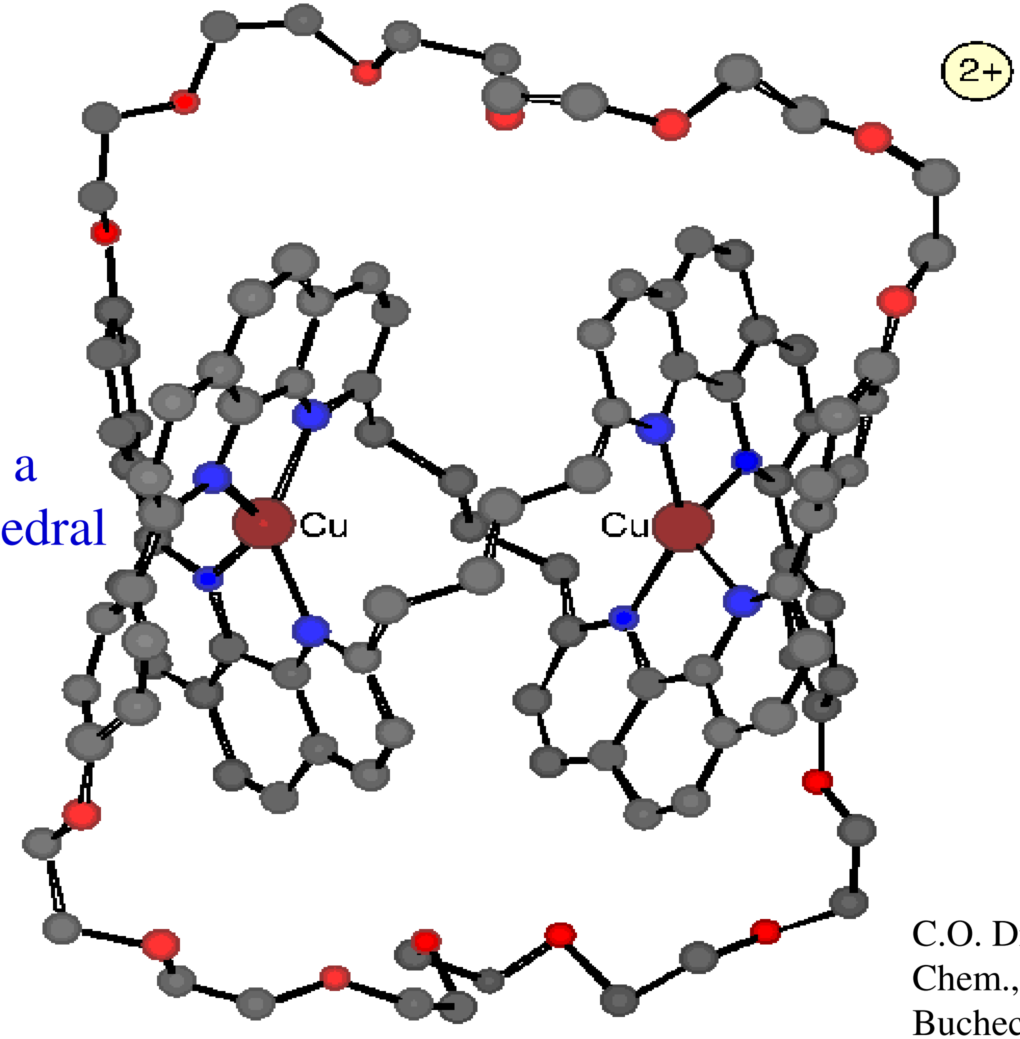


Dietrich-Buchecker, Guilhem, Pascard, Sauvage, *Angew. Chem., Int. Ed. Engl.,* 1990, **29**, 1154.

Linking ends of dinuclear helix then removing metals– three possible products:

- **Trefoil knot**
- **Large ring**
- **Two non-linked small rings**

X-ray Structure a double-helical complex of Cu(I) forming a trefoil knot



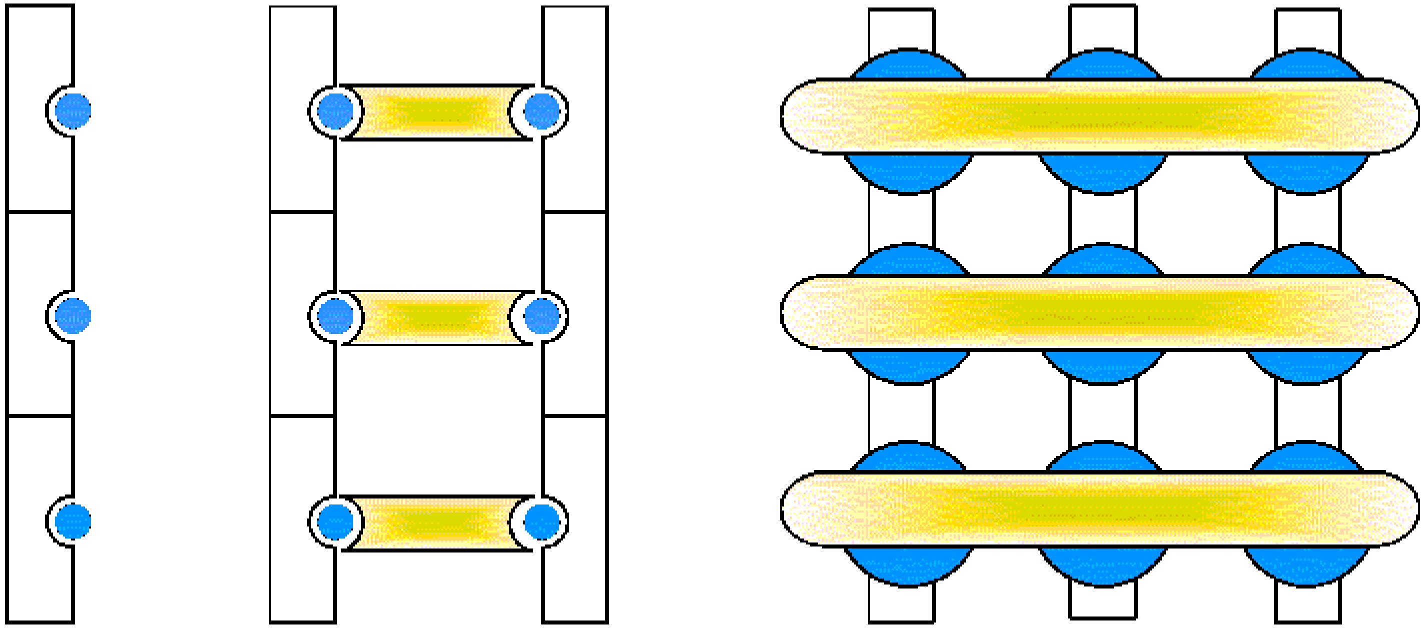
Each Cu(I) has a distorted tetrahedral geometry

C.O. Dietrich-Buchecker, *et al.*, *New J.* Chem., 1992, **16**, 931; C.O. Dietrich-Buchecker and J.-P. Sauvage, *Angew. Chem. Int. Ed. Engl.*, 1989, **28**, 189.

Molecular Racks, Grids and Ladders

Some further systems
illustrating the principles

Molecular Rack, Ladder and Grid

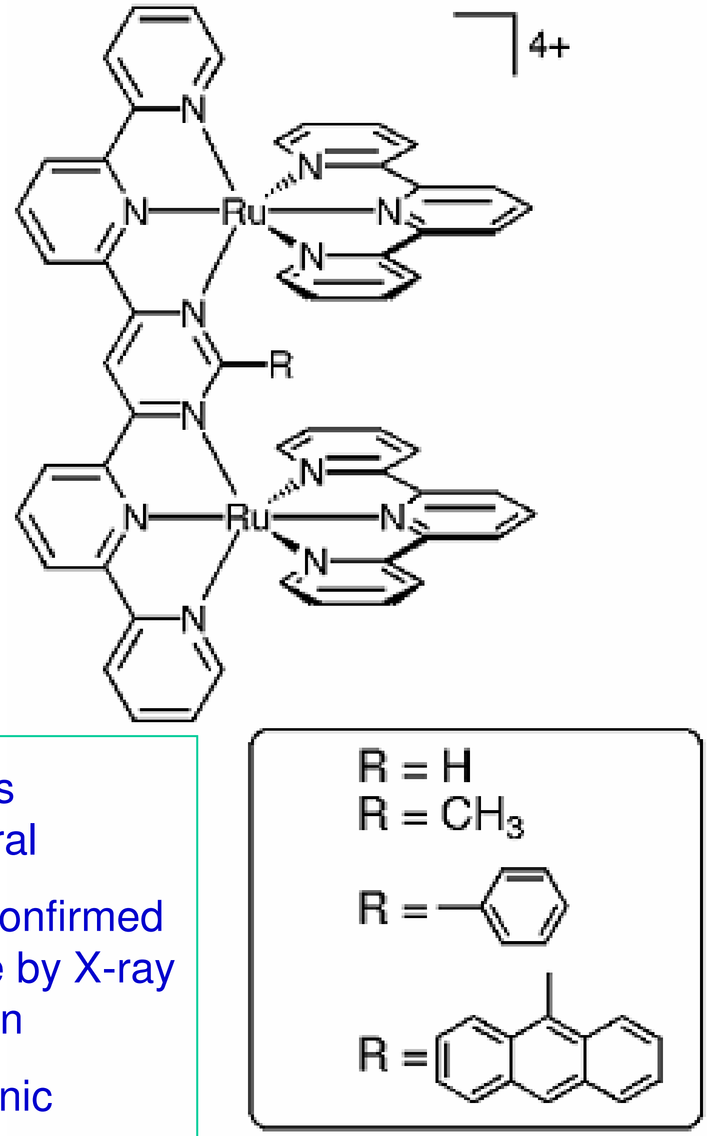


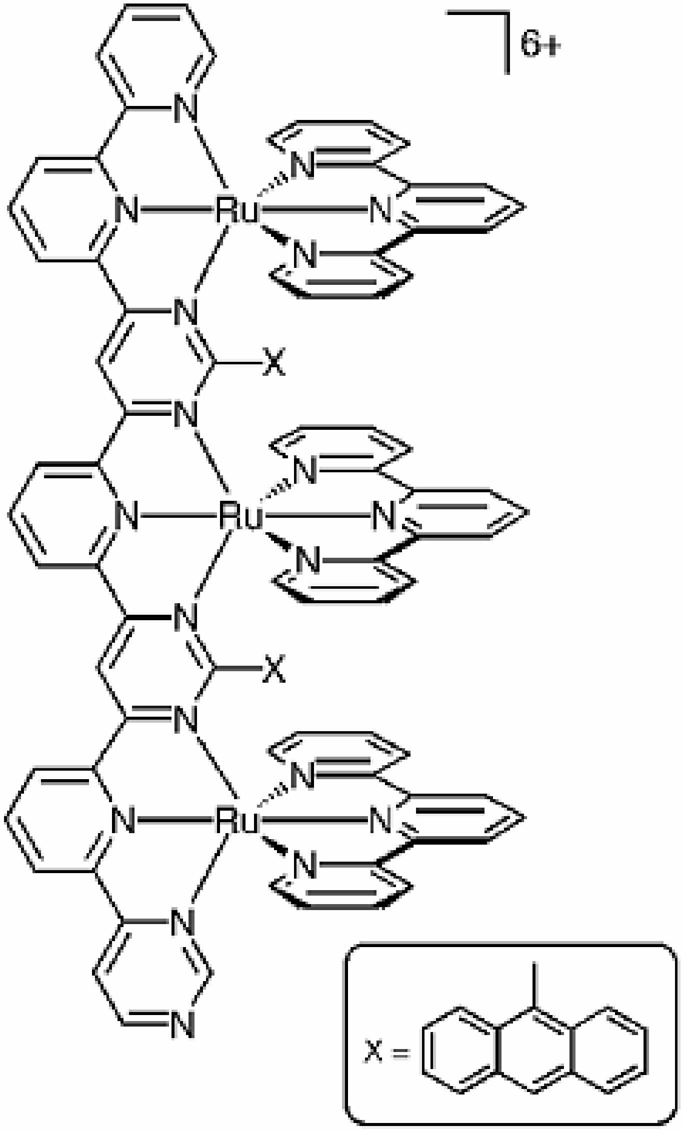
Two metal environments *Three metal environments*

Rack Ladder 3 x3 Grid

Redox modulated communication between metal centres?

MOLECULAR RACKS

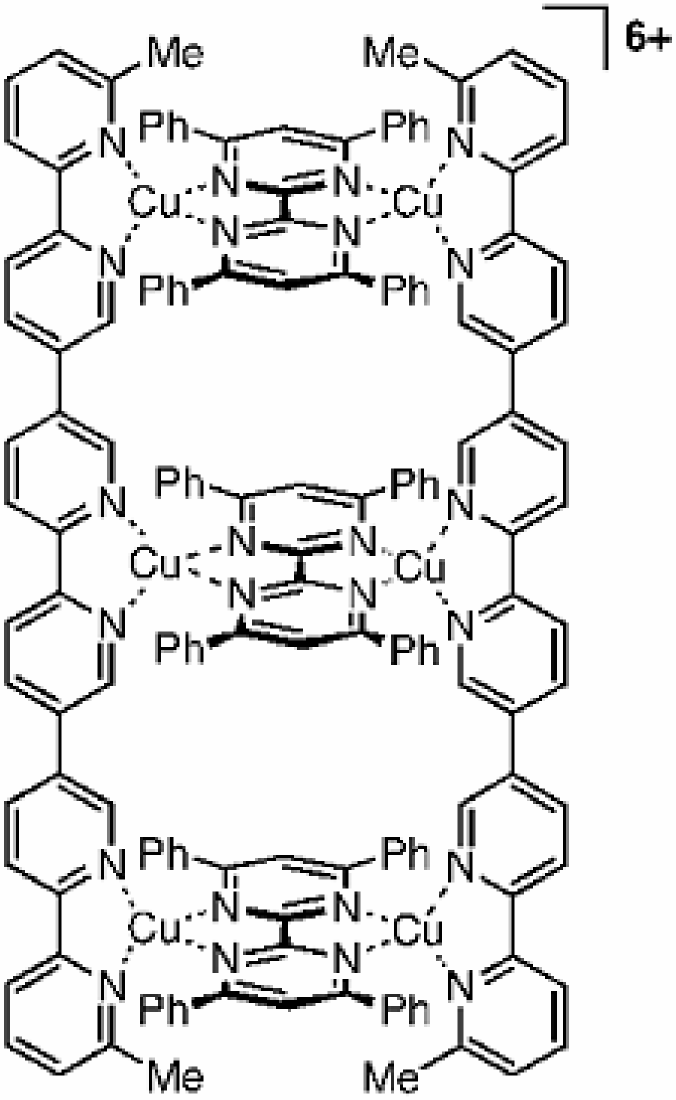




- Ru(II) is octahedral
- Have confirmed structure by X-ray diffraction
- Electronic mobility (conjugation)

G.S. Hanan, C.R. Arana, J.-M. Lehn, D. Fenske, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1122.

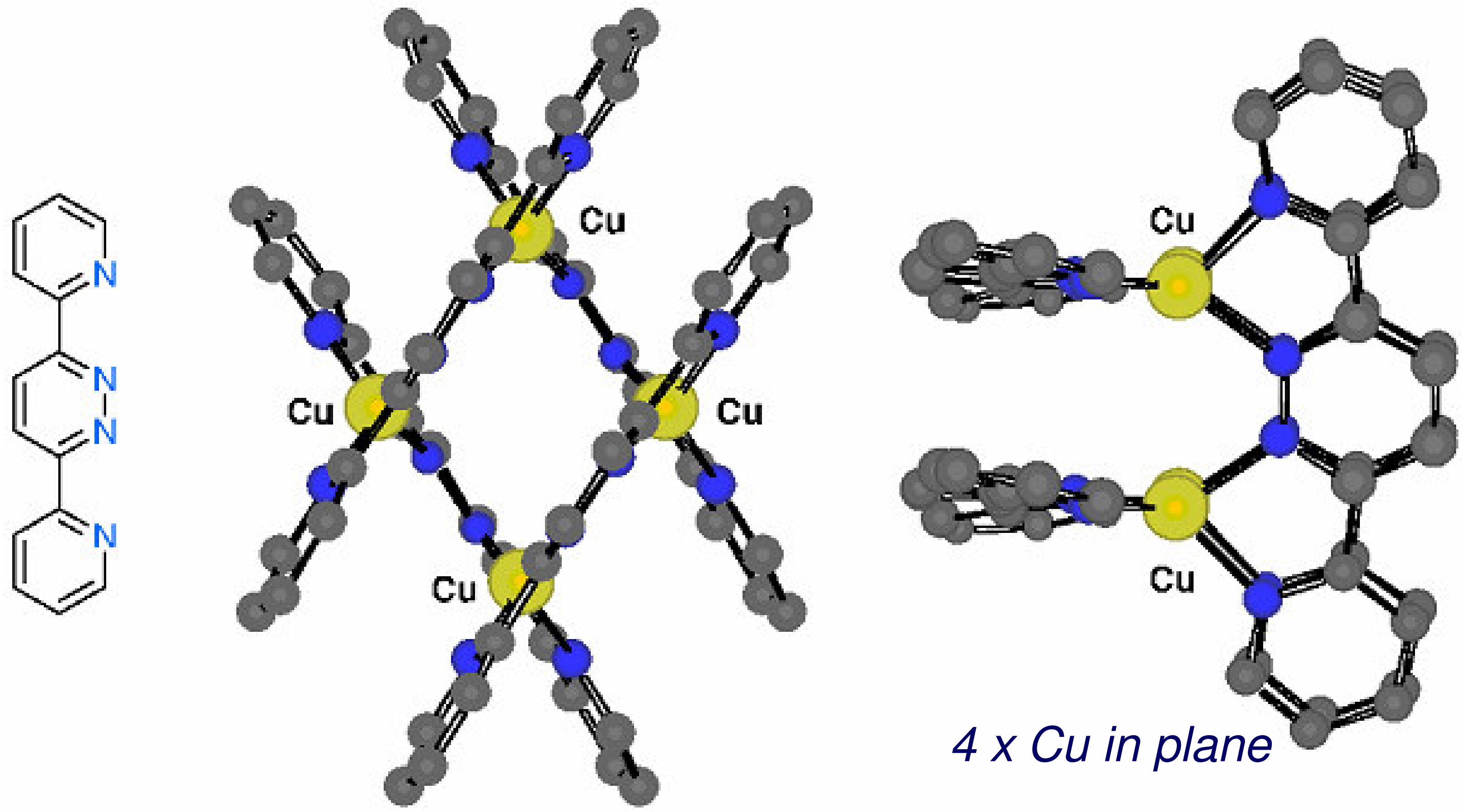
A MOLECULAR LADDER



Tris-Bipy + bipyrimidine + Cu(I)
gave self-assembly of ladder

P.N.W. Baxter, G.S. Hanan and J.-M. Lehn,
Chem. Commun., 1996, 2019.

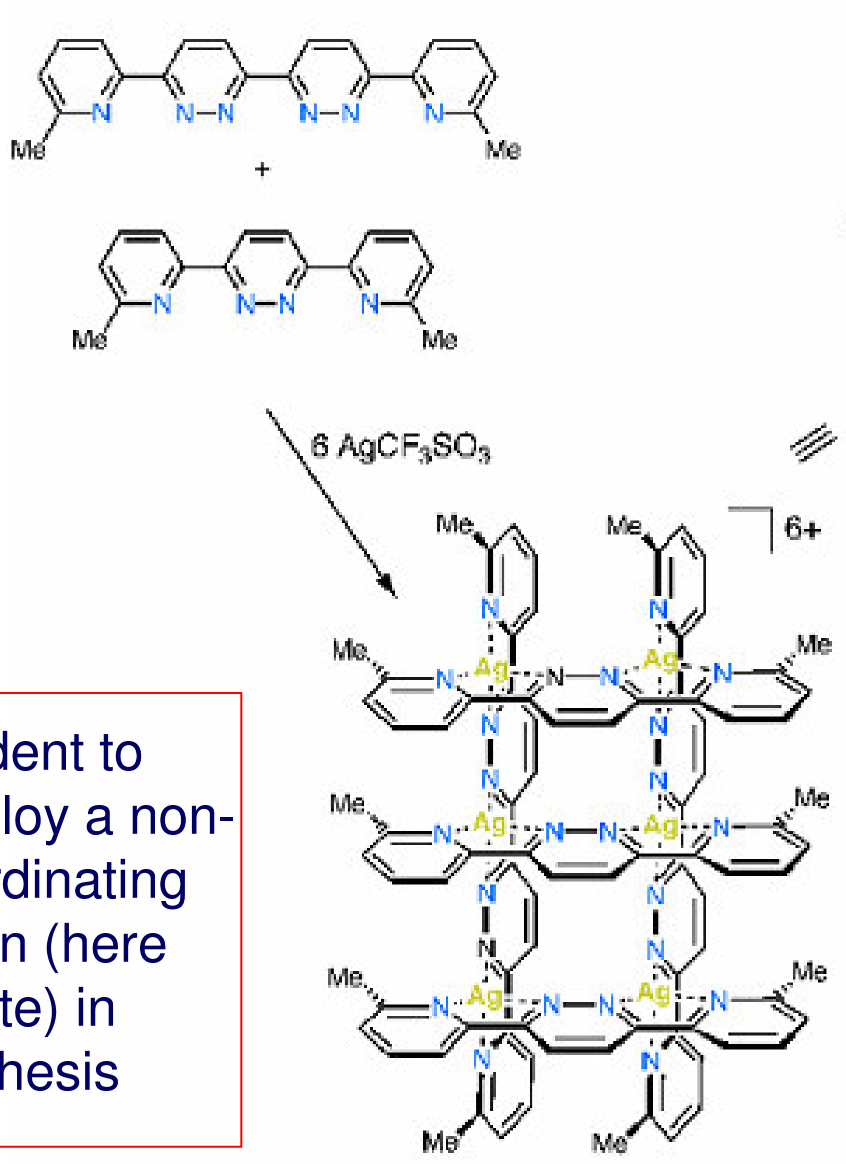
A Polynuclear grid based on a bis-bidentate Ligand

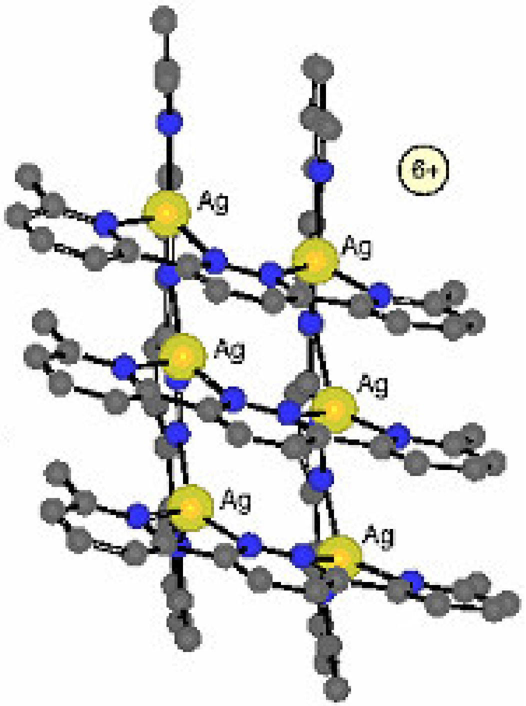


A planar arrangement of 4 Cu(I) at corners of a rhombus – 2 ligands above plane, 2 ligands below. Ligands parallel and offset, π - π stacked (3.47 Å)

P.N.W. Baxter, J.-M. Lehn, B.O. Kneisel and D. Fenske, *Chem. Commun.*, 1997, 2231.

A 3 x 2 Grid Incorporating Six Silver(I) Ions



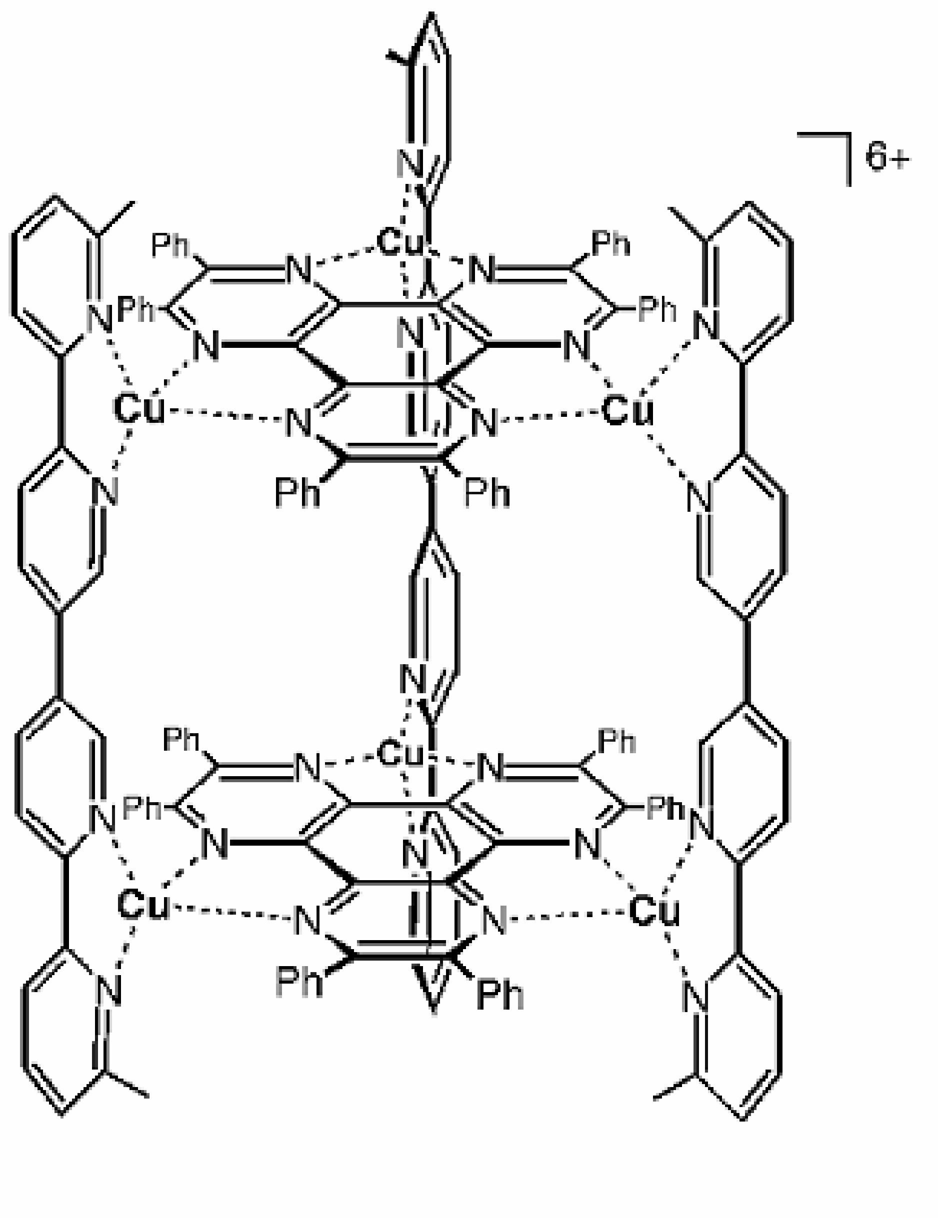


Prudent to employ a non-coordinating anion (here triflate) in synthesis

- 2 x 3 grid – a rhombus not a square
- Solvent molecules shown to be trapped in cavities
- For 3:3 grid ^{109}Ag NMR shows 4:4:1 singlets

P.N.W. Baxter, J.-M. Lehn, B.O. Kneisel and D. Fenske, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1978.

A Cylindrical Supramolecular Structure Assemblied from Eleven Particles



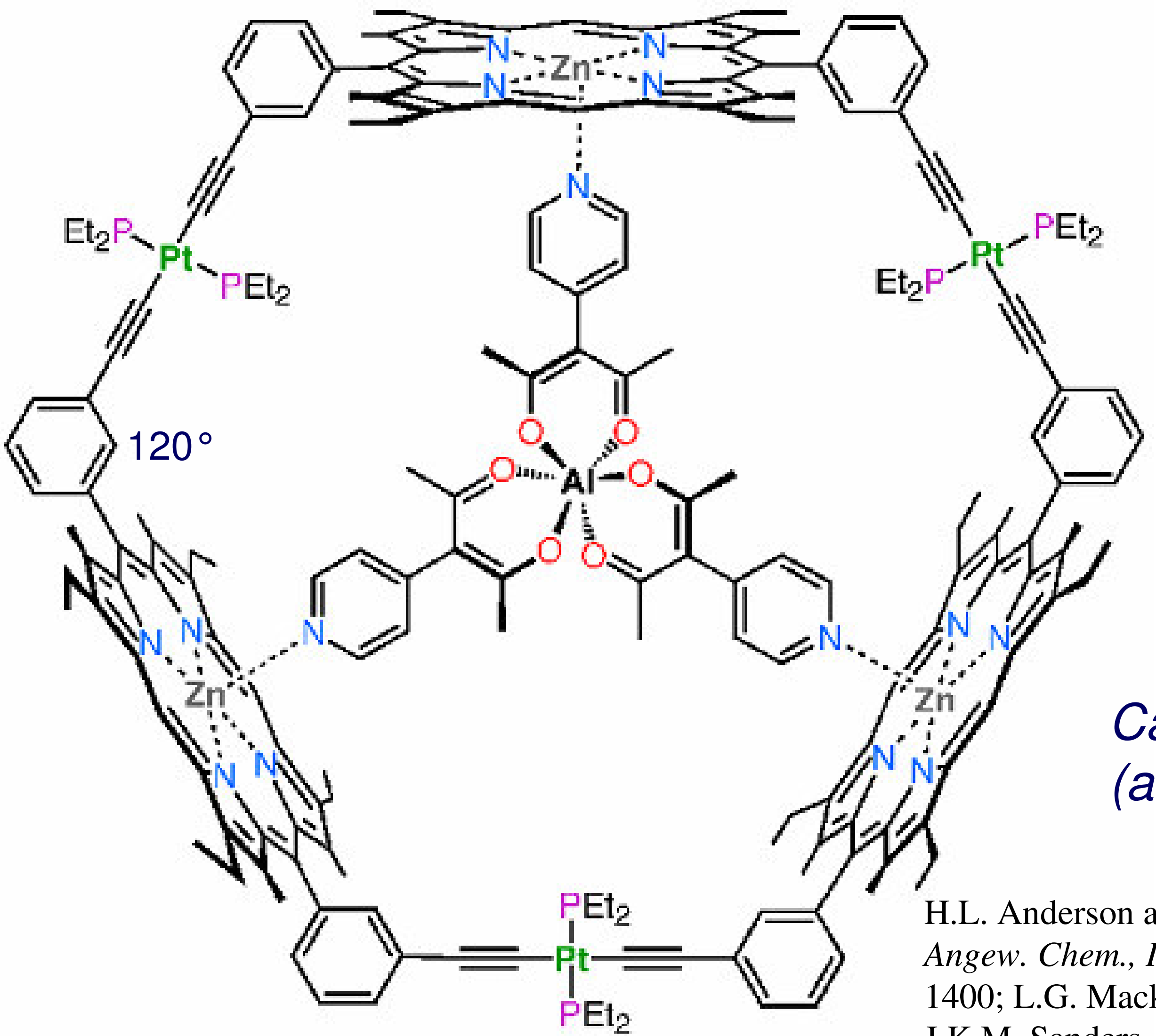
- Spontaneous assembly of 11 components
- Internal cavity ~ 4 x 4 Å
- Not quite as symmetric as drawn – helical twist
- Spectrophotometric titrations give information on positive cooperativity in this case
- Longer towers have subsequently also been constructed

A. Marquis-Rigault, *et al.*,
Inorg. Chem., 1996, **35**, 2307.

A Final Porphyrin System

(Exotica)

Zinc Porphyrin-Containing Assembled Array Formed Using Tris(pyridylaceto-acetato)aluminium(III) as a Template



Can remove Zn (and template)

H.L. Anderson and J.K.M. Sanders, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1400; L.G. Mackay, H.L. Anderson and J.K.M. Sanders, *J. Chem. Soc., Perkin Trans, 1*, 1995, 2269.

Final comment

- While the development of ‘organic’ supramolecular components has continued to develop at a rapid rate, researchers have been much more conservative in the utilisation of the vast range of metal ions (in their various oxidation states) provided by nature.

- ***Each and every metal ion represents a package of structural and electronic information*** whose uniqueness may potentially be harnessed to a given supramolecular enterprise.

- Exploitation of this aspect provides an enormous resource for future research.

Acknowledgement

Many of the figures used in this workshop are taken from the monograph: *Self-Assembly in Supramolecular Systems*, L. F. Lindoy and I. M. Atkinson, 2000, RSC, Cambridge, UK and are reproduced with permission of the Royal Society of Chemistry