Synthesis of Metal Based Interlocked Architectures: Spanning through Oxidation States, Geometries and Coordination Motifs

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Alla Mia Mamma e al Mio Papá.

Grazie per l'Amore Infinito del quale mi avete sommerso in ogni momento da quando sono al mondo:

Non sarei Nulla senza la Vostra Guida ed il Vostro Appoggio.

To My Mum and My Dad.

Thanks for the Infinite Love with which you have been covering me in every moment since I was born:

I would be Nothing without Your Guidance and Support.

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Abstract

Original synthetic procedures for preparing catenanes and rotaxanes are appearing in the current literature with escalating frequency as a result of the attention these mechanically interlocked molecules are receiving because of their potential as molecular switches, devices and machines. Coordination complexes in which rotaxanes act as ligands for transition metals are amongst the most celebrated examples of mechanically interlocked molecular level architectures. This is not only because coordination chemistry makes possible a rich diversity of structures, but also because the metal can be locked in unusual environments for subsequent electrochemical, photochemical and catalysis studies.

Efficient synthetic methods have been developed for catenates and rotaxanes based on tetrahedral and trigonal bipyrimidal metal complexes using the metal-*bis*-phenanthroline synthon pioneered in Strasbourg. Given the key role played by metal-directed synthesis in the assembly of superstructures it is essential for chemists to expand the arrays of metals and ligands available in this endeavour.
The aim of this project was to address this need and investigate the possibility to synthesise mechanically interlocked architecture using metals with higher oxidation states, different geometries and higher coordination motifs.

Chapter Two describes the synthesis of a general ligand system for rotaxane complexes of ions that prefer octahedral coordination - the commonest ligand geometry amongst transition metals but up to now a rare coordination mode for rotaxanes. Simple mixing of the components at room temperature is sufficient to assemble a broad range of octahedrally coordinated metal-[2]rotaxanes in excellent yields. The reactions have few, if any, byproducts and proceed under thermodynamic control in the absence of a catalyst or any other external reagents.

Chapter Three reports the template-directed synthesis of a [2]catenate and a [2]rotaxane by a clipping approach around trivalent octahedral cobalt ions. Appropriately derivatised pyridine carboxamide based ligands, once deprotonated, stabilise the trivalent oxidation state facilitating the entry into higher oxidation states of these metal ions. Unlike ligands previously designed for metal templation which upon demetalation offer no recognition motif, the removal of the metal to these ligands results in a system which has the potential for hydrogen-bonding.

Chapter Four reports the design and investigation of the synthesis of pentacoordinate rotaxane around divalent zinc and cadmium metals. A clipping approach as well as a threading-and-capping approach were considered, leading to interesting results involving the kinetics and thermodynamics of each complex. Zinc was suitable for the self-assembling of the macrocycle about the metal-thread complex but failed to hold the unstoppered thread in place while undergoing capping reaction; cadmium on the contrary yielded rotaxane upon threading approach but lead to the formation of more thermodynamically stable hexacoordinate catenate upon ligand self-assembly via clipping approach.

Declaration

The scientific work described in this Thesis was carried out in the School of Chemistry at the University of Edinburgh between October 2001 and September 2004. Unless otherwise stated, it is the work of the author and has not been submitted in whole or in support of an application for another degree or qualification of this or any other University or institute of learning.

Attended Lectures and Meetings

1. Organic Research Seminars, School of Chemistry, University of Edinburgh 2001-2004.
2. MIPA (Mechanically Interlocked Polymer Architectures) Meeting, 10^{th} -12^{th} November 2001, Brussels – Belgium. Oral presentation: "Metal Based Pyridine Carboxyamide Catenates".
3. MIPA (Mechanically Interlocked Polymer Architectures) Meeting, 8^{th} March 2002, Catania – Italy. Oral presentation: "New Metal Templated Mechanically Interlocked Systems".
4. EURESCO Conference - INORGANIC CHEMISTRY: Euroconference on the Inorganic Side of Molecular Architecture, 31^{st} August – 5^{th} September 2002, San Feliu de Guixol - Spain. Poster presentation: "Interlocked Architectures through Coordination of Octahedral Divalent Metal Ions".
5. EMMMA Meeting, 8^{th} February 2003, Edinburgh – UK. Oral presentation: "Developments in Transition Metal Based Interlocked Architectures".
6. The 225^{th} ACS (American Chemical Society) National Meeting, 23^{rd} - 27^{th} March 2003, New Orleans, LA – U.S.A. Oral presentation: "Interlocked Architectures through Versatile Ligands Suitable for Coordination of Divalent Metal Ions".
7. EMMMA (Exploiting Mechanical Motion in Molecular Architechtures) Meeting, 27^{th} September 2003, Trieste – Italy. Oral presentation: "Transition Metal Based Interlocked Architectures".
8. RSC-Organic Division, Scottish Regional Meeting, 17 December 2003, University of Edinburgh, UK. Poster presentation: "Interlocked Architectures through Coordination of Octahedral Divalent Metal Ions".
9. RSC-UK Macrocycles and Supramolecular Chemistry, 8-9 January 2004, University of Sheffield, UK. Poster presentation: "A Simple General Ligand System for Assembling Octahedral Metal-Rotaxane Complexes".

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Thanks to **Dr. Paul J. Lusby** for his direct supervision over these three years of work: with his calm spirit, positively traditionalist attitude and rigorous approach that at times conflicted with mine he taught me lessons in patience, perseverance and method. Much gratitude for all the times in which he cheered me up from my darkest moments with words such as: "Don't worry: everything will fall into place.". Thanks for his kindness and friendship.

Thanks to the Italians: **Elena**, **Giovanni** "Giacomino", **Andrea** "La Massaia Abruzzese", **Viviana** "Tortellino", **Andrea** "Piolin", **Giuseppe** "Bracco Baldo Perturbato" and **Ale Basso**, **Emiliano**, **Francesca**, **Michele** and **Chicco**: Miiii', senza di voi non mi passava piu'!!! Listing all the things they did for me and that I am so very grateful for would take another four pages, so I will just go for a: Grazie grazie grazie, per tutto!!

A very special thanks goes to **Louise Hogg**. Thanks for helping the entire lab to run smoothly, doing incredibly tedious, lengthy underestimated jobs, that no one would consider doing but that are so vital to our efficiency. Thanks for always willingly accept any task I asked her to help me with. Thanks for feeding me cake when you made a special one and never disappointing me when I asked history/general culture questions of any sort. Thanks for her visit to the hospital when I was ill, and the organic plums, and the flowers and the elderflower drink.

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I would like to acknowledge a few people outside the University.

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Finally, thank to **God**, for blessing me with a truly lucky life.

"It's a sign of mediocrity when you demonstrate gratitude with moderation"

Roberto Benigni

Italian actor, comedian, and director (1952 -)

List of Abbreviations

ACN: Acetonitrile

BOC: tert-Butyloxycarbonyl

Calcd.: Calculated

COSY: Correlated Spectroscopy

δ: Chemical shift

DCC: Dynamic Covalent Chemistry

DCM: Dichloromethane

DEPT: Distortionless Enhancement through Polarization Transfer

DMF: *N*,*N*': Dimethylformamide

DMSO: Dimethylsulphoxide

4-DMAP: 4-Dimethylaminopyridine

DNA: Deoxyribonucleic Acid

E: Trans isomer

EDTA: Etylenediaminotetracetate

EtOAc: Ethyl acetate

Et: Ethyl

EtOEt: Diethyl ether

FAB: Fast Atom Bombardment

g: Grams

HDPE: High-Density Polyethylene

HMBC: Heteronuclear Multiple Bond Connectivity

HMQC: Heteronuclear Multiple Quantum Coherence

hs: Hours

HRMS: High Resolution Mass Spectrometry

I.R.: Infra Red (Spectroscopy)

Me: Methyl

mins: Minutes

mL: Millilitres

m.p.: Melting Point

mmol: Millimoles

NMR: Nuclear Magnetic Resonance

NOESY: Nuclear Overhauser Effect Spectroscopy

Pyr: Pyridine

ppm: Part Per Million

RCM: Ring Closing Metathesis

RNA: Ribonucleic Acid

RT: Room Temperature

SMC: Supramolecular Chemistry

THF: Tetrahydrofurane

TLC: Thin Layer Chromatography

Z: *Cis* isomer

General Remarks of Experimental Data

Unless stated otherwise, all reagents and anhydrous solvents were purchased for Aldrich Chemicals and used without further purification. Column chromatography was performed using Kiesegel C60 (Merck, Germany) as the stationary phase. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV 400 instrument, at a constant temperature of 25 °C. Chemical shifts are reported in parts per million from low to high field and referenced to TMS. Coupling constants (*J*) are reported in hertz. Standard abbreviations indicating multiplicity are used as follows: br = broad, d = doublet, q = quadruplet, t = triplet, s = singlet. FAB mass spectrometry was carried out by the services at the University of Edinburgh. Melting points (m.p.) were determined using a Electrotermal 9100 melting point apparatus and are uncorrected.

Introduction

"If I have ever made any valuable discoveries, it has been owing more to patient attention, than to any other talent"
Isaac Newton (1643 - 1727)
English physicist & mathematician

.... And that would explain the value of my discoveries!
Ale: Thoughts on my Ph.D. work (2001-2004)

Chapter 1. Introduction

1.1 Background

"Nature does nothing uselessly.... In all things of nature there is something of the marvellous."

Aristotle (384 BC - 322 BC), Politics

Mankind's fascination for Nature goes a long way back: through the millennia it has been a source of awe and inspiration, often stimulating extraordinary discoveries and progress, up to these days, when it is still taken as an example and mimicked in a variety of different ways. In the chemistry arena, over the past few decades, the natural world has been used as model in a new field known as supramolecular chemistry, SMC, the chemistry of the noncovalent, intermolecular bond.[1] Nobel prize Jean-Marie Lehn described it as "chemistry beyond the molecule, concerning the structure and functions of the entities formed by the association of two or more chemical species".[1c] The objective has been to employ well-defined groups of molecules to perform tasks by functioning together, which the distinct components cannot do. The better understanding of the principles directing the function and mechanisms of biological processes and their dependence on noncovalent forces and self-assembly phenomena has provided to the synthetic chemists new models and ideas. Supramolecular chemistry is in fact the highly interdisciplinary merging of host-guest chemistry, molecular recognition,[2] self-assembly[3,4,5] and template-directed synthesis.[6]

Some concepts are crucial in SMC: *molecular recognition*, the selective interaction between two or more components in a self-process; *self-organization*, the spontaneous capability, under a particular set of conditions, to arrange complementary components

into definite, functional architectures; *self-assembly*, the elemental step that leads to self-organization; *(supra) molecular programming*, the specific design of the components to generate molecular recognition. Many times, one specific component is regarded as responsible for the organization and assembly of all the others: such a component is known as *template*.[7] DNA, RNA, protein and enzyme-substrate complexes are examples of supramolecular arrays in which nature relies on a variety of relatively weak forces to promote assembly. Namely, these forces are hydrogen bonding, van der Waals forces, Coulombic interactions and dipole-dipole interactions. Molecular systems held together by multiple weak forces have the advantage of being more flexible than the correspondingly strong forces assembled. Moreover, a large number of weak forces induce specificity as the most thermodynamically stable structure is produced in response of annealing processes.

1.2 Components of Chemical Templates — Anchors, Turns, Threadings, and Cross-overs

As Busch describes it, "a chemical template organizes an assembly of atoms, with respect to one or more geometric loci, in order to achieve a particular linking of atoms".[8] A deep thorough understanding of the mechanisms through which templates work and control sequences of organised steps is fundamental to be able to conceive and carry out template-directed synthesis. It is therefore important to identify and comprehend the elements crucial for the efficacy of a template and their role within the self-assembly.

The first component (a metal ion, ion pair complement, partial charge complement, or hydrogen bonded partner) in any chemical template is called an *anchor*: a function of an anchor is to hold one or more appropriate conjugate components. These conjugate components, held by the anchor, create a turn into the growing structure and are thus

called a *molecular turn*. These molecular turns, endowed with two or more terminal reactive groups oriented in a key direction, can either be intrinsically bent, (**Figure 1**, a.), or can attain their folded conformation upon reaction with the anchor (**Figure 1**, b.).

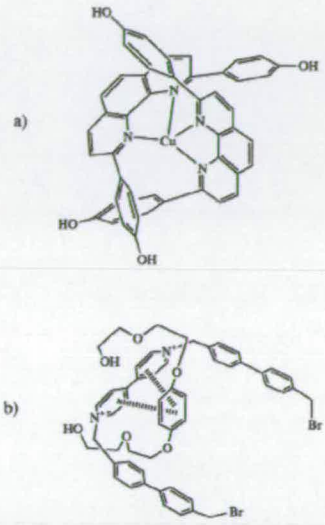


Figure 1: Examples of anchor/turn template complexes: (a) Sauvage's CuI anchor and phenanthroline turn, (b) Stoddart's π-donor and π-acceptor conjugate.[9]

Mechanically interlocked architectures are among the topologically intriguing structures constructed thanks to the greater understanding of non-covalent interactions and template synthesis. In the case of chemical templates targeted to the synthesis of mechanically interlocked architectures two elemental components must be added to molecular turns and anchors: *molecular threading* and *molecular cross-overs*.[10] Molecular threading involves the anchoring of a cyclic molecule and a linear molecule, or a molecular turn, in a fashion that inserts the linear part, called *thread*, through the center of the large ring. A molecular cross-over is given by the connection of an anchor with two non-parallel molecular turns (**Figure 2**, a.).

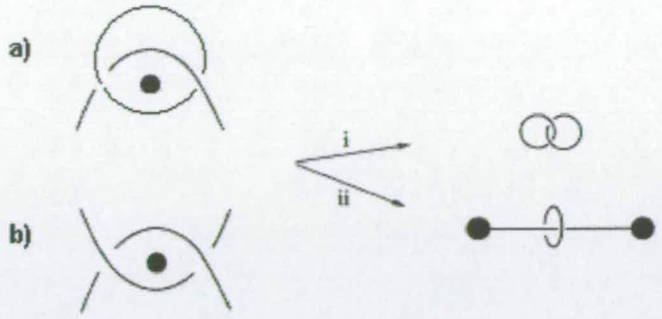
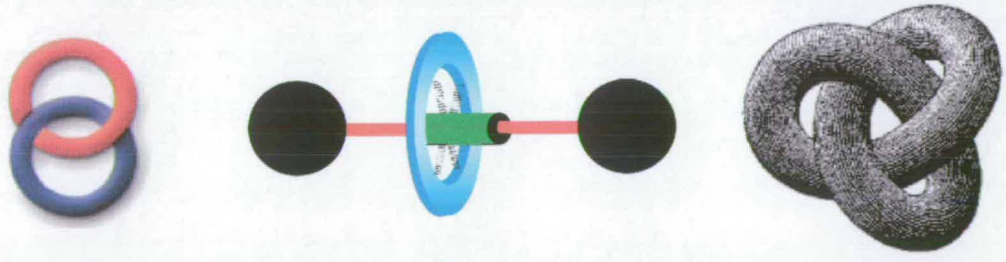


Figure 2: (a) Molecular threading and (b) a simple cross-over gives (i) a catenane upon two ring closures or (ii) a rotaxane upon one ring closure and capping.[9]

1.3 Interlocked Molecular Architectures - Nomenclature and Terminology

After introducing some of the terminology associated with the elemental components of chemical templates it is mandatory to familiarise with the vocabulary related to interlocked molecular architectures and their synthesis.

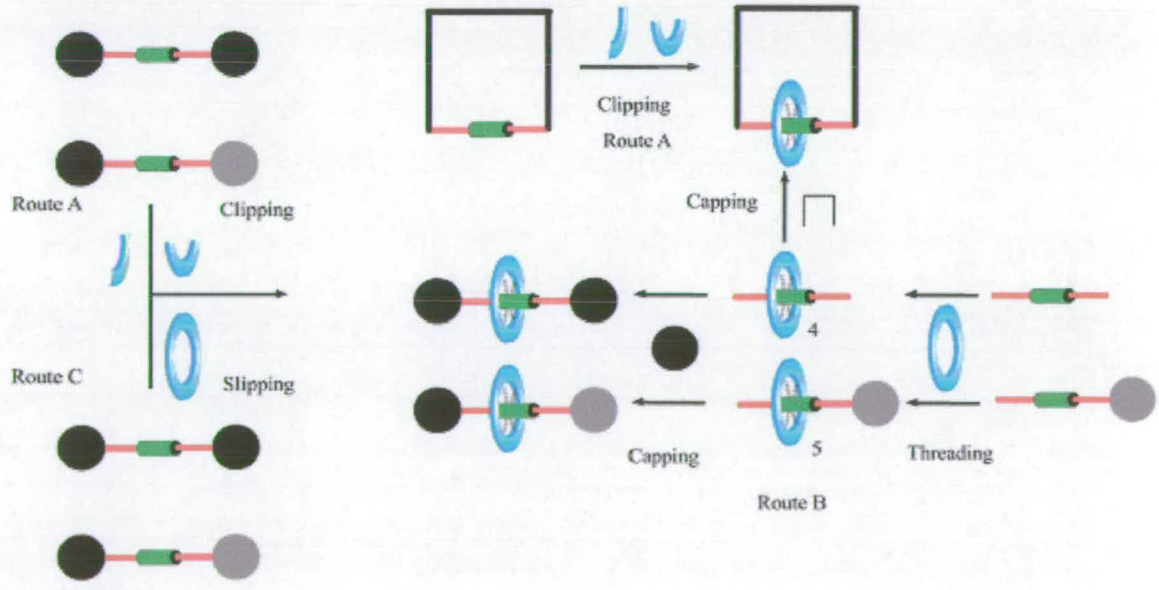


1 2 3

Figure 3: The simplest interlocked structures represented in cartoon format: 1. a [2]catenane, 2. a [2]rotaxane and 3. a trefoil knot.

The assembly of two or more interlocked rings is named *catenane*, from the Latin "catena" meaning chain. The word *catenate* is used to distinguish a catenane assembled under transition metal based template; upon removal of the metal the resulting interlocked architecture - by all means and purposes a catenane - is named *catenand* to

reveal its origin and potential coordinating characteristics.[11] *Rotaxanes* are made of one or more macrocycles surrounding a dumbbell-shaped thread-like molecule; dethreading of the system is prevented by the presence of bulky groups, called *stoppers*, at the ends of the linear moiety. Again the name is of Latin origin, "rota" meaning wheel, and "axis" meaning axle. The number in square brackets positioned before the words catenane, catenates or rotaxane indicates the number of interlocked components within the compound described. In **Figure 3** are illustrated a [2]catenane, **1**, and a [2]rotaxane **2**. Even though the components are not covalently connected, catenanes and rotaxanes are single molecules – not supramolecular complexes – as covalent bonds must be broken in order to separate the constituent parts. Mathematicians describe a *knot* as a cord that is intertwined with itself, with its loose ends joined so that it cannot become untangled. The chemical species denominated with this name presents exactly the same features. The simplest knot has three crossing points and is thus named a trefoil knot (**Figure 3**, 3.). The nomenclature related with more complex molecular entanglements is more complicated and will not be considered any further here.[12]



Scheme 1: Possible synthetic strategies towards interlocked molecular architectures.

There are three general strategies for synthesizing interlocked molecular architectures (**Scheme 1**), namely the *clipping*, *threading-and-capping* and *slipping* approach. The clipping approach, (**Scheme 1**, Route A), involves the ring closing on a molecular cross-over of one or more macrocycles. Depending on the nature of the molecular cross-over both rotaxanes and catenanes can be assembled this way. The clipping around a dumbbell shaped thread and another preformed macrocycle generates respectively a rotaxane and a catenane. Catenanes can also be produced by two ring closings on a molecular cross-over, each ring closing process making use of a single molecular turn. The threading approach, (**Scheme 1**, Route B), involves the template elemental step called molecular threading whereby a linear component is threaded through a macrocycle: capping reaction with bulky stopper groups affords rotaxane, while capping with a "u-shape" leads to catenane formation. The unstoppered system afforded by the anchoring of a cyclic molecule and a linear molecule is named *pseudo*-rotaxane, (**Scheme 1**, 4.)[13], or *semi*-rotaxane (**Scheme 1**, 5.). Another method for synthesising rotaxanes is the so-called slipping approach, (**Scheme 1**, Route C), and requires that a macrocycle slips over a preformed dumbbell overcoming the kinetic obstacle presented by the bulky groups thanks to elevated temperature (or pressure).

By combining these synthetic methods scientists involved in research in this field have been able to direct intricate successions of steps (threadings, cross-overs, ring closings, and other linkages) in order to arrange complicated organized molecular entanglements. Moreover, the simultaneous employment of a number of orthogonal[14] recognition motifs/algorithms[15] for the construction of elaborate multicomponent superarchitectures has enabled synthetic chemists to diversify the series of self-assembled[16] superstructures.[17] A more complete sequence of the various structural motifs that have been built through chemical templates are displayed in **Figure 4**.

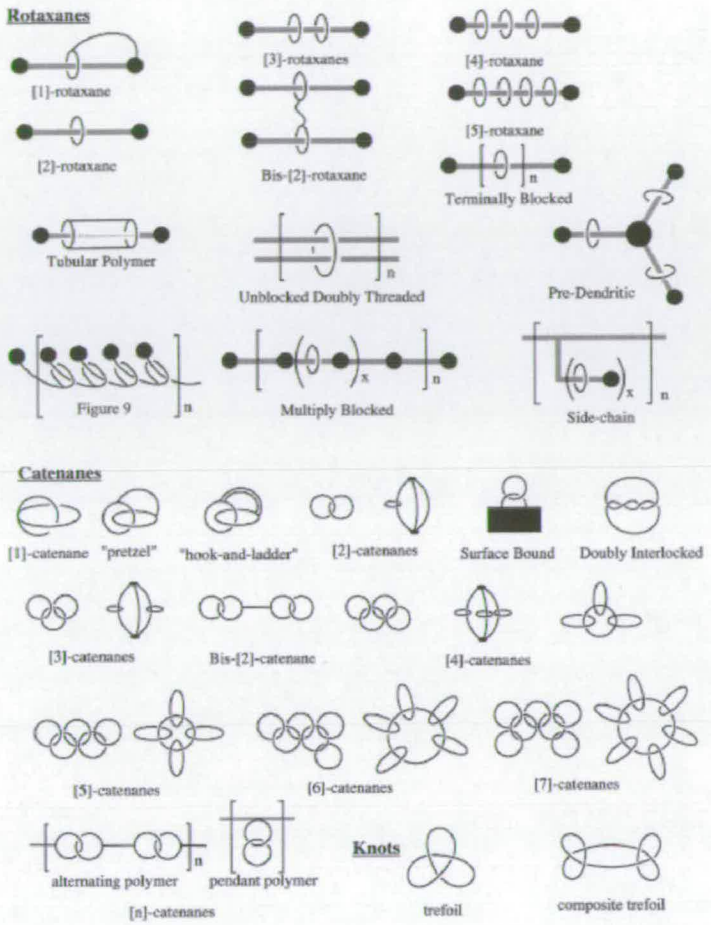


Figure 4: Cartoon representations of a variety of interlocked structures resulted from template syntheses: rotaxanes, catenanes, and knots.[9]

1.4 Coordination Chemistry - Metal Ion Templates

In the past twenty years coordination chemistry has played an increasingly important role expanding beyond the interactions of metal ions with organic and inorganic ligands and emerging into the field of supramolecular chemistry.[1a,b,g, 18] The coordination number of the metal ion, the geometry preference, and, in some instances, the rigid structure can orientate ligands in a precise spatial manner: this feature can be exploited

during critical bond formations. In addition, the metals can display properties such as light absorption and luminescence, catalysis and redox processes at accessible potential values, which can be used to carry out valuable tasks.[19]

A vast number of fascinating supramolecular species have been synthesised and investigated: here a short review which is by no means exhaustive discusses some of the principal examples of interlocked compounds and other supramolecular metal complexes that can be considered as prototypes of molecular-level devices.[19c,20,21]

The discovery that transition metals act as templates in the synthesis of macrocycles was first reported by Curtis in the 1961.[22] This finding initiated a new trend where metals were used as templates in the rational synthesis of macrocycles. A few years later, the Busch group proved that the planar nickel(II) ion exerts a kinetic template effect by arranging a tetradentate ligand into a turn and thus bringing its two reactive terminal groups into adjacent positions. This imposed proximity assists cyclization by reaction of the terminal groups with a reagent that is a second molecular turn (**Figure 5**).[23]

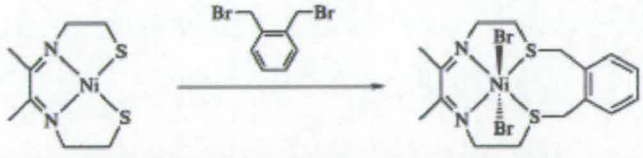
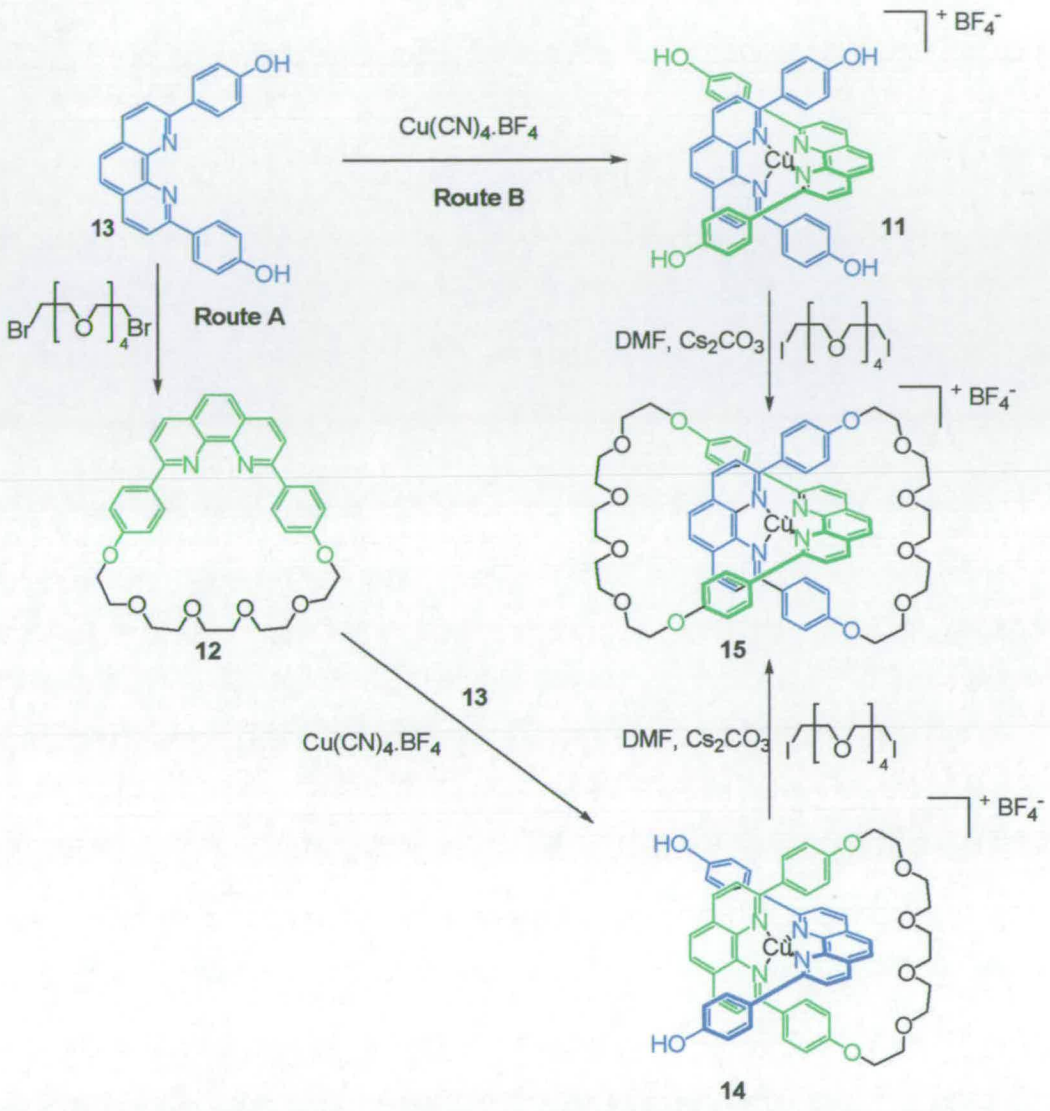


Figure 5: The seminal metal ion template macrocyclization[9]

Another advantage of this template-directed synthesis is that metal ion anchors can often be easily removed leaving the structure in one piece after the cyclization reaction.[24] The majority of the examples invoking transition metal 'templates' are two-dimensional, however there are some cases where the transitional metal positions the ligands in a three-dimensional manner.[25]

1.5 Overview of Mechanically Interlocked Architectures Using a Transition Metal Template

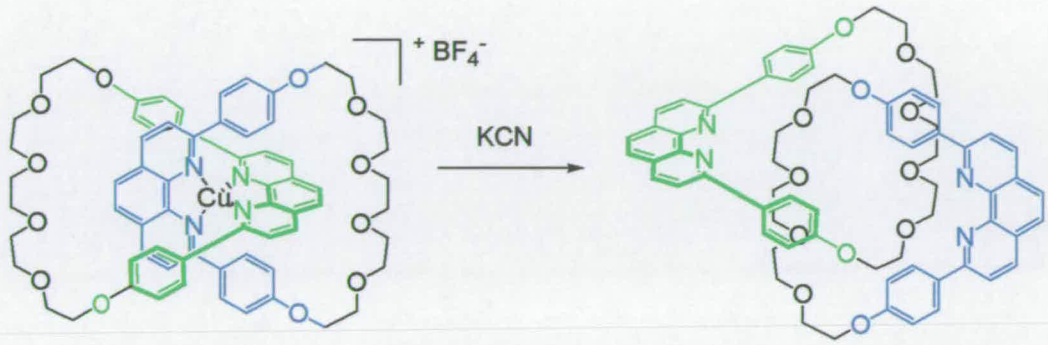
Interlocked molecules are characterised by non-planar structures and thus they require the template action of appropriate non-planar metal ions as anchors to compose the 'three-dimensional' arrangement. Sauvage and Dietrich-Buchecker pioneered this field offering the seminal example of transition metal/organic ligand complexes deployment to obtain interlocked molecular architectures.[26, 27] They developed a system based on copper(I) to exploit the '3D' nature of tetrahedral metal complexes. In this synthon, complex **11**, two bidentate phenanthroline ligands are held in a mutually orthogonal manner as shown in **Scheme 2**.[28] In order to obtain the desired catenate they attempted both a threading and a clipping approach. In the first case a preformed macrocycle is threaded with a molecular turn followed by ring closing dual capping. Macrocycle **12** endowed with a bidentate phenanthroline ligand was treated with $Cu(MeCN)_4BF_4$ and a diphenolic phenanthroline ligand **13** to give complex **14** (**Scheme 2**, Route A). Catenate **15** was obtained in 42 % yield by reaction of complex **14** with pentaethyleneglycol diiodide. In the clipping approach complex **11** was reacted directly with pentaethyleneglycol dibromibe in a two ring closing reaction to give catenate **15** in a 27 % yield (**Scheme 2**, Route B). Even though more risky and frequently lower yielding this strategy became the most common for the synthesis of symmetrical systems.



Scheme 2: The synthesis of Cu^{I}-based catenate **15**.[28]

These Cu(I) based catenates were shown to be more stable to demetalation than analogous non-interlocked ligand systems. This phenomenon, known as the catenand effect, is due to the topological confinement of the ligands within the interlocked superstructure.[29] Nevertheless, demetalation of catenate **15** was achieved by exposure to KCN giving the corresponding catenand **16** (**Scheme 3**). This new, more flexible structure does not experience the effect of the coordination to the copper and π-π

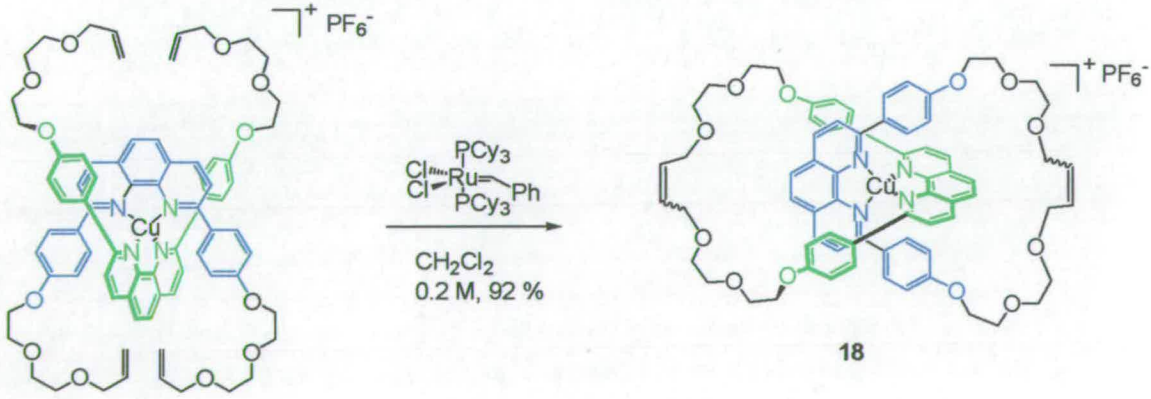
stacking between units and rearranges in order to minimise unfavourable interactions between the phenanthroline groups.



15 **16**

Scheme 3: Demetalation of catenate **15** to afford corresponding catenand **16.**[29]

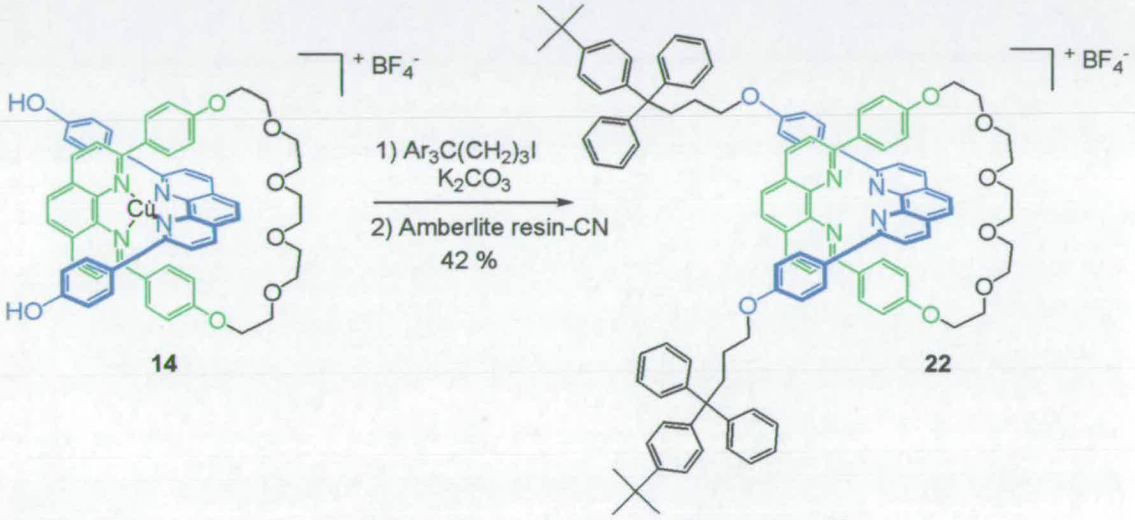
In the late 1990's the same Cu(I)/phenanthroline synthon, appropriately derivatised with terminal olefins, was used to afford catenate **18** via ring-closing metathesis, RCM, in an excellent yield of 92% (**Scheme 4**).[30] Alkene metathesis had been used in one of the earliest syntheses of catenanes,[31] but the development of the currently so famous Grubbs' catalyst, with its high activity and an excellent range of functional group tolerance,[32] moved the ring closure reaction to a new level.



17 **18**

Scheme 4: High-yielding synthesis of Cu^{I} catenates by ring closing metathesis.[30]

In 1991 Gibson *et al.* reported the synthesis of the first example of metal based rotaxane. Sauvage's Cu(I)/phenanthroline motif was used to deliver the pseudo-rotaxane **14** via a threading approach.[33] Treatment with a trityl-terminated alkyl halide, followed by acidic resin demetalation yielded rotaxane **22** in a 42 % yield (**Scheme 5**).



14 **22**

Scheme 5: Synthesis of a [2]rotaxane using a Cu^{I} template.[33]

Through the 90's, building on the usual tetrahedral coordination unit the Sauvage group published studies on a variety of transition metal-based rotaxanes where the trityl stoppers were replaced by chromophores. The spherical shape of fullerenes acted as an ideal endgroup for the dumbbell component.[34] Under light irradiation electron transfer took place between the Cu(I) central complex and one of the C_{60} stoppers working as electron acceptor (**Figure 6**, a.). [2]Rotaxane **22b** comprised metal-complexes fragments as stoppers. By taking advantage of the different coordination requirements of copper(I) and ruthenium(II) they assembled this system simply using coordination chemistry (**Figure 6**, b.).[35] The employment of porphyrine as stoppers due to their interesting electro and photo-active properties was of particular appeal in the development of models to simulate natural cofactors such as hemes and chlorophylls.[36]

Upon light irradiation the zinc porphyrin transfers an electron to the gold porphyrin acceptor. When these two bis-porphyrin chelates act as a molecular cross-over coordinating about a copper metal, the electron transfer occurs at much higher rate than in the free system. By complexing two bis-porphyrin threads around a single metal the undesirable interligand photoinduced electron transfer[37] is possible as well as the wanted intramolecular transfer. Incorporating the bis-porphyrin unit in rotaxane **22c** avoided dimerization of bis-porphyrin in a complex, allowing discrimination between the two possible electron transfer pathways (**Figure 6**, c).[38] This work was further investigated producing a series of transition metal-based rotaxanes incorporating porphyrins as stoppers in attempts to mimic the array of tetrapyrrolic chromophores, found at the heart of bacterial photosynthetic reaction centres.[39]

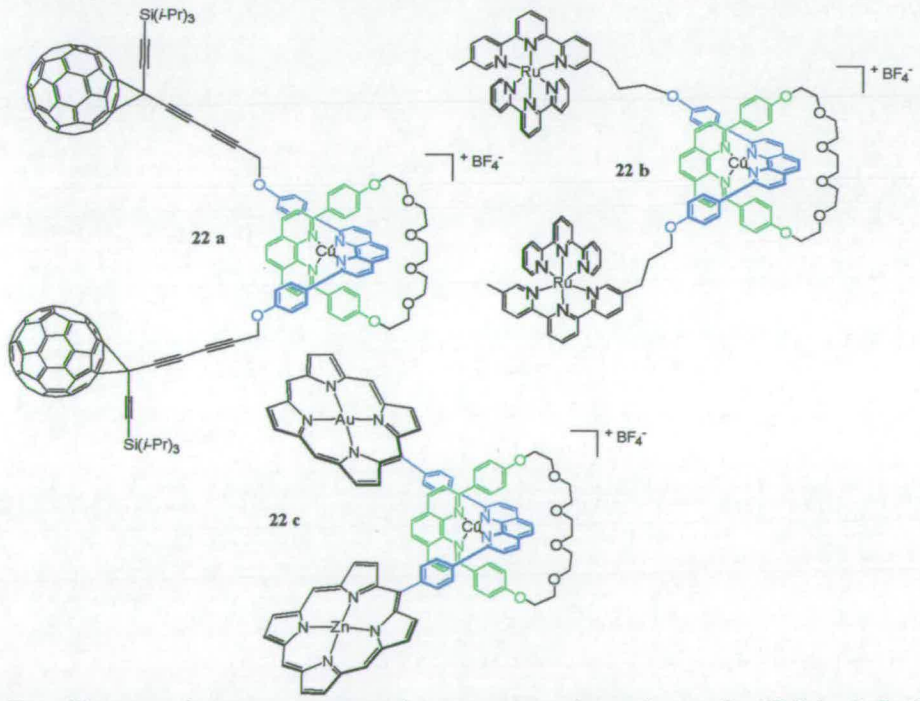
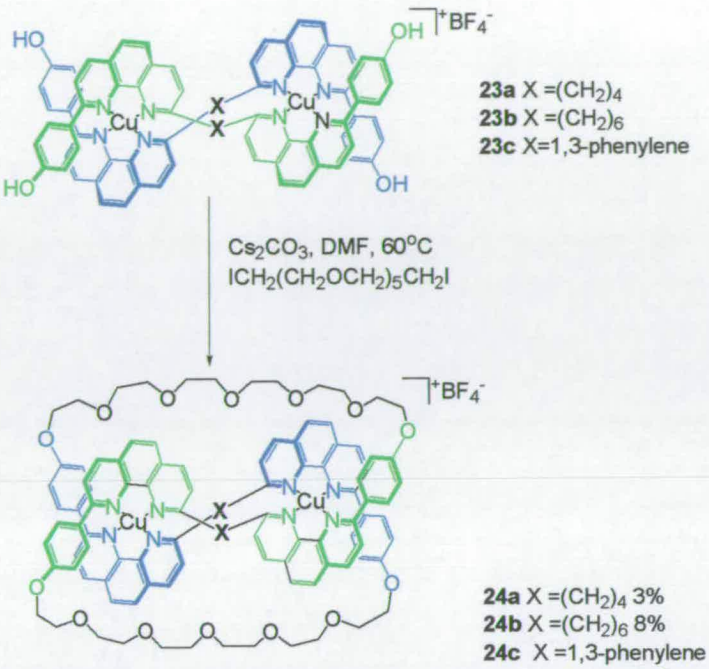


Figure 6: Chromophores stoppered rotaxanes based on Cu(I)/bis-2,9-diphenyl-1,10-phenanthroline complex: a. A C_{60}-stoppered rotaxane; b. Ru(terpyridine)$_2$-stoppered rotaxane and c. Porphyrine-stoppered rotaxane (Substituents of the porphyrins have been omitted for clarity).[33,34,37]

In similar fashion Loeb reported the synthesis of a rotaxane which utilizes square planar metal complexes as the stoppers.[40]

The use of transition metals represented a real breakthrough in the synthesis of molecular knots, whose appearance in the literature preceded the interlocked molecular architectures.[41] The first example of knot was reported in 1989 by Sauvage and Dietrich-Buchecker. Two Cu(I)/phenanthroline-based molecular turns linked by alkyl chain linkers **X** (**Scheme 6**) were used to create a pair of linked turns. Complexation of such ligand successfully formed a double helical complex **23a** containing two Cu(I) centres, along with a mixture of undesired products containing only one copper centre. The cyclization of the double helical precursor by reaction with a pair of polyglycol chains produced a knotted system **24a** in yield between 3 and 8% depending on the alkyl spacer.[42] Replacement of such linkers with a 1,3-phenylene moiety in the thread **23c** increased the yield of the corresponding knot **24c** to 29 %.[43] A further improvement to the synthesis of a trefoil knot was accomplished in 1997 by combining the use of the 1,3-phenylene spacer and Grubbs' catalyst mediated ring closing alkene metathesis: this procedure granted a remarkable 74 % yield of the requisite trefoil knot.[44]



Scheme 6: The synthesis of trefoil knots assembled with a Cu^{I} template.[42]

Sauvage, in collaboration with Geerts, reported the synthesis of polymeric catenanes containing alternating units of [2]catenanes prepared by the usual Sauvage template chemistry and covalently linked spacer groups. Each ring of the catenate was derivatised with a reactive peripheral hydroxyl group which upon polycondensation with a diacid spacer yielded the poly-[2]-catenane polymer (**Figure 7**). Even though the polymerization process did not take place through catenane formation this is the first example of a polymer held together by catenane linkages.[45]

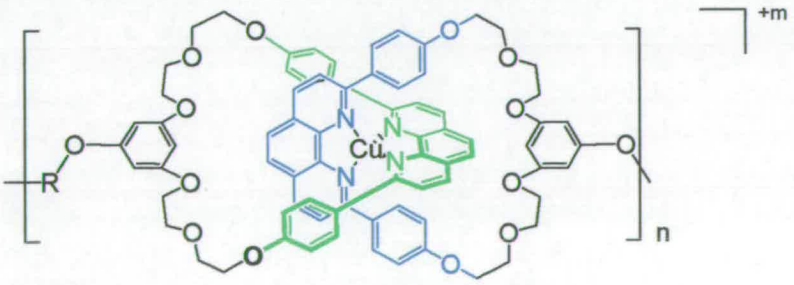


Figure 7: Polymer held together by catenane linkages.[44]

Collaborating efforts between Lehn, Baxter and Airola produced a variety of rigid-rack multimetallic pseudo-rotaxanes, (**Figure 8**), again using the Cu(I)/phenanthroline system.[46] Coordination with copper(I) of the phenanthroline macrocycle developed by Sauvage around a series of bipyridine/phenanthroline derivatised rod-type linear ligands represented an advance towards the synthesis of more extended polyrotaxanes.

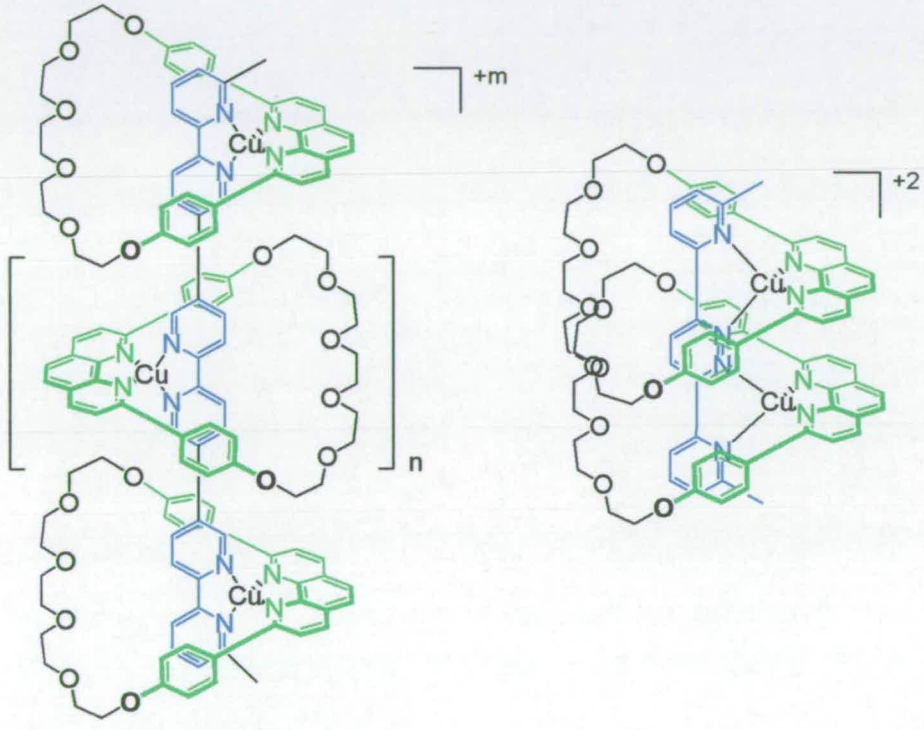
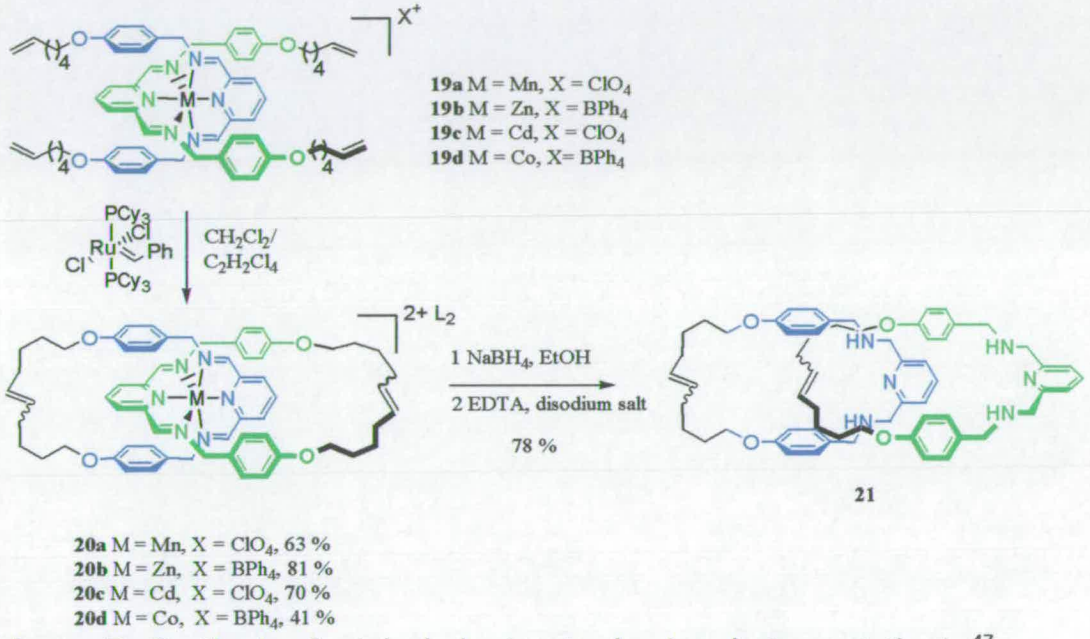


Figure 8: Rigid Rack pseudo-rotaxanes.[46]

Expanding on the tetrahedral Cu(I)/phenanthroline geometry, in 2001 Leigh *et al.* reported a simple, general and efficient synthesis of catenates with octahedral coordination geometry.[47] Inspired by Busch and co-workers,[48] they exploited a benzylic 2,6-diiminopyridine molecular turn to provided three coordination sites on a N_3 Mer conformation in an appropriately derivatised "u-shape" ligand. After complexation with a variety of divalent transition metals, complexes **19a-d**, catenates **20a-d** were obtained by RCM in good to excellent yields (**Scheme 7**). The exceptional kinetic stability

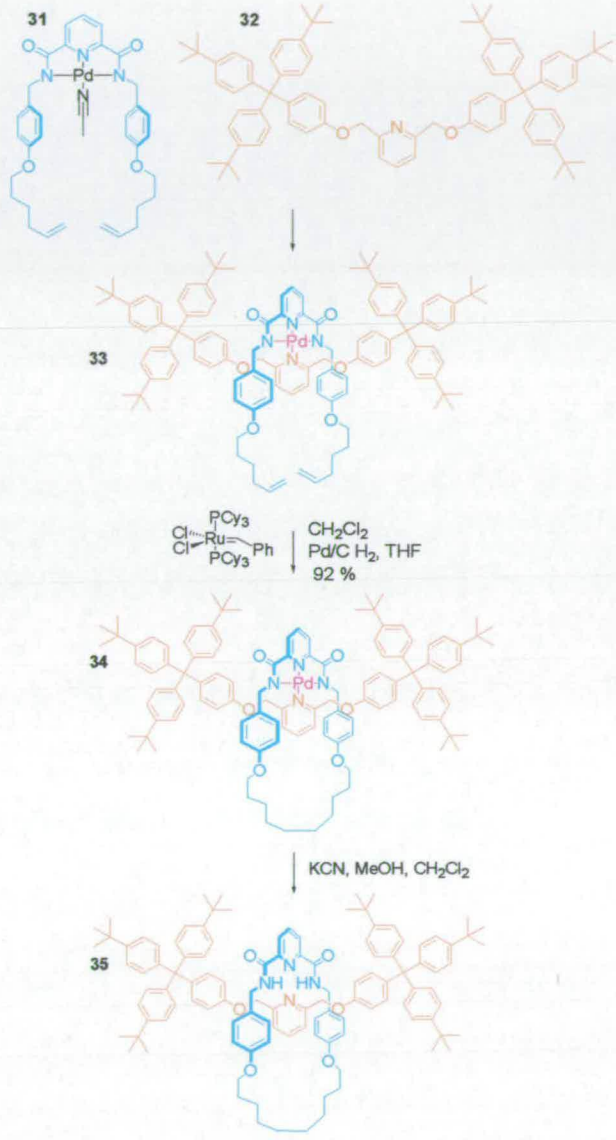
attributed to mechanically interlocked molecules was confirmed by these octahedral complexes, which were inert to demetalation attempted with EDTA. The reduction of the imines to amines was necessary in order to achieve demetalation and attain catenand **21**.



Scheme 7: Synthesis of octahedral catenates by ring closing metathesis.[47] further discussion here.

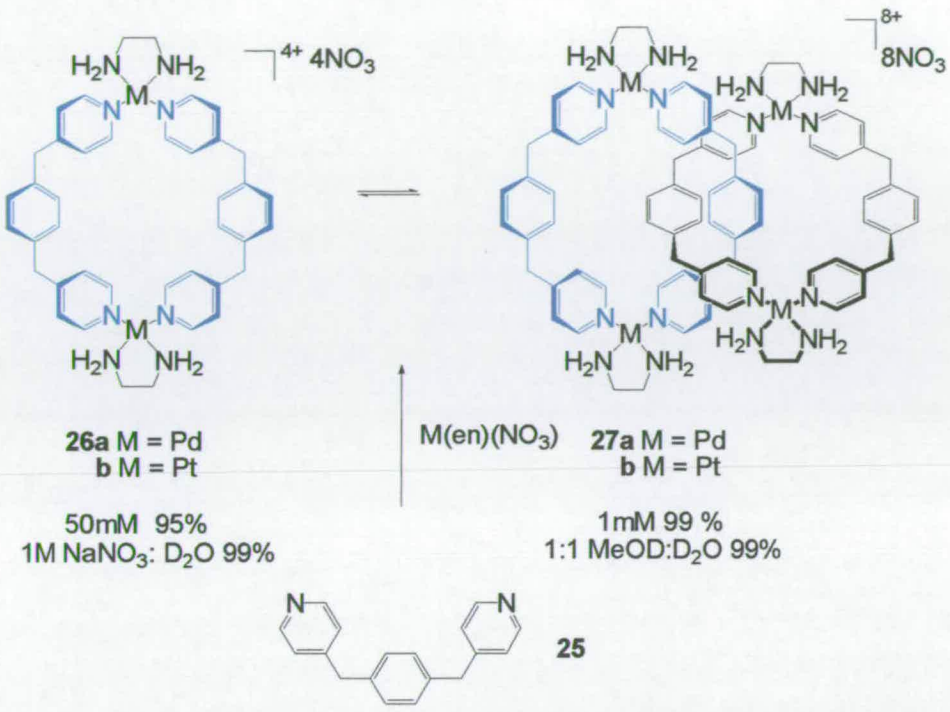
More recently Sauvage described the assembly of a pseudo-rotaxane based on four-coordinate square planar metal complex[49] but it is only at the beginning of this year that Leigh reported the metal template synthesis of a [2]rotaxane based on such geometry.[50] This proved that three dimensional interlocked architectures can also be assembled from two dimensional coordination templates, using steric and electronic restrictions to control the synthesis in the third dimension. Rotaxane **34** was obtained by clipping approach of an appropriately derivatised 2,6-dicarboxyamidepyridine unit which provided the palladium ligating moiety.[51] The thread bearing a pyridine donor with appropriately bulky stoppers aligns orthogonally to the plane defined by the "u-shape" tridentate donor in the square planar complex.[52] Ring closing metathesis followed by

catalytic hydrogenation gives rotaxane **34** in an overall 69% yield. Demetalation was accomplished using potassium cyanide to generate the free [2]rotaxane **35** in 97% yield.



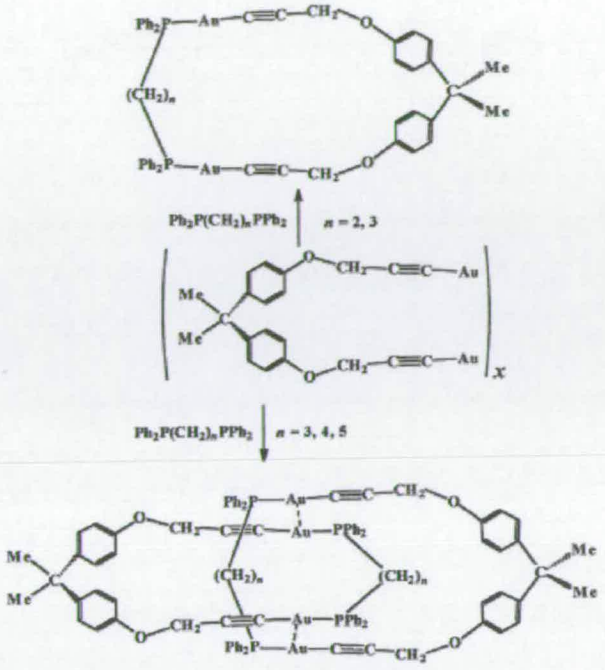
Scheme 8: The synthesis of [2]rotaxane around divalent palladium with square planar coordination.[51]

Within the contest of the present discussion, it is worth describing supramolecular systems containing different types of coordination modes, so-called "hybrid" systems. Fujita *et al.* synthesised a [2]catenane containing square planar palladium(II)-pyridine coordination units.[53] The fundamental difference between the two synthetic strategies is that in the Sauvage/Gibson complexes the copper(I) act as template organizing the self-assembly of the interlocked products and in the Japanese system removal of the metal results in collapse of the structure. In the latter case the molecular cross-over is not provided by a metal anchor but by hydrophobic interactions. In catenane **27a,b**, the metal is used in conjunction with ethylenediamine (en) and ligand **25** as component of the macrocycle self-assembling via clipping approach. In attempts to assemble the coordination macrocycle **26a,** it rapidly equilibrates in solution with [2]catenane **27a,** (**Scheme 9**), the efficient contact between the aromatic rings of the two macrocycles being the driving force for the formation of the interlocked products. For this reason interlocking is improved in polar solvent and optimised in aqueous solutions. Concentration also plays a key role pushing the equilibrium towards the catenane. The interconversion of the two species undergoes via a proposed Möbius strip mechanism and possible due to the kinetically labile nature of the palladium-pyridine coordination bonds.



Scheme 9: The synthesis of "magic rings" containing palladium and platinum.[53]

The kinetics of a similar system were studied after replacement of palladium(II) with platinum(II).[54] By mixing ligand **25** and Pt(en)(NO_3) macrocycle **26b** is the sole product and is not in equilibrium with other structures. Catenane formation is achieved after treatment with $NaNO_3$ and heating 100 °C: under these conditions the interlocked product is greatly favoured. Upon cooling at room temperature and removing $NaNO_3$ the catenane remains the majority species. This lack of interconversion between macrocycle and catenane, described as "locking" of the equilibrium between the two species, can be attributed to the properties of the coordination bonds between platinum-pyridine which are much less labile than those of palladium. The analogy between the locking and unlocking of the equilibrium process inspired Fujita to call this platinum-based system a "molecular lock".



Scheme 10: Puddephatt gold(I) based catenanes.[56]

Catenanes have also been assembled with gold(I) centers in the macrocyclic backbone. Mingos and co-workers[55] initiated this work which was further extended by Puddephatt and co-workers.[56] The coordination number of two of Au(I), characterised by linear stereochemistry,[57] is exploited to assemble rings and interlocked architectures by introducing molecular bends such as diphosphines and diacetylides or phosphinoacetylides. π-Stacking between ligands aryl groups or, more commonly, intermolecular Au···Au bonding are responsible for the assembly of these systems.[58] Catenation depends on the size of the rings or, more specifically on the size of the cavity available for molecular crossover. The digold(I) complex with $Ph_2P(CH_2)_nPPh_2$ illustrated in **Scheme 1** is a simple ring when n=2, exists in solution as an equilibrium between ring and catenane when n=3, and exists as a catenane only when n=4 or 5.

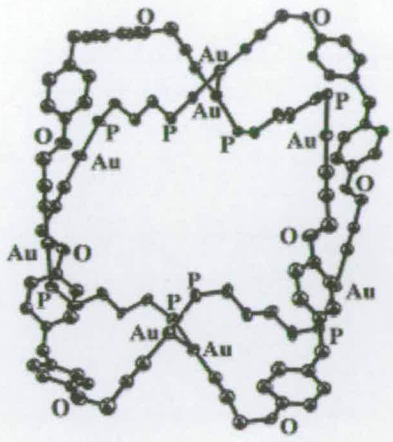
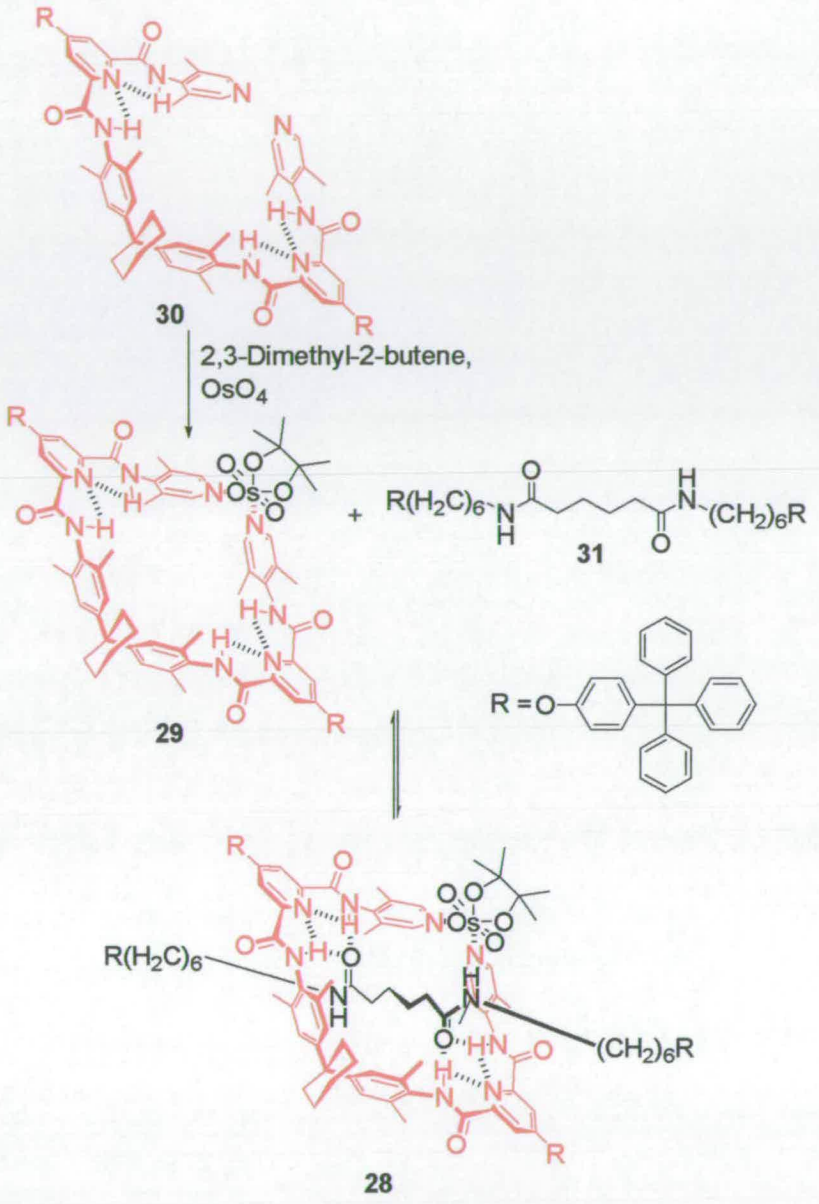


Figure 9: Structure of the double braid [2]-catenane.[56]

Remarkably, major changes in the gold(I) chemistry are obtained by changing the pivot atom X in the compounds $X(C_6H_4OCH_2CCH)_2$. When X=O or S the products are simple rings,[59] when $X=Me_2C$ catenane is formed. Unexpectedly reaction with the $X=C_6H_{10}$ (cyclohexylidene) substituted compound gave a novel double braid catenane, which self-assembles very selectively from eight components in high yield (**Figure 9**).



Scheme 11: The synthesis of [2]rotaxane containing osmium in the macrocyclic component.[60]

Another example of hybrid interlocked structure was reported by Jeong *et al.* in 2000.[60] Reaction of acyclic pyridine containing component **30**, OsO_4 and 2,3-dimethylbutene (**Scheme 11**) yields the formation of coordination macrocycle **29.** Upon treatment with

the adipamide thread **31** the hydrogen bonding interactions taking place between ring and thread in the interlocked species act as anchor and drive the molecular cross-over. [2]rotaxane **28** is obtained quantitatively. Again, the metal is part of the ring and is not engaged in template activity. The rotaxane forms due to the macrocycle ring opening/ ring-closing at the osmium/ pyridine bonds, i.e. by reversible clipping. However, the rotaxane **28** is not kinetically robust, an inherent limitation of all the products discussed in this section that contain metals within their macrocyclic framework. Jeong and co-workers have used the same methodology to produce corresponding [3]rotaxanes.[61]

A highlight of supramolecular chemistry appeared on Science early on 2004: Stoddart, Atwood and coworkers reported the synthesis of molecular Borromean rings (BRs).[62] BRs consist of three rings, not mutually interlocked, but entangled in a way that prevents separation from one another (**Figure 10**). Opening of one ring results in the falling apart of the whole assembly. This topologically achiral system was self-assembled by reaction of 18 components in an incredible nearly quantitative yield. The success of the construction of this intricate compound from individual pieces depended on the accurate programming of each individual piece in the molecular self-assembly process. 12 imine and 30 dative bonds were formed while three interlocked macrocycles, each tetranucleating and decadentate overall, coordinate a total of six zinc(II) ions stabilised by a total of 12 π-π stacking interactions. Each macrocycle was endowed with two *exo*-bidentate bipyridyl and two *endo*-diiminopyridyl ligands which upon penta-coordination with the zinc(II) ions provide precisely controlled molecular cross-overs. Kinetically labile zinc(II) was the metal of choice granting flexibility and reversibility in the coordination spheres. Reversibility was also provided by the dynamic Schiff base condensation between 2,6-diformylpyridine (DFP) and a diamine (DAB) which resulted in the formation of the endo-tridentate ligating moiety and ultimately in the formation of the macrocycles by [2+2] macrocyclization. This work represents an example of

cooperative use of coordination, supramolecular, and dynamic covalent chemistry as extraordinary for its elegance as well as for its simplicity.

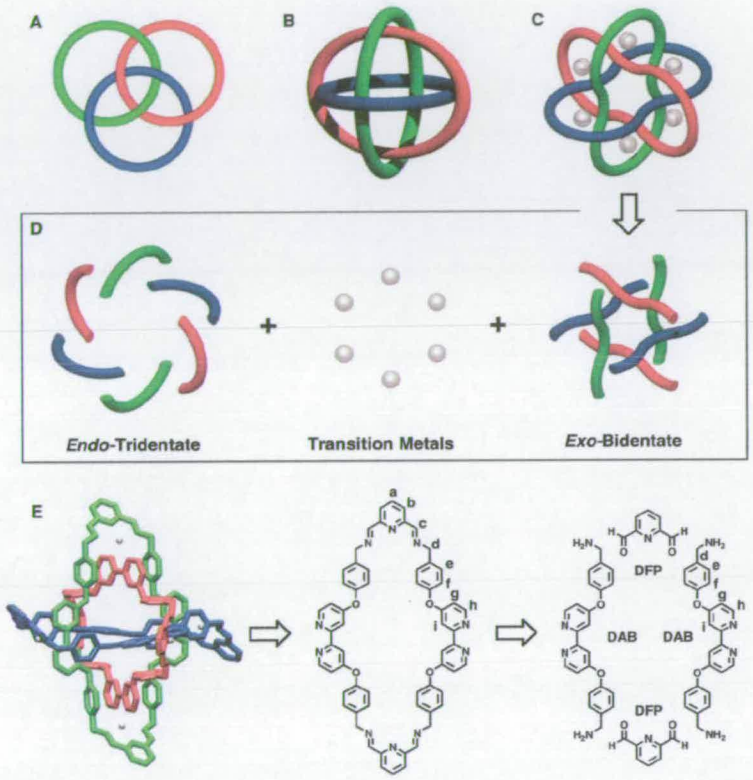


Figure 10: Cartoon representation of the Borromean rings: (**A**) planar Venn representation; (**B**) orthogonal arrangement and (**C**) illustration containing templating features shown as silver spheres. (**D**) Relatively straightforward retrosynthetic disconnection of the BRs. (**E**) The retrosynthesis in chemical terms.[63]

1.6 Controlling Motion in Interlocked Systems Containing Transition Metal Ions

As previously described, the synthesis of interlocked molecular architecture using transition metals has been very prolific. Intramolecular motions can be considerably preferred over intermolecular exchange due to kinetic stability of metal-ligand binding

interactions and accurate structural design.[64] Transition metals redox properties should permit the use of techniques, such as electrochemistry and photochemistry, to induce this motion. [65] For this reason, metal-based interlocked molecular architecture are good candidates for molecular-level machines. In such species the electroactive units are the metal ion and the ligands. Changes in the interaction of these units can be imparted by electrochemical oxidation or reduction. The structure and properties of the overall supramolecular assembly can be controlled through electrochemical stimuli acting on the metals whose stereoelectronic requirements depend on its oxidation state. Appropriately designed systems programmed to contain suitable metal ions and ligands can yield molecular rearrangements. If a large amplitude displacement of some components of the supramolecular architecture with respect to the others is consequence of the electrochemically induce rearrangement the system can be said to behave as an electrochemically driven molecular machine. [66]

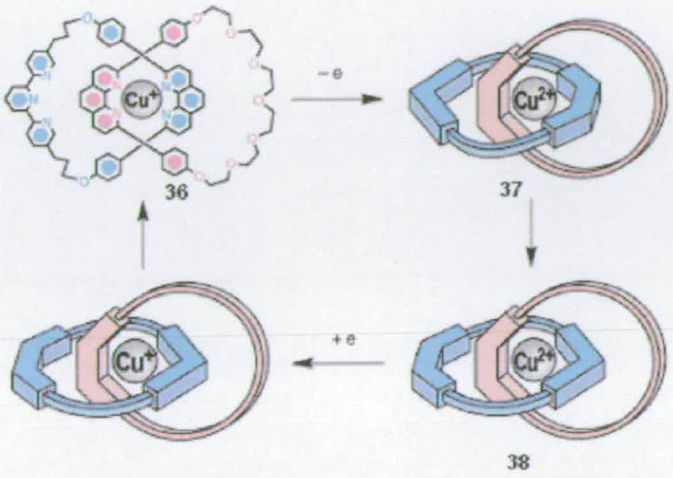
The definition of molecular machine and what differentiates them from other molecular devices is still moot and under debate.[67] After the initial iconic classification of molecules as machines, based on the imaginative resemblance between the structures and pieces of machinery, a more useful approach distinguished between 'device' and 'machine' on etymological basis. While both molecular devices and a machines are "*assembly of a discrete number of molecular components designed to perform a specific function*" the word 'machine' necessarily involves mechanical movement. The inferred definition can be therefore stated as: "*an assembly of molecular components that can move relative to each other in response to an external stimulus, provided that movement can be used to modify, apply or transmit energy*".[68] In other words 'molecular machines' are a "subset of molecular devices in which some stimulus triggers the controlled, large amplitude mechanical motion of one component relative to another (or of a substrate relative to the machine) which results in a net task being performed.".[69]

A number of pseudo-rotaxane based devices have been made with functions such as: reversible formation and de-threading of the interlocked species using a number of stimuli;[70] switching between different preferred guests;[71] and control of intramolecular electron transfer reactions.[72]

Controlled mechanical behaviour is attained on condition that the kinetic stability of the pseudo-rotaxanes provides sufficient restrictions on the motions of the unbound species: in this case the system can be called molecular machine.[73] In these kinetically associated species,[74] the mechanical bond conveys a restriction in the degrees of freedom for relative movement of the components, while frequently allowing extremely large amplitude motion in the permitted vectors. Biological motors exploit equivalent type of movement restriction by structural tracks,[75] and for this reason interlocked structures have withdrawn such an interest in the development of synthetic molecular machines.[76]

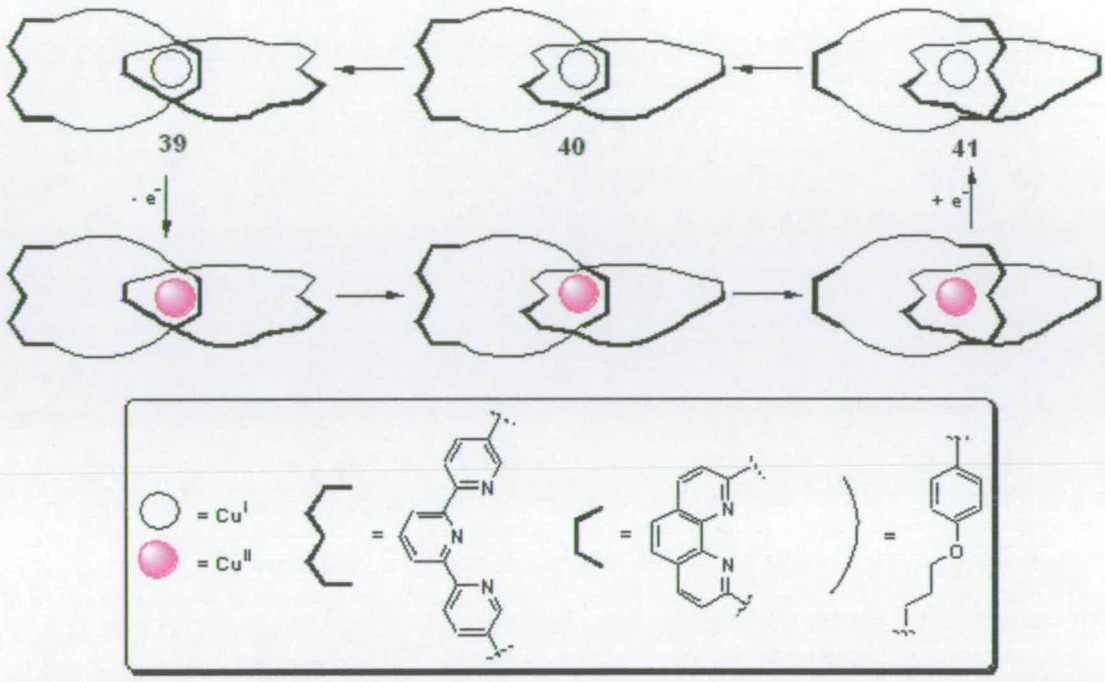
Sauvage and co-workers reported a prototypical example of a redox-switchable [2]catenate.[77] Exploiting the unique properties (among the first row transition metals at least) of copper – in particular, the strong stereoelectronic requirements for the mono- and divalent cations[78] they designed a system where satisfaction of the coordination requirements induced ring pirouetting. Catenate **36**, (**Scheme 12**), was assembled using Cu(I) as anchor and two bidentate phenanthrolines and molecular turns. One of the two macrocycle was endowed with an extra station, a tridentate 2,2':6',2''-terpyridine (terpy) ligand, to provide the means for 5-coordinate arrangement. Copper(I) prefers coordination number four while copper(II) favours coordination number five. The Cu(I) template coordinates to the two phenanthroline units in the expected tetrahedral arrangement Oxidation of the Cu^{I} catenate by chemical, electrochemical or photochemical[79] means, affords metastable Cu^{I} four coordinate system **37**, which upon pirouetting of one ring through the other gives the stable 5-coordinate Cu(II) catenate **38**. Reduction of catenate **38** reverses the order of preference for coordination numbers:

accordingly a circumrotation to regenerate the starting Cu(I) complex **36** in a completely reversible manner.



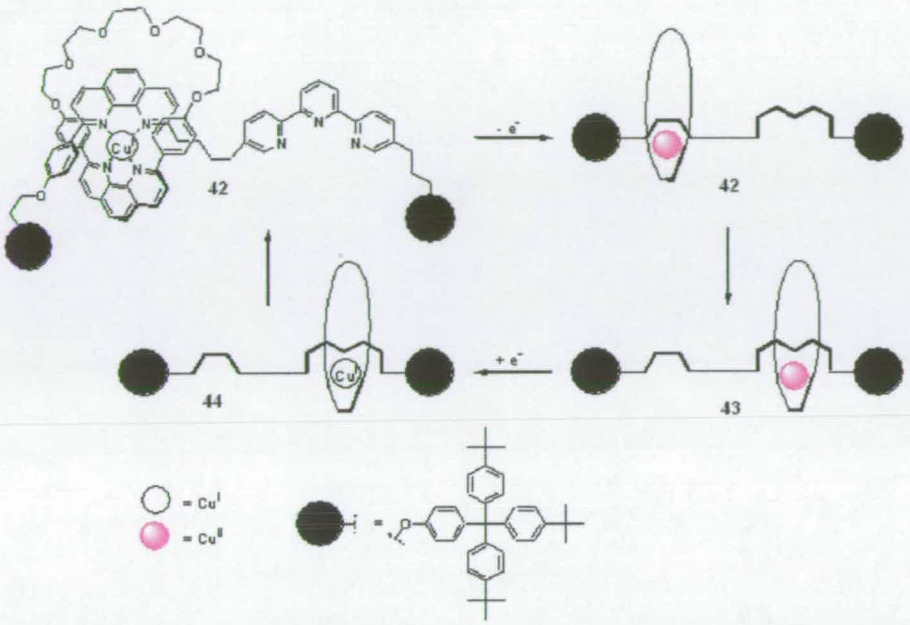
Scheme 12: An electrochemically-switchable copper-based catenate.[78]

The synthesis and properties of a symmetric [2]catenate incorporating two terpy and two phenanthroline ligands was described by Sauvage *et al.* two years later.[80] Circumrotation of the macrocycles around the metal anchor leads to the formation of three distinct geometries within its central core, tetra-, penta- and hexa-coordinate, corresponding to three translational 'isomers'(**Scheme 13**, respectively **39**, **40**, **41**). Taking into account the different metal oxidation states it can be said that this catenate presents six different states. Again, chemical and electrochemical methods can be utilized to trigger the switching process.



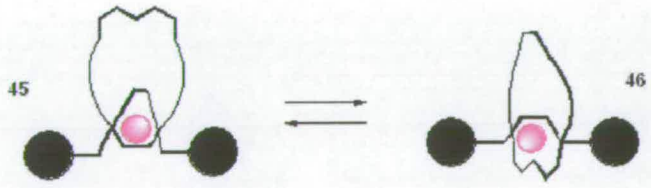
Scheme 13: Oxidation state controlled switching of [2]catenate **39** between three distinct co-conformations.[80]

Sauvage has also synthesised [2]rotaxanes using similar structural motifs to make transition metals based redox-responsive molecular shuttles.[81] A macrocycle containing a bidentate phenanthroline unit, is locked around a thread incorporating two different coordinating units, a phenanthroline and a tridentate terpy ligand. The geometrical preferences of Cu(I) and Cu(II)-based complexes drive the co-conformational changes. Both of the phenanthroline ligands (thread precursor and macrocycle) are used to complex Cu(I) in a tetracoordinate fashion, templating the synthesis of the fully stoppered rotaxane (**Scheme 14**, **42**). Upon electrochemical oxidation[82] of Cu(I) to Cu(II) the tetrahedral geometry is destabilized and the new preferred co-conformer is that where the macrocycle resides over the terpyridine unite, allowing Cu(II) to form a five-coordinate species (**Scheme 14**, **43**). The shuttling process can also be achieved via photochemical oxidation. The reverse reductive step cannot be carried out photochemically but proceed successfully using ascorbic acid as chemical reductant.



Scheme 14: Redox-switched shuttling in a metal-templated [2]rotaxane.[81]

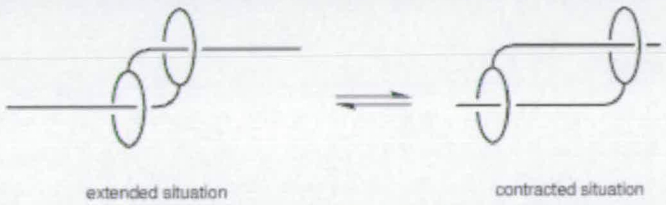
Sauvage and co-workers used the macrocycle bearing two ligating moieties designed for the synthesis of catenate **36** to assemble a [2]rotaxane. Electrochemical methods induced pirouetting of the ring component around the phenanthroline derivatised thread **(Scheme 15)**.[83]



Scheme 15: An electrochemically-switchable copper-based [2]rotaxane.[83]

The principles of shuttling in metal-templated rotaxanes can be applied to the synthesis of a so-called molecular muscle,[84] i.e. a system in which the submolecular motion

results in lengthening and contraction of the molecule in a manner which mimics the actin-myosin linear motor found in skeletal muscles.[85] The realization of such an assembly was reported in 2000 by Sauvage and co-workers.[86] It is a dimeric system comprising two identical units consisting of a bidentate phenanthroline site embedded in a macrocyclic ring; this ring is joined to a thread portion endowed with a phenanthroline ligand as well as a tridentate terpyridine, (**Figure 11**), site in a doubly threaded topology as shown in **Scheme 16**.



Scheme 16: Cartoon representation of doubly threaded topology-the precursor to a molecular muscle.[84]

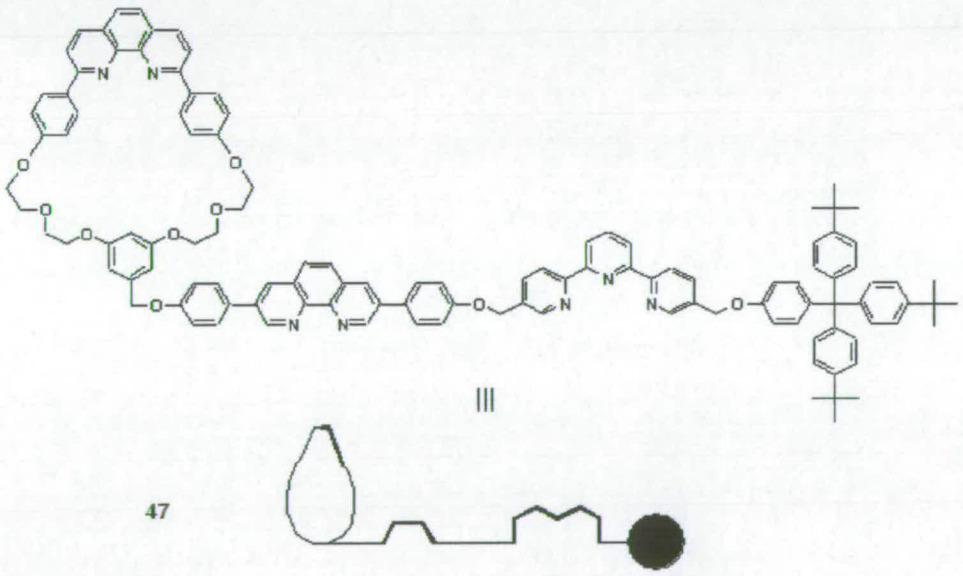
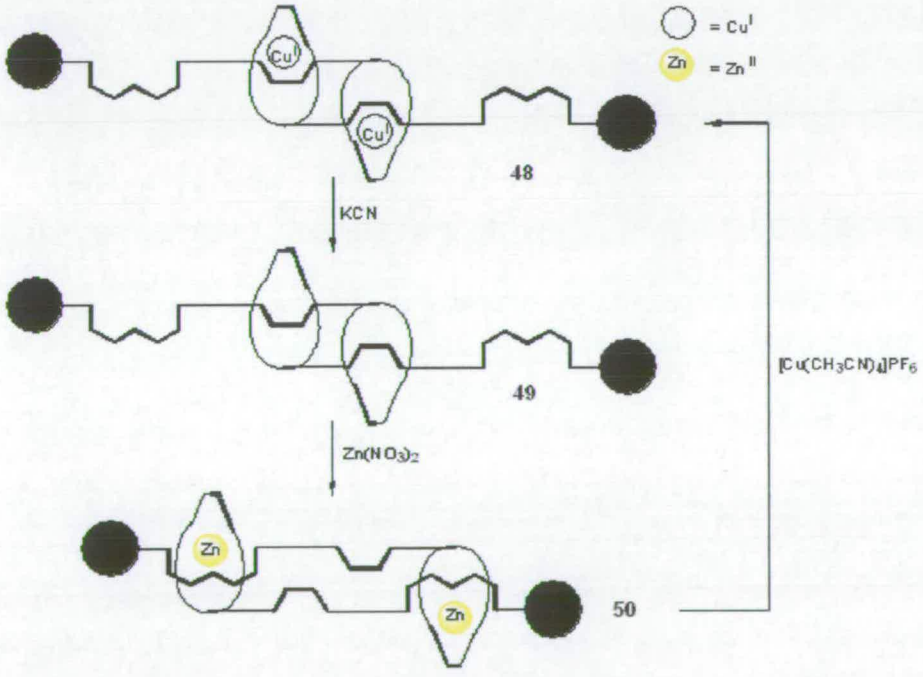


Figure 11: Monomer unit for the construction of artificial molecular muscle rotaxane dimer. [84]

The molecule **48** was initially synthesized in its extended conformation: Cu(I) ions were used to template formation of the dimer coordinating to two phenanthroline units

each. Electrochemical oxidation to the Cu(II) was not sufficient to activate the switch and promote shuttling of the rings to the terpy station. In this instance the tetrahedral geometry proved sufficiently kinetically stable to prevent motion. Demetalation of **48** using KCN gave the free ligand system **49.** Contraction of the dimer was finally achieved upon treatment with Zn(II). **50** was produced in response to the new coordination requirements of the two Zn(II) cations each coordinating a phenanthroline and a terpyridine unit. Treatment with excess Cu(I) regenerated the original stretched conformation. While the distance between the metal centres increases, the overall length of the molecule decreases due to the gliding of the linear portions of the muscle over each other in result to the metal templated shuttling of the rings. A 24% contraction is obtained during this process, reducing from approximately 85 Å to 65 Å.



Scheme 17: Reversible switching between extended ($[62{\cdot}2Cu]^{2+}$) and contracted ($[62{\cdot}2Zn]^{4+}$) forms in a chemically-switched artificial molecular muscle. [84]

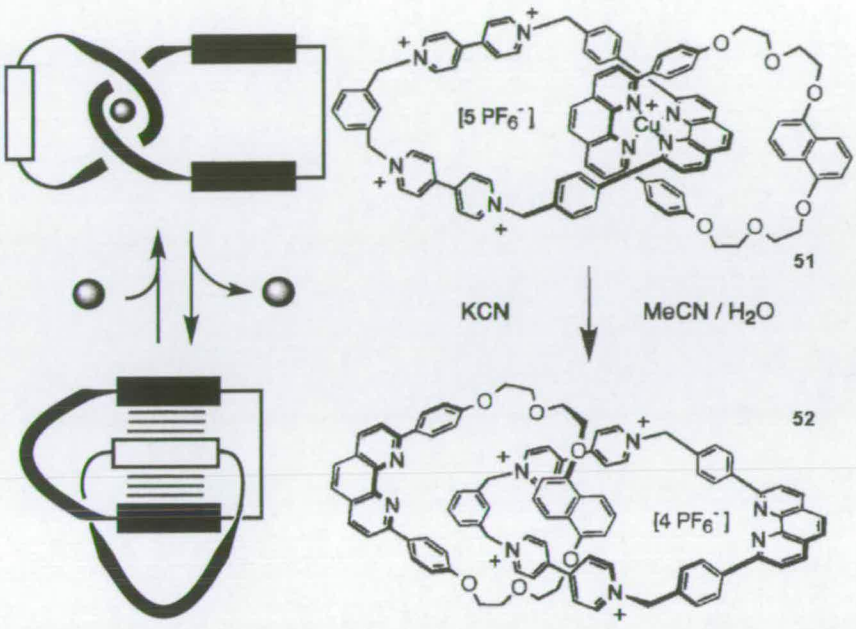


Figure 12: The concept behind a switchable [2]-catenane based on metal ion (dark ball) chelation and -electron donor (clear rectangle) to acceptor (dark rectangle) interactions. The molecule is switched by complexation or removal of the chelated ion.[87]

In 1996, Sauvage and Stoddart reported the copper(I) templated synthesis of a bimodal [2]catenane endowed with both metal complexation and charge-transfer interactions motifs.[87] The compound comprising two different rings was derivatised with both a transition metal coordination site (the usual phenathroline moiety) and a set of π-electron rich and π-electron deficient aromatic units suitable for the formation of acceptor-donor complexes (respectively 1,5- dioxynaphthalene and two equivalent bipyridinium units known as tetracationic cyclophane component).[88] This species shows one monoelectronic process concerning the oxidation of the Cu(I) complex, and two bielectronic processes corresponding to the simultaneous first and second reduction of the two equivalent bipyridinium units. Switching of the nature of the complex mode resulted in the circumrotation of one ring within the other. These two contrasting orientation, obtained by complete topographical rearrangement of the molecule, can be

triggered by adding or removing the cation center (Cu^+, Li^+, or H^+), bonded to the phenanthroline-containing complexing site.

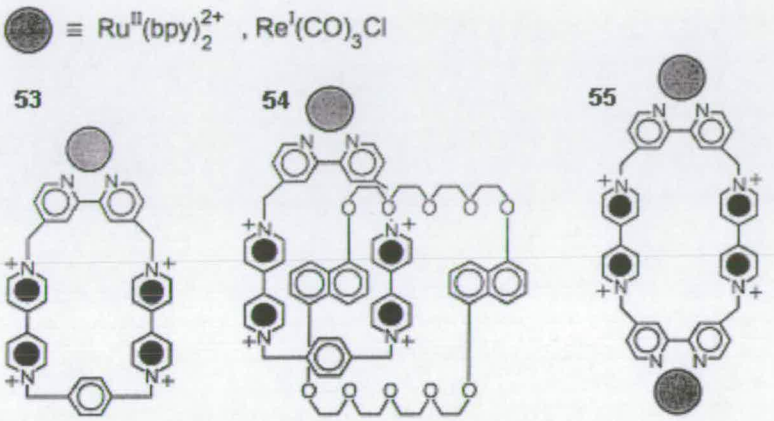
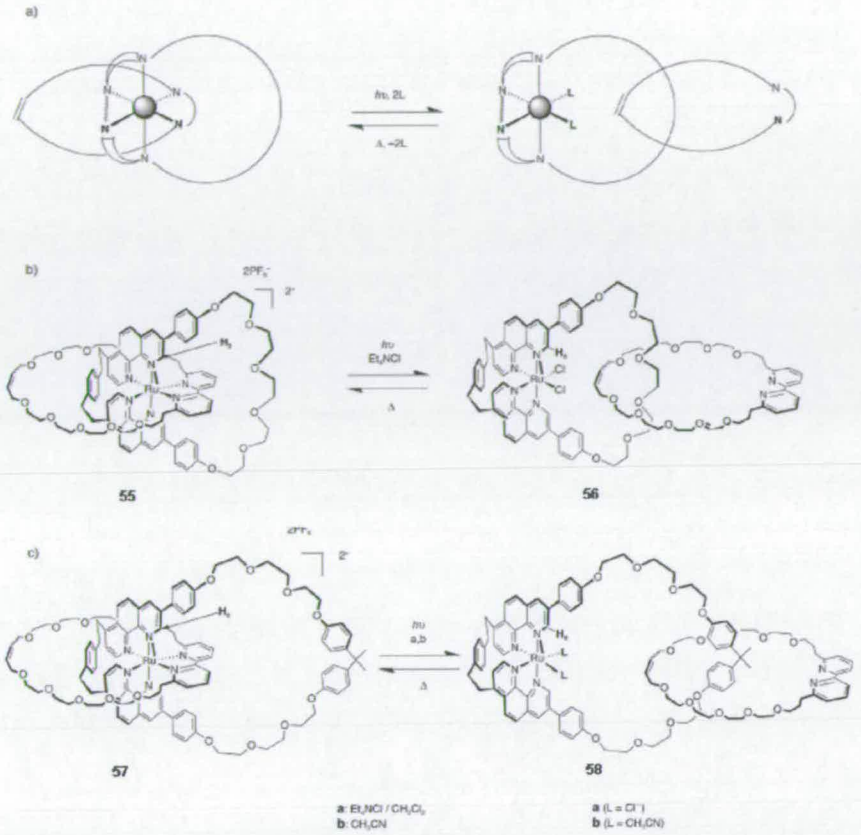


Figure 13: Structure formulae of mono and dinuclear Ru(II) and Re(I) complexes containing a cyclophane or a catenane ligand.[89]

The peculiar excited–state properties of transition-metal complexes, and specifically charge-transfer interactions, have been exploited in pseudorotaxane, rotaxane and catenane structures suitably designed to behave as photodriven molecular machines.[90] The covalently linked metal-based moiety plays the role of photosensitizer.[91] The synthesis of number of mono and dinuclear Ru(II) and Re(I) complexes based on a cyclophane containing one or two bpy coordination sites was reported.[92] Such complexes exhibit several interesting redox properties which will not be matter of further discussion here.



Scheme 18: a) Schematic representation of the photoinduced and thermal motions taking place in the present catenanes, b) and c) chemical structure of catenanes **55** and **57** and their photoproducts **56, 58a**, and **58b**. M42 is one of the constitutive rings containing the bpy fragment.[93]

In all the systems described so far the movements is triggered by an electrochemical or a chemical signal. Sauvage *et al.* have recently described multicomponent ruthenium(II) complexes in which motion is set photochemically: such system can be considered new prototypes of light-driven machines.[93] Using an octahedral ruthenium(II) templated synthesis they constructed a set of two [2]catenates in which the light-driven motions are based on the formation of dissociative excited states. The rings, one incorporating two phenanthroline units and the other a 2,2′-bipyridine group, are initially connected through the coordination of the ruthenium center. A photochemical reaction leads to

quantitative decomplexation of the bpy chelate from the ruthenium(II) center resulting in the disconnection of the two rings from each other, while simple heating regenerates the starting complex.

1.7 The Objectives of This Research

Undeniably, the generation of new interlocked molecular architectures has experienced extraordinary progress, both in the diversity and complexity of the molecules that have been synthesized and in the interpretation of the interactions, generalizations and principles that govern them. Metal template chemistry has played a large role in this maturation. The versatility of chemical templates becomes evident when one recognizes that the excellent display of structural motifs briefly reviewed here has been realized with a very small number of distinct chemical templates. Attention must be drawn to the fact that most of the above templates and topologically distinct products are the result of the clever use of very few metal/ligand anchor/turn pair or template.

The aim of this project was to address this need and investigate the possibility to synthesise novel types of metal based templates for interlocked structures.

This program of research was initiated shortly before my arrival with the synthesis of a series of [2]catenates based upon divalent metals with a preferred octahedral geometry.[47] In extending this work, Chapter Two describes the synthesis of a general ligand system for [2]rotaxane complexes with analogous coordination motif. Octahedrally coordinated metal [2]rotaxanes were obtained via a five component self-assembly procedure under thermodynamic control. This procedure proved successful with a variety of divalent transition metals affording the corresponding rotaxane in good to excellent yields.

Chapter Three reports the template-directed synthesis of a [2]catenate and a [2]rotaxane by a clipping approach around trivalent octahedral cobalt ions. Appropriately derivatised pyridine 2,6-dicarboxamide based ligands, once deprotonated, stabilise the trivalent oxidation state facilitating the entry into higher oxidation states of these metal ions. Unlike ligands previously designed for metal templation which upon demetalation offer no recognition motif, the removal of the metal to these ligands results in a system which has the potential for hydrogen-bonding.

Chapter Four reports the design and investigation of the synthesis of pentacoordinate rotaxane around divalent zinc and cadmium metals. A clipping approach as well as a threading-and-capping approach were considered, leading to interesting results involving the kinetics and thermodynamics of each complex. Zinc was suitable for the self-assembling of the macrocycle about the metal-thread complex but failed to hold the unstoppered thread in place while undergoing capping reaction; cadmium on the contrary yielded rotaxane upon threading approach but lead to the formation of more thermodynamically stable hexacoordinate catenate upon ligand self-assembly via clipping approach.

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[15] The expression 'algorithm' has been used by Lehn (Ref. 1f, pp. 143–144) to characterize programmed supramolecular systems whose response relies upon molecular information handling procedures. *Molecular programming* involves situating the information for a particular superstructure's construction in the covalent skeletons of its precursors. This information constitutes the molecular *program* which operates through noncovalent recognition *algorithms*.

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Chapter Two

A Simple General Ligand System for Assembling Octahedral Metal-Rotaxane Complexes

"Nature is trying very hard to make us succeed, but nature does not depend on us. We are not the only experiment"
R. Buckminster Fuller (April 30, 1978)
US architect & engineer (1895 - 1983)

.... Although we often think we are!
Ale: Thoughts on my Ph.D. work (2001-2004)

Chapter 2. A Simple General Ligand System for Assembling Octahedral Metal-Rotaxane Complexes.

2.1. Abstract

Coordination complexes in which rotaxanes act as ligands for transition metals are amongst the most celebrated examples of mechanically interlocked molecular level architectures.[1] This is not only because coordination chemistry makes possible a rich diversity of structures, but also because the metal can be locked in unusual environments for subsequent electrochemical,[2] photochemical[3] and catalysis[4] studies. Efficient synthetic methods have been developed for rotaxanes based on tetrahedral and trigonal bipyrimidal metal complexes using the metal-*bis*-phenanthroline synthon pioneered in Strasbourg.[1a,b, 5] Here we describe a general ligand system for rotaxane complexes of ions that prefer octahedral coordination - the commonest ligand geometry amongst transition metals but up to now a rare[6] coordination mode for rotaxanes. Simple mixing of the components at room temperature is sufficient to assemble a broad range of octahedrally coordinated metal-[2]rotaxanes in excellent yields. The reactions have few, if any, byproducts and proceed under thermodynamic control in the absence of a catalyst or any other external reagents.

2.2. Introduction

Within the success of coordination chemistry its application to the synthesis of mechanically interlocked molecular architectures plays a key role. The pioneer in the development of this field, J. P. Sauvage used copper(I) to exploit the '3D' nature of

tetrahedral metal complexes to provide the first template directed synthesis of catenanes (**Figure 1**).[7] Organizing appropriately derivatised phenanthroline ligands about Cu(I), a [2]catenate was synthesised in 27 % yield with the two-turn approach,[7] while the ring-turn approach yielded 42%.[8] Subsequent studies using Grubbs' ring-closing metathesis (RCM)[9] moved the ring closure reaction to a much greater distance boosting yields to near quantitative levels.[10]

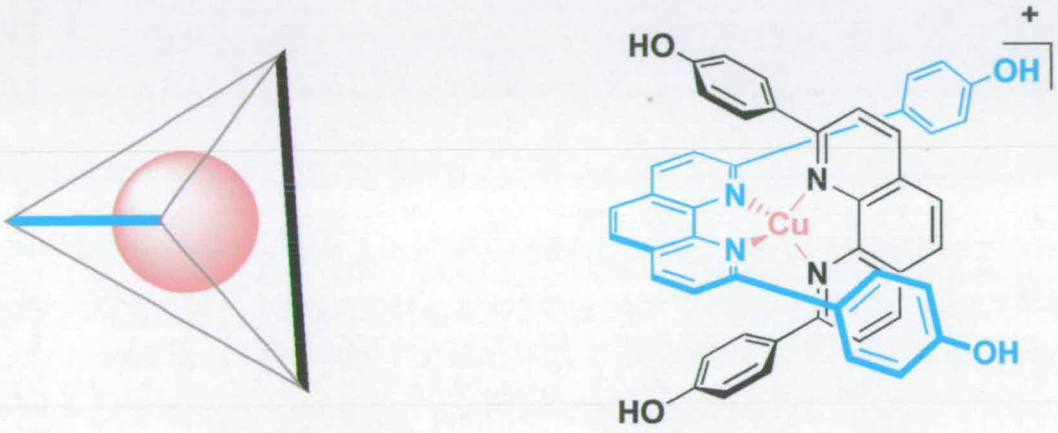


Figure 1: Sauvage tetrahedral Cu(I) based template complex.

Through clever modifications of this template system, the Sauvage group and others have accumulated a remarkable display of interlocked molecular architectures, including [n]catenates (n=2-8)[11] of varying complexity, catenands (the demetalated, but still interlocked ligands),[12] rotaxanes,[13] pseudo-rotaxanes,[14] and knots.[15]

In these, as well as in many other important developments, the required geometric control is granted by the appropriate design and use of a highly effective molecular turn. While the clever use of a single metal/ligand anchor/turn pair have proved very powerful to deliver different templates and topologically distinct products, so far only few distinct types of true templates for interlocked structures are available. It seems evident that the expansion to new arrays of templates would supply the synthetic chemists with a whole new tool box.

Some work has been done using octahedral metal ions to template syntheses, but those systems have not yet been so fully exploited. Pioneering work in this regard has been carried out by Schröder *et al.*,[16] and others,[17] and two octahedral catenates[18, 19] (and two knots[20,21]) have been described. Sauvage synthesised a [2]catenate based on octahedral Ru^{II} utilizing a 5,5′-disubstituted terpy ligand[22] reproducing through the geometry of the two tridentate chelates about an octahedral metal atom anchor, an orthogonal chelation similar to the one obtained with the two bidentate ligands about tetrahedral copper(I). In 1998 Busch *et al.*[23] designed and synthesised a new family of tridentate Schiff base ligands derived from 2,6-dicarbonyl pyridines and *para*-substituted anilines for use in octahedral molecular templates (**Figure 2**).[17] These systems offered the advantages that syntheses of the ligands and these complexes are straightforward, giving high yields in simple, one-pot reactions; besides reactions and structural variations are easily accomplished.

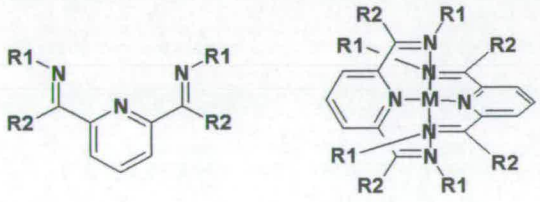


Figure 2: Busch's 2,6-dicarbonyl pyridines and *para*-substituted anilines for use in octahedral molecular templates.

As Busch shrewdly anticipated,[24] his work stimulated further work: Leigh *et al.* in 2001 reported the synthesis of a [2]catenate inspired by the very same tridentate Schiff base ligands.[25] Being very familiar with interlocked architectures based on hydrogen bonds (**Figure 3**), whereby the dynamic properties are tunable in a continuous range,[26,27] Leigh sought a route to catenates and rotaxanes characterized by a different type of dynamics. These systems should have been of a size and shape compatible and interchangeable in molecular devices with benzylic amide catenanes assembled by

hydrogen bonds and coordination chemistry offered the most appealing approach. In fact, with metal templates the strong coordination bonds present in catenates and rotaxanes lock the macrocyclic components in fixed positions but, upon removal of the metal, the rings rotate with virtually complete and uncontrolled freedom.

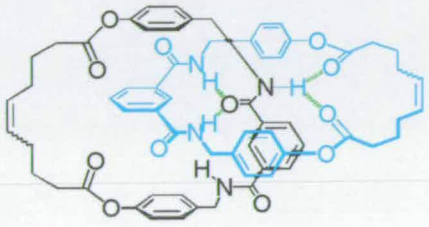


Figure 3: H-bond catenanes

Relating to the basic architecture of benzylic amide macrocycles frequently used,[28] the ligand designed for metal ion chelation (**Figure 4**) presented a rigid framework: the benzylic bis(2,6-diiminopyridine) moiety provided three coordination sites on a N_3 Mer conformation and represented a convenient spacer to hold the aromatic rings in a parallel arrangement at a distance ideal for stacking with an orthogonally bound guest. Unlike the diphenylphenanthroline unit that allows a 120° turn, the 1,3-linked benzylic motif guaranteed a complete 180° turn for each fragment holding the endgroups in positions that encourage intracomponent rather than intercomponent cyclizations. The importance of these structural features for promoting catenate formation was exemplified by a recent study which showed that it is not possible to produce octahedral catenates from terpy ligands which were not well preorganized for intracomponent cyclization.[29]

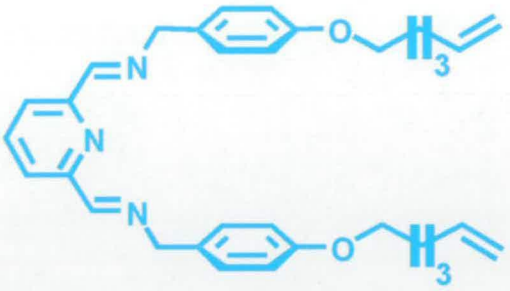


Figure 4: Ligand design for Octahedral Coordination.

Remarkably, the catenates (**Figure 5**) were obtained both via ring closing metathesis through the reaction of the α-olefins as well as via in situ assembling of the bis-amine with 2,6-pyridinedicarbaldehyde around the metal. In the latter case, the driving force enabling this elegant procedure is the reversible formation of four imine bonds from five components to satisfy the desired octahedral coordination geometry.

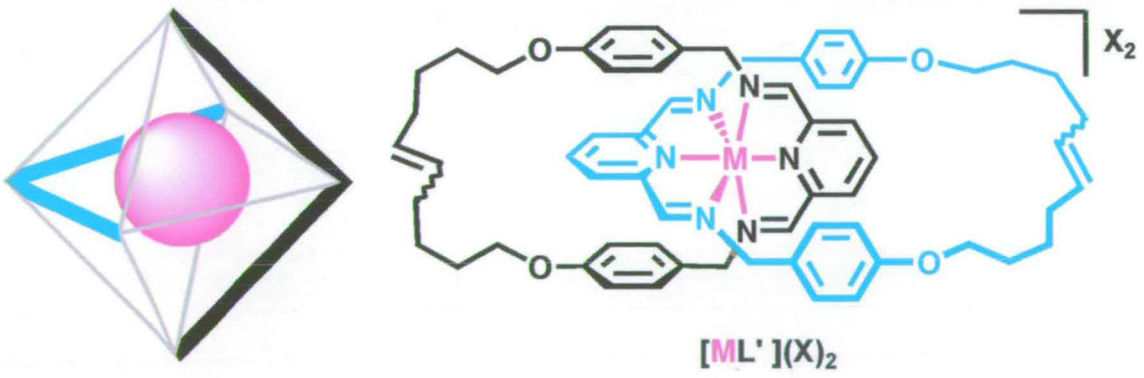
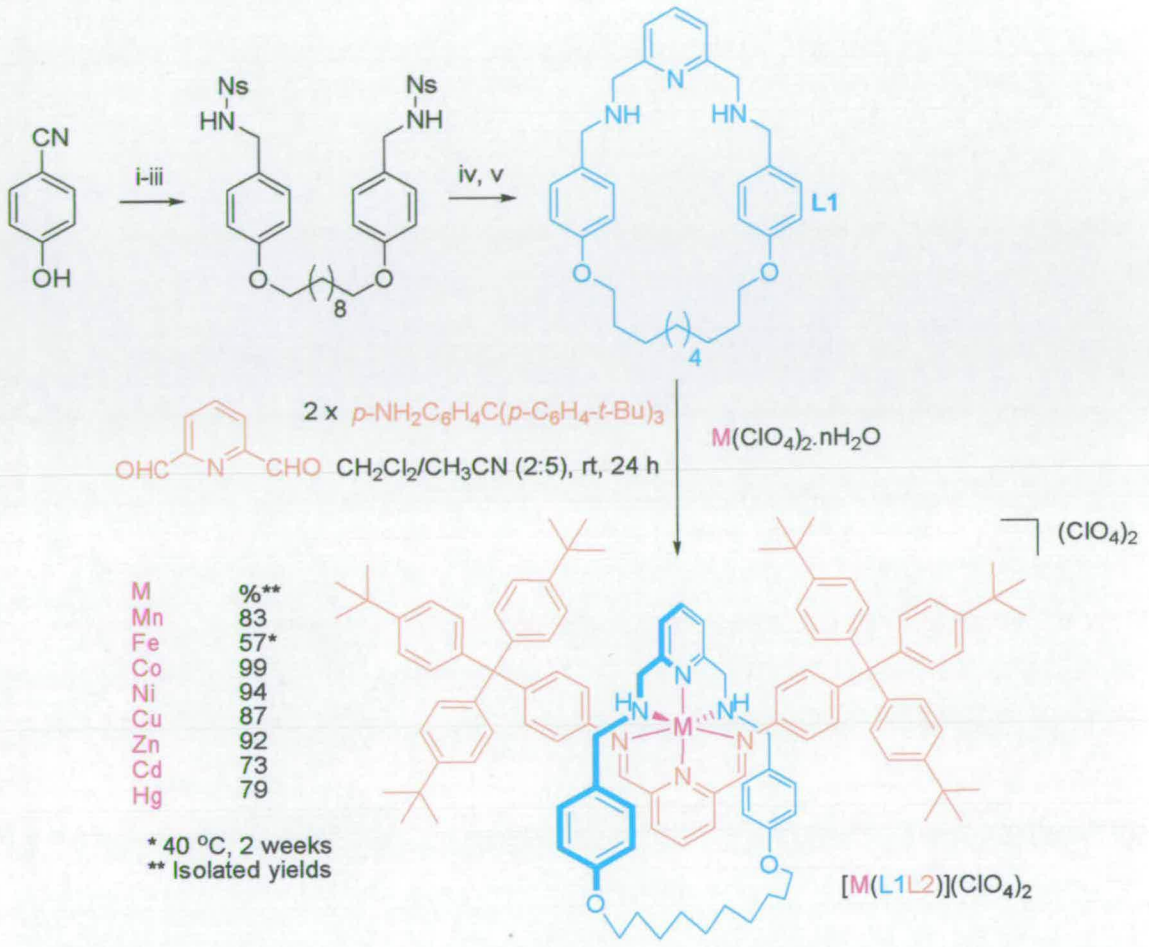


Figure 5: Catenates by orthogonalization of coordinated ligands about metal (M) templates with octahedral coordination preference. M: Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}.

This route was thought to be extendable to the synthesis of other metal-based interlocked architectures such as rotaxanes, shuttles, and knots: when I joined the Leigh group in the October 2001 the synthesis of rotaxanes based on this kind of chemistry was my first task.

2.3. Results and Discussion

As illustrated above, catenanes have previously been synthesized around octahedral metal templates by employing macrocycles containing tridentate 2,6-diiminopyridine chelating units.[25] This system is not well-suited to forming rotaxanes, however, because thread-thread-metal and macrocycle-macrocycle-metal (catenate) complexes can form in competition with the desired thread-macrocycle-metal assembly. Replacement of the macrocycle imine ligand set by non-labile amine groups removes the possibility of forming catenates and introduces a structural asymmetry that can potentially be tailored to favour rotaxane formation under dynamic exchange conditions.[30]



Scheme 1: Five component self-assembly of octahedral metal(II) rotaxanes, [M(**L1L2**)]$(ClO_4)_2$. Reagents and conditions: i. 1,10-dibromodecane, K_2CO_3, NaI, butanone, reflux, 18 h, 83%, ii. $LiAlH_4$, THF, 0-60 °C, 3 h, 92%, iii. 2-nitrobenzenesulfonyl chloride (NsCl), NEt_3, CH_2Cl_2, 18 h, 93%, iv. 2,6-dibromomethylpyridine, K_2CO_3, butanone, reflux, 18 h, 67%, v. mercaptoacetic acid, LiOH, DMF, 24 h, 80%.

After exploring several unsuccessful designs, we investigated the chemistry of macrocycle **L1**, which is prepared on a multigram scale in five steps from readily available materials (**Scheme 1**). The key step to **L1** is the macrocyclization of a *bis*-2-nitrobenzenesulfonamide (NsNH) derivative with 2,6-dibromomethylpyridine to give the protected macrocycle in 67% yield. Cyclization of the analogous Boc-protected diamine proceeded in low yield (<20%) and routes based on ring closing olefin

metathesis to form the C_{10} chain also proved uncompetitive. The use of aniline, rather than benzylamine, in the thread was designed to destabilize the dithread-metal complex with respect to the desired interlocked structure (*vide infra*).

Octahedral metal-rotaxane formation (**Scheme 1**) was achieved by sequential treatment of **L1** with $Zn(ClO_4)_2.6H_2O$ (0.8 equiv.), 2,6-diformylpyridine (1 equiv.) and (*p*-aminophenyl)tris(*p-tert*-butylphenyl)methane (2 equiv.). Remarkably, after 24 h at RT no metal-containing species other than the zinc(II)[2]rotaxane was evident by either ^1H NMR or electrospray mass spectrometry and the pure $[Zn(\mathbf{L1L2})](ClO_4)_2$ rotaxane was isolated in 92% yield by simply washing the crude product with diethyl ether. The generality of the reaction was explored using divalent metal ions both across and down the periodic table with respect to zinc (i.e. Mn←Zn and Zn→Hg). Pleasingly, each of $[M(\mathbf{L1L2})](ClO_4)_2$ ($M = Mn^{II}$, Co^{II}, Ni^{II}, Cu^{II}, Cd^{II}, Hg^{II}) could be efficiently prepared using the procedure in isolated yields ranging from 73 to 99% (**Scheme 1**). In all cases no other metal-containing species could be detected[31] after 24 h, suggesting near-quantitative formation of the interlocked metal-rotaxane complex. Formation of $[Fe(\mathbf{L1L2})](ClO_4)_2$ required a longer reaction time and gentle heating (CH_2Cl_2/CH_3CN, N_2, 40 °C, 2 weeks) and resulted in a lower yield of rotaxane (57%). The sluggish reaction rate is characteristic of the slow ligand exchange rate of low spin d^6 metals, but a potentially useful feature of the slower dynamics is that Fe^{II} therefore locks the rotaxane architecture in a particularly kinetically stable form.

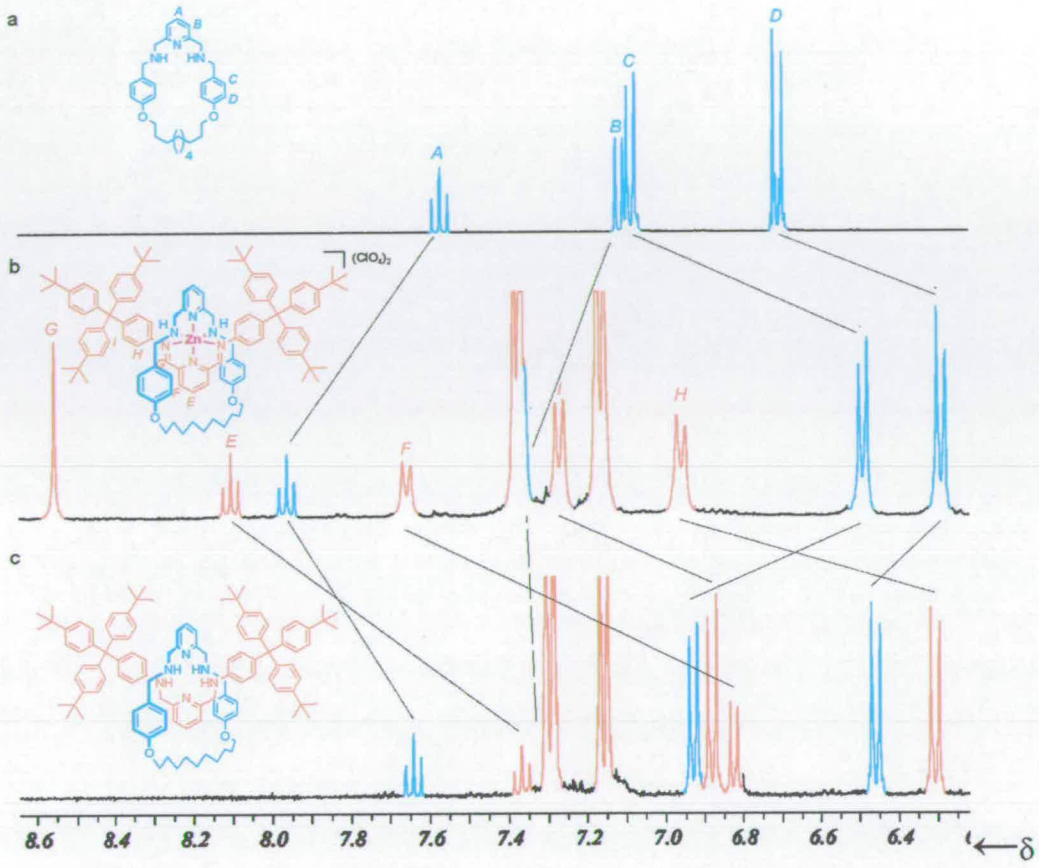


Figure 6: ^{1}H NMR spectra (400 MHz, CD_3CN, 298 K) of (a) macrocycle **L1** (b) zinc(II) rotaxane [Zn(**L1L2**)]$(ClO_4)_2$ (c) demetallated, reduced, rotaxane **L1**H_4**L2**.

The non-paramagnetic metal-rotaxane complexes all possess similar ^{1}H NMR spectra; those of the zinc(II) rotaxane [Zn(**L1L2**)]$(ClO_4)_2$ and macrocycle **L1** are shown in **Figure 6**.[32] The shielding of the H_C and H_D protons of the benzyl rings of the macrocycle and several protons of the thread indicate that extensive intercomponent π-stacking occurs in solution. Single crystals of [Cd(**L1L2**)]$(ClO_4)_2$ suitable for investigation by X-ray crystallography were obtained by slow vapor diffusion of diethyl ether into a solution of the rotaxane in acetonitrile.[33] The crystal structure (**Figure 7**) confirms the interlocked molecular architecture, the (pseudo-) octahedral geometry of the cadmium(II)

ion, and shows π-stacking of both macrocycle benzyl rings with the pyridyl unit and an imine group of the thread.

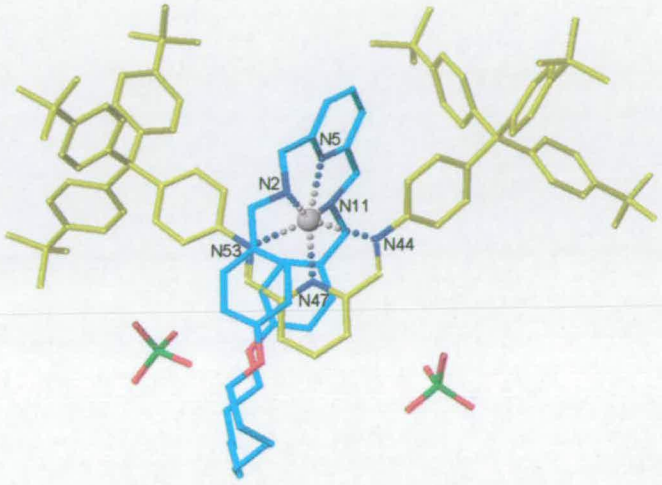
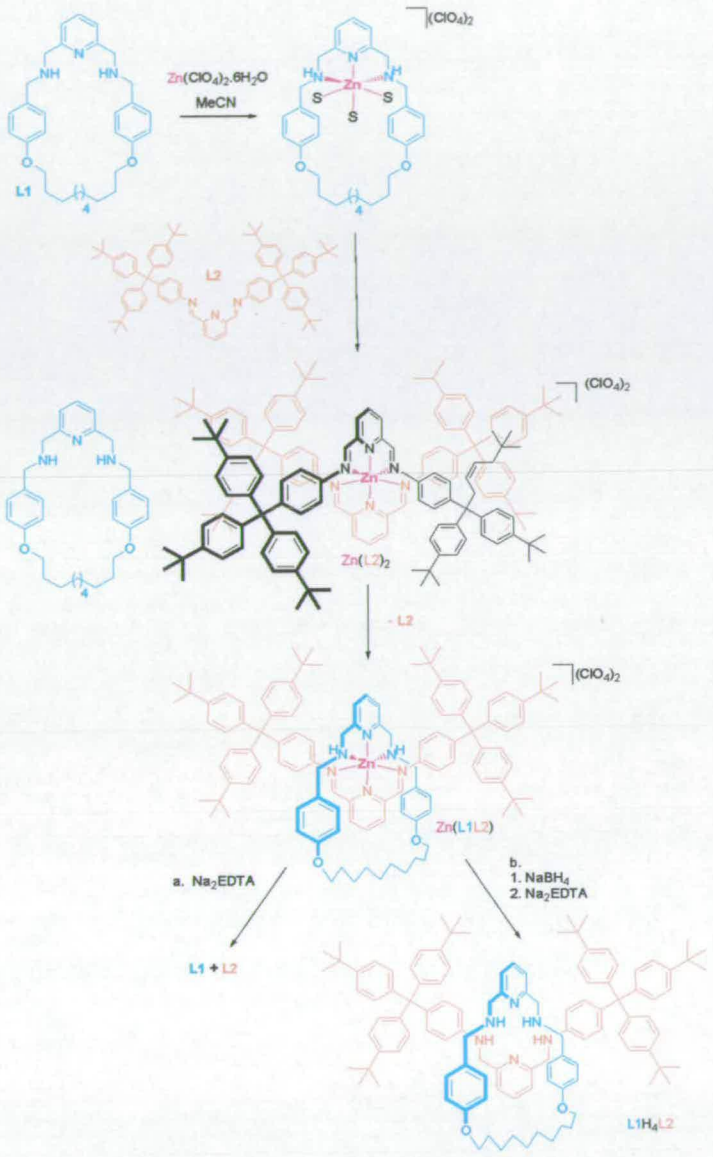


Figure 7: X-Ray crystal structure of [Cd(**L1L2**)]$(ClO_4)_2$.[11] Carbon atoms of the macrocycle, **L1**, are shown in light blue and those of the thread, **L2**, in yellow; oxygen atoms are red, nitrogen dark blue, chlorine green and cadmium grey. Hydrogen atoms and a molecule of acetonitrile are omitted for clarity. Selected bond lengths [Å]: Cd-N2 2.40, Cd-N5 2.30, Cd-N11 2.40, Cd-N44 2.52, Cd-N47 2.26, Cd-N53 2.38; other selected interatomic distances [Å]: N2-N11 4.52, N5-N47 4.52, N44-N53 4.59; ligand bite angles [°]: N2-Cd-N11 141.5, N44-Cd-N53 139.2.

The mechanism of the rotaxane-forming reaction provides insight into the reasons for the effectiveness of the ligand assembly. When **L1** is treated with $Zn(ClO_4)_2.6H_2O$ (CH_2Cl_2/CH_3CN, rt) followed by the preformed thread, **L2**, electrospray mass spectrometry shows that within 10 minutes the thread has extracted the zinc(II) ion from the macrocycle to form the dithread complex, [Zn(**L2**)$_2$]$(ClO_4)_2$ in >95% yield (**Scheme 2**). The [Zn(**L2**)$_2$]$(ClO_4)_2$ species is then quantitatively converted to the rotaxane [Zn(**L1L2**)]$(ClO_4)_2$ over 24 h.[34] Whilst the reversible nature of imine bond formation accounts for the dynamics of the system, the reasons for the rotaxane-metal complex being the thermodynamic product rather than the dithread-metal complex are



Scheme 2: Mechanism of formation and reactivity of [Zn(**L1L2**)]$(ClO_4)_2$. Rapid formation of Zn(**L2**)$_2$ is followed by quantitative conversion to Zn(**L1L2**) under thermodynamic control. Demetallation of the rotaxane using Na_2EDTA occurs both with (b) and without (a) prior reduction of the imine groups.

rather more subtle. In fact imine donors often form stronger coordination bonds than the corresponding amines,[35] which led to dithread-metal complexes being

thermodynamically favoured in other ligand systems we investigated. However, the use of aniline rather than, say, benzylamine groups in the thread does not allow geometries where the dithread-metal complex can form favourable intercomponent π-stacking interactions, such as those observed in the rotaxane between the benzyl groups of the macrocycle and the extended π-system of the thread in both solution (NMR) and the solid state (X-ray). We believe these favourable secondary interactions are important for the thermodynamic stability of the rotaxane over the other possible products of the reaction.

The 2,6-diminopyridyl motif imparts high kinetic stability in metal-coordinated interlocked structures. Tetra-imine metal(II) catenates are not demetallated by Na_2EDTA, requiring reduction to the more labile tetra-amine catenates in order for the metal to be extracted.[7] The [M(**L1L2**)]$(ClO_4)_2$ rotaxanes, which contain a combination of imine and amine donors, do react with excess Na_2EDTA under heating (10 equiv., CH_3CN/MeOH, 60 °C, 0.5 h) to remove the metal. However, without the stabilization provided by metal coordination the rotaxane decomposes through imine bond exchange and only free macrocycle and thread are observed experimentally (**Scheme 2**, path a). If the rotaxane imine bonds are reduced beforehand ([Zn(**L1L2**)]$(ClO_4)_2$, 10 eq. $NaBH_4$, CH_3CN/MeOH, Δ, 1.5 h), however, treatment with Na_2EDTA (10 equiv., CH_3CN/MeOH, 60 °C, 0.5 h) gives the demetallated, reduced, rotaxane **L1H$_4$L2** (88% yield) with no evidence of dethreading (**Scheme 2**, path b). The ^{1}H NMR of **L1H$_4$L2** is shown in **Figure 6c**. The downfield shift in the resonances of the benzyl groups with respect to [Zn(**L1L2**)]$(ClO_4)_2$ indicates that π-stacking with the thread is less pronounced in the demetallated rotaxane where there are no coordination bonds to organize the geometry of the components.

2.4. Conclusions

The field of supramolecular chemistry is growing at incredible pace leading rapidly to the development of machines at the molecular level. The world of catalysis is already being affected and, in the long run, could be revolutionized by the wide array of structures that this chemistry can afford. Coordination chemistry is playing a major role in the metal-directed synthesis of superstructures and we believe its involvement will be even greater in the improvement and implementation of catalytic systems.

This project was aimed at improve our understanding of metal-directed synthesis of supramolecular interlocked architectures.

During these months of research we have discovered a general ligand system for the efficient assembly of [2]rotaxanes around octahedral metal ions. The five component self-assembly reaction produces rotaxanes under true thermodynamic control in excellent yields without the need for large excesses of reagents, subsequent derivatization to stabilize the rotaxane architecture, chromatography or any other complicated purification processes. The system is remarkable in terms of its simplicity and expands both the range and geometry of metal ions that can be encapsulated within a rotaxane architecture. The procedure can be applied to a variety of divalent metals. This represents a step ahead in expanding the field of interlocked molecules to higher oxidation state transition metals. Besides, this is the first example of rotaxanes templated around a metal under thermodynamic control.

The ligand system utilized suggests application of further significance as it can be used, in slightly functionalized forms as catalyst for ethylene polymerization.

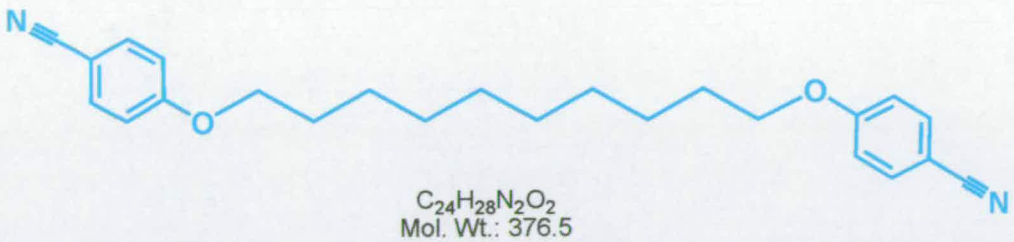
2.5. Experimental Section

2.5.1. *General*

Unless stated otherwise, all reagents and anhydrous solvents were purchased from Aldrich Chemicals and used without further purification. 2,6-Diformylpyridine and (*p*-aminophenyl)tris(*p-tert*-butylphenyl)methane were prepared according to literature procedures.[23, 36] Column chromatography was carried out using Kiesegel C60 (Merck, Germany) as the stationary phase, and TLC was performed on precoated silica gel plates (0.25 mm thick, $60F_{254}$, Merck, Germany) and observed under UV light.

All ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV 400 instrument at 25 °C. Chemical shifts are reported in parts per million from low to high field and referenced to TMS. Coupling constants (*J*) are reported in Hertz. Standard abbreviations indicating multiplicity were used as follows: br = broad, d = doublet, q = quadruplet, t = triplet, s = singlet. All melting points were determined using a Sanyo Gallenkamp apparatus and are reported uncorrected. ESI mass spectroscopy was performed with a Micromass Platform II Mass Spectrometer controlled using Masslynx v2.3 software while FAB mass spectroscopy and elemental analysis were carried out by the services at the University of Edinburgh.

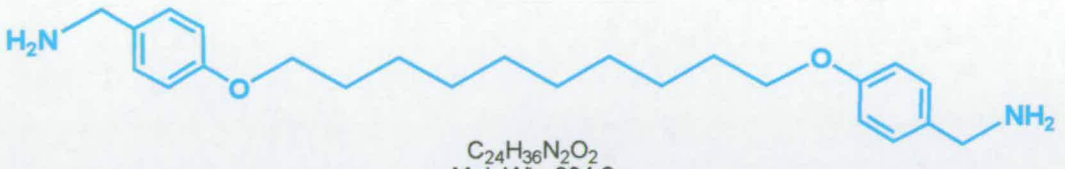
1,10-decoxybis(4-benzonitrile)



$C_{24}H_{28}N_2O_2$
Mol. Wt.: 376.5

4-Hydroxybenzonitrile (20.0 g, 168 mmol), potassium carbonate (209 g, 1.51 mol), 1,10-dibromodecane (25.2 g, 84.0 mmol) and sodium iodide (0.20 g, 1.30 mmol) were refluxed in butanone (500 L) under an Ar atmosphere for 18 h. Upon cooling the mixture was filtered, and the solvent removed in vacuo. The crude residue was dissolved in dichloromethane (50 mL) and filtered before methanol (300 mL) was added to induce precipitation. The precipitate was filtered off, washed with methanol and dried in air to yield the title compound as a colourless solid (26.2 g, yield = 83%). m.p. 126.2-127.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293K): δ=1.37 (bs, 8H; alkyl-H), 1.49 (m, 4H; alkyl-H), 1.84 (m, 4H; $OCH_2C\underline{H}_2$), 4.03 (t, J=6.5 Hz, 4H; OCH_2), 6.96 (d, J=8.9 Hz, 4H; ArH), 7.60 (d, J=8.9 Hz, 4H; ArH); ^{13}C NMR (100 MHz, $CDCl_3$, 293K): δ=26.3, 29.4, 29.7, 29.8, 68.8, 104.1, 115.6, 119.7, 134.4; ESI-MS: m/z = 377 $[MH]^+$; Anal. calcd. for $C_{24}H_{28}N_2O_2$ (376): C, 76.60%; H, 7.45%; N, 7.45%. Found: C, 76.46%; H, 7.43%; N, 7.22%.

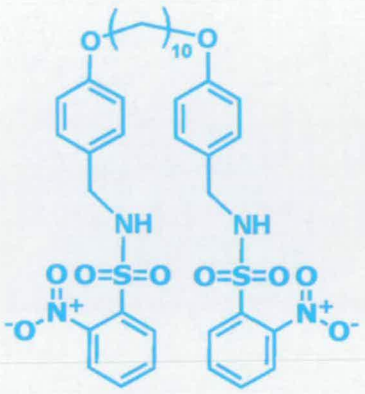
1,10-decoxybis(4-benzylamine)



$C_{24}H_{36}N_2O_2$
Mol. Wt.: 384.6

To a 1 mol dm^{-3} tetrahydrofuran solution of lithium aluminium hydride (200 mL, 200 mmol) under an atmosphere of argon at 0 °C, was added dropwise 1,10-decoxybis(4-benzonitrile) (12.5 g, 33.3 mmol) in anhydrous tetrahydrofuran (400 mL). Upon warming to room temperature, the solution was refluxed for 3 h. Once cool, the solution was cautiously quenched by dropwise addition of water (5.6 mL), 15% aq. NaOH solution (5.6 mL) and water (16.8 mL). The aluminium salts were filtered off and the solvent removed under reduced pressure to yield the title compound as a colourless solid (11.8 g, yield = 92%). m.p. 101.8-104.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ =1.37 (bs, 8H; alkyl-H), 1.51 (m, 4H; alkyl-H), 1.81 (m, 4H; $OCH_2C\underline{H}_2$), 3.83 (s, 4H; $ArC\underline{H}_2NH_2$), 3.98 (t, J=6.5 Hz, 4H; OCH_2), 6.90 (d, J=8.9 Hz, 4H; ArH), 7.24 (d, J=8.9 Hz, 4H; ArH); ^{13}C NMR (100 MHz $CDCl_3$, 298K): δ=26.0, 29.3, 29.4, 29.5, 45.9, 68.0, 114.5, 128.2, 135.3, 158.0; ESI-MS: m/z = 385 $[MH]^+$; Anal. calcd. for $C_{24}H_{36}N_2O_2$ (384): C, 75.00%; H, 9.37%; N, 7.29%. Found: C, 75.07%; H, 9.41%; N, 6.96%.

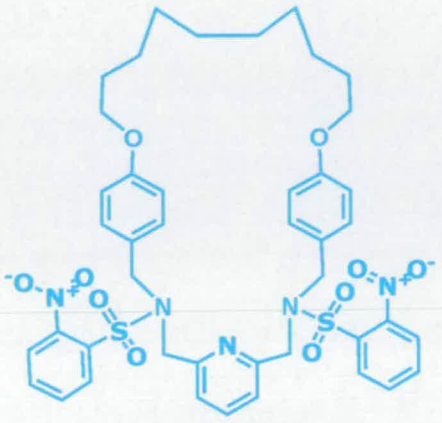
N,N'-di-2-nitrobenzenesulfonyl[1,10-decoxybis(4-benzylamine)]



$C_{36}H_{42}N_4O_{10}S_2$
Mol. Wt.: 754.9

To 1,10-decoxybis(4-benzylamine) (11.5g, 29.9 mmol) in chloroform (500 mL) was added triethylamine (9.28 mL, 65.9 mmol) and 2-nitrobenznesulfonyl chloride (13.3 g, 60.0 mmol). The solution was stirred at room temperature under an atmosphere of nitrogen for 18 h. The resulting precipitate was filtered off and dried in air to yield the title compound as a pale yellow solid (22.6 g, yield = 93%). m.p. 180.0-181.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ = 1.32 (bs, 4H; alkyl-H), 1.56 (bs, 8H; alkyl-H), 1.74 (m, 4H; $OCH_2C\underline{H}_2$), 3.89 (t, J=6.8 Hz, 4H; OCH_2), 4.23 (d, J=6.3 Hz, 4H; $C\underline{H}_2NHNs$), 5.61 (t, J=6.3Hz, $CH_2N\underline{H}Ns$), 6.73 (d, J=8.6 Hz, 4H; ArH), 7.10 (d, J=8.6 Hz, 4H; ArH), 7.67 (m, 4H; Ns-ArH), 7.82 (m, 2H; Ns-ArH), 8.03 (m, 2H; Ns-ArH). ^{13}C NMR (100 MHz $CDCl_3$, 298K): δ = 26.0, 29.1, 29.3, 29.4, 47.4, 68.0, 114.6, 125.2, 127.3, 129.2, 131.1, 132.6 133.3, 136.1, 138.8, 157.8. ESI-MS: m/z = 772 $[M\text{NH}_4]^+$;

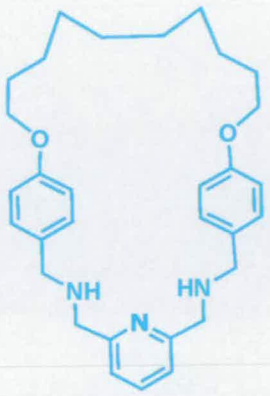
N,N'-2,6-dimethylpyridyl-N,N'- di-2-nitrobenzenesulfonyl [(1,10-decoxybis(4-benzylamine)]



$C_{43}H_{47}N_5O_{10}S_2$
Mol. Wt.: 858.0

N,N'-di-2-nitrobenzenesulfonyl[1,10-decoxybis(4-benzylamine)] (3.15 g, 4.18 mmol), 2,6-dimethylbromopyridine (1.11 g, 4.19 mmol) and potassium carbonate (75 g, 0.54 mol) were heated to reflux in butanone (2 L) under nitrogen for 24 h. The excess potassium carbonate was filtered off and the solvent removed under reduced pressure. The crude residue was purified by column chromatography (CH_2Cl_2/EtOAc 50:1) to yield the title compound as an off-white solid (2.42 g, yield = 68%). m.p. 181.9-184.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ = 1.30 (bs, 8H; alkyl-H), 1.40 (m, 4H; alkyl-H), 1.70 (m, 4H; $OCH_2C\underline{H}_2$), 3.88 (t, J=6.3 Hz, 4H; $OC\underline{H}_2$), 4.39 (s, 4H; $C\underline{H}_2NNs$), 4.41 (s, 4H; $C\underline{H}_2NNs$), 6.70 (d, J=8.6 Hz, 4H; ArH), 6.97 (d, J=8.6 Hz, 4H; ArH), 7.07 (d, J=7.8 Hz, 2H; pyridyl-H), 7.46 (t, J=7.8 Hz, 1H; pyridyl-H), 7.6-7.74 (m, 6H; Ns-ArH), 8.00 (m, 2H; Ns-ArH); NMR (100 MHz $CDCl_3$, 298K): δ = 25.1, 27.7, 28.0, 28.4, 50.9, 51.5, 67.6, 114.6, 121.0, 124.2, 126.4, 130.2, 131.0, 131.8, 133.6, 133.9, 137.3, 147.9, 155.5, 158.8; ESI-MS: m/z = 858 $[M]^+$.

N,N'-2,6-dimethylpyridyl[(1,10-decoxybis(4-benzylamine)] L1

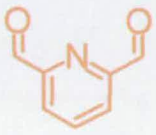


$C_{31}H_{41}N_3O_2$
Mol. Wt.: 487.7

To N,N'-2,6-dimethylpyridyl-N,N'-di-2-nitrobenzenesulfonyl [(1,10-decoxybis(4-benzylamine)] (2.42 g, 2.82 mmol) in dimethylformamide (20 mL) was added lithium hydroxide (2.36 g, 56.1 mmol) and mercaptoacetic acid (1.93 mL, 27.7 mmol). The reaction was stirred for 18 h at room temperature. The solvent was removed under reduced pressure and the resulting residue partitioned between ethylacetate (50 mL) and saturated sodium bicarbonate solution (50 mL). The organic layer was separated and washed with further sodium bicarbonate solution (5x50 mL). The organic solution was then dried over sodium sulphate, filtered and the solvent removed under reduced pressure. The crude residue was purified using column chromatography ($CHCl_3$/MeOH/NH_4OH 90:9.75:0.25) to leave the title compound as a colourless oil. A colourless solid was obtained by adding water to a methanolic solution of the title compound (1.21 g, yield = 88%). m.p. 67.4-69.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ=1.33 (bs, 4H; alkyl-CH_2), 1.46 (m, 4H; alkyl-CH_2), 1.76 (m, 4H; alkyl-CH_2), 2.32 (m, 4H; $OCH_2C\underline{H_2}$), 3.76 (s, 4H; $ArC\underline{H_2}NH$), 3.88 (s, 4H; Pyridyl-$C\underline{H_2}NH$), 3.95 (t, J=6.3 Hz, 4H; $OC\underline{H_2}$), 6.81 (d, J=8.5 Hz, 4H; ArH), 7.16 (d, J=7.5 Hz, 2H; Pyridyl-H), 7.20 (d, J=8.5 Hz, 4H; ArH), 7.59 (t, J=7.5 Hz, 1H; Pyridyl-H); ^{13}C NMR (100 MHz, $CDCl_3$, 298K): δ=25.9, 28.4, 28.9, 29.0, 53.5, 54.6, 67.9, 114.9, 121.0, 129.9, 132.3,

137.2, 158.6, 159.4; ESI-MS: m/z = 488 $[MH]^+$. Anal. calcd. for $C_{31}H_{41}N_3O_2$ (487): C, 76.35%; H, 8.47%; N, 8.62%; Found: C, 76.43%; H, 8.49%; N, 8.52%.

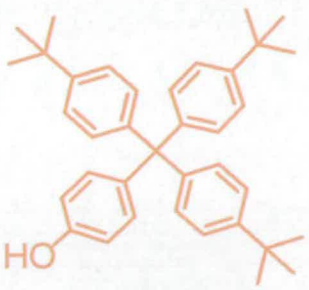
2,6-Diformylpyridine



$C_7H_5NO_2$
Mol. Wt.: 135.1

This compound was prepared as described in A. L. Vance, N. W. Alcock, J. A. Heppert, D. H. Busch, *Inorg.. Chem*, **1998**, 37, 6912 – 6920 and showed identical spectroscopical data to those reported therein.

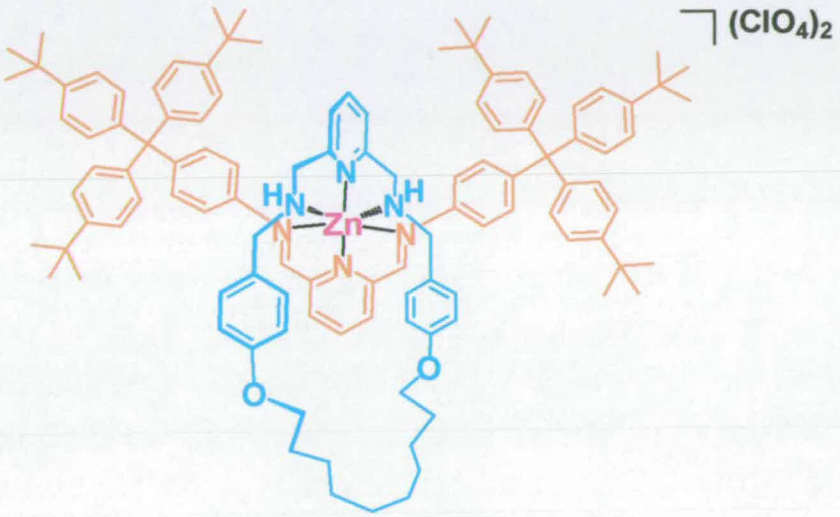
4-[Tris-(4-*tert*-butyl-phenyl)-methyl]-phenol



$C_{37}H_{44}O$
Mol. Wt.: 504.7

This compound was prepared as described in H. W. Gibson, S. H. Lee, P. T. Engen, P. Lecavalier, J. Sze, Y. X. Shen, M. Bheda, J. Org. Chem, **1993**, *58*, 3748 – 3756 and showed identical spectroscopical data to those reported therein.

[N,N'-2,6-dimethylpyridylbis(1,10-decoxy-4-benzylamine)]-[2,6-diacetylpyridinebis[(*p*-iminophenyl)tris(*p*-*tert*-butylphenyl)methyl]zinc(II) perchlorate [Zn(L1L2)](ClO$_4$)$_2$



$C_{112}H_{132}Cl_2N_6O_{10}Zn$
Mol. Wt.: 1858.6

Method 1: 5 component self assembly

To **L1** (0.200 g, 0.410 mmol) in acetonitrile (10 mL) was added zinc(II) perchlorate hexahydrate (0.127 g, 0.342 mmol) in acetonitrile (5 mL). After stirring at room temperature for 5 min., 2,6-diformylpyridine (0.055 g, 0.410 mmol) in acetonitrile (10 mL) was added. After a further 5 min., (*p*-aminophenyl)tris(*p*-*tert*-butylphenyl)methane (0.413 g, 0.820 mmol) in dichloromethane (10 mL) was added, and the solution stirred at room temperature for 24 h. The solvent was removed under reduced pressure, the crude residue dissolved in acetonitrile (30 mL), filtered and the solvent removed under reduced pressure. The crude residue was stirred in diethyl ether (30 mL), for 10 min., filtered off and dried in air to give the title compound as a bright yellow solid (0.582 g,

yield=92%). M.p. 266 °C (dec). ^{1}H NMR (400 MHz, CD_3CN, 298K): δ = 1.32 (s, 54H; $C(CH_3)_3$), 1.48-1.68 (bm, 12H; alkyl-H), 1.79 (m, 4H; OCH_2,$C\underline{H}_2$), 3.84 (br, 4H; OCH_2), 4.06-4.55 (br, 8H; Pyr$C\underline{H}_2$NH$C\underline{H}_2$Ar), 6.29 (d, J=8.6 Hz, 4H; macrocycle ArH), 6.49 (d, J=8.6 Hz, 4H; macrocycle ArH), 6.96 (d, J=8.6 Hz, 4H; thread ArH), 7.16 (d, J=8.6 Hz, 12H; thread ArH), 7.27 (d, J=8.6 Hz, 4H; thread ArH), 7.37 (m, 14H; thread ArH + macrocycle pyridyl-H), 7.65 (d, J=7.8 Hz, 2H; thread pyridyl-H), 7.96 (t, J=7.8 Hz, 1H; macrocycle pyridyl-H), 8.11 (t, J=7.8 Hz, 1H; thread pyridyl-H), 8.57 (s, 2H; thread HC=N); ^{13}C NMR (100 MHz, $CDCl_3$, 298K): δ = 25.6, 28.4, 28.5, 29.4, 31.5, 34.5, 52.2, 55.3, 63.9, 67.4, 114.1, 120.8, 123.0, 124.1, 124.3, 124.6, 127.0, 128.5, 130.6, 141.5, 141.9, 143.3, 143.4, 145.9, 148.9, 149.0, 155.0, 158.2, 158.7; IR (KBr pressed pellet): ν = 3465, 2960, 2865, 1611, 1582, 1513, 1464, 1395, 1363, 1251, 1180, 1109, 1089, 1017, 840, 823, 637, 625, 582 cm^{-1}; LRESI-MS: m/z = 829 [Zn(**L1L2**)]$^{2+}$, 1758 [Zn(**L1L2**)]$(ClO_4)^+$; HRFAB-MS (3-NOBA matrix): m/z = 1657.97065 (calcd. for $^{12}C_{111}{}^{13}CH_{132}N_6O_2{}^{64}Zn$ [Zn(**L1L2**)], 1657.97363).

Method 2: From [2,6-diacetylpyridinebis[(p-iminophenyl)tris(p-tert-butylphenyl)methyl]

To **L1** (0.034 g, 0.0687 mmol) in acetonitrile (5 mL), was added zinc(II) perchlorate hexahydrate (0.021 g, 0.0572 mmol) in acetonitrile (5 mL). After stirring at room temperature for 5 min., **L2** (0.076 g, 0.0687 mmol) in dichloromethane (5 mL) was added. The reaction was stirred at room temperature, being followed to completion by ESI-MS (ca. 48 h). The solvent was removed under reduced pressure, acetonitrile added (10 mL), and the solution filtered. The solvent was then removed and diethyl ether added to the crude residue. After stirring for 10 min. the residue was filtered and dried in air to give the title compound as bright yellow solid (0.085 g, yield = 80%). Analysis same as for method 1.

Method 3: From Bis[2,6-diacetylpyridinebis[(p-iminophenyl)tris(p-tert-butylphenyl)methyl]zinc(II) perchlorate $[Zn(L2)_2](ClO_4)_2$

To an acetonitrile (5 mL) solution of $[Zn(\mathbf{L2})_2](ClO_4)_2$ (0.100 g, 0.404 mmol), was added **L1** (0.020 g, 0.0404 mmol) in dichloromethane (5 mL). The reaction was stirred at room temperature, being followed to completion by ESI-MS (ca. 48 h). The solvent was removed under reduced pressure, acetonitrile added (10 mL), and the solution filtered. The solvent was then removed and diethyl ether added to the crude residue. After stirring for 10 min. the residue was filtered and dried in air to give the title compound as bright yellow solid (0.062 g, yield = 83%). Analysis same as for method 1.

[N,N'-2,6-dimethylpyridylbis(1,10-decoxy-4-benzylamine)]-[2,6-diacetylpyridinebis[(p-iminophenyl)tris(p-tert-butylphenyl)methyl]cadmium(II) perchlorate $[Cd(L1L2)](ClO_4)_2$

Reaction of **L1** (0.150 g, 0.307 mmol), cadmium(II) perchlorate hydrate (0.076 g, 0.245 mmol), 2,6-diformylpyridine (0.042 g, 0.307 mmol) and (*p*-aminophenyl)tris(*p*-*tert*-butylphenyl)methane (0.309 g, 0.614 mmol) as described for the preparation of $[Zn(\mathbf{L1L2})](ClO_4)_2$, gave the title compound as a bright yellow solid (0.340 g, yield = 73%). m.p. 254 °C (dec); ^{1}H NMR (400 MHz, [D$_6$]acetone, 298K): δ = 1.31 (s, 54H; $C(CH_3)_3$), 1.45-1.70 (b, 12H; alkyl-H), 1.80 (bm, 4H; OCH_2,$C\underline{H}_2$), 3.71- 4.49 (br, 12H; OCH_2 + Pyr$C\underline{H}_2NHC\underline{H}_2$Ar), 6.30 (d, *J*=8.6 Hz, 4H; macrocycle ArH), 6.78 (d, *J*=8.6 Hz, 4H; macrocycle ArH), 7.12 (d, *J*=8.6 Hz, 12H; thread ArH), 7.28 (bm, 8H; thread ArH), 7.39 (d, *J*=8.6 Hz, 12H; thread ArH), 7.44 (d, *J*=7.8 Hz, 2H; macrocycle pyridyl-H), 8.00 (t, *J*=7.8 Hz, 1H; macrocycle pyridyl-H), 8.18 (bs, 2H; thread pyridyl-H), 8.42 (bs, 1H; thread pyridyl-H), 9.02(bs, 2H; thread HC=N); ^{13}C NMR (100 MHz, $CDCl_3$, 298K): δ = 25.7, 28.1, 28.2, 28.5, 31.3, 34.5, 51.9, 54.7, 63.9, 67.3, 113.7, 121.0, 123.5, 124.0, 124.6, 127.9, 128.8, 130.6, 133.0, 141.1, 141.7, 142.7, 143.3, 144.4, 146.1, 148.8,

155.0, 158.2, 158.7; IR (KBr pressed pellet): ν = 3465, 2960, 1611, 1583, 1514, 1463, 1394, 1363, 1251, 1180, 822, 624, 592 cm^{-1}; LRESI-MS: *m/z* = 853 $[Cd(\mathbf{L1L2})]^{2+}$, 1806 $[Cd(\mathbf{L1L2})](ClO_4)^+$. HRFAB-MS (3-NOBA matrix): *m/z* = 1707.94303 (calcd. for $^{12}C_{111}{}^{13}CH_{132}N_6O_2{}^{114}Cd$ $[Cd(\mathbf{L1L2})]$, 1707.94813).

[N,N'-2,6-dimethylpyridylbis(1,10-decoxy-4-benzylamine)]-[2,6-diacetylpyridinebis[(*p*-iminophenyl)tris(*p-tert*-butylphenyl)methyl]mercury(II) perchlorate [Hg(L1L2)](ClO$_4$)$_2$

Reaction of **L1** (0.150 g, 0.307 mmol), mercury(II) perchlorate hydrate (0.098 g, 0.242 mmol), 2,6-diformylpyridine (0.042 g, 0.307 mmol) and (*p*-aminophenyl)tris(*p-tert*-butylphenyl)methane (0.310 g, 0.614 mmol) as described for the preparation of $[Zn(\mathbf{L1L2})](ClO_4)_2$, gave the title compound as a bright yellow solid (0.378 g, yield = 79%). M.p. 244 °C (dec). ^{1}H NMR (400 MHz, CD_3CN, 298K): δ = 1.30 (s, 54H; $C(CH_3)_3$), 1.41 (bs, 8H; alkyl-H), 1.55 (4H, m; Alkyl-H), 1.75 (4H, m; alkyl-H), 3.67 (t, *J*=6.6 Hz, 4H; OCH_2), 3.94 (br, 8H; $ArC\underline{H}_2NHC\underline{H}_2Py$), 6.06 (d, *J*=8.6 Hz, 4H; macrocycle ArH), 6.44 (d, *J*=8.6 Hz, 4H; macrocycle ArH), 6.92 (d, *J*=8.6 Hz, 4H; thread ArH), 7.19 (d, *J*=8.6 Hz, 12H; thread ArH), 7.25 (d, *J*=8.6 Hz, 4H; thread ArH), 7.38 (m, 14H; thread ArH + macrocycle pyridyl-H), 7.93 (t, *J*=7.8 Hz, 1H; macrocycle pyridyl-H), 8.06 (d, *J*=7.8 Hz, 2H; thread pyridyl-H), 8.43 (t, *J*=7.8 Hz, 1H; thread pyridyl-H), 8.66 (s, 2H; N=CH). ^{13}C NMR (100 MHz, CD_3CN, 298K): δ = 25.1, 27.9, 28.1, 28.3, 30.4, 33.9, 50.4, 53.9, 63.5, 67.4, 113.5, 121.1, 124.2, 124.7, 128.1, 128.5, 130.0, 130.4, 131.7, 132.4, 141.1, 142.9, 143.6, 145.4, 146.2, 148.8, 149.1, 153.5, 158.5. IR (KBr pressed pellet): ν = 3466, 2961, 2861, 1611, 1583, 1513, 1461, 1394, 1363, 1252, 1179, 1121, 1108, 1018, 842, 823, 637, 624, 594 cm^{-1}. LRESI-MS: *m/z* = 897 $[Hg(\mathbf{L1L2})]^{2+}$, 1894 $[Hg(\mathbf{L1L2})](ClO_4)^+$. HRFAB-MS (3-NOBA matrix): *m/z* = 1796.01909 (calcd. for $^{12}C_{111}{}^{13}CH_{132}N_6O_2{}^{202}Hg$ $[Hg(\mathbf{L1L2})]$, 1796.01517).

[N,N'-2,6-dimethylpyridylbis(1,10-decoxy-4-benzylamine)]-[2,6-diacetylpyridinebis[(*p*-iminophenyl)tris(*p*-*tert*-butylphenyl)methyl]copper(II) perchlorate [Cu(L1L2)](ClO$_4$)$_2$

Reaction of **L1** (0.150 g, 0.307 mmol), copper(II) perchlorate hexahydrate (0.091 g, 0.245 mmol), 2,6-diformylpyridine (0.042 g, 0.307 mmol) and (*p*-aminophenyl)tris(*p*-*tert*-butylphenyl)methane (0.309 g, 0.614 mmol) as described for the preparation of [Zn(**L1L2**)](ClO$_4$)$_2$, gave the title compound as a green solid (0.398 g, yield = 87%). M.p. 260 °C (dec). IR (KBr pressed pellet): ν = 3465, 2960, 1612, 1586, 1515, 1461, 1394, 1363, 1253, 1181, 1121, 1108, 1017, 842, 822, 623, 583 cm^{-1}; LRESI-MS: *m/z* = 828 [Cu(**L1L2**)]$^{2+}$, 1757 [Cu(**L1L2**)](ClO$_4$)$^+$. HRFAB-MS (3-NOBA matrix): *m/z* = 1656.97501 (calcd. for $^{12}C_{111}{}^{13}CH_{132}N_6O_2{}^{63}Cu$ [Cu(**L1L2**)], 1656.97433).

[N,N'-2,6-dimethylpyridylbis(1,10-decoxy-4-benzylamine)]-[2,6-diacetylpyridinebis[(*p*-iminophenyl)tris(*p*-*tert*-butylphenyl)methyl]nickel(II) perchlorate [Ni(L1L2)](ClO$_4$)$_2$

Reaction of **L1** (0.150 g, 0.308 mmol), nickel(II) perchlorate hexahydrate (0.088 g, 0.242 mmol), 2,6-diformylpyridine (0.042 g, 0.308 mmol) and (*p*-aminophenyl)tris(*p*-*tert*-butylphenyl)methane (0.310 g, 0.616 mmol) as described for the preparation of [Zn(**L1L2**)](ClO$_4$)$_2$, gave the title compound as a reddish brown solid (0.423 g, yield = 94%). m.p. 240 °C (dec); IR (KBr pressed pellet): ν = 3501, 2960, 2865, 1611, 1582, 1515, 1461, 1394, 1363, 1253, 1181, 1108, 1017, 839, 822, 623, 586 cm^{-1}; LRESI-MS: *m/z* = 826 [Ni(**L1L2**)]$^{2+}$, 1752 [Ni(**L1L2**)](ClO$_4$)$^+$. HRFAB-MS (3-NOBA matrix): *m/z* = 1651.97955 (calcd. for $^{12}C_{111}{}^{13}CH_{132}N_6O_2{}^{58}Ni$ [Ni(**L1L2**)], 1651.97983).

[N,N'-2,6-dimethylpyridylbis(1,10-decoxy-4-benzylamine)]-[2,6-diacetylpyridinebis[(*p*-iminophenyl)tris(*p-tert*-butylphenyl)methyl]cobalt(II) perchlorate [Co(L1L2)](ClO$_4$)$_2$

Reaction of **L1** (0.189 g, 0.387 mmol), cobalt(II) perchlorate hexahydrate (0.113 g, 0.310 mmol), 2,6-diformylpyridine (0.052 g, 0.387 mmol) and (*p*-aminophenyl)tris(*p-tert*-butylphenyl)methane (0.390 g, 0.774 mmol) as described for the preparation of [Zn(**L1L2**)](ClO$_4$)$_2$, gave the title compound as a pale brown solid (0.570 g, yield = 99%). m.p. 257 °C (dec); IR (KBr pressed pellet): ν =3501, 2960, 2865, 1611, 1581, 1515, 1462, 1394, 1363, 1253, 1181, 1108, 1017, 841, 822, 623, 586 cm^{-1}; LRESI-MS: *m/z* = 827 [Co(**L1L2**)]$^{2+}$, 1753 [Co(**L1L2**)](ClO$_4$)$^+$. HRFAB-MS (3-NOBA matrix): *m/z* = 1652.97916 (calcd. for $^{12}C_{111}{}^{13}CH_{132}N_6O_2{}^{59}Co$ [Co(**L1L2**)], 1652.97773).

[N,N'-2,6-dimethylpyridylbis(1,10-decoxy-4-benzylamine)]-[2,6-diacetylpyridinebis[(*p*-iminophenyl)tris(*p-tert*-butylphenyl)methyl]iron(II) perchlorate [Fe(L1L2)](ClO$_4$)$_2$

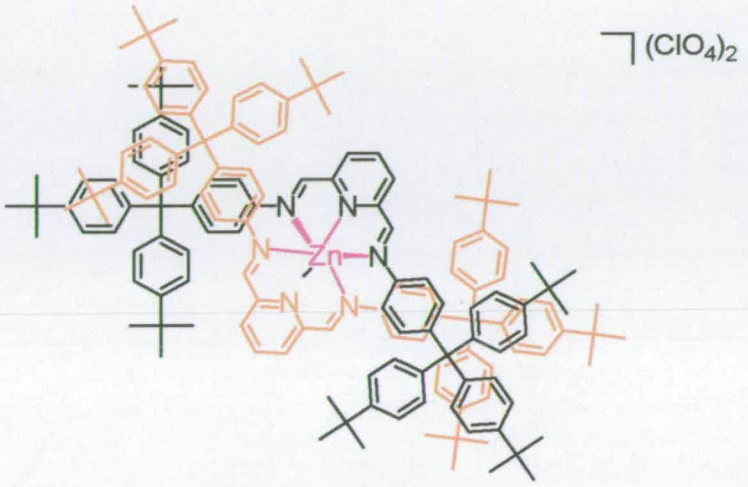
To **L1** (0.075 g, 0.154 mmol) in dichloromethane (10 mL) was added sequentially over 5 min. periods iron(II) perchlorate hexahydrate (0.033 g, 0.128 mmol) in acetonitrile (5 mL), 2,6-diformylpyridine (0.021 g, 0.154 mmol) in acetonitrile (5 mL) and (*p*-aminophenyl)tris(*p-tert*-butylphenyl)methane (0.155 g, 0.307 mmol) in dichloromethane (5 mL). The resulting solution was heated to reflux, under an atmosphere of nitrogen, for two weeks. Upon cooling, the solvent was removed under reduced pressure, the crude residue dissolved in acetonitrile (30 mL), filtered and the solvent removed under reduced pressure. The crude residue was stirred in diethyl ether (30 mL), for 10 min., filtered off and dried in air to give the title compound as a dark purple solid (0.136 g, yield =57%). m.p. 270 °C (dec); IR (KBr pressed pellet): cm^{-1}; 3470, 2960, 2864, 1612,

1560, 1512, 1458, 1400, 1364, 1253, 1180, 1109, 1017, 823, 623; LRESI-MS: m/z = 824 $[Fe(\mathbf{L1L2})]^{2+}$.

[N,N'-2,6-dimethylpyridylbis(1,10-decoxy-4-benzylamine)]-[2,6-diacetylpyridinebis[(*p*-iminophenyl)tris(*p*-*tert*-butylphenyl)methyl]manganese(II) perchlorate [Mn(L1L2)](ClO$_4$)$_2$

Reaction of **L1** (0.150 g, 0.307 mmol), manganese(II) perchlorate hexahydrate (0.88 g, 0.245 mmol), 2,6-diformylpyridine (0.042 g, 0.307 mmol) and (*p*-aminophenyl)tris(*p*-*tert*-butylphenyl)methane (0.309 g, 0.614 mmol) as described for the preparation of [Zn(**L1L2**)](ClO$_4$)$_2$, gave the title compound as a tan coloured solid (0.376 g, yield = 83%). M.p. 259 °C (dec); IR (KBr pressed pellet): ν = 3465, 2959, 2864, 1611, 1581, 1514, 1464, 1394, 1363, 1252, 1180, 1109, 1018, 823, 624, 585 cm^{-1}; LRESI-MS: m/z = 824 $[Mn(\mathbf{L1L2})]^{2+}$, 1749 [Mn(**L1L2**)](ClO$_4$)$^+$. HRFAB-MS (3-NOBA matrix): m/z = 1648.98280 (calcd. for $^{12}C_{111}{}^{13}CH_{132}N_6O_2{}^{55}Mn$ [Mn(**L1L2**)], 1648.98263).

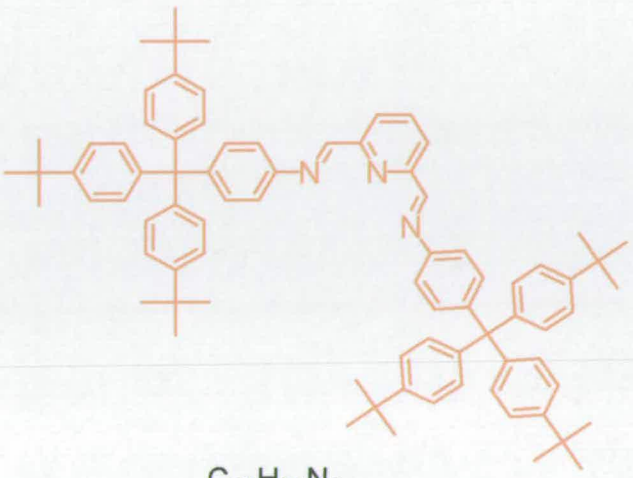
Bis[2,6-diacetylpyridinebis[(*p*-iminophenyl)tris(*p*-*tert*-butylphenyl)methyl]zinc(II) perchlorate $[Zn(L2)_2](ClO_4)_2$



$C_{162}H_{182}Cl_2N_6O_8Zn$
Mol. Wt.: 2477.5

To 2,6-diformylpyridine (0.020 g, 0.149 mmol) in acetonitrile (5 mL) was added zinc(II) perchlorate hexahydrate (0.028 g, 0.0745 mmol) in acetonitrile (5mL), and (*p*-aminophenyl)tris(*p*-*tert*-butylphenyl)methane (0.150 g, 0.298 mmol) in dichloromethane (5 mL). The reaction was stirred at room temperature for 24 h. The solvent was then removed under reduced pressure, re-dissolved in acetonitrile (5 mL) and filtered. The solvent was removed under reduced pressure and diethyl ether was added to the crude residue. After stirring for 10 min, the residue was filtered off and dried in air to yield the title compound as a bright yellow solid (0.163 g, yield = 88%). ^{1}H NMR (400 MHz, [D_6]acetone, 298K): δ = 1.27 (s, 108H; $C(CH_3)_3$), 6.77 (d, J=8.8 Hz, 8H; stopper ArH), 7.02 (d, J=8.8 Hz, 8H; stopper ArH), 7.05 (d, J=8.8 Hz, 24H; stopper ArH), 7.32 (d, J=8.8 Hz, 24H; stopper ArH), 8.36 (d, J=7.6 Hz, 4H; pyridyl-H), 8.49 (t, J=7.6 Hz, 2H; pyridyl-H), 9.15 (s, 4H; CH=N); ^{13}C NMR (100 MHz, $CDCl_3$, 298K): δ = 31.6, 34.9, 64.4, 121.7, 122.9, 125.4, 131.2, 132.9, 143.6, 144.5, 146.1, 147.7, 149.4, 149.9, 159.7; LRESI-MS: m/z = 1139 $[Zn(\mathbf{L2})_2]^{2+}$.

2,6-diacetylpyridinebis[(*p*-iminophenyl)tris(*p*-*tert*-butylphenyl)methyl L2



$C_{81}H_{91}N_3$
Mol. Wt.: 1106.6

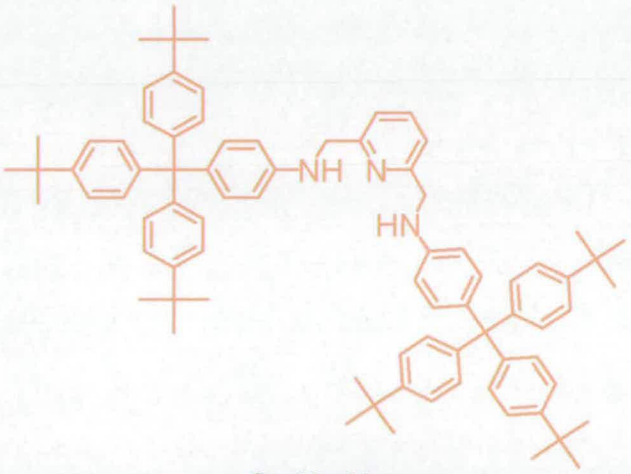
Method 1: From [Zn(L2)$_2$](ClO$_4$)$_2$

To [Zn(**L2**)$_2$](ClO$_4$)$_2$ (0.150 g, 0.0605 mmol) in acetonitrile (10 mL) and methanol (20 mL), was added EDTA, disodium salt (2.03 g, 6.05 mmol). The mixture was heated at 60 °C for 1 hour. Upon cooling, the solvent was removed under reduced pressure and dichloromethane (30 mL) added to the residue. After stirring for 20 min., the solid was filtered off, and the filtrate reduced to dryness under reduced pressure. Acetone (20 mL) was added to the crude residue, and the resulting precipitate filtered off, and dried in air to yield the title compound as a pale yellow solid (0.119 g, yield = 89%). ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ = 1.32 (s, 54H; $C(CH_3)_3$), 7.05 (d, J=8.6 Hz,12H; ArH), 7.17 (m, 20H; ArH), 7.84 (t, J = 7.8 Hz, 1H; pyridylH), 8.19 (d, J =7.8 Hz, 2H; pyridylH), 8.63 (s, 2H; N=CH); ^{13}C NMR (100 MHz, $CDCl_3$, 298K): δ = 31.4, 34.3, 62.1, 120.1, 122.9, 123.1, 130.7, 132.1, 137.7, 143.8, 146.5, 148.0, 148.5, 154.7, 159.5; LRESI-MS: m/z = 1123 [M]NH_4^+.

Method 2: From [Zn(L1L2)](ClO$_4$)$_2$

To [Zn(**L1L2**)]$(ClO_4)_2$ (0.100 g, 0.0538 mmol) in acetonitrile (10 mL) and methanol (20 mL), was added EDTA, disodium salt (1.81 g, 5.38 mmol). The mixture was heated at 60 °C for 1 hour. Upon cooling, the solvent was removed under reduced pressure and dichloromethane (30 mL) added to the residue. After stirring for 20 min., the solid was filtered off, and the filtrate reduced to dryness under reduced pressure. Acetone (20 mL) was added to the crude residue, and the resulting precipitate filtered off, and dried in air to yield the title compound as a pale yellow solid (0.045 g, yield = 76%). Characterisation as above.

2,6-diacetylpyridinebis[(*p*-aminophenyl)tris(*p*-*tert*-butylphenyl)methyl H_4L2

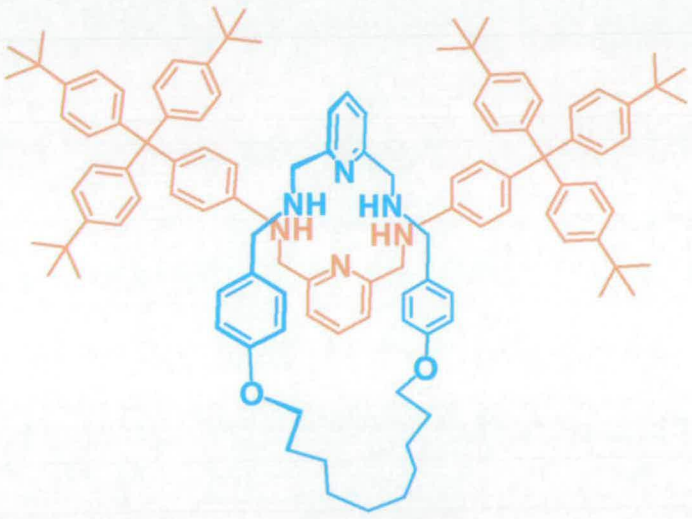


$C_{81}H_{95}N_3$
Mol. Wt.: 1110.6

To [Zn(**L2**)$_2$]$(ClO_4)_2$ (0.150 g, 0.0605 mmol) in acetonitrile (10 mL) and methanol (20 mL), was added sodium borohydride (0.046 g, 1.21 mmol). The resulting solution was refluxed for 2 hours. Upon cooling, the solvent was removed under reduced pressure, and the residue dissolved in a mixture of dichloromethane (5 mL) and methanol (15 mL). EDTA, disodium salt (2.03 g, 6.05 mmol) was added, and the mixture heated at 40 °C for 1 hour. Upon cooling, the solvent was removed under reduced pressure and

dichloromethane (30 mL) added to the residue. After stirring for 20 min., the solid was filtered off, and the filtrate reduced to dryness to yield the title compound as an off-white solid (0.116 g, yield = 87%). m.p. 220 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ = 1.31 (s, 54H; $C(CH_3)_3$), 4.46 (s, 4H; pyridyl$C\underline{H}_2$NH), 6.57 (d, J=8.6 Hz, 4H; ArH), 7.00 (d, J=8.6 Hz, 4H; ArH), 7.10 (d, J=8.6 Hz, 12H; ArH), 7.23 (d, J=8.6 Hz, 12H; ArH), 7.26 (d, J=7.6 Hz, 2H; pyridyl-H), 7.63 (t, J=7.6 Hz, 1H; pyridyl-H); ^{13}C NMR (100 MHz, $CDCl_3$, 298K): δ = 30.4, 33.2, 48.3, 61.9, 110.8, 119.0, 122.9, 129.7, 131.1, 135.6, 136.4, 143.3, 144.5, 147.1, 157.0; LRESI-MS: m/z = 1110 $[M]H^+$.

[N,N'-2,6-dimethylpyridylbis(1,10-decoxy-4-benzylamine)]-[2,6-diacetylpyridinebis[(*p*-aminophenyl)tris(*p*-*tert*-butylphenyl)methyl] L1H$_4$L2



$C_{112}H_{136}N_6O_2$
Mol. Wt.: 1598.3

To [Zn(**L1L2**)]$(ClO_4)_2$ (0.418 g, 0.225 mmol) in dichloromethane (10 mL) and methanol (30 mL) was added sodium borohydride (0.085 g, 2.25 mmol). Once the initial effervescence had subsided the solution was heated to reflux for 2 h. Na_2EDTA (0.837

g, 2.25 mmol) was then added and the mixture heated for a further 1.5 h. Upon cooling, the solvent was removed under reduced pressure and dichlomethane (20 mL) added to the residue. The solution was then filtered and the solvent removed under reduced pressure. The crude residue was recrystallised from methanol to yield the title compound as an off-white solid (0.317 g, yield = 88%). m.p. 145 °C (dec); ^{1}H NMR (400 MHz, [D$_6$]acetone, 298K): δ = 1.05 (br, 8H; alkyl-H), 1.29 (br, 58H; C(CH$_3$)$_3$ + alkyl-H), 1.58 (m, 4H; OCH$_2$C$\underline{H}_2$), 3.68 (s, 4H; ArC$\underline{H}_2$NHCH$_2$Py), 3.70 (s, 4H; ArCH$_2$NHC$\underline{H}_2$Py), 3.73 (t, J=6.6 Hz, 4H; OCH$_2$), 3.95 (s, 4H; PyC$\underline{H}_2$NHC$_6$H$_4$), 6.30 (d, J= 8.6 Hz, 4H; thread ArH), 6.44 (d, J= 8.6 Hz, 4H; macrocycle ArH), 6.78 (d, J=7.8 Hz, 2H; thread pyridyl-H), 6.89 (d, J= 8.6Hz, 4H; thread ArH), 6.93 (d, J= 8.6 Hz, 4H; macrocycle ArH), 7.16 (d, J= 8.6 Hz, 12H; thread ArH), 7.29 (m, 15H; thread ArH + thread pyridyl-H + macrocycle pyridyl-H), 7.64 (t, J=7.6 Hz, 1H; macrocycle pyridyl-H); ^{13}C NMR (100 MHz, [D$_6$]acetone, 298K): δ = 26.4, 29.3, 29.8, 29.9, 31.7, 34.8, 49.7, 53.8, 54.4, 63.8, 67.6, 112.4, 115.0, 119.7, 120.9, 124.9, 130.1, 131.5, 132.2, 132.9, 135.8, 137.8, 137.9, 145.8, 147.4, 148.8, 148.6, 159.7, 160.9; LRESI-MS: m/z = 1598[MH]$^+$; HRFAB-MS (3-NOBA matrix): m/z = 1599.08047 (calcd. for ^{12}C$_{111}$^{13}CH$_{137}$N$_6$O$_2$, [**L1**H$_4$**L2**]H$^+$, 1599.08366).

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[31] Reactions were monitored by electrospray mass spectrometry in all cases and by ^{1}H NMR for systems not containing paramagnetic metals.

[32] The **L1** and **L2** resonances in [Zn(**L1L2**)]$(ClO_4)_2$] were distinguished by a combination of COSY and ROESY experiments.

[33] Cd(**L1L2**)]$(ClO_4)_2$: $C_{124}H_{154}CdCl_2N_6O_{12}$, M = 2103.83, colorless block, crystal size 0.15 × 0.12 × 0.10 mm, monoclinic Cc, a = 31.636(2), b = 22.4269(14), c = 22.2668(15) Å, β = 133.7570(10) °, V = 11410.8(13) Å^3, Z = 6 , ρ_{calcd} = 1.837 Mg m^{-3}; $Mo_{K\alpha}$ radiation (graphite monochromator, λ = 0.71073 Å), μ = 0.450 mm^{-1}, T = 150(2) K. data (22992 unique, R_{int} = 0.03170, 1.27 <θ< 28.96 °), were collected on a Siemens SMART CCD diffractometer using narrow frames (0.3° in ω), and were corrected semiempirically for absorption and incident beam decay. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 values of all data (G. M. Sheldrick, SHELXTL manual, Siemens Analytical *X*-ray Instruments, Madison WI, USA, 1994, version 5) to give $wR = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ = 0.1692, conventional R = 0.0643 for F

give $wR = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2} = 0.1692$, conventional $R = 0.0643$ for F values of 22992 reflections with $F_o^2 > 2\sigma(F_o^2)$, $S = 0.984$ for 1324 parameters. Residual electron density extremes were 1.209 and -0.918 eÅ^{-3}. Hydrogens were added in calculated positions and constrained to a Riding model. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-XXX-XXX. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk.

[34] Under identical experimental conditions the reduced thread, H_4**L2**, does not afford [Zn(**L1**H_4**L2**)]$(ClO_4)_2$, precluding the possibility of a 'slippage' mechanism.

[35] G. J. P. Britovesk, V. C. Gibson, S. Mastroianni, D. C. H. Oakes, C. Redshaw, G. A. Solan, A. J. P. White, D. J. Williams, *Eur. J. Inorg. Chem.* **2001**, 431-437. The greater stability of octahedral metal-imine complexes *cf.* metal-amine complexes is also illustrated by the facile demetallation of amine - but not imine - octahedral metal catenates

[36] H. W. Gibson, S. H. Lee, P. T. Engen, P. Lecavalier, J. Sze, Y. X. Shen, M. Bheda, J. Org. Chem, **1993**, *58*, 3748 – 3756.

Getting Harder: Synthesis of a [2]Catenate and a [2]Rotaxane with Trivalent Metal

"Any sufficiently advanced technology is indistinguishable from magic"
Arthur C. Clarke
English physicist & science fiction author (1917 -)

.... And anything is indistinguishable from technology with sufficiently advanced magic!
Ale: Thoughts on my Ph.D. work (2001-2004)

Chapter 3. Getting Harder: Synthesis of a [2]Catenate and a [2]Rotaxane with Trivalent Metal.

3.1. Abstract

Original synthetic procedures for preparing catenanes and rotaxanes are appearing in the current literature[1] with escalating frequency as a result of the attention[2] these mechanically interlocked molecules[3] are receiving because of their rapidly growing potential as molecular switches for developing devices[4] and molecular machines[5]. Coordination chemistry has provided some elegant recognition motifs that produced a variety of interlocked molecular level architectures.[6] Given the key role played by metal-directed synthesis in the assembly of superstructures it is essential for chemists to expand the arrays of metals and ligands available in this endeavour. Here, we report the template-directed synthesis of a [2]catenate and a [2]rotaxane by a clipping approach around trivalent octahedral cobalt ions. Appropriately derivatised 2,6-dicarboxamide pyridine based ligands, once deprotonated, stabilise the trivalent oxidation state facilitating the entry into higher oxidation states of these metal ions. Along with the palladium four-coordinate square planar metal complex[7] and the divalent metal-directed[8] synthesis of interlocked architectures recently developed in our group they broaden the series of mechanically interlocked ligands for common transition metal geometries started by Sauvage in 1983. In addition, unlike interlocked architectures prepared via metal templation which, upon demetalation show no intercomponent recognition, the removal of the metal in these carboxamide systems results in a species which has the potential for hydrogen-bonding.

3.2. Introduction

Along with their potential applications in area such as molecular recognition,[9] catalysis[10,11] and material design,[12] the template directed synthesis of mechanically interlocked structures based on metal coordination chemistry has been one of the interesting aspects for which cation binding receptors have drawn much attention. The carboxamide [–C(O)NH–] group, recurrent ubiquitously throughout nature in the primary structure of proteins, represents an important ligand construction unit. A number of reports have described the synthesis and study of systems whereby this moiety appears next to pyridine units delivering classes of multidentate ligands available from straightforward condensation reactions.[13] Pyridine carboxamide ligands have proven very versatile, being employed in asymmetric catalysis,[14] molecular receptors,[15] dendrimer synthesis[16] and platinum(II) complexes with antitumour properties.[13d] Mascharak[17] and others[18] in the past 10 years have developed several synthetic protocols to isolate discrete metal complexes of ligands with the tridentate pyridine-2,6-dicarboxamide group. More specifically, the coordination chemistry of iron(III) [19, 20, 21] and cobalt(III)[22,23,24,25,26] with nonmacrocyclic chelating ligands containing an amide functionality has been investigated. Through these studies it has become clear that the anionic nature of the deprotonated nitrogens of organic amides allows a significant stabilization of the trivalent oxidation state enabling therefore a facile entry into higher oxidation states of these metal ions.[22]

2:1 complex. The crystal structure of pyridine-2,6-dicarboxylic acid *bis*benzylamide(PDBA) is illustrated in **Figure 2**.

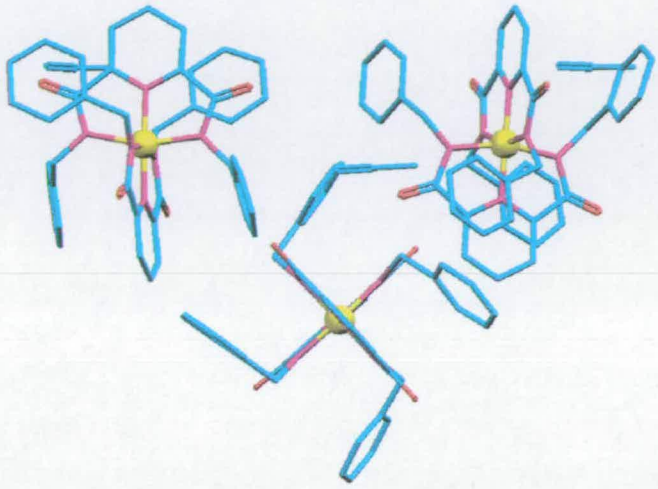


Figure 2: X-ray crystal structure of Grossel's paddle-type complex, [**(PDBA)**$_2$Co(III)]K.[26]

In the previous chapter it was described how we moved from copper based mechanically interlocked molecular architectures built on tetrahedral geometry to catenate and rotaxanes where divalent metals are coordinated with an octahedral motif. Bearing in mind that the goal of this research was the expansion of this simple concept to different metal ions/ligand types, in this chapter it will be described how an octahedral trivalent metal ion and a 2,6-pyridine dicarboxamide motif were used to assemble interlocked architectures.

3.3. Results and Discussion

The ligand designed for the purpose of synthesising catenates and rotaxanes about a trivalent octahedral metal atom was an elegant combination of the system developed for

the imine-based interlocked architectures and the benzylic amide catenanes assembled by hydrogen bonds (**Figure 3**).[27]

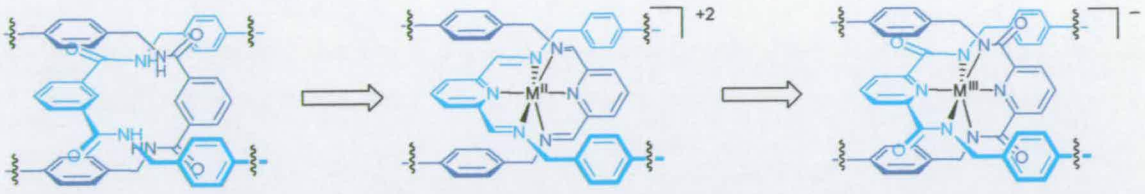


Figure 3: Ligand designed for catenates and rotaxanes about trivalent octahedral metals; combination of the benzyl imine-based interlocked architectures and the benzylic amide catenanes assembled by hydrogen bonds.

The basic architecture of the benzylic amide macrocycles produced in our group was quite compatible with assembly processes of different nature. The rigid framework placed multiple donor groups so that they come together towards the centre of the cavity. The benzylic *bis*(2,6-dicarboxyamidepyridine) moiety, once deprotonated, provided three coordination sites on a N_3 Mer conformation which has been shown to stabilize metal higher oxidation states with an orthogonal chelation. It also represented a convenient spacer to hold the aromatic rings in a parallel arrangement at a distance ideal for stacking with an orthogonally bound guest and it grants a complete 180° turn that promoted intracomponent over intercomponent cyclizations. Finally, the derivatization with the α-olefin, as devised for the imine-based catenate, enabled ring closing metathesis (RCM).

As opposed to the rotaxane which required separate designs for the thread and the macrocycle, the catenate could be assembled from identical ligands: such symmetrical nature simplified the design conception and the synthetic implementation. For these reasons it was chosen as the first target.

3.3.1. Catenate and "Figure-of-eight" Syntheses

The strategy devised for the catenate involves a synthesis via a clipping approach: two "u-shape" tridentate ligands coordinate orthogonally the metal centre and can then undergo a double macrocyclization to produce the catenate. Looking back at the ligand developed for the synthesis of the imine-based catenate - described in the previous chapter - replacement of the imines with amide groups produces a ligand suitable for the synthesis of interlocked architectures about a trivalent metal ion (**Figure 4**).

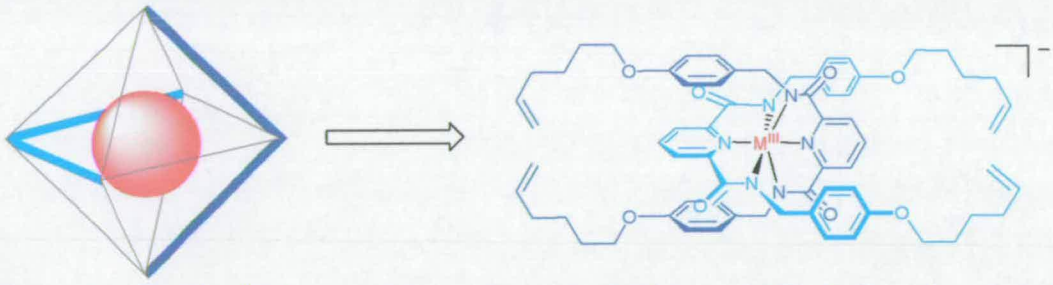
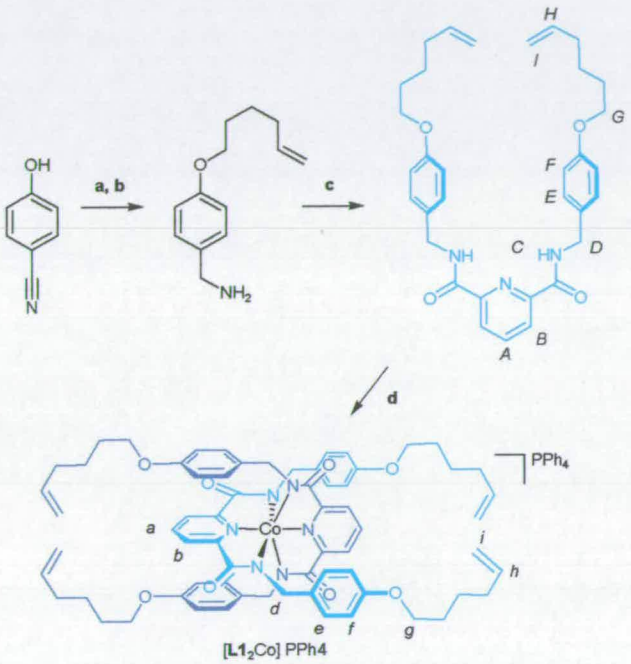


Figure 4: Octahedral geometry and coordination motif of ligands around a trivalent metal.

The 2,6-pyridine dicarboxamide ligand, H_2**L1**, was conveniently prepared on a multigram scale in three steps from readily available materials (**Scheme 1**, a. – c.). 4-Cyanophenol was reacted with 6-bromo-1-hexene under Williamson ether conditions to produce 5-hex-5'-enyloxybenzonitrile in 92% yield. Reduction of the nitrile group with lithium alluminium hydride generates the corresponding amine which was then reacted with 2,6-pyridinedicarbonyl chloride to give the "u-shape" ligand H_2**L1** in an overall yield of 86%. This ligand was then converted into the corresponding sodium salt, Na_2**L1**, by treatment with sodium hydride in dimethylformamide in anaerobic conditions and directly reacted with a cobalt(II) hexahydrate. A colour change from blue to red was indicative of Co(II) coordination. The kinetically labile cobalt(II) sodium complex, [Co**L1**$_2$]Na_2, undergoes air oxidation to the more inert cobalt(III) complex, [Co**L1**$_2$]Na: a further colour change from red to green was observed upon reaction. Finally,

displacement of the sodium ions is achieved by reaction with tetraphenylphosphonium chloride, the precipitation of sodium chlorides out of solution being the driving force. The cobalt(III) tetraphenylphosphonium complex, [**L1**$_2$Co]PPh$_4$, was isolated with an overall yield of 91% as a dark green solid (**Scheme 1**, d.).[17r]



Scheme 1: Synthesis of ligand H_2**L1** and formation of octahedral acyclic complex [**L1**$_2$Co]PPh$_4$. Reagents and conditions: a) 6-Bromo-1-hexene, K_2CO_3, NaI, butanone, reflux, 18 h, 92%, b) $LiAlH_4$, THF, 0-60 °C, 3 h, 94%, c) 2,6-pyridinedicarbonyl chloride, NEt_3, CH_2Cl_2, reflux, 18 h, 91%, d) i. NaH, DMF, 20 min, ii. $CoCl_2 \cdot 6H_2O$, DMF, 10 min, iii. Air, 30 min, 91%, iv. PPh_4Cl, CH_2Cl_2.

Both FAB mass spectrometry (*m/z*= 1138, [H**L1**$_2$**Co**]$^+$) and ^{1}H NMR confirm that the ligand is coordinated to the metal in the deprotonated form. ^{1}H NMR spectra of free ligand H_2**L1** and [**L1**$_2$Co] PPh$_4$ are shown in **Figure 5.** Comparison between the two clearly points to metal coordination: the amide protons, H_C, are absent and the pyridine resonances, H_A and H_B, switch positions. The doublets due to the benzylic protons of both ligands, H_D, present an upfield shift of almost 1.5ppm and are changed into singlets. Shielding of the benzylic aromatic rings (H_E and H_F) is indicative of π-stacking

due to the entwined architecture, as previously observed in our benzylic imine catenanes and rotaxanes.

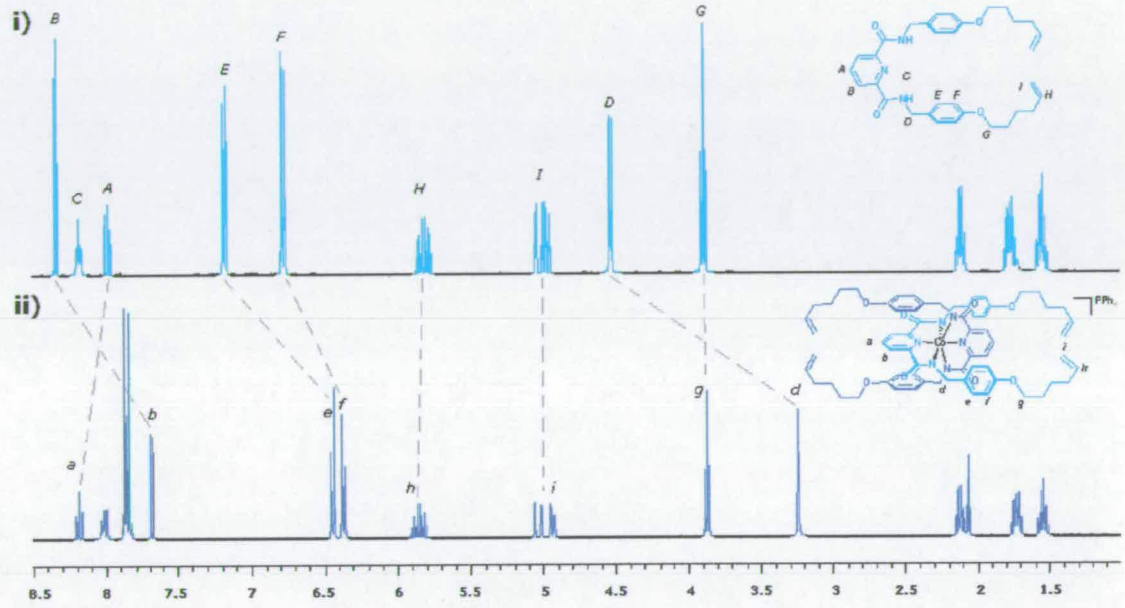
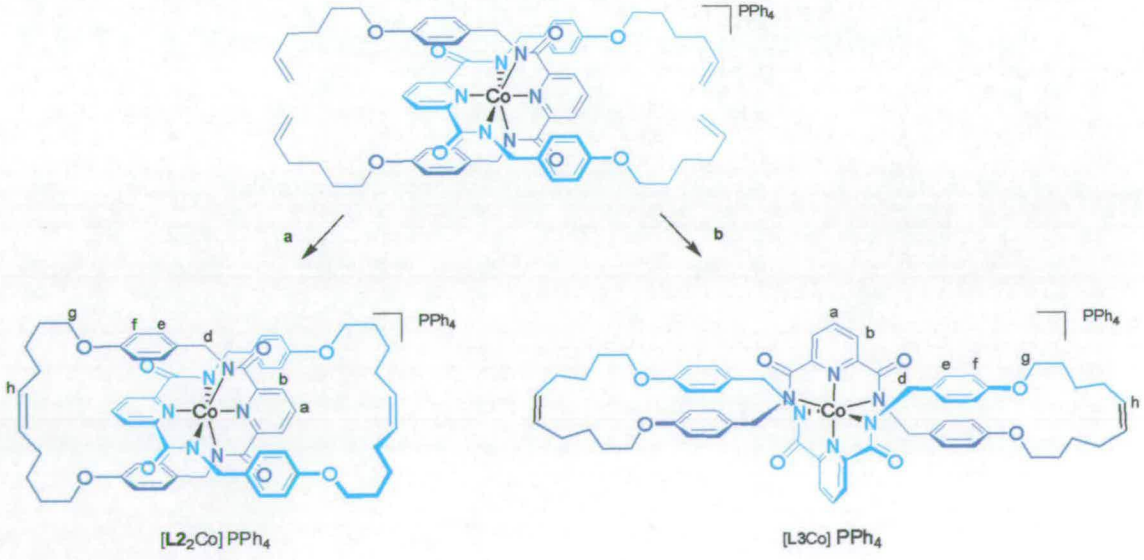


Figure 5: ^{1}H NMR spectra (400 MHz, Acetone-d_6, 298 K) of i) free "u-shape" ligand [H_2**L1**], ii) cobalt(III) tetraphenylphosphonium complex [**L1**$_2$Co]PPh_4.



[**L2**$_2$Co] PPh_4 [L3Co] PPh_4

Scheme 2: Double macrocyclization of Co(III) PPh_4 complex: unexpected formation of both catenate, [**L1**$_2$Co]PPh_4, and "figure-of-eight" [**L3'**Co] PPh_4. Reagents and conditions: Grubbs' catalyst, CH_2Cl_2, RT, 4 days; Yields: a) 38%, b) 42%.

The tetraolefin complex [**L1**$_2$Co]PPh_4 was subjected to ring closing metathesis using first generation Grubbs' catalyst ([Ru(=CHPh)$(PCy_3)_2Cl_2$], CH_2Cl_2, Ar, RT, 4 days) (**Scheme 2**). While crude ^{1}H NMR revealed the consumption of external alkenes thus indicating RCM was complete, two species were clearly observable by thin layer chromatography (TLC) (Silica gel, 1:39:60 $Et_3N/(CH_3)_2CO/CH_2Cl_2$), and were thus separated via standard column chromatography techniques. Mass spectrometry revealed the compounds had identical molecular weights (Negative ESI mass spectrometry showed: m/z = 1081, corresponding to the negatively charged complex without tetraphenylphosphonium counterion, [**L2**$_2$Co]$^-$ and [**L3'**Co]$^-$, and FAB mass spectrometry: m/z = 1421, corresponding to the neutral complex with an added extra proton, [**L2**$_2$CoPPh$_4$H]$^+$ and [**L3**CoPPh$_4$H]$^+$), proving we had obtained isomeric compounds. The ^{1}H NMR of both isomers and the precursor complex are shown in **Figure 6**.

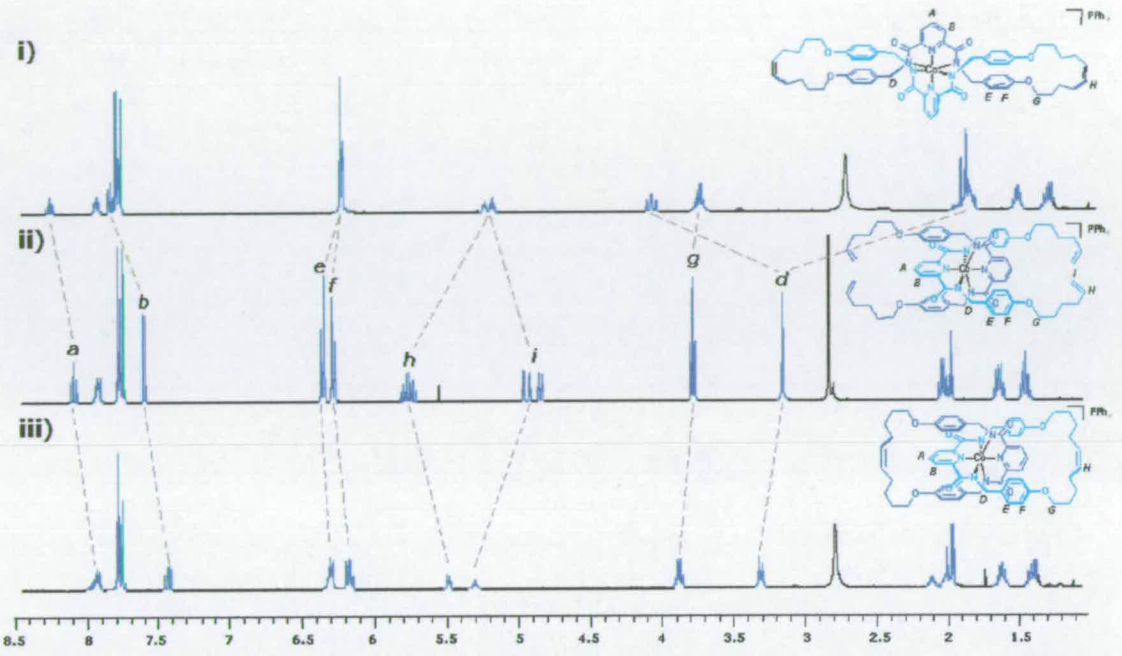
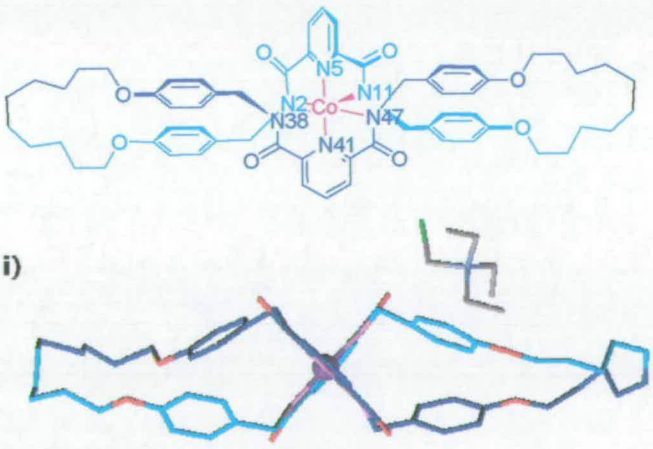


Figure 6: Partial ^{1}H NMR spectra (400 MHz, Acetone-d_6, 298 K) of i) cobalt(III) tetraphenylphosphonium "figure-of-eight" [**L3**Co]PPh4, ii) cobalt(III) tetraphenylphosphonium acyclic precursor complex [$\mathbf{L1_2}$Co]PPh_4, iii) cobalt(III) tetraphenylphosphonium catenate [$\mathbf{L2_2}$Co]PPh_4.

The isolation of crystals suitable for X-ray crystallography was attempted with both isomeric compounds. One species generated green crystals from a saturated acetone solution, which confirmed the hypothesis that one of the two compounds was the "figure-of-eight" complex, (**Figure 7**, i.), produced by intermolecular reaction between distinct "u-shape" ligands complexed to the same metal, (**Scheme 2**, ii.). The crystal structure of [**L3'**Co]$(CH_2Cl)(C_2H_5)_3N$ is illustrated in **Figure 7**. Curiously, the tetraphenylphosphonium counterion had been replaced by a 2-chloromethyl-triethylammonium cation. Although initially surprising, this must have occurred during the process of column chromatography, whereby dichloromethane reacted with triethylamine in the presence of silica to give chloromethyltriethylammonium chloride, and small amount of this salt exchanged with [**L3**Co]PPh_4. The X-ray structure clearly illustrated the octahedral geometry around the coordinated cobalt centre, with the N_3 bite

angles of N2-Co-N11 164.04, N38-Co-N47 162.80, (**Figure 7**, ii.). Metal coordination necessarily buried the polar amide groups at the centre of the molecular structure with the alkyl chains to the outside; a similar overall co-conformation to that observed in the solid state for amphiphilic benzylic amide catenanes.[27a] The π-stacking between the benzylic groups and the pyridine rings, which in solution gave significant ^{1}H NMR shifts, (see NMR data in **Figure 6**, i.) and which was also clearly present in the precursor complex [$L1_2Co$] PPh_4, was considerably offset in the solid state (**Figure 7**, iii.). Comparison with the X-ray crystal structure of Grossel's paddle-type complex, [(**PDBA**)$_2$Co(III)] K, (**Figure 2**) revealed exactly the same behaviour: it is no surprise then that it contributed to intercomponent rather than intracomponent cyclization during RCM. Analysis of the crystal structure also explained the splitting of the resonance frequences corresponding to the benzylic groups due to the different environments to which they were exposed in each orientation. The two protons, H_d, are locked into different environments, with one proton pointing towards the metal, the other away from it.[28]



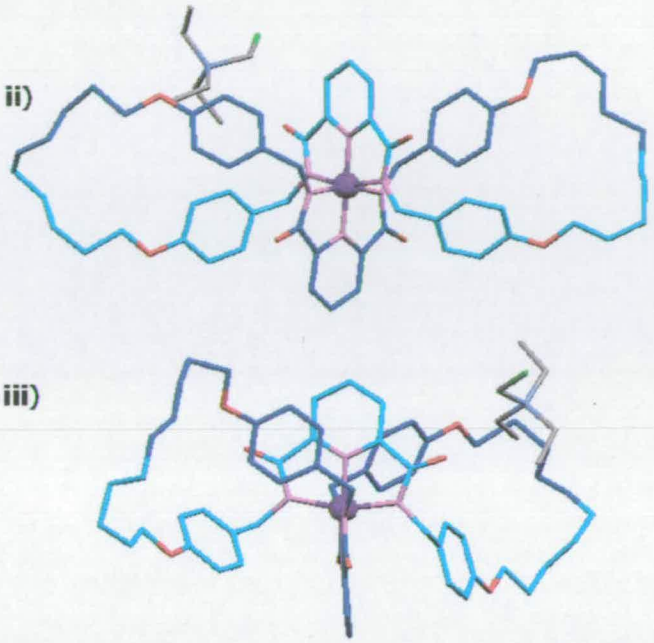
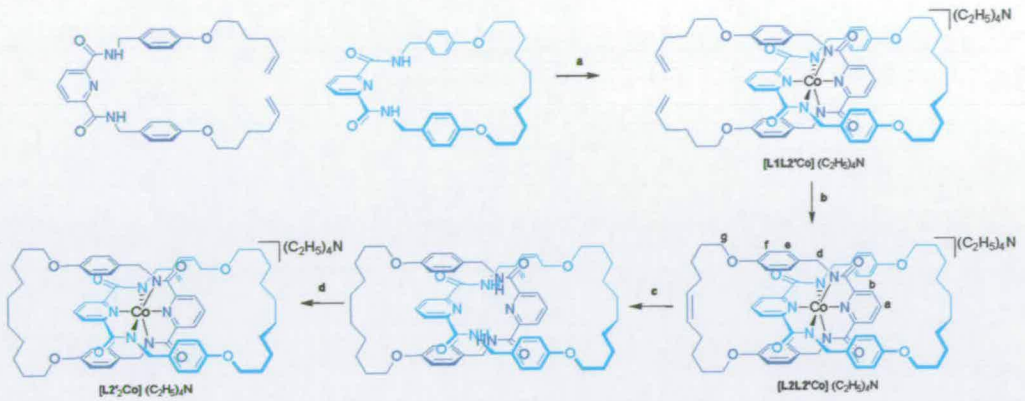


Figure 7: Structure of "figure-of-eight" [**L3'**Co](CH_2Cl)(C_2H_5)$_3$N as determined by X-ray crystallography.[29] Carbon atoms originally part of distinct "u-shape" ligands are shown in light and dark blue; oxygen atoms are red, nitrogen lilac, chlorine green, and cobalt violet. Hydrogen atoms and a molecule of acetone are omitted for clarity. Selected bond lengths [Å]: Co-N2 1.965, Co-N5 1.823, Co-N11 1.959, Co-N38 1.952, Co-N41 1.855, Co-N47 1.967; other selected interatomic distances [Å]: N2-N11 3.885, N5-N41 3.677, N38-N47 3.874; ligand bite angles [°]: N2-Co-N11 164.04, N38-Co-N47 162.80.

The ring closing metathesis reaction of [**L1**$_2$Co]PPh_4 was reinvestigated (**Scheme 2**). Extending the reaction time from four to fifteen days resulted in the sole production of the "figure-of-eight" complex, [**L3**Co]PPh_4, strongly suggesting that the reaction was under thermodynamic control with this complex being the favoured product. This situation was verified by subjecting the unsaturated catenate, [**L2**$_2$Co]PPh_4, to the Grubbs catalyst in dichloromethane, and after a similar amount of time (15 days), again the sole product isolated was "figure-of-eight" complex.



Scheme 3: Single macrocyclization via precatenate complex [**L1L2'**Co]Et_4N generating catenate [**L2'**$_2$Co]Et_4N. Reagents and conditions: a) i. NaH, DMF, 20 min, ii. $CoCl_2$•$6H_2O$, DMF, 10 min, iii. Air, 30 min, 91%, iv. $(C_2H_5)_3NCl$, CH_2Cl_2; b) Grubbs' catalyst, CH_2Cl_2, RT, 4 days, 57%; c) i. H_2/Pd-C, MeOH, RT, 12 h, ii. Zn, CH_3COOH, MeOH, RT, 20 min, 81%; d) NaH, DMF, 20 min, ii. $CoCl_2$•$6H_2O$, DMF, 10 min, iii. Air, 30 min, 91%.

An alternative and unambiguous approach to the synthesis of a cobalt(III) catenate was via the single macrocyclization of a threaded precatenate species, [**L1L2'**$_2$Co]Et_4N, to prevent the formation of the "figure-of-eight" complex. This precatenate species was prepared by treating equimolar amounts of preformed saturated macrocycle, H_2**L2'**, and "u-shape", H_2**L1**, with sodium hydride, cobalt chloride hexahydrate and tetraethyl ammonium chloride[30], using the methodology as previously described (**Scheme 3**). After column chromatography, [**L1L2'**$_2$Co]Et_4N was isolated in 44% yield and subjected to RCM ([Ru(=CHPh)$(PCy_3)_2Cl_2$], CH_2Cl_2, Ar, RT, 18 hours) affording the monounsaturated cobalt(III) tetraethylammonium catenate [**L2L2'**$_2$Co]Et_4N in a 57% yield. Hydrogenation (H_2, MeOH, RT, 12 h) of the double bond resulted in partial demetalation of the catenand; this compound was therefore treated *in situ* with zinc powder and acetic acid in methanol to complete the conversion to the free saturated catenand [**L2'**$_2$Co]Et_4N (**Scheme 3**, c). This choice of conditions was adapted from similar Co(III) cryptands demetalation procedures, where the kinetically inert trivalent metal is reduced to the divalent state under acidic conditions thus facilitating the

removal.[31] Reinsertion of the metal ion was achieved by the standard procedure using sodium hydride and cobalt(II) chloride hexahydrate in dimethylformamide.

Partial ^{1}H NMR spectra of free macrocycle H_2**L2'**, the cobalt(III) precatenate complex [**L1L2'**Co] Et_3N and the saturated cobalt(III) catenate [**L2'**$_2$Co]Et_4N are shown in **Figure 8.** Several features confirmed the formation of the precursor complex: a 1:1 ratio of **L1** and **L2'** fragments, loss of the amide protons, π-stacking between pyridines and aromatic rings and upfield shift of the benzylic protons. After macrocyclization the π-stacking seemed to be slightly attenuated and the aromatic protons were shifted downfield of about 0.3 ppm with respect to the precursor complex. The benzylic shifts presented a similar behaviour.

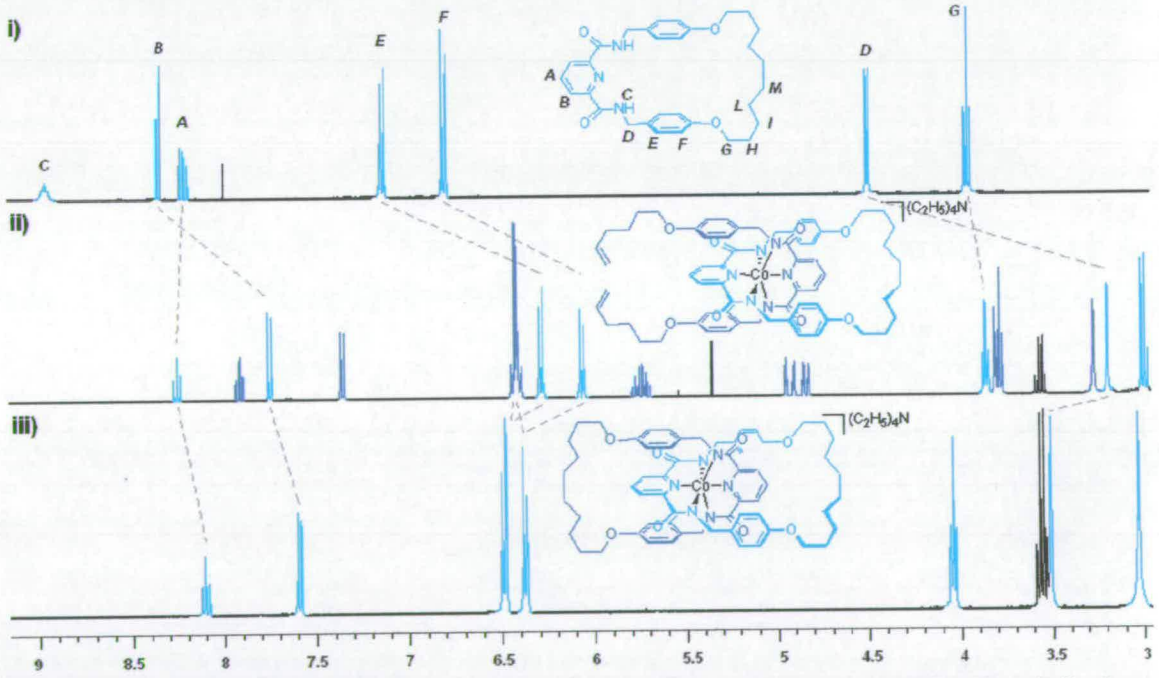
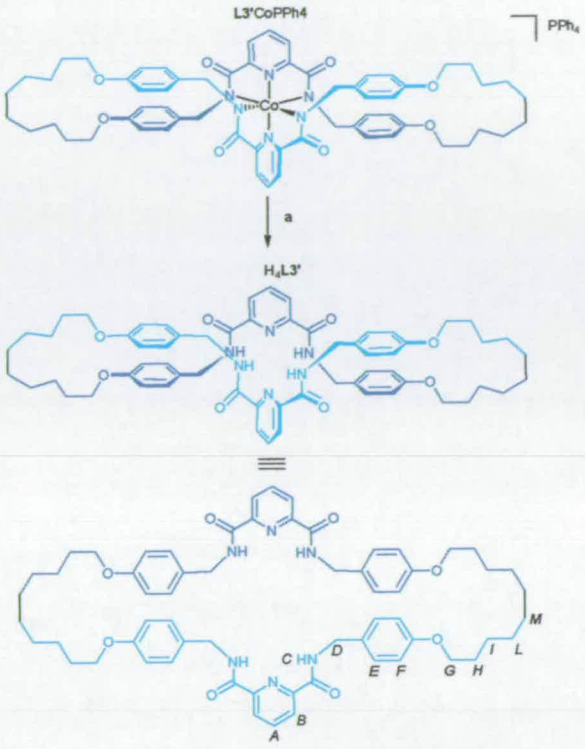


Figure 8: Partial ^{1}H NMR spectra (400 MHz, Acetone-d_6, 298 K) of i) free macrocycle [H_2**L2'**], ii) cobalt(III) tetraethylammonium precursor complex [**L1L2'**Co]Et_4N, iii) hydrogenated cobalt(III) tetraethylammonium catenate [**L2'**$_2$Co]Et_4N. The assignments correspond to the lettering shown in **Scheme 2.**

To compare with the properties of the catenand, which had already been isolated, the "figure-of-eight" complex was also demetallated using a similar procedure (reaction with zinc powder in methanol in the presence of acetic acid over a 20 minutes period) yielding the double sized macrocycle [H_4**L3'**] (**Scheme 4**). Due to its interlocked nature the catenand immediately presented very different physical properties from its constitutional isomer, the macrocyclic counterpart; [(H_2**L2'**)$_2$] dissolved readily in chloroform and dichloromethane, whereas the big macrocycle, "big-mac", [H_4**L3'**] was characterised by very poor solubility in all solvents except dimethylformamide and dimethylsulphoxide. A rationale for this observation was that the rotation of the interlocked macrocycles within the catenand readily allowed an arrangement that permitted self-satisfying hydrogen bonding. In contrast, the two 2,6-dicarboxamide units within[H_4**L3'**] would require a high energy conformational change to undergo internal hydrogen bonding.



Scheme 4: Demetalation of (i) catenate yielding catenand , [**L2'**$_2$], and of (ii) "figure-of-eight" yielding double sized macrocycle, [**L3'**]. Reagents and conditions: a) Zn, CH_3COOH, MeOH, RT, 20 min. Yields: i) 92%, ii) 95%. H-bond assembled catenanes **1**.

Partial ^{1}H NMR spectra of catenand [(H_2**L2'**)$_2$], free macrocycle [H_2**L2'**], and double sized macrocycle [H_4**L3'**] are shown in **Figure 9**. The shielding of the aromatic phenoxy groups in the catenand compared to the free macrocycle and the "big-mac", confirmed the interlocked architecture. The π-stacking influenced also the nearby benzylic protons, H_D, as well as the alkyloxy ones, H_G, which were shifted upfield respectively by 0.2 and 0.4 ppm. It should be noted that these spectra were recorded in deuterated dimethylsulphoxide due to the solubility properties of [H_4**L3'**]. This solvent usually tends to form strong hydrogen bonding with amide groups, reflected by considerable downfield shifts compared to the resonances measured in less polar aprotic chlorinated solvents. By comparison, the macrocycle amide protons resonated at 7.75

ppm in $CDCl_3$ corresponding to a shift greater than 2 ppm, (**Figure 10**). In the catenand the lesser extent of the downfield shift induced by the solvent suggested interaction between the interlocked rings, preventing complete solvation. Not surprisingly the spectra of macrocycles **H_2L2'** and **H_4L3'** were virtually identical except for the "big-mac" broadening due to its poor solubility.

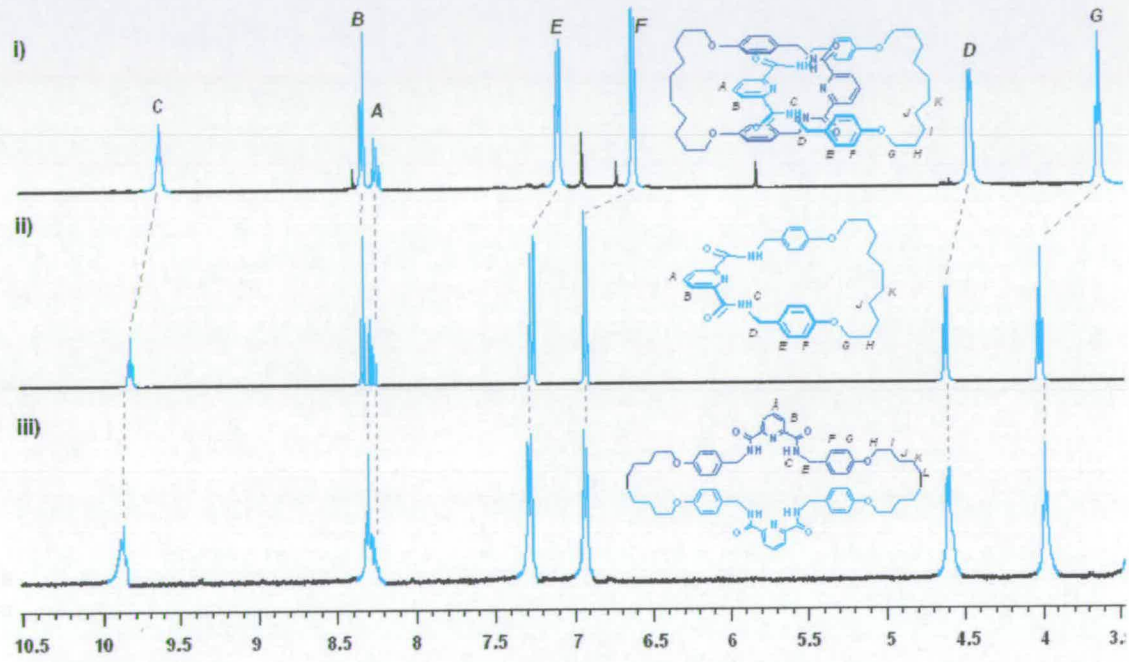


Figure 9: Partial ^{1}H NMR spectra (400 MHz, Dimethylsulfoxide-d_6, 298 K) of i) Catenand [H_2**L2'**]$_2$, ii) free macrocycle [H_2**L2'**], iii) double sized macrocycle [H_4**L3**]. The assignments correspond to the lettering shown in **Scheme 2.**

To assess the effects of mechanical bonding in the catenand in a non-hydrogen bonding solvent, the ^{1}H NMR spectrum of [H_2**L2'**]$_2$ was also taken in deuterated chloroform and compared directly with the small macrocycle, H_2**L2'** (**Figure 10**). The effects of interlocking were significantly accentuated. With the exception of the amide protons, H_c, which moved downfield by ca. 0.5 ppm thus confirming their self association, all other catenand resonances were shielded with respect to the free macrocycle, a common spectral feature of interlocked architectures. More significantly, both aromatic signals,

H_e and H_f, were moved upfield by over 0.5 ppm, thus confirming $\pi-\pi$ stacking, an interaction present due to the conformation imposed by hydrogen bonding between the pyridine-2,6-dicarboxamide groups.

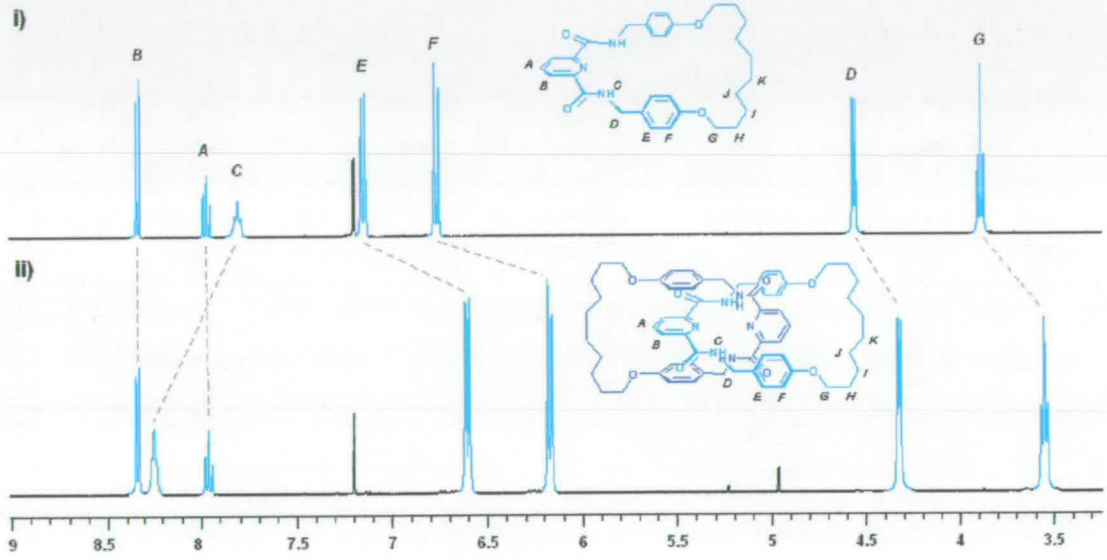


Figure 10: Partial ^{1}H NMR spectra (400 MHz, Chloroform-d, 298 K) of i) free macrocycle [H_2**L2'**] and ii) Catenand [H_2**L2'**]$_2$.

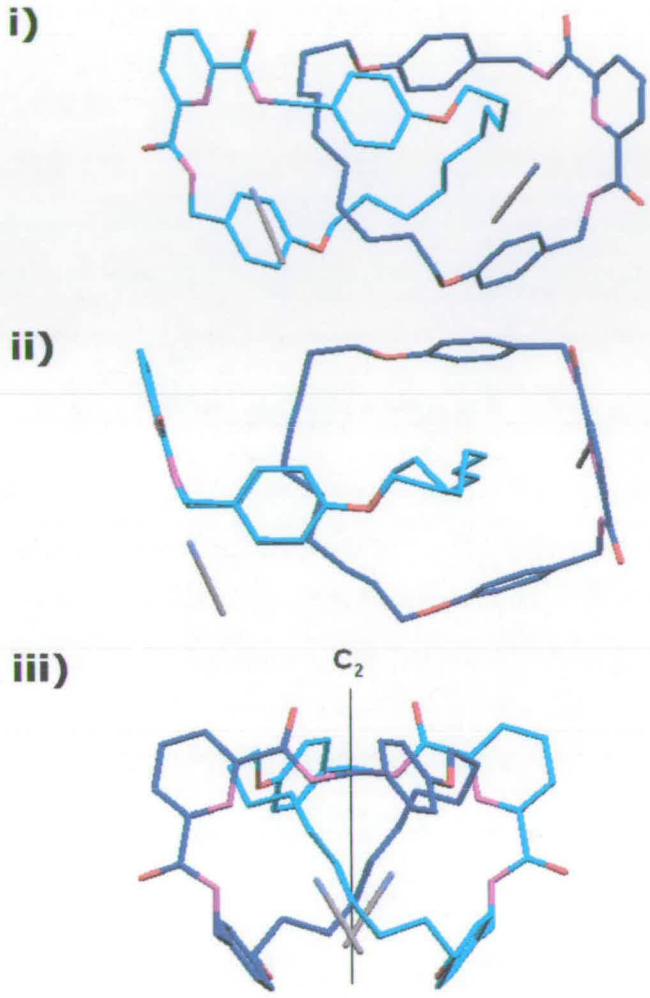


Figure 11: Structure of catenand $[(H_2\mathbf{L2})_2]$ as determined by X-ray crystallography.[32] Carbon atoms part of distinct rings ligands are shown in light and dark blue; oxygen atoms are red and nitrogen lilac. Hydrogen atoms are omitted for clarity.

The isolation of single crystals suitable for X-ray crystallography were obtained from a saturated acetonitrile solution, confirming unequivocally the interlocked nature of the catenand, (**Figure 11**, Surprisingly, the crystal structure of $[(H_2\mathbf{L2})_2]$, illustrates that in the solid state the two rings are oriented in a manner that places internally the alkyl

chains while the pyridine-2,6-dicarboxamide units are externally oriented, with hydrogen bonding being satisfied by interactions with two molecules of acetonitrile. This behaviour is opposite to the one observed by ^{1}H NMR in chloroform, where the pyridine-2,6-dicarboxamide groups gather towards the cavity of the system driven by mutual hydrogen-bonding. The discrepancy between solid and solution conformation can be attributed to a combination of factors including interactions with different solvents and also crystal packing effect. The third view of the crystal structure, (**Figure 11**, iii.), shows the symmetry of the system, presenting a C_2 axis.

3.3.2. Rotaxane Synthesis

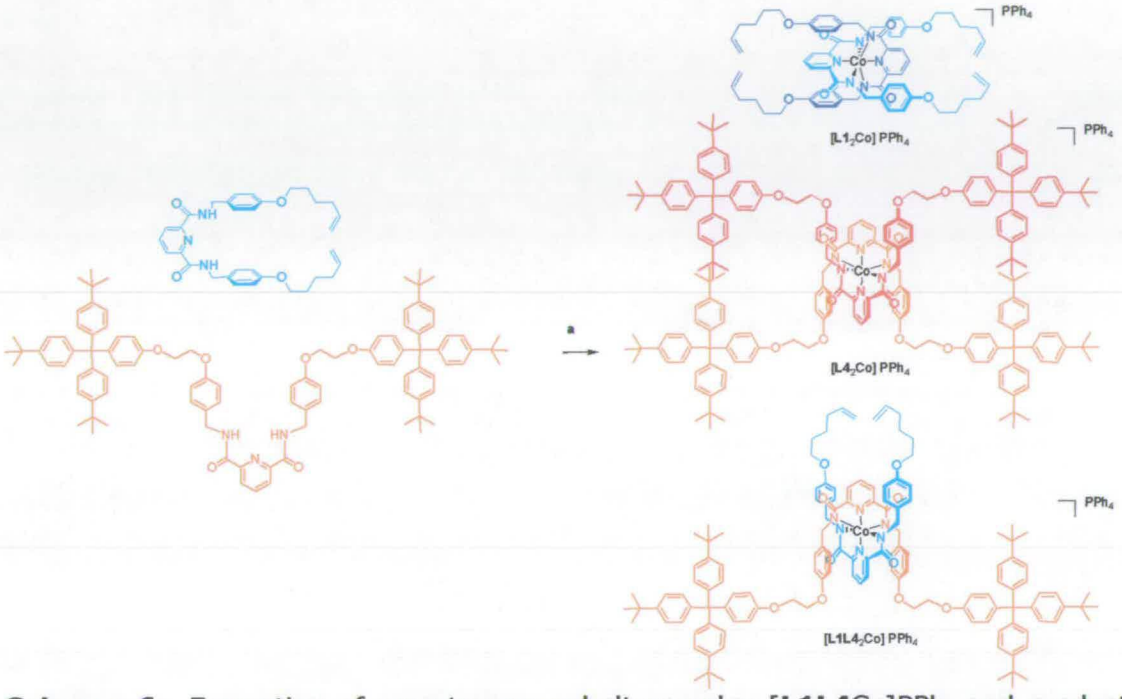
Despite the richness of examples of [2]rotaxane prepared utilising H-bonding and π-π stacking, there are relatively few examples of metal ions being utilised to template rotaxane formation. Our discovery of a general ligand system for the efficient assembly of [2]rotaxanes around octahedral metal ions represents a step forward to the work on tetrahedral Cu(I) *bis*-phenanthroline synthon reported by Sauvage.[6a] After the realization of a catenate based on a Co(III) *bis*-2,6-pyridinedicarboxamido synthon, it was apparent that we could exploit this unit in a rotaxane synthesis. Furthermore, with H_2**L1** to hand, a clipping strategy could be used around a suitable thread. By replacing the hexenyl groups of H_2**L1** by linked stopper groups, we readily arrived to such a thread.

Scheme 5: Synthesis of ligand H_2**L4**. Reagents and conditions: a) i. 1,2-dibromoethane, K_2CO_3, NaI, butanone, reflux, 10 h, 96%; ii. 4-tris(4-*tert*-butylphenyl)phenol, K_2CO_3, NaI, butanone, reflux, 18 h, 56%; iii. $LiAlH_4$, THF, 0 °C to reflux, 3 h, 98%, b) 2,6-pyridinedicarbonyl chloride, NEt_3, CH_2Cl_2, reflux, 2 h, 95%.

The thread H_2**L4** was prepared in four steps from readily available starting materials: (**Scheme 5**). 4-Cyanophenol was reacted with an excess of 1,2-dibromoethane to yield the monosubstituted 4-(2-bromo-ethoxy)-benzonitrile in 96% yield. A second substitution reaction with 4-tris(4-*tert*-butylphenyl)phenol[33] using analogous conditions, followed by lithiumalluminium hydride reduction gave 4-(2-{4-[Tris-(4-tert-butylphenyl)-methyl]-phenoxy}-ethoxy)-benzylamine. Finally, reaction with 2,6-pyridinedicarbonyl chloride using triethylamine generated the thread H_2**L4** as white solid in a 95% yield.

Our approach to prepare the acyclic prerotaxane complex was to undertake a non selective cross complexation between H_2**L1** and H_2**L4** and subsequently separate the three different products via chromatographic techniques (**Scheme 6**). Thus, equimolar amounts of H_2**L1** and H_2**L4** in dimethylformamide under anaerobic conditions were treated first with sodium hydride and then with cobalt chloride hexahydrate. Subsequent exposure to air gave a colour change as previously observed (red to green, Co(II) to Co(III)). Initial analysis by thin layer chromatography (Silica gel, 1:39:60 $Et_3N/(CH_3)_2CO/CH_2Cl_2$) showed our anticipated three products, [**L1**$_2$Co]Na, [**L4**$_2$Co]Na

and [**L1L4**Co]Na, and the desired unsymmetrical complex was successfully isolated, following column chromatography, in 41 % yield.



Scheme 6: Formation of prerotaxane cobalt complex [**L1L4**Co]PPh_4 and products of cross-complexation, [**L1**$_2$Co]PPh_4 and [**L4**$_2$Co]PPh_4. Reagents and conditions: a) i. NaH, DMF, 20 min, ii. $CoCl_2 \cdot 6H_2O$, DMF, 10 min, iii. air, 30 min; ii. PPh_4Cl, CH_2Cl_2.

The ^{1}H NMR spectrum of the precursor complex [**L1L4**Co]Na is shown in **Figure 12**, alongside the spectra of the free protonated ligands [H_2**L1**] and [H_2**L4**] for comparison (**Figure 12**, i. and iii. respectively). The spectrum of [**L1L4**Co]Na clearly shows a 1:1 ratio of **L1** to **L4**. Further indications of metal coordination were the absence of the amide protons, $H_{C,c}$, and the shifting of the pyridine resonances, $H_{A,a}$ $H_{B,b}$. The doublets due to the benzylic protons of both ligands, $H_{D,d}$, were shifted upfield by approximately 2ppm and were converted into singlets. Shielding of the benzylic aromatic rings (particularly H_E and H_F) was indicative of the entwined architecture.

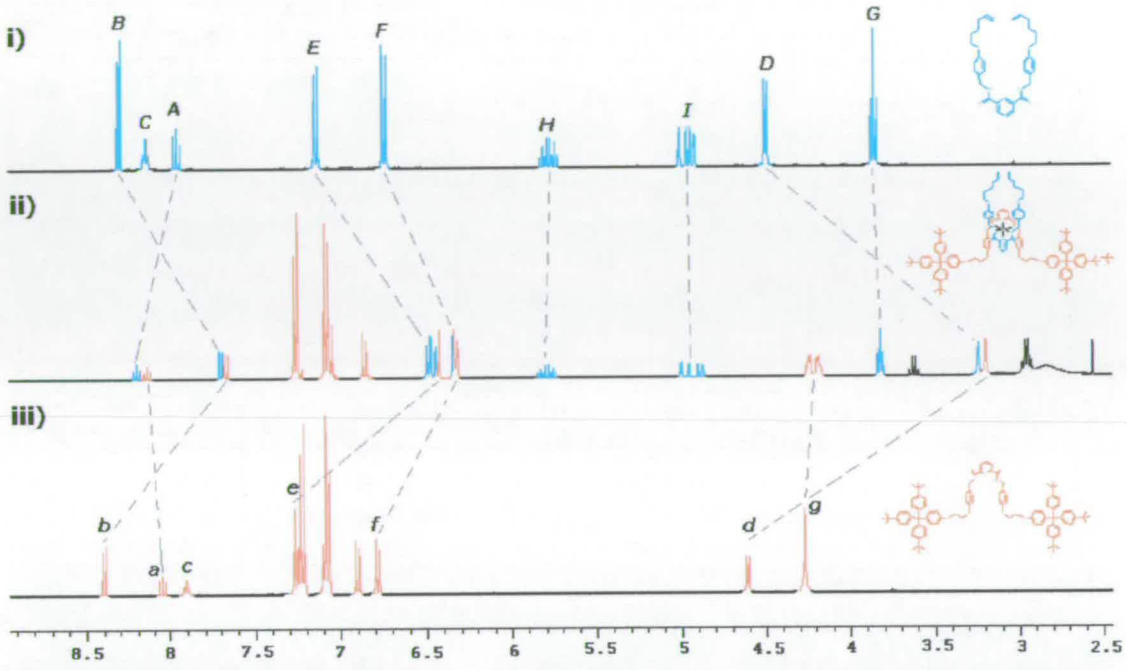
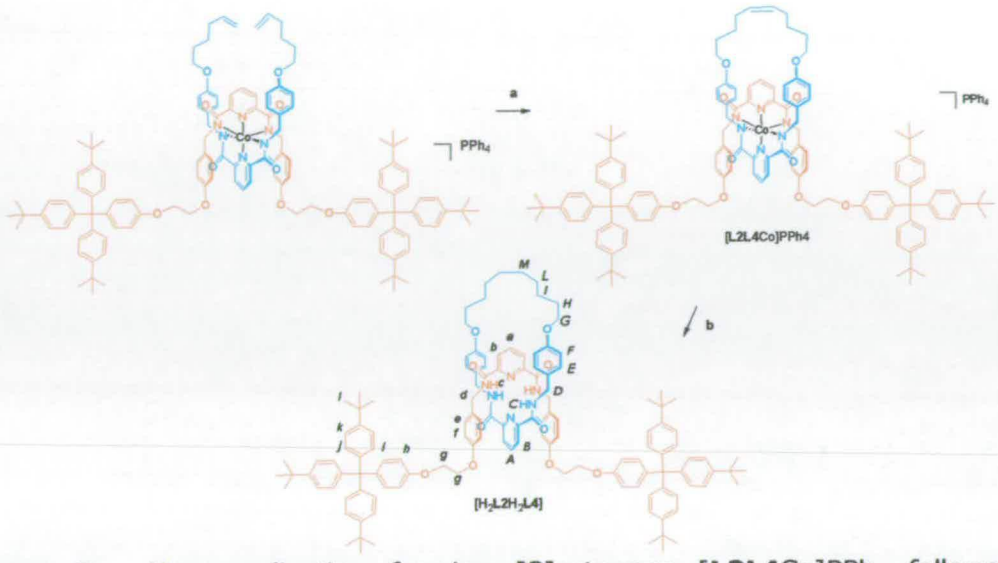


Figure 12: Partial ^{1}H NMR spectra (400 MHz, Acetone-d_6, 298 K) of i) free "u-shape" ligand [H_2**L1**], ii) cobalt(III) sodium precursor complex [**L1L4**Co]Na, iii) free thread ligand [H_2**L4**]. The assignments correspond to the lettering shown in **Scheme 7**.

To aid solubility the sodium ion was displaced with tetraphenylphosphonium as previously described. [**L1L4**Co]PPh_4 was macrocyclized by ring closing metathesis with Grubbs' catalyst, ([Ru(=CHPh)$(PCy_3)_2Cl_2$], CH_2Cl_2, Ar, RT, 1 day) to give the unsaturated rotaxane [**L2L4**Co]PPh_4, (**Scheme 7**), in 72% yield as a mixture of the *E* and *Z* diastereoisomers. Hydrogenation of the double bond was achieved by exposure to dihydrogen in the presence of palladium on carbon catalyst, in methanol at room temperature. The saturated rotaxane [**L2'L4**Co]PPh_4 underwent demetalation upon reaction with zinc powder in acidic environment generating the free [2]rotaxane H_2**L2**H_2**L4** in 97% yield, thus confirming the mechanically interlocked nature of this system architecture.



Scheme 7: Macrocyclization forming [2]rotaxane [**L2L4**Co]PPh_4 followed by hydrogenation and demetalation generating [H_2**L2**H_2**L4**]. Reagents and conditions: a) Grubbs' catalyst, CH_2Cl_2, RT, 1 day, 72%, b) i. H_2/Pd-C, MeOH, RT, 18h, 89%;ii. Zn, CH3COOH, MeOH, RT, 20 min, 97%.

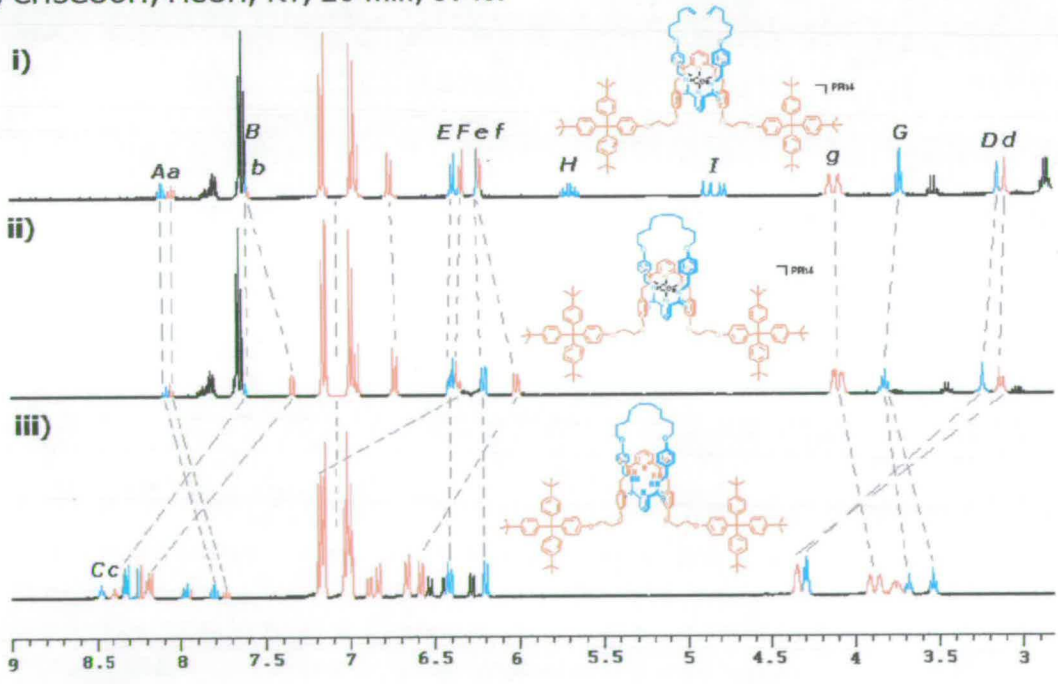


Figure 13: Partial ^{1}H NMR spectra (400 MHz, Acetone-d_6, 298 K) of i) cobalt(III) tetraphenylphosphonium precursor complex [**L1L4**Co]PPh_4, ii) cobalt(III) tetraphenylphosphonium rotaxane [**L2L4**Co]PPh_4, iii) demetalated rotaxane [H_2**L2**H_2**L4**]. The assignments correspond to the lettering shown in **Scheme 7**.

Comparison of the ^{1}H NMR spectrum of the precursor complex, [**L1L4**Co]PPh_4, and the cobalt(III) tetraphenylphosphonium rotaxane, [**L2L4**Co]PPh_4, confirmed the loss of terminal alkene protons (**Figure 13**). Minor but noteworthy differences of all the non-alkyl chain resonances were a sign of ligand rearrangement during rotaxane formation. Upon demetalation and reprotonation of the amide moieties, the corresponding signals reappeared on the spectrum of the free rotaxane, [H_2**L2**H_2**L4**] (**Figure 13**, iii.).

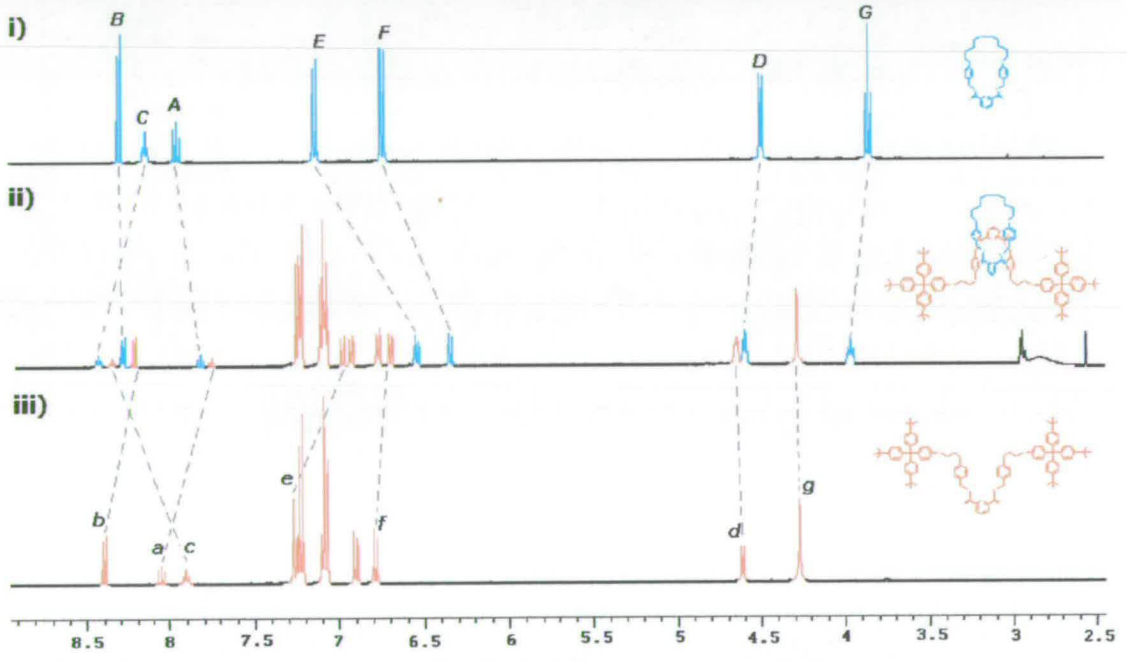


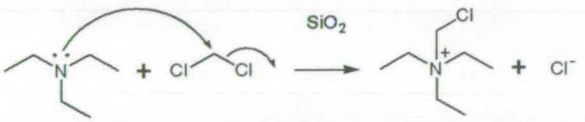
Figure 14: Partial ^{1}H NMR spectra (400 MHz, Chloroform-d, 298 K) of i) free macrocycle [H_2**L2'**], ii) demetalated rotaxane [H_2**L2'**H_2**L4**], iii) free thread [H_2**L4**]. The assignments correspond to the lettering shown in **Scheme 7**.

Figure 14 shows the ^{1}H NMR spectra of [H_2**L2**H_2**L4**], (ii.) and its uninterlocked constituents, (i., iii.). The shielding of the aromatic benzyl groups in the rotaxane compared to the free macrocycle, confirmed the interlocked architecture. In addition, the unusual proximity of the amide polar groups in chlorinated solvents promoted

specific hydrogen bonding interactions between the thread and the macrocycle to which corresponded a downfield shift in the amide protons ($H_{C,c}$).

3.3.3. Serendipitous Quaternisation of Triethylamine with Dichloromethane

Finally, this work on cobalt(III) complexes lead to the serendipitous discovery of another interesting reaction. Purification via chromatography (Silica gel, 1:39:60 $Et_3N/(CH_3)_2CO/CH_2Cl_2$) of the cobalt(III) complexes resulted in the unpredictable formation of chloromethyl-triethylammonium chloride, produced on silica by reaction between triethylamine and dichloromethane, **(Scheme 8)**.



Scheme 8: Quaternisation of triethylamine with dichloromethane.

It is worth commenting on this reaction because it is known that dichloromethane is inert towards reaction with most tertiary amines under atmospheric conditions. In order to react it with a variety of tertiary amines to produce α-chloro quaternary ammonium, it requires pressures in the order of 10^6 Torr,[34 a] or irradiation (High-pressure mercury lamp, λ <290 nm).[34 b] Although further investigation is essential to better understand the conditions and mechanism of such substitution, in the case here reported reaction seemed to occur at atmospheric pressure and without irradiation. In order to identify the factors involved, a study was conducted: a series of "blank" reactions was carried out excluding systematically one parameter at the time, e.g. silica gel, cobalt(III) complex, light. The observations lead to the conclusion that reaction between triethylamine and

dichloromethane takes place in the presence of silica and neither cobalt complexes nor light are necessary for the substitution to take place.

3.4. Conclusions

While the field of supramolecular chemistry is merging rapidly with the development of machines at the molecular level, the creative utilization of old pieces of knowledge to yield novel building blocks and assemble original structures is particularly prolific. Given the key role played by coordination chemistry in the metal-directed synthesis of superstructures it is essential for chemists to expand the arrays of metals available in this endeavour. This project was planned to investigate the feasibility of using trivalent octahedral cobalt ions metals in the metal-directed synthesis of supramolecular interlocked architectures based on a 2,6-pyridine dicarboxamide ligand system. We have shown that it is possible to synthesise both [2]catenate and [2]rotaxane via a clipping strategy. Stabilised by the anionic nature of the deprotonated nitrogens of the amides, the [2]catenate and the [2]rotaxane here reported are the first derived from a higher oxidation state coordinated metal. Along with the palladium four-coordinate square planar metal complex[7] the divalent metal-directed[8] synthesis of interlocked architectures recently developed in our group they broaden the series of mechanically interlocked ligands for common transition metal geometries started by Sauvage in 1983. Moreover, this work resulted in the serendipitous discovery of a silica catalysed reaction whereby triethylamine substitutes a chloride in dichloromethane.

3.5. Experimental Section

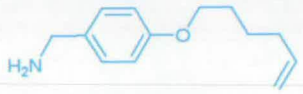
3.5.1. *General*

Unless stated otherwise, all reagents were purchased and techniques were carried out as specified in Chapter 2.

X-ray structure determination was carried out by the services at the University of St. Andrews using a a Bruker SMART CCD diffractometer.

3.5.2. Catenate Synthesis

4-(Hex-5-enyloxy)benzylamine

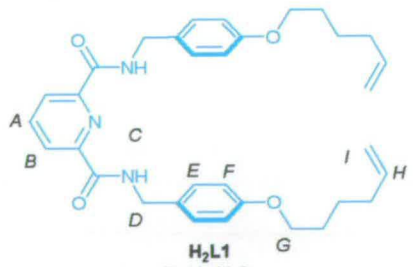


$C_{13}H_{19}NO$
Mol. Wt.: 205.3

This Compound was prepared as described in D. A. Leigh,* P. J. Lusby, S. J. Teat, A. J. Wilson, J. K. Y. Wong, *Angew. Chem.Int. Ed.*, **2001**, *40*, 1538-1543. and showed identical spectroscopical data to those reported therein.

***N, N'- bis*[4-(hex-5-enyloxy)benzyl]-2,6-pyridinedicarboxamide**

H_2L1



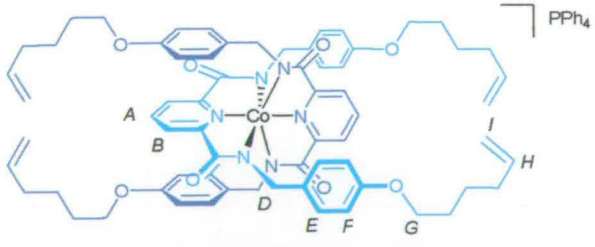
H_2L1
$C_{33}H_{39}N_3O_4$
Mol. Wt.: 541.7

To a solution of 4-(hex-5-enyloxy)benzylamine (2.18 g, 10.6 mmol) and triethylamine (1.07 g, 10.6 mmol) in dichloromethane (50 mL) at 0 °C under an atmosphere of nitrogen was added slowly 2,6-pyridinedicarbonyl dichloride (1.08 g, 5.30 mmol). The reaction was then stirred at room temperature for 18 h. The solvent was removed under

reduced pressure and the crude residue purified by column chromatography (Silica gel, 1:9 EtOAc/CH_2Cl_2) and then recrystallised from acetonitrile to yield the title compound as a colorless crystalline solid (2.61 g, yield = 91%). m.p. 141.2-143.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293K): δ = 1.46 (m, 4H, alkyl-H), 1.68 (m, 4H, $OCH_2C\underline{H}_2$), 2.02 (m, 4H, alkyl-H), 3.81 (t, J=6.6 Hz, 4H, $OC\underline{H}_2CH_2$), 4.44 (d, J=6.3 Hz, 4H, $CONHC\underline{H}_2$), 4.90 (m, 4H, $CH=C\underline{H}_2$), 5.73 (m, 2H, $C\underline{H}=CH_2$), 6.68 (d, J=8.8 Hz, 4H, ArH), 7.11 (d, J=8.8 Hz, 4H, ArH), 7.90 (t, J=7.8 Hz, 1H, pyridyl-H), 8.22 (d, J=7.8 Hz, 2H, pyridyl-H), 8.62 (t, J=6.3 Hz, 2H, $CON\underline{H}CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$, 293K): δ = 25.3, 28.7, 33.4, 42.9, 67.8, 114.6, 114.8, 125.2, 129.0, 129.9, 138.5, 138.9, 148.8, 158.5, 163.5; LRFAB-MS (3-NOBA matrix): m/z = 541 $[M]^+$, 564 $[M\text{Na}]^+$; HRFAB-MS (3-NOBA matrix): m/z = 541.29425 (calcd. for $C_{33}H_{39}N_3O_4$, 541.29406).

***bis*{(*N,N'*- *bis*[4-(hex-5-enyloxy)benzyl]-2,6-pyridinedicarboxamido)cobalt(III)} tetraphenylphosphonium**

[$L1_2Co$] PPh_4



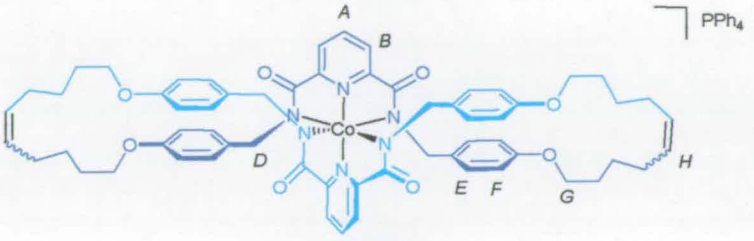
$L1_2CoPPh_4$
$C_{90}H_{94}CoN_6O_8P$ (Mol. Wt.: 1477.6)
$C_{66}H_{74}CoN_6O_8$ (Mol. Wt.: 1138.3)

To H_2**L1** (1.083 g, 2.000 mmol) in anhydrous dimethylformamide (100 mL) was added a suspension of 40% sodium hydride in mineral oil (0.160 g, 4.000 mmol). The reaction was stirred at room temperature under an atmosphere of nitrogen for 20 minutes and then a solution of cobalt (II) chloride hexahydrate (0.238 g, 1.000 mmol) in anhydrous dimethylformamide (50 mL) was added to it via double ended needle technique. A

colour change from blue to deep red was observed. The reaction was stirred at room temperature under an atmosphere of nitrogen for 10 minutes then the flask was opened and the solution bubbled with compressed air for 30 minutes. A further change in colour from red to dark green was observed. The solvent was removed under reduced pressure and the resulting solid was stirred in ethylacetate (50 mL) with sonnicating for 60 minutes and then filtered under gravity. The resultant green solid was dissolved in dichloromethane (25 mL) and tetraphenylphoshonium chloride (0.375 g, 1.000 mmol) was added to it and stirred for 30 minutes. The solution was filtered and the solvent removed under reduced pressure to yield the title compound as a dark green solid (1.345 g, yield = 91%). m.p. 166 °C (dec); ^{1}H NMR (400 MHz, Acetone-d_6, 293K): δ = 1.48-1.58 (m, 8H, alkyl-H), 1.67-1.77 (m, 8H, $OCH_2C\underline{H}_2$), 2.03-2.07 (m, 4H, alkyl-H), 2.07-2.15 (m, 8H, alkyl-H) 3.23 (s, 8H, $CONCoC\underline{H}_2$), 3.86 (t, J=6.6 Hz, 8H, $OC\underline{H}_2CH_2$), 4.80-4.96(m, 8H, $CH=C\underline{H}_2$), 5.79-5.90 (m, 4H, $C\underline{H}=CH_2$), 6.35 (d, J=8.6 Hz, 8H, ArH), 6.43 (d, J=8.6 Hz, 8H, ArH), 7.67 (d, J=7.8 Hz, 4H, pyridyl-H), 7.81-7.88 (m, 12H, PPh_4 ArH), 7.97-8.03 (m, 8H, PPh_4 ArH), 8.17 (t, J=7.8 Hz, 2H, pyridyl-H); ^{13}C NMR (100 MHz, Acetone-d_6, 293K): δ = 26.1, 30.0, 34.2, 46.7, 68.2, 114.2, 118.8, 123.0, 123.1, 129.1, 131.4, 131.5, 135.6, 135.7, 136.4, 139.7, 157.9, 159.3, 169.1- LRFAB-MS (3-NOBA matrix): m/z = 1138 $[\mathbf{L1_2Co}]^+$, HRFAB-MS (3-NOBA matrix): m/z = 1138.49776 (calcd. for $C_{66}H_{75}CoN_6O_8$, 1138.49784).

{[H_4L3]cobalt(III)} tetraphenylphosphonium

[L3Co]PPh_4

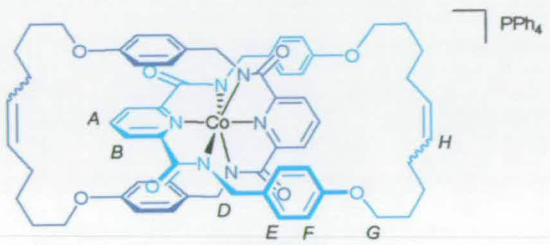


L3CoPPh$_4$
$C_{86}H_{86}CoN_6O_8P$
Mol. Wt.: 1421.5

Grubbs' metathesis catalyst [Ru(=CHPh)(PCy_3)$_2Cl_2$] (0.056 g, 0.068 mmol, 20 mol %) was placed in a sealed, argon-purged, flame-dried Schlenk tube, and subjected to a constant stream of argon for ten minutes. A degassed and argon-purged solution of the **[$L1_2$Co] PPh_4** complex (0.500 g, 0.338 mmol) in anhydrous dichloromethane (500 mL) was transferred to the Schlenk tube by injection over ten minutes. Reaction was allowed to continue until all the starting material was consumed as evidenced by TLC (typically 4 days). The resulting solution was added with 2 mL of methanol, evaporated to dryness and purified by chromatography (Silica gel, 1:39:60 Et_3N/$(CH_3)_2CO$/CH_2Cl_2) to give the figure of eight **[L3Co] PPh_4** as a dark green solid.: *FRACTION A*: (0.201 g, yield = 42%). m.p. 170-173 °C; ^{1}H NMR (400 MHz, Acetone-d_6, 293K): δ = 1.33-1.38 (m, 8H, alkyl-H), 1.41-1.52(m, 8H, $OCH_2C\underline{H}_2$), 1.65-1.78 (m, 12H, alkyl-H+ $CONCoC\underline{H}_2$), 3.72-3.84 (m, 8H, $OC\underline{H}_2CH_2$), 4.12 (t, J=12.38 Hz, 4H, $CONCoC\underline{H}_2$), 5.19-5.28 (m, 4H, $C\underline{H}$=$C\underline{H}$),, 6.28 (d, J=1.76 Hz, 8H, ArH), 6.27 (d, J=1.76 Hz, 8H, ArH), 7.88 (d, J=7.83 Hz, 4H, pyridyl-H), 8.31 (t, J=7.58 Hz, 2H, pyridyl-H); ^{13}C NMR (100 MHz, Acetone-d_6, 293K): δ = 27.1, 28.6, 32.4, 46.6, 67.5, 114.2, 123.1, 130.3, 130.7, 131.5, 134.1, 135.6, 135.8, 136.4, 139.8, 157.6, 159.4, 169.3 - LRFAB-MS (3-NOBA matrix): m/z = 1082 **[L3Co]$^+$**, HRFAB-MS (3-NOBA matrix): m/z = 1421.56234 (calcd. for $C_{86}H_{87}CoN_6O_8P$, 1421.56550) **[$L1_3$CoPPh$_4$H]$^+$**.

[2]-{*bis*[(*N,N'*-1,10-dec-5-enyloxydibenzyl)-2,6-pyridinedicarboxamido]cobalt(III)} tetraphenylphosphonium

[$L2_2Co$] PPh_4

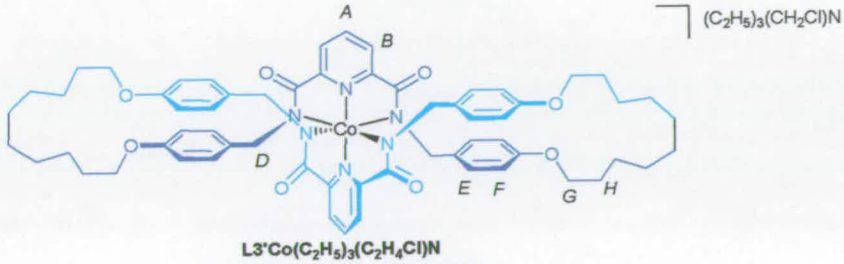


$L2_2CoPPh_4$
$C_{86}H_{86}CoN_6O_8P$
Mol. Wt.: 1421.5

Grubbs' metathesis catalyst [Ru(=CHPh)(PCy_3)$_2Cl_2$] (0.056 g, 0.068 mmol, 20 mol %) was placed in a sealed, argon-purged, flame-dried Schlenk tube, and subjected to a constant stream of argon for ten minutes. A degassed and argon-purged solution of the **[$L1_2Co$] PPh_4** complex (0.500 g, 0.338 mmol) in anhydrous dichloromethane (500 mL) was transferred to the Schlenk tube by injection over ten minutes. Reaction was allowed to continue until all the starting material was consumed as evidenced by TLC (typically 4 days). The resulting solution was added with 2 mL of methanol , evaporated to dryness and purified by chromatography (Silica gel, 1:39:60 Et_3N/$(CH_3)_2CO$/CH_2Cl_2) to give the catenate [$L2_2Co$] PPh_4 as a green solid.: *FRACTION B*: (0.180 g, yield = 38%). m.p. 161 - 164 °C ; ^1H NMR (400 MHz, Acetone-d_6, 293K): δ = 1.40-1.50 (m, 8H, alkyl-H) 1.63-1.72 (m, 8H, alkyl-H), 2.00-2.04 (m, 8H, alkyl-H), 1.99-3.36 (d, J=9.8 Hz, 8H, CONCoC$\underline{H}_2$), 3.90-3.97 (m, 8H, OC$\underline{H}_2$CH_2), 5.52-5.56 (m, 4H, C$\underline{H}$=C$\underline{H}$), 6.22 (d, J=8.3 Hz, 8H, ArH), 6.34 (d, J=8.3 Hz, 8H, ArH), 7.45-7.41 (m, 4H, pyridyl-H), 7.79-7.85 (m, 16H, PPh_4 ArH), 7.95-8.03 (m, 6H, pyridyl-H+ PPh_4 ArH); ^{13}C NMR (100 MHz, Acetone-d_6, 293K): δ = 26.2, 28.6, 32.5, 46.5, 67.9, 114.9, 122.5, 128.8, 131.1, 131.3, 134.8, 135.6, 135.8, 136.4, 138.5, 157.0, 157.5, 158.9 - LRFAB-MS (3-NOBA matrix): m/z = 1083 [$L2_2Co$]$^-$, HRFAB-MS (3-NOBA matrix): m/z = 1421. 56011 (calcd. for $C_{86}H_{87}CoN_6O_8P$, 1421.56550) [$L1_2CoPPh_4H$]$^+$.

{[H_4L3']cobalt(III)} 2- chloromethyl-triethylammonium

[L3'Co] $(C_2H_5)_3(CH_2Cl)N$

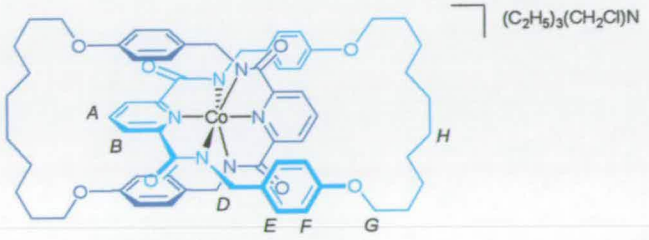


L3'Co$(C_2H_5)_3(C_2H_4Cl)N$
$C_{70}H_{89}ClCoN_7O_8$ (Mol. Wt.: 1250.8)
$C_{68}H_{86}CoN_7O_6^+$ (Mol. Wt.: 1188.4)

To **[L3Co]PPh_4** (0.142 g, 0.100 mmol) in anhydrous methanol(30 mL) was added 10% w/w Pd-C (0.020 g) and was stirred under an atmosphere of H_2 for 18 h. The Pd-C was then removed by filtration through a plug of Celite, and the solvent was removed under reduced pressure. The crude mixture was purified using column chromatography (Silica gel, 1:39:60 $Et_3N/(CH_3)_2CO/CH_2Cl_2$) to give the product as a dark green solid.(0.106g, yield = 85%). m.p. 166 - 170 °C; ^{1}H NMR (400 MHz, Acetone-d_6, 293K): δ = 1.15 (t, 9H, J = 7.3, $C\underline{H}_3CH_2N$), 1.32-1.37 (m, 16H, alkyl-H), 1.58 (t, 2H, J = 6.3, $ClCH_2C\underline{H}_2N$), 1.65-1.75 (m, 8H, alkyl-H), 2.01-2.10 (m, 12H, alkyl-H+CONCoC$\underline{H}_2$), 3.04 (q, 6H, J = 7.3, $CH_3C\underline{H}_2N$), 3.81 (t, 2H, J = 6.3, $ClC\underline{H}_2CH_2N$), 3.87-3.97 (m, 8H, $OC\underline{H}_2CH_2$), 4.29 (d, 4H, CONCoC$\underline{H}_2$), 5.28 (t, J=3.78 Hz, 2H, CH=C$\underline{H}_2$), 6.25-6.48 (m, 16H, ArH), 7.88 (d, J=7.71 Hz, 4H, pyridyl-H), 8.31 (t, J=7.71 Hz, 2H, pyridyl-H); ^{13}C NMR (100 MHz, Acetone-d_6, 293K): δ = 7.5, 25.8, 27.7, 28.4, 28.6, 46.5, 53.3, 67.9, 114.6, 124.2, 130.1, 134.5, 138.1, 141.4, 158.1, 159.2 - LRFAB-MS (3-NOBA matrix): m/z = 1087 **[L3CoH_2]$^+$**, HRFAB-MS (3-NOBA matrix): m/z= 1087.47427 (calcd. for $C_{62}H_{72}CoN_6O_8$, 1087.47436).

[2]- {*bis* [(*N,N'*-1,10-decanyloxydibenzyl)-2,6-pyridinedicarboxamido]cobalt(III)} 2-2- chloromethyl-triethylammonium

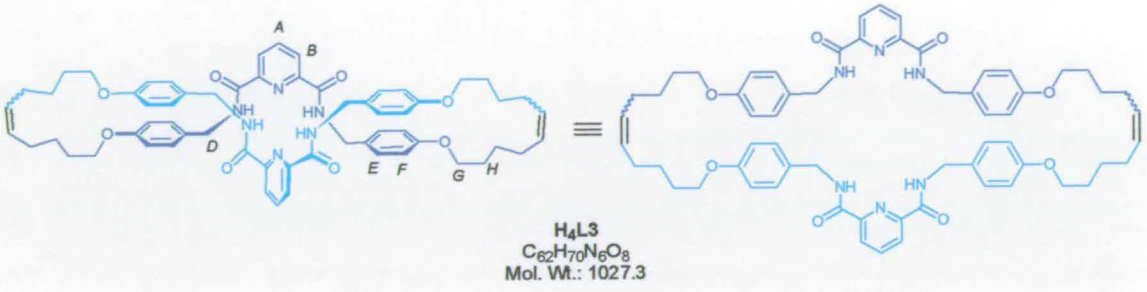
[$L2_2$'Co] $(C_2H_5)_3(CH_2Cl)N$



[$L2_2$'Co]$(C_2H_5)_3(C_2H_4Cl)N$
$C_{70}H_{89}ClCoN_7O_8$ (Mol. Wt.: 1250.8)
$C_{62}H_{70}CoN_6O_8^+$ (Mol. Wt.: 1086.2)

To **[$L2_2$Co] PPh_4** (0.100 g, 0.070 mmol) in anhydrous methanol (30 mL) was added 10% w/w Pd-C (0.015 g) and was stirred under an atmosphere of H_2 for 18 h. The Pd-C was then removed by filtration through a plug of Celite, and the solvent was removed under reduced pressure. The crude mixture was purified using column chromatography (Silica gel, 1:39:60 $Et_3N/(CH_3)_2CO/CH_2Cl_2$) to give the product as a dark green solid.(0.071 g, yield = 81%). m.p. 162 -166 °C; ^{1}H NMR (400 MHz, Acetone-d_6, 293K): δ = 1.41-1.56 (m, 36H, alkyl-H + $C\underline{H}_3CH_2N^+$), 1.84-1.75 (m, 8H, alkyl-H), 3.50 (s, 4H, $CONCoC\underline{H}_2$), 3.55 (q, 8H, J = 7.3, $CH_3C\underline{H}_2N^+$), 4.03 (t, 8H, $OC\underline{H}_2CH_2$), 6.37 (d, *J*=8.3 Hz, 8H, ArH), 6.48 (d, *J*=8.3 Hz, 8H, ArH), 7.58 (d, *J*=7.7 Hz, 4H, pyridyl-H), 8.09 (t, *J*=7.70 Hz, 2H, pyridyl-H); ^{13}C NMR (100 MHz, Acetone-d_6, 293K): δ = 16.5, 26.1, 28.2, 28.7, 46.4, 52.7, 53.1, 67.7, 115.4, 122.5, 129.2, 134.8, 138.5, 157.2, 159.3, 169.1 - LRFAB-MS (3-NOBA matrix): *m/z* = 1087 **[$L2_2$'CoH]$^+$**, 516 **[L2H]$^+$**, HRFAB-MS (3-NOBA matrix): *m/z* = 1086.46523 (calcd. for $C_{62}H_{71}CoN_6O_8$, 1086.46654), ESI -ve: *m/z* = 1086 **[$L2_2$'Co]$^-$**.

Macrocycle H_4L3

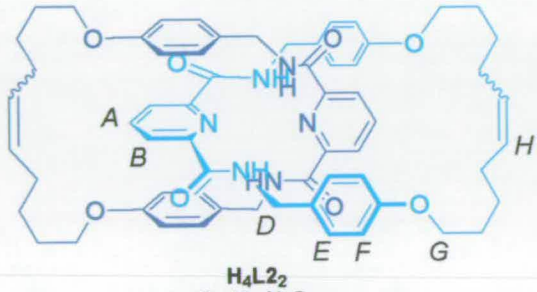


H_4L3
$C_{62}H_{70}N_6O_8$
Mol. Wt.: 1027.3

To **[L3Co]PPh$_4$** (0.071 g, 0.050 mmol) in anhydrous methanol (10 mL) was added zinc powder (0.005 g, 0.077 mmol) and glacial acetic acid (0.5 mL). The reaction was stirred at room temperature in aerobic conditions for 20 minutes. A change in colour from green to pale pink was observed. The suspension was filtered through a plug of Celite and the filtrate was added dropwise to an aqueous sodium carbonate solution stirring on top of a chloroform layer: the product precipitated out of solution in the form of white powder (0.048 g, yield = 95%). m.p. 290 °C (dec); ^{1}H NMR (400 MHz, N,N-Dimethylformamide-d$_7$, 293K): δ = 1.59-1.69 (m, 8H, alkyl-H), 1.82-1.93 (m, 8H, alkyl-H), 2.16-2.30 (m, 8H, alkyl-H), 4.07-4.15 (t, J=5.8 Hz, 8H, OC$\underline{H}_2$CH$_2$), 4.65 (d, J=6.2 Hz, 8H, CONHC$\underline{H}_2$), 5.53-5.63 (m, 4H, C$\underline{H}$=C$\underline{H}$), 7.01 (d, J=8.4 Hz, 8H, ArH), 7.36 (d, J=8.4 Hz, 8H, ArH), 8.41 (t, J=9.0 Hz, 2H, pyridyl-H), 8.48 (d, J=9.0 Hz, 4H, pyridyl-H), 9.85 (t, J=6.2 Hz, 4H, CON$\underline{H}$CH$_2$); ^{13}C NMR (100 MHz, Acetone-d$_6$, 293K): δ = 26.9, 28.7, 32.4, 42.2, 67.7, 114.4, 124.6, 129.1, 130.0, 130.6, 139.7, 158.1, 167.3- LRFAB-MS (3-NOBA matrix): m/z = 1027 [**L3H**]$^+$, HRFAB-MS (3-NOBA matrix): m/z = 1027.53393 (calcd. for $C_{62}H_{71}N_6O_8$, 1027.53334).

[2]-*bis*(*N,N'*-1,10-decanyloxydibenzyl)-2,6-pyridinedicarboxamide

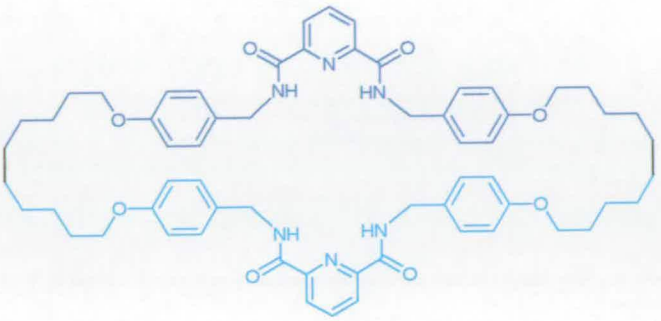
$(H_2L2)_2$



H_4L2_2
$C_{62}H_{70}N_6O_8$
Mol. Wt.: 1027.3

To **[$L2_2$]** (0.050 g, 0.035 mmol) in anhydrous methanol (10 mL) was added zinc powder (0.005 g, 0.077 mmol) and glacial acetic acid (0.5 mL). The reaction was stirred at room temperature in aerobic conditions for 20 minutes. A change in colour from green to pale pink was observed. The suspension was filtered through a plug of Celite and the filtrate was added dropwise to an aqueous sodium carbonate solution stirring on top of a chloroform layer: the product precipitated out of solution in the form of white powder (0.033 g, yield = 92%). m.p. 86 - 93 °C; ^{1}H NMR (400 MHz, Chloroform-d, 293K): δ= 1.20-1.30 (m, 8H, alkyl-H), 1.36-1.48 (m, 8H, alkyl-H), 1.69-1.76 (m, 8H, alkyl-H), 3.61 (t, *J*=6.3 Hz, 8H, $OC\underline{H}_2CH_2$), 4.39 (d, *J*=5.6 Hz, 8H, $CONHC\underline{H}_2$), 5.50-5.53 (m, 4H, $C\underline{H}$=$C\underline{H}$), 6.24 (d, *J*=8.3 Hz, 8H, ArH), 6.68 (d, *J*=8.3 Hz, 8H, ArH), 8.03 (t, *J*=7.8 Hz, 2H, pyridyl-H), 8.29 (t, *J*=5.6 Hz, 4H, $CON\underline{H}CH_2$), 8.40 (d, *J*=7.8 Hz, 4H, pyridyl-H); ^{13}C NMR (100 MHz, Chloroform-d, 293K): δ= 25.9, 27.9, 31.5, 43.2, 66.8, 113.8, 125.8, 128.3, 128.8, 130.4, 138.6, 149.2, 157.5, 163.3 - LRFAB-MS (3-NOBA matrix): *m/z* = 1027 **[$L2_2$H]**$^+$, 514 **[L2H]**$^+$, HRFAB-MS (3-NOBA matrix): *m/z* = 1027.53181 (calcd. for $C_{62}H_{71}N_6O_8$, 1027.53334).

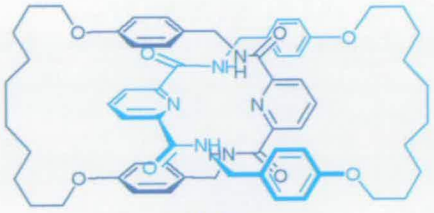
Macrocycle H_4L3'



H_4L3'
$C_{62}H_{74}N_6O_8$
Mol. Wt.: 1031.2

To **[L3'Co]PPh_4** (0.063 g, 0.050 mmol) in anhydrous methanol (10 mL) was added zinc powder (0.005 g, 0.077 mmol) and glacial acetic acid (0.5 mL). The reaction was stirred at room temperature in aerobic conditions for 20 minutes. A change in colour from green to pale pink was observed. The suspension was filtered through a plug of Celite and the filtrate was added dropwise to an aqueous sodium carbonate solution stirring on top of a chloroform layer: the product precipitated out of solution in the form of white powder (0.047 g, yield = 92%). m.p. 292 °C (dec); ^{1}H NMR (400 MHz, N,N-Dimethylsulphoxide-d_6, 293K): δ = 1.15-1.33 (m, 16H, alkyl-H), 1.33-1.42 (m, 8H, alkyl-H), 1.61-1.75 (m, 8H, alkyl-H), 4.11 (t, J=5.8 Hz, 8H, OC$\underline{H}_2$CH_2), 4.65 (d, J=6.2 Hz, 8H, CONHC$\underline{H}_2$), 7.00 (d, J=8.4 Hz, 8H, ArH), 7.35 (d, J=8.4 Hz, 8H, ArH), 8.41 (t, J=9.0 Hz, 2H, pyridyl-H), 8.48 (d, J=9.0 Hz, 4H, pyridyl-H), 9.85 (t, J=6.2 Hz, 4H, CON$\underline{H}$CH$_2$); ^{13}C NMR (100 MHz, Acetone-d_6, 293K): δ = 25.9, 27.7, 32.3, 42.3, 67.7, 114.3, 124.6, 129.0, 130.0, 130.5, 139.7, 158.4, 167.3- LRFAB-MS (3-NOBA matrix): m/z = 1031 [**L3'**H]$^+$, HRFAB-MS (3-NOBA matrix): m/z = 1031.56328 (calcd. for $C_{62}H_{75}N_6O_8$, 1031.56464).

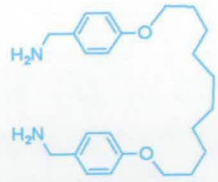
[2]-[Pyridine-2,6-dicarboxylic acid 1,10-di(4-phenoxymethylamide)decane] $(H_2L2')_2$



$H_4L2'_2$
$C_{62}H_{74}N_6O_8$
Mol. Wt.: 1031.29

To **$[L2_2'Co]$ $(C_2H_5)_3(C_2H_4Cl)N$** (0.062 g, 0.050 mmol) in anhydrous methanol (10 mL) was added zinc powder (0.005 g, 0.077 mmol) and glacial acetic acid (0.5 mL). The reaction was stirred at room temperature in aerobic conditions for 20 minutes. A change in colour from green to pale pink was observed. The suspension was filtered through a plug of Celite and the filtrate was added dropwise to an aqueous sodium carbonate solution stirring on top of a chloroform layer: the product precipitated out of solution in the form of white powder (0.046 g, yield = 89%). m.p. 81-90 °C; ^{1}H NMR (400 MHz, Chloroform-d, 293K): δ = 1.19-1.32 (m, 16H, alkyl-H), 1.35-1.46 (m, 8H, alkyl-H), 1.64-1.74 (m, 8H, alkyl-H), 3.61 (t, J=6.3 Hz, 8H, $OC\underline{H}_2CH_2$), 4.39 (d, J=5.6 Hz, 8H, $CONHC\underline{H}_2$), 6.23 (d, J=8.3 Hz, 8H, ArH), 6.67 (d, J=8.3 Hz, 8H, ArH), 8.02 (t, J=7.8 Hz, 2H, pyridyl-H), 8.30 (t, J=5.6 Hz, 4H, $CON\underline{H}CH_2$), 8.40 (d, J=7.8 Hz, 4H, pyridyl-H); ^{13}C NMR (100 MHz, Chloroform-d, 293K): δ = 25.4, 28.2, 29.0, 34.2, 43.2, 66.7, 113.9, 125.5, 125.7, 128.2, 138.7, 149.2, 157.8, 163.4- LRFAB-MS (3-NOBA matrix): m/z = 1031 $[L3'H]^+$, HRFAB-MS (3-NOBA matrix): m/z = 1031.56328 (calcd. for $C_{62}H_{75}N_6O_8$, 1031.56464).

1,10-di(4-phenoxymethylamine)decane

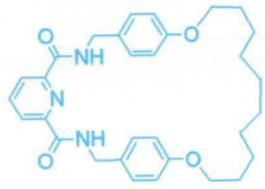


$C_{24}H_{36}N_2O_2$
Mol. Wt.: 384.6

This Compound was prepared as described in D. A. Leigh,* P. J. Lusby, S. J. Teat, A. J. Wilson, J. K. Y. Wong, *Angew. Chem.Int. Ed.*, **2001**, *40*, 1538-1543. and showed identical spectroscopical data to those reported therein.

Pyridine-2,6-dicarboxylic acid 1,10-di(4-phenoxymethylamide)decane

H_2L2'



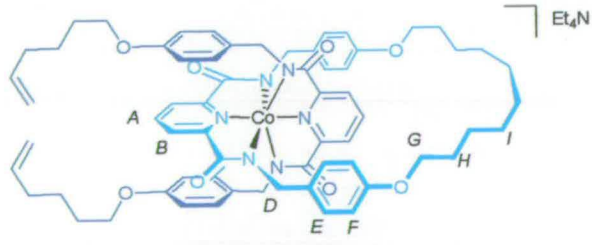
H_2L2'
$C_{31}H_{37}N_3O_4$
Mol. Wt.: 515.6

To chloroform (2.5 L), in a sealed, argon-purged, flame-dried Schlenk tube at 0°C, was added dropwise simultaneously 1,10-di(4-phenoxymethylamine)decane (3.00 g, 7.80 mmol) and triethylamine (1.74 g, 17.2 mmol) in chloroform (250 mL), and 2,6-pyridine dicarbonyl dichloride (1.59 g, 7.80 mmol) in chloroform (250 mL). The solution was stirred at room temperature for 18 h, after which the solvent was removed by rotary evaporation and the crude residue purified by column chromatography (Silica gel, 1:1 EtOAc/$CHCl_3$), and recrystallised from chloroform and EtOEt to yield the product as a white solid (2.29 g, 4.44 mmol, 57%). m.p. 258.5-260.0°C; ^{1}H NMR (400 MHz, Acetone-d_6, 293K): δ = 1.22-1.34 (m, 8H, Alkyl-H), 1.37-1.46 (m, 4H, Alkyl-H), 1.64-

1.74 (m, 4H, J = 6.7 Hz, Alkyl-H), 3.96 (t, 4H, J = 6.0 Hz, OC$\underline{H}_2$ CH_2), 4.50(d, 4H, J = 6.3 Hz, CONHC$\underline{H}_2$), 6.80 (d, 4H, J = 8.5 Hz, ArH), 7.13 (d, 4H, J = 8.5 Hz, ArH), 8.20 (t, 1H, J = 8.3 Hz, pyridyl-H), 8.35 (d, 2H, J = 8.3 Hz, pyridyl-H), 8.96 (t, 2H, J = 6.3 Hz, CON$\underline{H}$$CH_2$); (400 MHz, Chloroform-d, 293K): δ = 1.28-1.32 (m, 8H, Alkyl-H), 1.45 (t, 4H, J = 6.6 Hz, Alkyl-H), 1.72-1.77 (m, 4H, J = 6.7 Hz, Alkyl-H), 3.94 (t, 4H, J = 6.2 Hz, OC$\underline{H}_2$ CH_2), 4.62(d, 4H, J = 5.9 Hz, CONHC$\underline{H}_2$), 6.80 (d, 4H, J = 8.6 Hz, ArH), 7.19 (d, 4H, J = 8.6 Hz, ArH), 7.95 (t, 2H, J = 5.9 Hz, CON$\underline{H}$$CH_2$), 8.03 (t, 1H, J = 7.6 Hz, pyridyl-H), 8.37 (d, 2H, J = 7.6 Hz, pyridyl-H); ^{13}C NMR (100 MHz, Acetone-d_6, 293K): δ = 26.2, 28.9, 29.1, 29.5, 42.7, 67.7, 115.3, 125.5, 129.7, 131.9, 140.1, 150.2, 158.7, 163.9 - (100 MHz, Chloroform-d, 293K): δ = 25.4, 28.1, 28., 28.7, 42.9, 67.4), 114.8, 125.4, 129.2, 129.8, 138.9, 148.8, 158.7, 163.3- LRFAB-MS (3-NOBA matrix): m/z = 516 $[\mathbf{H_2L2'H}]^+$, HRFAB-MS (3-NOBA matrix): m/z = 516.28571 (calcd. for $C_{31}H_{38}N_3O_4$, 516.28623).

{[*N, N'- bis*[4-(hex-5-enyloxy)benzyl]-2,6-pyridinedicarboxamido]-[Pyridine-2,6-dicarboxylic acid 1,10-di(4-phenoxymethylamide)decane]cobalt(III)} tetraethylammonium

[L1L2'Co] $(C_2H_5)_4N$



L1L2'Co$(C_2H_5)_4N$
$C_{72}H_{92}CoN_7O_8$ (Mol. Wt.: 1242.5)
$C_{64}H_{72}CoN_6O_8$ (Mol. Wt.: 1112.2)

To H_2**L2'** (0.206 g, 0.400 mmol) in anhydrous dimethylformamide (50 mL) was added a suspension of 40% sodium hydride in mineral oil (0.035 g, 0.880 mmol). The reaction

was stirred at room temperature under an atmosphere of nitrogen for 20 minutes and then a solution of cobalt(II) chloride hexahydrate (0.090 g, 0.380 mmol) in anhydrous dimethylformamide (25 mL) was added to it via double ended needle technique. A colour change from blue to dark brown was observed. The reaction was stirred at room temperature under an atmosphere of nitrogen for 60 minutes then it was added with a solution of H_2**L1** (0.108 g, 0.200 mmol) in anhydrous dimethylformamide (25 mL), separately reated with a suspension of 40% sodium hydride in mineral oil (0.018 g, 0.440 mmol), was added to it. The reaction was stirred at room temperature under an atmosphere of nitrogen for 120 minutes then the flask was opened and the solution bubbled with compressed air for 30 minutes. A further change in colour from dark brown to brown green was observed. The suspension was filtered under gravity; the solvent was removed to the filtrate under reduced pressure and the resulting solid was stirred in ethylacetate (50 mL) with sonnicating for 60 minutes and then filtered under gravity. The resultant green solid was dissolved in dichloromethane (25 mL) and tetraethylammonium acetate (0.523 g, 0.200 mmol) was added to it and stirred for 30 minutes. The solution was filtered and the solvent removed under reduced pressure; it was then purified using column chromatography (Silica gel, 1:39:60 $Et_3N/(CH_3)_2CO/CH_2Cl_2$) to give the product as a dark green solid (0.109 g, yield = 44%). m.p. 151-156 °C (dec); ^{1}H NMR (400 MHz, Acetone-d_6, 293K) Ushape: δ = 1.24-1.28 (m, 8H, alkyl-H), 1.36-1.45 (m, 8H, alkyl-H), 1.55-1.63 (m, 8H, $OCH_2C\underline{H}_2$), 1.94-2.01 (m, 4H, $C\underline{H}_2CH=CH_2$), 3.16 (br s, 4H, $CONCoC\underline{H}_2$), 3.24 (br s, 4H, $CONCoC\underline{H}_2$), 3.75 (t, J=6.6 Hz, 4H, $OC\underline{H}_2CH_2$), 3.82 (t, J=6.3 Hz, 4H, $OC\underline{H}_2CH_2$), 4.78-4.92(m, 4H, $CH=C\underline{H}_2$), 5.65-5.76 (m, 2H, $C\underline{H}=CH_2$), 6.02 (d, J=8.4 Hz, 4H, ArH), 6.25 (d, J=8.4 Hz, 4H, ArH), 6.36 (d, J=8.7 Hz, 4H, ArH), 6.40 (d, J=8.7 Hz, 4H, ArH), 7.33 (d, J=7.8 Hz, 4H, pyridyl-H), 7.72 (d, J=7.6 Hz, 4H, pyridyl-H), 7.87 (t, J=7.8 Hz, 2H, pyridyl-H) 8.20 (t, J=7.6 Hz, 2H, pyridyl-H); ^{13}C NMR (100 MHz, Acetone-d_6, 293K): δ = 9.16, 22.9, 26.2, 26.3, 28.9, 28.9,34.8, 46.7, 53.5, 67.7, 67.8, 68.2, 114.6, 114.9, 115.0, 122.7, 123.5, 128.3, 129.7, 133.5, 134.7, 134.8, 139.6, 139.8, 157.62,

158.1, 158.6, 159.1, 168.9, 169.3 - LRFAB-MS (3-NOBA matrix): *m/z* = 1113 **[L1L2'CoH]**$^+$, HRFAB-MS (3-NOBA matrix): *m/z* = 1113.48999 (calcd. for $C_{64}H_{74}CoN_6O_8$, 1113.49001), ESI -ve: *m/z* = 1112 **[L1L2'CoH]**$^-$.

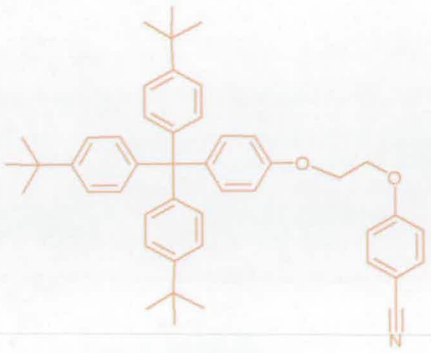
3.5.3. Rotaxane Synthesis

4-(2-bromo-ethoxy)-benzonitrile

C_9H_8BrNO
Mol. Wt.: 226.1

To a solution of 4-cyanophenol (5.950 g, 0.050 mol) and 1,2-dibromoethane (37.60 g, 0.200 mol) in ethylmethylketone (750 mL) under an atmosphere of nitrogen was added potassium carbonate (69.00 g, 0.500 mol) and sodium iodide (0.112 g, 0.005 mol). The reaction was refluxed for 10 hours then it was filtered under gravity. The solvent was removed under reduced pressure, the crude residue purified by column chromatography (Silica gel, 5:25 EtOAc/CH_2Cl_2) and then recrystallised from n-hexane to yield the title compound as a colorless crystalline solid (10.85 g, yield = 96%). m.p. 48.0-50.1; ^{1}H NMR (400 MHz, Chloroform-d, 293K): δ = 3.65 (t, *J*=6.0 Hz, 2H, $OCH_2\underline{CH_2}Br$), 4.33 (t, *J*=6.0 Hz, 2H, $OCH_2\underline{CH_2}Br$), 6.96 (d, *J*=8.8 Hz, 2H, ArH), 7.59 (d, *J*=8.8 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, 293K): δ = 28.4, 67.9, 104.7, 115.3, 119.0, 134.1, 161.3 -RFAB-MS (3-NOBA matrix): *m/z* = 226 [*M*H]$^+$; HRFAB-MS (3-NOBA matrix): *m/z* = 225.98650 (calcd. for C_9H_9BrNO, 225.98675).

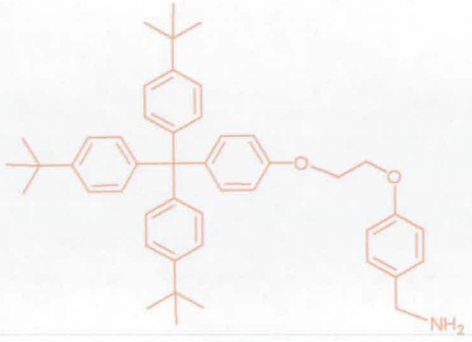
4-(2-{4-[Tris-(4-*tert*-butylphenyl)-methyl]-phenoxy}-ethoxy)-benzonitrile



$C_{46}H_{51}NO_2$
Mol. Wt.: 649.9

A solution of 4-tris(4-*tert*-butylphenyl)phenol (8.310 g, 16.50 mmol) and 4-(2-bromo-ethoxy)-benzonitrile (3.910 g, 17.30 mmol) in ethylmethylketone (140 mL) containing potassium carbonate (22.00 g, 160.0 mmol) was heated at reflux overnight under an atmosphere of argon. The solution was filtered and the solvent removed under reduced pressure. The residue was dissolved in minimum dichloromethane. Addition of diethyl ether and refrigeration of the solution resulted in the precipitation of the pure product as a white solid (6.010 g, yield = 56%). m.p. 238.2-240.1 °C; ^{1}H NMR (400 MHz; Chloroform-d, Me_4Si, 293K): δ = 1.30 (s, 27H, $C(CH_3)_3$), 4.32-4.34 (m, 4H, $O(CH_2)_2O$), 6.80 (d, 2H, J = 8.8 Hz, ArH), 6.99 (d, 2H, J = 8.5, ArH), 7.08 (d, 6H, J= 8.5 Hz, ArH), 7.11 (d, 2H, J = 8.8 Hz, ArH), 7.23 (d, 6H, J = 8.5 Hz, ArH), 7.59 (d, 2H, J = 8.5 Hz, ArH); ^{13}C NMR (100 MHz, Chloroform-d, Me_4Si, 293K): δ = 31.8, 34.7, 63.5, 66.4, 67.3, 104.8, 113.5, 115.8, 119.5, 124.5, 131.1, 132.8, 134.4, 140.8, 144.4, 148.8, 156.6, 162.4 - LRFAB-MS (3-NOBA matrix): m/z = 649 $[M]^+$, HRFAB-MS (3-NOBA matrix): m/z = 649.39250 (calcd. for $C_{46}H_{51}NO_2$, 649.39198).

4-(2-{4-[Tris-(4-*tert*-butylphenyl)-methyl]-phenoxy}-ethoxy)-benzylamine

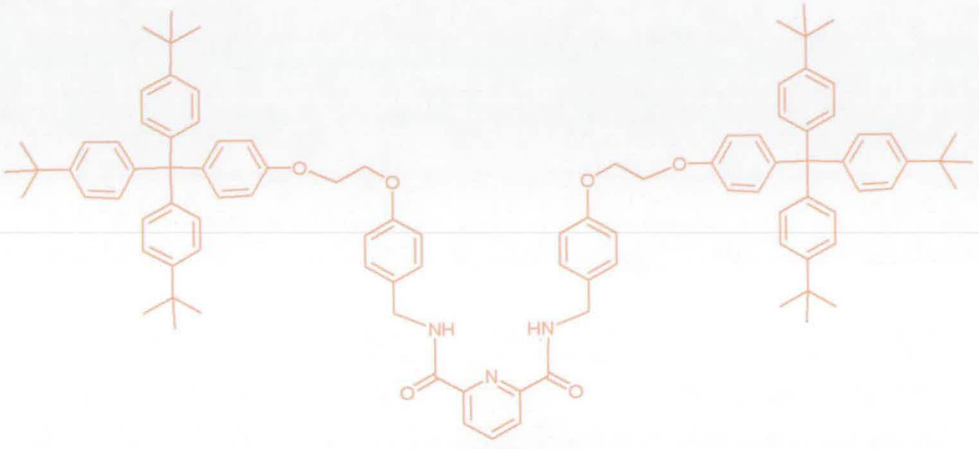


$C_{46}H_{55}NO_2$
Mol. Wt.: 653.9

A solution of 4-(2-{4-[Tris-(4-*tert*-butylphenyl)-methyl]-phenoxy}-ethoxy)-benzonitrile (5.880 g, 9.050 mmol) in anhydrous tetrahydrofuran (100 mL) was added dropwise to a cooled at 0 °C solution of lithium aluminium hydride in tetrahydrofuran (1.0 M solution, 37 mL) under an atmosphere of argon. The resultant solution was heated at reflux for 3 hours, then allowed to cool to room temperature. The solution was cooled in an ice bath and water (1 mL), 15% aqueous sodium hydroxide solution (1 mL) then water (3 mL) were added cautiously with vigorous stirring. The resultant precipitate was filtered out and discarded. The solvent was removed under reduced pressure to yield the title compound as a white solid (5.800 g, yield = 98%). m.p. 98.0-99.5 °C; ^{1}H NMR (400 MHz; $CDCl_3$, Me_4Si, 293K): δ = 1.34 (s, 27H, $C(CH_3)_3$), 3.84 (s, 2H, $C\underline{H}_2NH_2$), 4.34 (s, 4H, OCH_2), 6.85 (d, 2H, J = 8.8 Hz, ArH), 6.96 (d, 2H, J = 8.8 Hz, ArH), 7.12 (d, 8H, J = 8.8 Hz, ArH), 7.27 (d, 8H, J = 8.8 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si, 293K): δ = 31.8, 34.7, 46.3, 63.5, 66.8, 67.0, 113.6, 115.2, 124.5, 128.7, 131.1, 132.71, 136.4 , 140.5, 144.5, 148.7, 156.8, 158.0 - LRFAB-MS (3-NOBA matrix): *m/z* = 654 $[M]^+$, HRFAB-MS (3-NOBA matrix): *m/z* = 654.43179 (calcd. for $C_{46}H_{56}NO_2$, 654.43111).

[Pyridine-2,6-dicarboxylic acid *bis*-[4-(2-{4-[Tris-(4-*tert*-butylphenyl)-methyl]-phenoxy}-ethoxy)-benzylamide]

[H_2L4]



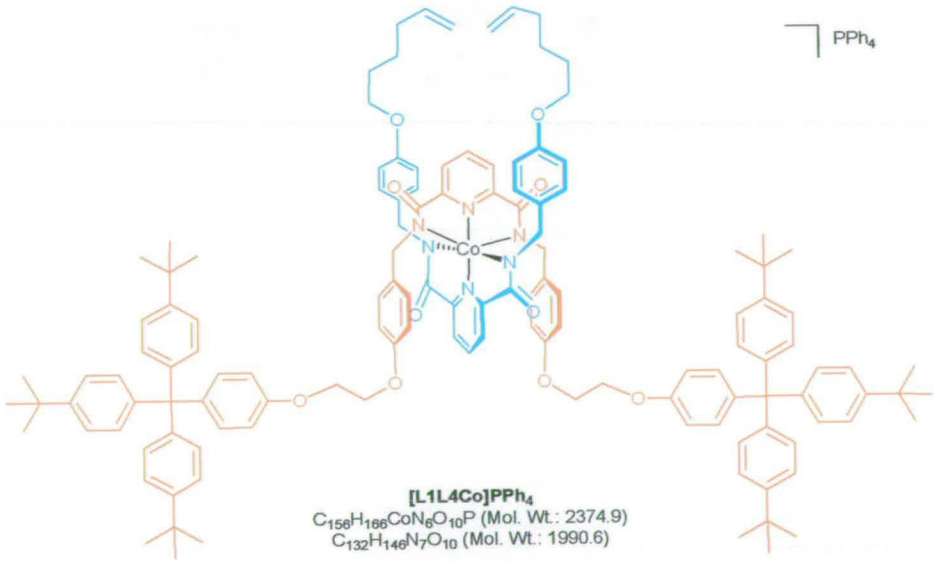
H_2L4
$C_{99}H_{111}N_3O_6$
Mol. Wt.: 1439.0

A solution of 4-(2-{4-[Tris-(4-*tert*-butylphenyl)-methyl]-phenoxy}-ethoxy)-benzylamine (3.970 g, 6.070 mmol), and triethylamine in dry dichloromethane (50 mL) was cooled to 0 °C under an atmosphere of argon. A solution of pyridine-2,6-dicarbonyl dichloride (0.619 g, 3.040 mmol) in anhydrous dichloromethane was added dropwise under argon. The reaction was stirred at 0 °C for 2 hours then it was allowed to warm to room temperature. The solvent was removed under reduced pressure and the residue dissolved in ethyl acetate. The solution was passed through a plug of silica then the solvent was removed under reduced pressure. The residue was dried in a vacuum oven overnight to yield the title compound as a white solid (4.144 g, yield = 95%). m.p. 180.3-182.1 °C; ^{1}H NMR (400 MHz; $CDCl_3$, Me_4Si, 293K): δ = 1.28 (s, 54H, $C(CH_3)_3$), 4.20 (s, 8H, $O(CH_2)_2O$), 4.51 (d, 4H, J = 6.0, CONHC$\underline{H}_2$), 6.74 (d, 4H, J = 8.8, ArH), 6.80 (d, 4H, J = 8.8, ArH), 7.06-7.09 (m, 16H, ArH), 7.16 (d, 4H, J = 8.8, ArH), 7.23 (d, 12H, J =8.8, ArH), 7.96 (t, 1H, J = 7.8, pyridyl-H), 8.23 (t, 2H, J = 6.0 CON$\underline{H}$CH$_2$), 8.33 (d, 2H, J = 7.8, piridyl-H); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si, 293K): δ = 31.8, 34.7, 42.95, 63.1,

66.2, 66.6, 113.1, 114.7, 123.8, 125.3, 129.1, 130.9, 131.0, 132.3, 139.3, 140.5, 144.5, 148.7, 149.2, 156.7, 158.5, 163.9 - LRFAB-MS (3-NOBA matrix): m/z = 1438 $[M\mathrm{H}]^+$, 1461 $[M\mathrm{Na}]^+$, HRFAB-MS (3-NOBA matrix): m/z = 1438.85059 (calcd. for $C_{99}H_{111}N_3O_6$, 1438.85064), ESI +ve: m/z = 1438 $[M\mathrm{H}]^+$.

[Pyridine-2,6-dicarboxylic acid *bis*-[4-(2-{4-[Tris-(4-*tert*-butylphenyl)-methyl]-phenoxy}-ethoxy)-benzylamide]- [*N, N'*- *bis*[4-(hex-5-enyloxy)benzyl]-2,6-pyridinedicarboxamide]cobalt(III)} tetraphenylphosphonium

[Co(L1)(L4)]PPh_4

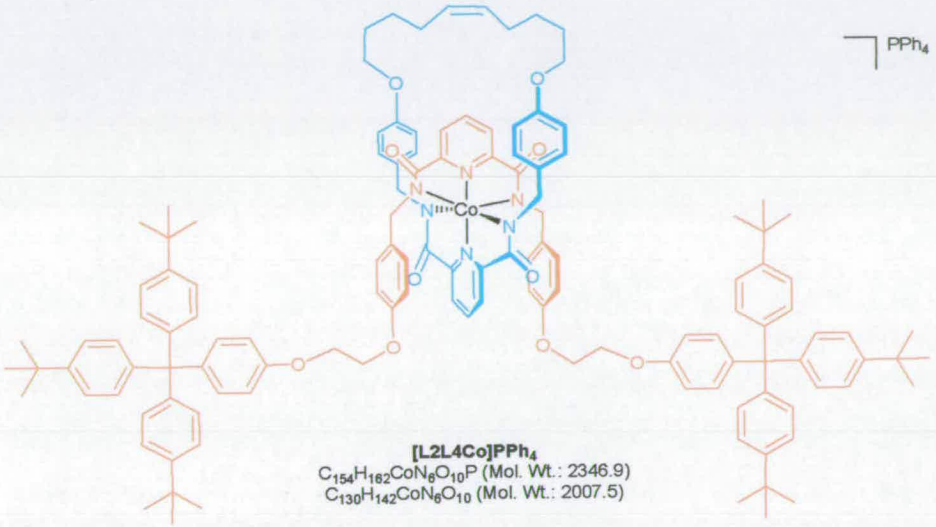


To pyridine-2,6-dicarboxylic acid *bis*-[4-(2-{4-[Tris-(4-*tert*-butylphenyl)-methyl]-phenoxy}-ethoxy)-benzylamide], H_2**L4,** (0.500 g, 0.345 mmol) and 2,6-diacetylpyridine *bis*(5-hex-5'-enyloxybenzylamide), H_2**L1,** (0.187 g, 0.345 mmol) in anhydrous dimethylformamide (100 mL) was added a suspension of 40% sodium hydride in mineral oil (0.112 g, 2.800 mmol). The reaction was stirred at room temperature under an atmosphere of nitrogen for 20 minutes and then a solution of cobalt (II) chloride

hexahydrate (0.082 g, 0.345 mmol) in anhydrous dimethylformamide (3 mL) was added to it via double ended needle technique. A colour change from blue to red-brown was observed. The reaction was stirred at room temperature under an atmosphere of nitrogen for 10 minutes then the flask was opened and the solution bubbled with compressed air for 30 minutes. A further change in colour from red to green was observed. The solvent was removed under reduced pressure and the resulting solid was stirred in ethylacetate (50 mL) with sonnicating for 60 minutes and then filtered under gravity. The resultant green solid was dissolved in dichloromethane (25 mL) and tetraphenylphoshonium chloride (0.129 0.345 mmol) was added to it and stirred for 30 minutes. The solution was filtered and the solvent removed under reduced pressure. The crude mixture was purified using column chromatography (Silica gel, 1:39:60 $Et_3N/(CH_3)_2CO/CH_2Cl_2$) to give the product as a dark green solid (0.333 g, yield = 41%). m.p. 136.5-138.4 °C; ^{1}H NMR (400 MHz, Acetone-d_6, 293K): δ = 1.12 (s, 54H, $C(CH_3)_3$) 1.37-1.42 (m, 4H, Alkyl-H), 1.54-1.60 (m, 4H, $OCH_2C\underline{H}_2$), 1.94-2.05 (m, 4H, $C\underline{H}_2CH{=}CH_2$), 3.08 (s, 4H, $CONHC\underline{H}_2$), 3.12 (s, 4H, $CONHC\underline{H}_2$), 3.71 (t, 4H, J = 6.6, OCH_2), 4.06-4.15 (m, 8H, OCH_2CH_2O), 4.77-4.91 (m, 4H, $CH{=}C\underline{H}_2$), 5.64-5.75 (m, 2H, $C\underline{H}{=}CH_2$), 6.19-6.34 (m, 16H, ArH), 6.77 (d, 4H, J = 8.8 ArH), 6.96 (d, 4H, J = 8.8 ArH), 6.99 (d, 12H, J = 8.6, ArH), 7.16 (d, 12H, J = 8.6, ArH), 7.50 (d, 2H, J = 7.8, pyridyl-H), 7.56 (d, 2H, J = 7.6, pyridy-H), 7.69-7.72 (m, 16H, PPh_4), 7.82-7.88 (m, 4H, PPh_4), 7.95 (t, 1H, J = 7.8, pyridyl-H), 8.06 (t, 1H, J = 7.6, pyridyl-H).); ^{13}C NMR (100 MHz, Acetone-d_6, 293K): δ = 26.2, 29.3, 31.7, 34.2, 34.9, 46.8, 53.5, 63.9, 67.3, 67.5, 68.2, 114.2, 114.3, 114.8, 115.0, 123.0, 123.1, 123.8, 125.1, 129.1, 129.2, 130.9, 131.0, 131.4, 131.5, 132.8, 134.2, 134.9, 136.4, 139.6, 139.7, 140.4, 145.3, 148.7, 149.1, 157.6, 157.8, 158.0, 158.6, 168.9, 170.0 - LRFAB-MS (3-NOBA matrix): m/z = 2040 $[\boldsymbol{L1L4}Co\mathrm{H}_2]^+$, HRFAB-MS (3-NOBA matrix): m/z = 2037.06353 (calcd. for $C_{132}H_{148}CoN_6O_{10}$, 2037.06225) $[\boldsymbol{L1L4}Co]^+$, ESI -ve: m/z = 2035 $[\boldsymbol{L1L4}Co]^-$

[Pyridine-2,6-dicarboxylic acid *bis*-[4-(2-{4-[Tris-(4-*tert*-butylphenyl)-methyl]-phenoxy}-ethoxy)-benzylamide]-[*bis*{[(*N,N'*-1,10-dec-5-enyloxydibenzyl)-2,6-pyridinedicarboxamido]cobalt(III)} tetraphenylphosphonium

[L2L4Co]PPh4



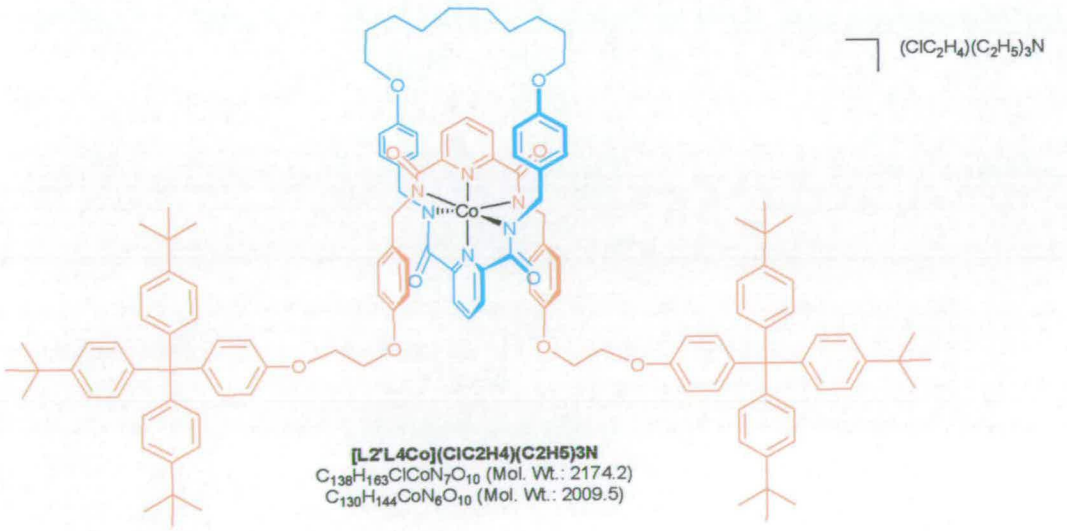
Grubbs' metathesis catalyst [Ru(=CHPh)(PCy_3)$_2Cl_2$] (0.037 g, 0.045 mmol, 20 mol %) was placed in a sealed, argon-purged, flame-dried Schlenk tube, and subjected to a constant stream of argon for ten minutes. A degassed and argon-purged solution of the **[L1L4Co]PPh$_4$** complex (0.532 g, 0.224 mmol) in anhydrous dichloromethane (500 mL) was transferred to the Schlenk tube by injection over ten minutes. Reaction was allowed to continue until all the starting material was consumed as evidenced by TLC (typically 1 day). 2 mL of methanol were added to the resulting solution, which was then evaporated to dryness and purified by chromatography (Silica gel, 1:39:60 $Et_3N/(CH_3)_2CO/CH_2Cl_2$) to yield the title compound as a green solid (0.379 g, yield = 72%). m.p. 165 °C (dec); ^{1}H NMR (400 MHz, Acetone-d_6, 293K): δ = 1.15 (s, 54H, $C(CH_3)_3$), 1.33-1.39 (m, 4H, Alkyl-H), 1.55-1.60 (m, 4H, $OCH_2C\underline{H}_2$), 1.94-2.11 (m, 4H, $C\underline{H}_2CH{=}CH_2$), 3.10 (d, 4H, J = 9.6, $CONHC\underline{H}_2$), 3.22 (s, 4H, $CONHC\underline{H}_2$), 3.81 (m, 4H, OCH_2), 4.08-4.14 (m, 8H, OCH_2CH_2O), 5.26 (t, 1.1H, J = 4.5, CH=CH trans) 5.44 (t,

0.9H, J = 3.8, CH=CH cis), 5.97-6.01 (m, 4H, ArH), 6.18-6.21 (m, 4H, ArH), 6.32-6.41 (m, 8H, ArH), 6.76 (d, 4H, J = 8.8 ArH), 6.95 (d, 4H, J = 8.8 ArH), 6.98 (d, 12H, J = 8.6, ArH), 7.16 (d, 12H, J = 8.6, ArH), 7.32 (d, 2H, J = 7.6, pyridyl-H), 7.61-7.66 (m, 2H, pyridyl-H), 7.69-7.72 (m, 16H, PPh_4), 7.82-7.88 (m, 4H, PPh_4), 8.03 (q, 1H, J = 8.3, pyridyl-H); ^{13}C NMR (100 MHz, Acetone-d_6, 293K): δ = 26.2, 29.3, 31.2, 34.8, 36.4, 46.9, 55.0, 63.9, 67.4, 67.5, 68.10, 114.1, 114.6, 115.1, 118.5, 119.4, 122.5, 124.7, 125.5, 129.3, 130.1, 131.4, 131.5, 131.7, 131.9, 132.8, 134.4, 135.7, 136.4, 138.7, 139.4, 140.4, 145.3, 149.1, 157.0, 157.5, 158.8, 159.4, 169.1, 169.2 - LRFAB-MS (3-NOBA matrix): m/z = 2010 $[L1L4CoH_2]^+$, HRFAB-MS (3-NOBA matrix): m/z = 2008.02607 (calcd. for $C_{130}H_{143}CoN_6O_{10}P$, 2008.02313) [*L1L4Co*H], ESI -ve: m/z = 2008 $[L1L4Co]^-$

.

[Pyridine-2,6-dicarboxylic acid *bis*-[4-(2-{4-[Tris-(4-*tert*-butylphenyl)-methyl]-phenoxy}-ethoxy)-benzylamide]-[Pyridine-2,6-dicarboxylic acid 1,10-di(4-phenoxymethylamide)decane]cobalt(III)} tetraphenylphosphonium

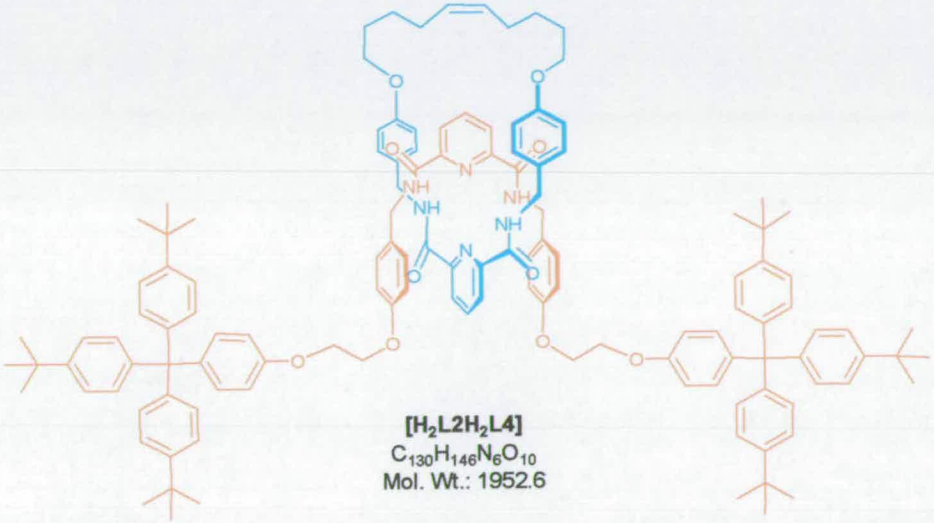
$[L2'L4Co](ClC_2H_4)(C_2H_5)_3N$



To **[L2'L4Co]PPh4** (0.059 g, 0.025 mmol) in anhydrous methanol(30 mL) was added 10% w/w Pd-C (0.010 g) and was stirred under an atmosphere of H_2 for 18 h. The Pd-C was then removed by filtration through a plug of Celite, and the solvent was removed under reduced pressure. The crude mixture was purified using column chromatography (Silica gel, 1:39:60 $Et_3N/(CH_3)_2CO/CH_2Cl_2$) to give the product as a dark green solid.(0.022g, yield = 89%). m.p. 160-175 °C (dec); ^{1}H NMR (400 MHz, Acetone-d_6, 293K): δ= 1.15 (s, 54H, $C(CH_3)_3$), 1.16 (t, 9H, J = 7.3, $C\underline{H}_3CH_2N$), 1.34-1.39 (m, 12H, Alkyl-H), 1.57 (t, 2H, J = 6.3, $ClCH_2C\underline{H}_2N$), 1.53-1.60 (m, 4H, $OCH_2C\underline{H}_2$), 1.92 (m, 9H, $C\underline{H}_3CH_2N$), 3.04 (q, 6H, J = 7.3, $CH_3C\underline{H}_2N$), 3.17 (d, 4H, J = 9.6, $CONHC\underline{H}_2$), 3.24 (s, 4H, $CONHC\underline{H}_2$), 3.79 (m, 4H, OCH_2), 3.80 (t, 2H, J = 6.3, $ClC\underline{H}_2CH_2N$), 4.03-4.12 (m, 8H, OCH_2CH_2O), 6.00 (d, 4H, J = 8.6, ArH), 6.23 (d, 4H, J = 8.8, ArH), 6.34 (d, 4H, J = 8.6, ArH), 6.42 (d, 4H, J = 8.6, ArH), 6.71 (d, 4H, J = 8.8 ArH), 6.93 (d, 4H, J = 8.6 ArH), 6.97 (d, 12H, J = 8.6, ArH), 7.14 (d, 12H, J = 8.6, ArH), 7.34 (d, 2H, J = 7.6, pyridyl-H), 7.71 (d, 2H, J = 7.6, pyridyl-H), 7.85 (t, 1H, J = 8.3, pyridyl-H), 7.94 (t, 1H, J = 8.3, pyridyl-H); ^{13}C NMR (100 MHz, Acetone-d_6, 293K): δ = 9.53, 26.3, 27.7, 28.9, 29.0, 31.7, 34.9, 42.8, 42.9, 46.8, 50.9, 63.9, 67.4, 67.5, 67.80, 114.1, 115.8, 122.8, 125.4, 125.7, 128.3, 128.4, 129.6, 129.8, 130.1, 131.1, 131.4, 131.5, 132.6, 140.3, 140.4, 142.2, 145.3, 149.0, 149.1, 157.7, 157.7, 158.9 - LRFAB-MS (3-NOBA matrix): m/z = 2011 $[\mathbf{L1'L4}CoH_2]^+$, HRFAB-MS (3-NOBA matrix): m/z = 2011.04660 (calcd. for $C_{130}H_{146}CoN_6O_{10}$, 2011.04735) $[\mathbf{L1'L4}CoH_2]^+$, ESI -ve: m/z = 2009 $[\mathbf{L1'L4}Co]^-$.

[Pyridine-2,6-dicarboxylic acid *bis*-[4-(2-{4-[Tris-(4-*tert*-butylphenyl)-methyl]-phenoxy}-ethoxy)-benzylamide]-[*bis*{[(*N,N'*-1,10-dec-5-enyloxydibenzyl)-2,6-pyridinedicarboxamido]

[H_2L2H_2L4]



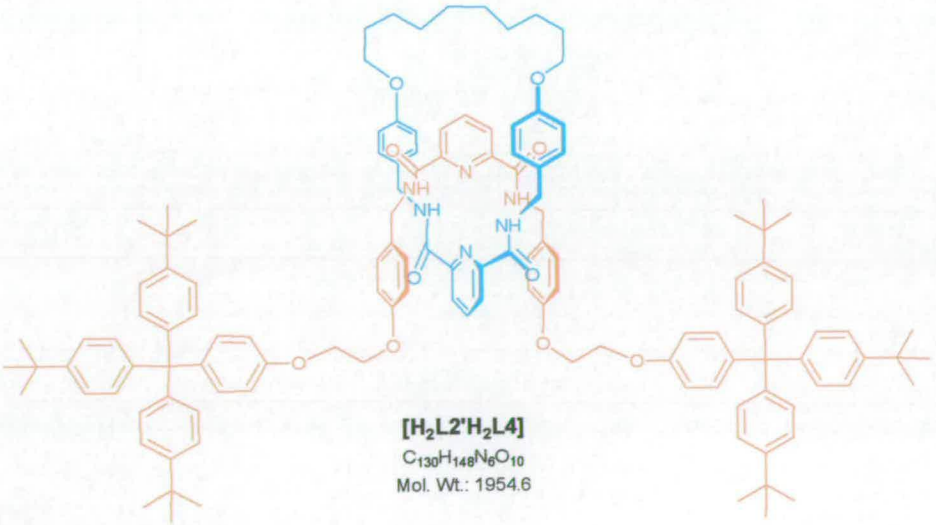
[H_2L2H_2L4]
$C_{130}H_{146}N_6O_{10}$
Mol. Wt.: 1952.6

To **[L2L4Co]PPh_4** (0.117 g, 0.050 mmol) in anhydrous methanol (20 mL) was added zinc powder (0.005 g, 0.077 mmol) and glacial acetic acid (0.5 mL). The reaction was stirred at room temperature in aerobic conditions for 20 minutes. A change in colour from green to pale pink was observed. The suspension was filtered through a plug of Celite and the filtrate was added dropwise to an aqueous sodium carbonate solution stirring on top of a chloroform layer: the product precipitated out of solution in the form of white powder (0.095 g, yield = 97%). m.p. 140-144 °C; ^{1}H NMR (400 MHz, Acetone-d_6, 293K): δ = 1.29 (s, 54H, $C(CH_3)_3$) 1.36-1.49 (m, 4H, Alkyl-H), 1.58-1.68 (m, 4H, $OCH_2C\underline{H}_2$), 1.94-2.05 (m, 4H, $C\underline{H}_2CH{=}CH_2$), 3.61 (t, J = 6.6, 2H, $OC\underline{H}_2CH_2O$), 3.75 (t, 2H, J = 6.6, $OC\underline{H}_2CH_2O$), 3.78-3.88 (m, 3H, $PhOC\underline{H}_2$) 3.90-4.01 (s, 5H, $PhOC\underline{H}_2$), 4.36 (t, 4H, J = 5.2, $CONHC\underline{H}_2$), 4.42 (t, 4H, J = 4.5, $CONHC\underline{H}_2$), 4.06-4.15 (m, 8H,), 5.30-5.41 (m, 4H, $C\underline{H}{=}C\underline{H}$), 6.20 (d, 4H, J = 8.6, ArH), 6.41 (d, 4H, J = 8.6, ArH), , 6.44 (d, 4H, J = 8.6, ArH), 6.58 (d, 4H, J = 8.6, ArH), 6.66 (d, 4H, J = 8.6, ArH),

6.83 (d, 4H, J = 8.6, ArH), 7.03 (d, 12H, J = 8.4, ArH), 7.16 (d, 12H, J = 8.4, ArH), 7.74 (t, 1H, J = 7.8, pyridyl-H), 7.81 (t, 1H, J = 7.6, pyridyl-H), 8.18 (d, 2H, J = 7.8, pyridyl-H), 8.25 (d, 2H, J = 7.6, pyridy-H), 8.39 (t, 16H, J = 5.6, CONHCH$_2$), 8.48 (t, 4H, J = 5.6, CONHCH$_2$); **(NB: Some signals appear to be doubled due to near 1:1 *cis- trans*-product ratio.)** ^{13}C NMR (100 MHz, Chloroform-d, 293K): δ = 25.3, 25.8, 31.4, 34.3, 42.9, 43.0, 43.3, 63.0, 65.8, 66.0, 67.0, 113.6, 114.2, 124.1, 125.5, 125.6, 128.9, 129.9, 130.1, 130.4, 130.6, 132.2, 138.8, 140.2, 144.0, 148.3, 149.0, 149.1, 155.7, 157.3, 157.6, 163.5, 163.7 - LRFAB-MS (3-NOBA matrix): m/z = 514 [**L2**H$_3$]$^+$, 1440 [**L3**H$_3$]$^+$, 1953 [H$_2$**L2**H$_2$L3H]$^+$, HRFAB-MS (3-NOBA matrix): m/z =1952.11678 (calcd. for $C_{130}H_{146}N_6O_{10}$, 1952.11340), ESI -ve: m/z = 1951 [H**L2**H$_2$**L3**]$^-$.

[Pyridine-2,6-dicarboxylic acid *bis*-[4-(2-{4-[Tris-(4-*tert*-butylphenyl)-methyl]-phenoxy}-ethoxy)-benzylamide]-[Pyridine-2,6-dicarboxylic acid 1,10-di(4-phenoxymethylamide)decane]

H$_2$L2'H$_2$L4



[H$_2$L2'H$_2$L4]
$C_{130}H_{148}N_6O_{10}$
Mol. Wt.: 1954.6

To **[H_2L2H_2L4]** (0.109 g, 0.050 mmol) in anhydrous methanol (30 mL) was added 10% w/w Pd-C (0.015 g) and was stirred under an atmosphere of H_2 for 18 h. The Pd-C was then removed by filtration through a plug of Celite, and the solvent was removed under reduced pressure. The crude mixture was purified using column chromatography (Silica gel, 1:39:60 $Et_3N/(CH_3)_2CO/CH_2Cl_2$) to give the product as a white solid. (0.093 g, yield = 95%). m.p. 135-140 °C; ^{1}H NMR (400 MHz, Acetone-d_6, 293K): δ = 1.22-1.34 (m, 8H, Alkyl-H), 1.29 (s, 54H, $C(CH_3)_3$), 1.37-1.46 (m, 4H, Alkyl-H), 1.58-1.67 (m, 4H, $OCH_2C\underline{H}_2$), 3.60 (t, J = 6.6, 2H, $OC\underline{H}_2CH_2O$), 3.75 (t, 2H, J = 6.6, $OC\underline{H}_2CH_2O$), 3.78-3.88 (m, 3H, $PhOC\underline{H}_2$) 3.90-4.01 (s, 5H, $PhOC\underline{H}_2$), 4.36 (t, 4H, J = 5.2, $CONHC\underline{H}_2$), 4.42 (t, 4H, J = 4.5, $CONHC\underline{H}_2$), 4.05-4.13 (m, 8H,), 6.45 (d, 4H, J = 8.6, ArH), 6.54 (d, 4H, J = 8.6, ArH), , 6.75 (d, 4H, J = 8.6, ArH), 6.86 (d, 4H, J = 8.6, ArH), 6.92 (d, 4H, J = 8.6, ArH), 6.99 (d, 4H, J = 8.6, ArH), 7.03 (d, 12H, J = 8.4, ArH), 7.16 (d, 12H, J = 8.4, ArH), 7.74 (t, 1H, J = 7.8, pyridyl-H), 7.81 (t, 1H, J = 7.6, pyridyl-H), 8.18 (d, 2H, J = 7.8, pyridyl-H), 8.25 (d, 2H, J = 7.6, pyridy-H), 8.39 (t, 16H, J = 5.6, $CONHCH_2$), 8.48 (t, 4H, J = 5.6, $CONHCH_2$); ^{13}C NMR (100 MHz, Chloroform-d, 293K): δ = 13.4, 25.3, 25.7, 26.3, 31.2, 34.2, 42.9, 43.1, 43.4, 63.0, 65.8, 66.1, 67.0, 113.5, 114.2, 124.1, 125.6, 125.7, 128.9, 129.9, 130.0, 130.4, 130.5, 138.9, 140.2, 144.1, 148.3, 149.1, 149.1, 155.7, 157.4, 157.6, 163.7, 163.8 - LRFAB-MS (3-NOBA matrix): m/z = 516 [**L2**H_3]$^+$, 1440 [**L3**H_3]$^+$, 1955 [H_2**L2**H_2L3H]$^+$, HRFAB-MS (3-NOBA matrix): m/z = 1954.13411 (calcd. for $C_{130}H_{149}N_6O_{10}$, 1954.13352), ESI -ve: m/z = 1953 [H**L2**H_2**L3**]$^-$.

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[28] Another potential interpretation assigns different resonances to couple of protons adjacent to the same carbon. At each time, one aromatic ring from each original "u-shape" ligand is engaged in π-stacking with the pyridine unit while the other is twisted nearly perpendicularly to it. Π-stacking augments the electron density on the aromatics and the benzylic groups therefore inducing an upfield shift; on the other side, the aromatic perpendicular to the pyridine unit, experience a negligible effect and it resonates similarly to the free ligand.

[29] ***X*-ray crystallographic structure determination,** **[L3'Co](C_2H_4Cl)(C_2H_5)$_3$N**: $C_{70}H_{86}ClCoN_7O_8$, M = 1247.84, green prism, 0.20 × 0.08 × 0.08 mm, orthorhombic, $P2_12_12_1$, a = 14.142(4), b = 20.476(7), c = 23.569(11) Å, V = 6825(4) Å^3, Z = 4, ρ_{calcd} = 1.214 mg m^{-3}; $Mo_{K\alpha}$ radiation (graphite monochromator, λ = 0.71073 Å), μ = 0.348 mm^{-1}, T = 93(2) K. 42876 data (12313 unique, R_{int} = 0.0709, 1.75 < θ < 25.35°), were collected on a Bruker SMART CCD diffractometer using narrow frames (0.3° in ω), and

were corrected semiempirically for absorption and incident beam decay. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 values of all data (G. M. Sheldrick, SHELXTL manual, Bruker AXS, Madison WI, USA, 1994, version 5) to give $wR = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2} = 0.3125$, conventional $R = 0.1138$ for F values of 12313 reflections with $F_o > 4\sigma(F_o)$, $S = 1.066$ for 812 parameters. Residual electron density extremes were 0.821 and –0.610 eÅ^{-3}. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-229418. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk.

[30] The counterion tetraphenylphosphonium, chosen in the first place to help solubility, was replaced with tetraethylammonium to assist crystallization.

[31] J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle, *Comprehensive Supramolecular Chemistry*, Elsevier, NY, **1996** (Volume 1).

[32] *X*-ray crystallographic structure determination, [2]Catenand $[H_2\mathbf{L2'}]_2$: C_{66} H_{80} N_8 O_8, M = 1113.38, colourless prism, 0.20 x 0.20 x 0.20 mm^3, Triclinic, P_{212121}, a = 10.2200(14) Å, b = 15.396(3) Å, c = 19.845(3) Å, V = 3005.8(8) Å^3, Z = 2, ρ_{calcd} = 1.230 mg m^{-3}; $Mo_{K\alpha}$ radiation (graphite monochromator, λ = 0.71073 Å), μ = 0.082 mm^{-1}, T = 93(2) K. 10447 data (10447 unique, R_{int} = 0.0210, 2.03° < θ < 25.35°), were collected on a Bruker SMART CCD diffractometer using narrow frames (0.3° in ω), and were corrected semiempirically for absorption and incident beam decay. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 values of all data (G. M. Sheldrick, SHELXTL manual, Bruker AXS, Madison WI, USA, 1994, version 5) to give $wR = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2} = 0.3125$, conventional $R = 0.1138$ for F values of 12313 reflections with $F_o > 4\sigma(F_o)$, $S = 1.066$ for 812 parameters. Residual

electron density extremes were 0.821 and –0.610 eÅ^{-3}. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-229418. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk.

[33] H. W. Gibson, S-H. Lee, P. T. Engen, P. Lecavalier, J. Sze, Y. X. Shen and M. Bheda, *J. Org. Chem.*, **1993**, *58*, 3748-3756.

[34] A) B. Almarzoqi, A. V. George and N. S. Isaacs, *Tetrahedron*, **1986**, *42*, 601-607; B) R. Erra-Balsells, A. R. Frasca, *Aust. J. Chem.*, 1988, *41*, 103-110.

Chapter Four

Synthesis of Penta-coordinate Zinc(II) and Cadmium(II) [2]Rotaxanes

"Creativity is...seeing something that doesn't exist already. You need to find out how you can bring it into being and that way be a playmate with God"
Michele Shea

.... And that's what I enjoyed the most in a Synthetic Lab.!
Ale: Thoughts on my Ph.D. work (2001-2004)

Chapter 4. Synthesis of Penta-coordinate Zinc(II) and Cadmium(II) [2]Rotaxanes.

4.1. Abstract

In this work we describe the synthesis of [2]rotaxanes with metal centres (Zn^{2+} and Cd^{2+}) that can adopt pentacoordinate geometry as templates. Two strategies were investigated. In the threading approach a tridentate macrocycle is reacted with a linear synthon incorporating a bipyrirdyl unit and cadmium(II) perchlorate to give the pseudo-rotaxane. Both ends of the thread are then functionalised with bulky stoppers, via the Mitsunobu reaction, to give the desired mechanically interlocked architecture. Attempts carried out with zinc(II) perchlorate afforded unintertwined thread due to fast ligand exchange, characteristic of this metal.

In the clipping approach the macrocycle self-assembles through Schiff base condensation reactions around a preformed metal-thread complex. Zinc(II) perchlorate reacts promptly with the free ligands to form the kinetic product, the 5-coordinate rotaxane; this compound converts over a period of 12 hours into the more stable octahedral hexacoordinate [2]catenate. Cadmium(II) perchlorate on the contrary reacts in a more slow fashion to generate directly the thermodynamic product.

4.2. Introduction

The importance of pentacoordinate metal complexes has been stressed in reaction intermediates of a variety of metal enzymes.[1] The synthesis of new aza-macrocycles mimicking biologically occurring macrocyclic ligands and their complexes has attracted

much attention not only from a biological standpoint but also because of the potential applications in area such as electrocatalysis and electrochemical corrosion.[2] In a recent paper, Adams and Najera discuss the pentacoordinate complexes forming interactions of Cu(II), Ni(II), Ag(I), Zn(II) and Pb(II) with a pyridinyl-derived macrocycle (**Figure 1**).[3]

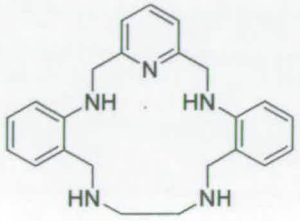


Figure 1: Adams' and Najera's macrocycle.

Comparison between the complexes obtained with the different metals proved that "*a priori*" arguments are unreliable in predicting the geometry of a particular complex".[3] In fact, the number of counter ions and the stereochemical requirements of chelating ligands are crucial features in defining the specific geometry of these pentacoordinate complexes which can range from distorted square-pyramidal, like in the silver complex, to distorted trigonal-bipyramidal, like with zinc, and again to an even more distorted structure where the lead metal, being too large to fit the cavity, is placed out of the main plane with the macrocycle sitting on one side and the anions sitting on the other (**Figure 2**).

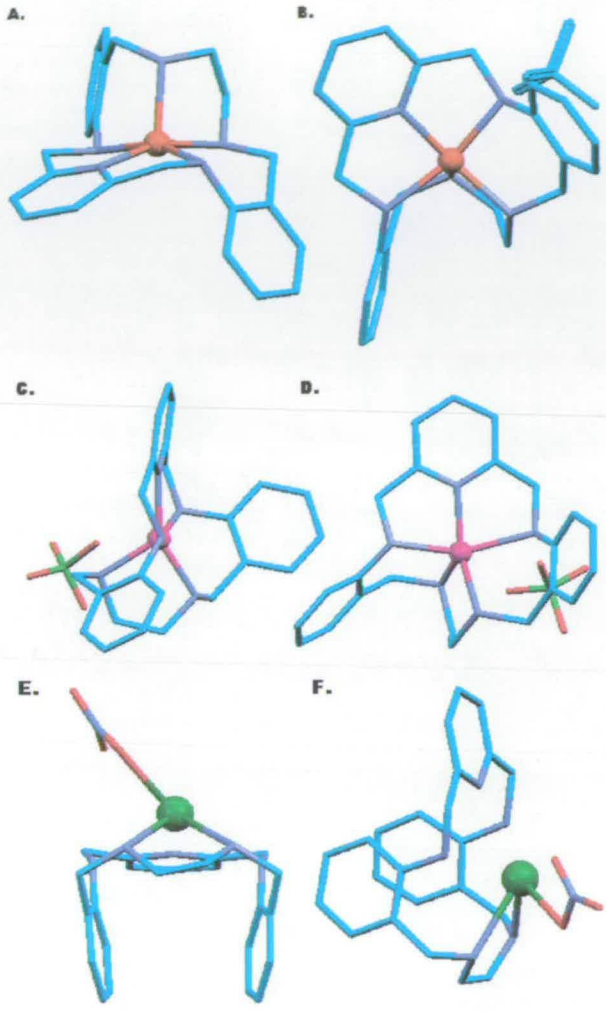


Figure 2: X-ray crystallography of Adams' and Najera's distorted square-pyramidal silver complex, A. and B., zinc distorted trigonal-bipyramidal complex, C. and D., and "out-of-the-plane" lead complex, E. and F..

The flexibility and relative unpredictability of the pentacoordinate geometry, as well as the kinetically unstable nature of the corresponding complexes has accounted for its lower usage in the development of mechanically interlocked architectures. The first examples of rotaxanes containing a pentacoordinate motif were reported by Sauvage *et al.* in 1999.

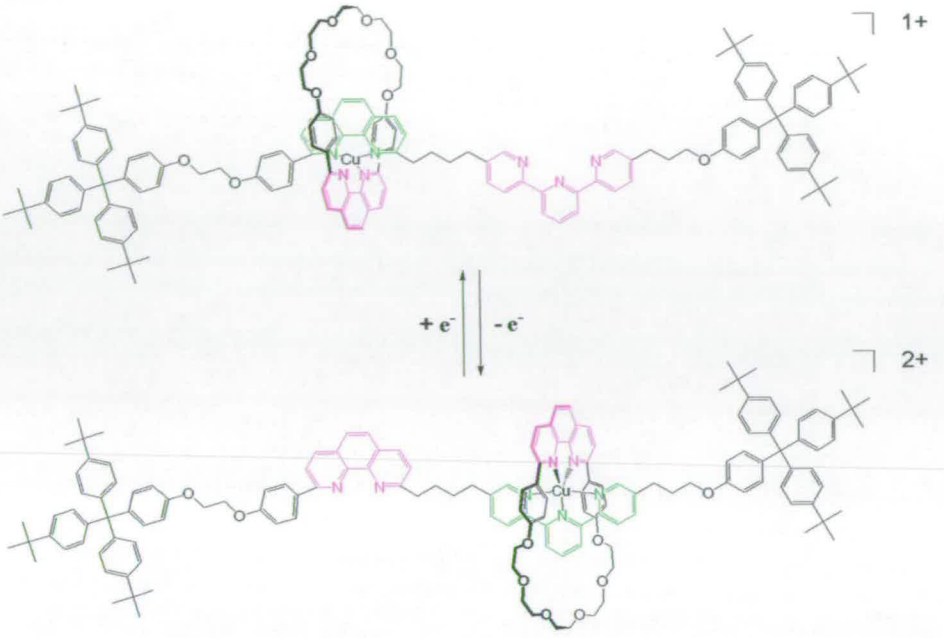


Figure 3: Sauvage's copper based redox-responsive [2]rotaxane presenting a thread derivatised with a bidentate and a tridentate station.

In the *J.A.C.S.* paper they presented the metal based redox-responsive molecular shuttle where the different preferred coordination number, respectively 4 and 5 for copper(I) and copper(II), is exploited to induce movement of the macrocycle along the thread. In this [2]rotaxane, (**Figure 3**), a phenanthroline derivatised macrocycle provides a bidentate ligand for the coordination sphere surrounding the metal. The thread bears two coordinating units, a bidentate phenanthroline and a tridentate terpyridine. Reduction and oxidation of the metal generates systems with the mentioned different preferred coordination number. Satisfaction of such coordination requirements is achieved selectively binding to either one of the two stations built in the thread. While adjusting to the appropriate geometry the macrocycle achieves controlled large-amplitude molecular motion.[4]

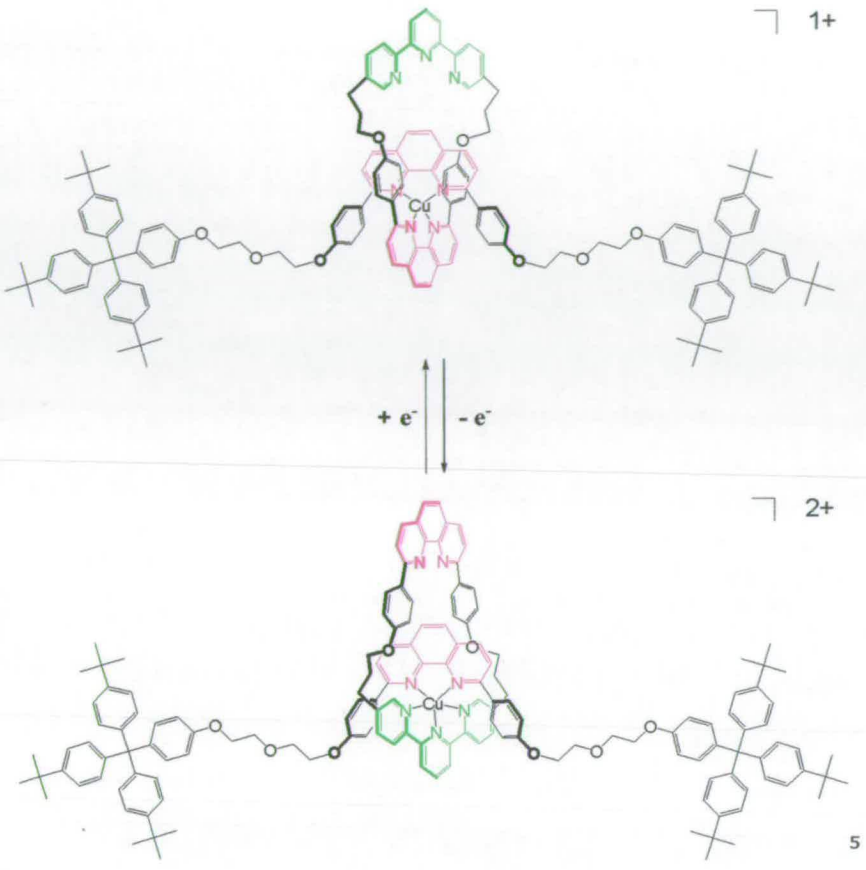


Figure 4: Sauvage's redox-responsive [2]rotaxane presenting a macrocycle derivatised with a bidentate and a tridentate station.

The very same principle was used to develop a system where the macrocycle carries two stations, a bidentate phenanthroline and a tridentate terpyridine, while the thread is functionalised only with a phenanthroline moiety (**Figure 4**). Rather than shuttling, reduction and oxidation of the metal induces controlled pirouetting of the macrocycle around the thread.[6]

While the examples shown in **Figure 3** and **Figure 4** yield architectures mechanically interlocked about a pentacoordinate geometry, this specific motif is not actually used as a template to direct the synthesis of such systems. The assembly of the macrocyclic and

unstoppered thread units takes place using Sauvage's tetrahedral copper(I) *bis*-phenanthroline synthons.

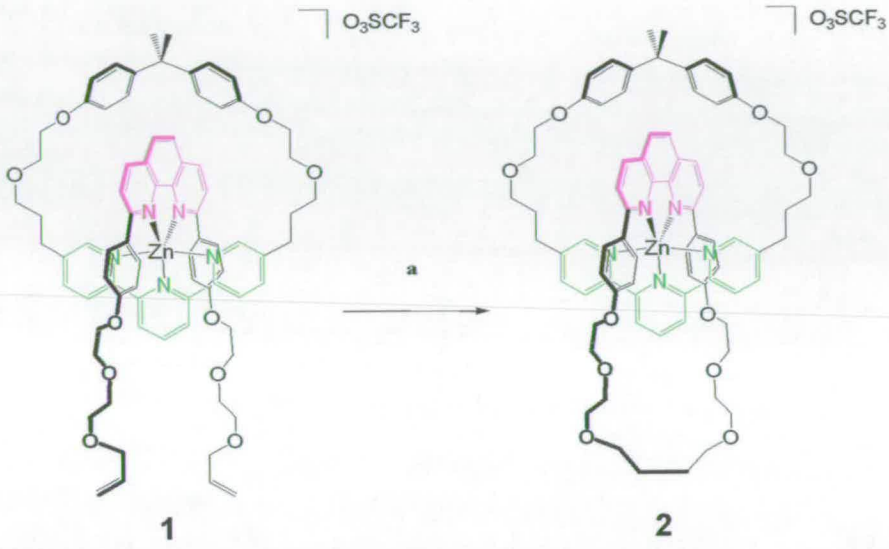


Figure 5: First example of template directed synthesis about a pentacoordinate metal: zinc(II) [2]catenate consisting of two different cycles, containing with a bidentate and a tridentate ligand respectively. Reagents and conditions: a) Grubbs' catalyst, CH_2Cl_2, RT, b) H_2/Pd-C, MeOH, RT.

The first example of using a 5-coordinate metal as a template for synthesising a mechanically interlocked system came once again from the Strasbourg group in 2003.[7] They presented the assembly of a [2]catenate consisting of two different macrocycles, one bidentate and the other tridentate (**Figure 5**, 2). While zinc is known to form quite stable pentacoordinate complexes with nitrogen containing ligands, the formation of hexacoordinate complexes remains favoured. To prevent two tridentate ligands from assembling about a single zinc atom, an endotopic tridentate terpyridine unit was incorporated into a macrocycle. The formation of the pentacoordinate complex **1** was therefore obtained via threading of a bidentate ligand through the pre-formed zinc macrocycle complex; a clipping reaction between the appropriately derivatised ends of the "u-shape" ligand then delivered the corresponding catenate. The zinc(II) preferred

coordinate geometry prevented the formation of tetracoordinate complexes between two bidentate open-ended ligands. Grubbs' catalyst mediated ring closing metathesis on the "u-shape" terminal olefins generated the desired catenate. The catenate carrying the double bond is reported to be quite unstable and easily demetalated. Hydrogenation of the double bond generated catenate **2** with an overall yield of 40%.

The aim of this project was to synthesise [2]rotaxanes by template directed synthesis about a pentacoordinate metal. To the best of our knowledge this had not been done or reported. This endeavour represented another step ahead towards the investigation of the construction of mechanically interlocked architectures about a range of diverse metals, moving from octahedral 6-coordinate to 5-coordinate motifs (**Figure 6**).

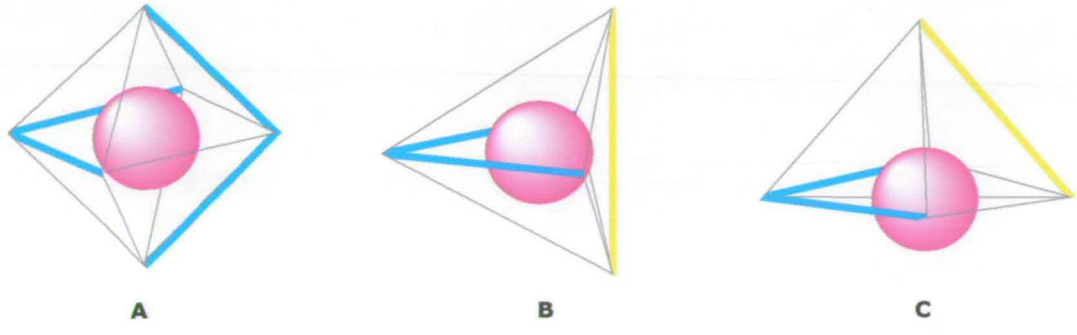


Figure 6: The progression from (a), octahedral 6-coordinate motif, to (b), 5-coordinate trigonalbipyramidal, and, (c), Square-pyramidal.

4.3. Results and Discussion

The system design exploited the tridentate macrocyclic ligands developed and studied for the chemistry involving mechanically interlocked architectures about hexacoordinate metals with octahedral geometry, as described in Chapter 2 (**Figure 7**). For the very

same argument discussed with the 5-coordinate [2]catenate with regard to the competing formation of hexacoordinate complexes, the tridentate station had to be placed within the macrocycle. The thread, derivatised with a bidentate station, provided the proper number of nitrogens to create a pentacoordinating environment. A 5,5'-disubstituted-2,2'-bipyridine unit was the bidentate station selected.

Two different synthetic paths were conceived to potentially deliver the desired rotaxane. The first strategy involved a clipping approach whereby an imine-based macrocycle self-assembled through Schiff base condensation around the preformed metal-thread complex (**Figure 7**, a.). On the other hand, the insertion of an unstoppered thread into a preformed macrocycle-metal complex followed by reaction with a bulky stopper to prevent slippage (threading and capping approach) offered an alternative method to the construction of the interlocked system (**Figure 7**, b.).

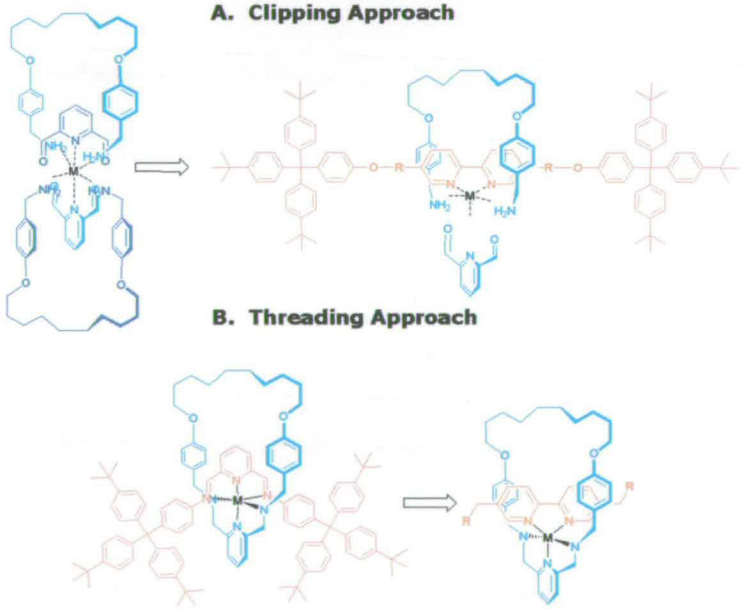


Figure 7: Pentacoordinate [2]rotaxane design using ligands developed for octahedral geometry: A) Imine-based *clipping* approach: the macrocycle *self*-assembles about the metal and the thread through Schiff base condensation; B)

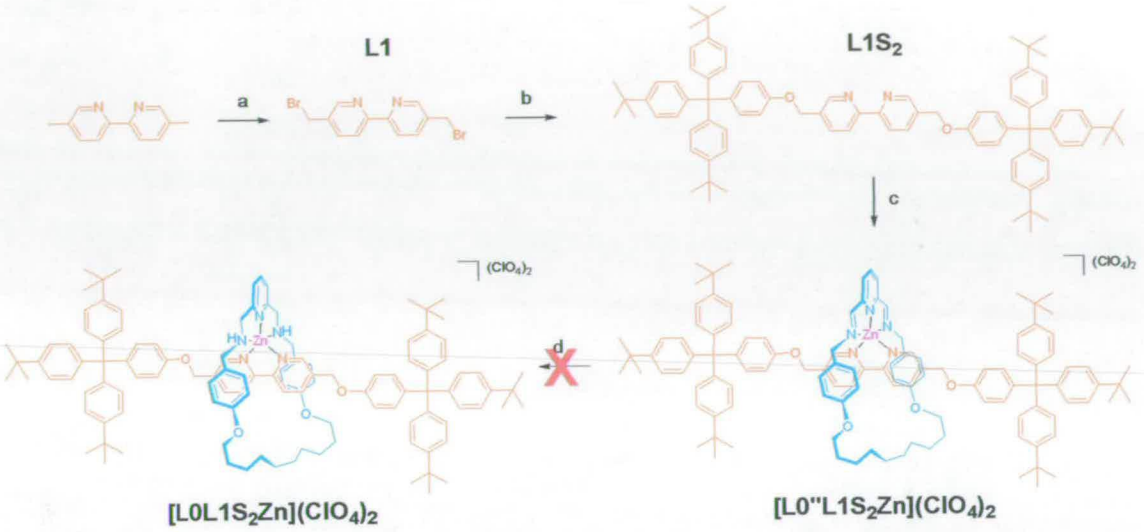
Amine-based *threading* approach: an unstoppered thread slip through a preformed macrocycle-metal complex.

4.3.1. Thread *L1S₂*

The Clipping Approach – 1.

In order to proceed with a clipping approach the thread was synthesised in advance. {4-[5'-(4-Hydroxymethyl-phenoxymethyl)-[2,2']bipyridinyl-5-ylmethoxy]-phenyl}-methanol, **L1S₂**, was the first and simplest bipyridyl thread made. It was prepared in three steps from readily available materials (**Scheme 1**, a. – b.). 5,5'-Dimethyl-[2,2']dipyridyl was reacted with N-bromosuccinimide in the presence of 2,2'-azo-*bis*-isobutyronitrile and irradiated with white light for four hours to give 5,5'-*bis*-bromomethyl-[2,2']bipyridyl, **L1**, according to a literature procedure.[8] Initial attempts to substitute the bromine atoms with the stopper, 4-[Tris-(4-*tert*-butyl-phenyl)-methyl]-phenol, **S**, under under Williamson ether conditions - i.e. reacting with potassium carbonate in ethylmethylketone catalysed by sodium iodide - were unsuccessful[9] leading to procedures using stronger bases and higher temperatures. The thread was finally obtained by reaction with sodium hydride in dimethylformamide as a white solid in a 46% yield. Complexation of **L1S₂** with zinc(II)perchlorate in the presence of 1,10-decoxybis(4-benzylamine) and 2,6-diformylpyridine in a mixture of dichloromethane and methanol lead to the formation of complex, **[L0"L1S₂Zn]**$(ClO_4)_2$ as detected from ESI-mass spectrometry, (m/z = 1835), where **L0** is the imine macrocycle. Any attempt of isolation and purification of the product failed and no acceptable NMR spectrum of this system was recorded. Sodium borohydride reduction of the imine double bond to kinetically stabilise the rotaxane was attempted: NMR spectrum of the crude confirmed the loss of the imine protons, yet isolation of the clean rotaxane was not achieved despite

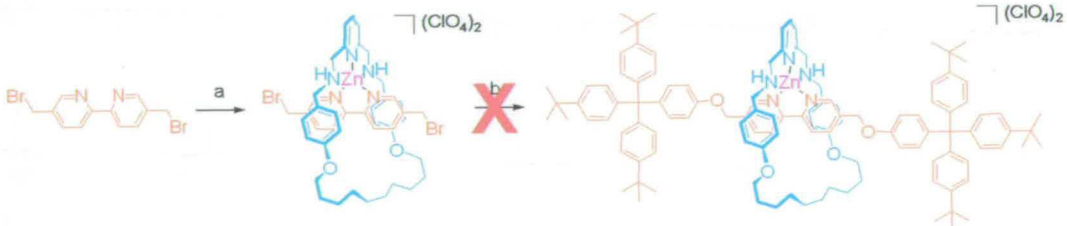
the different purification strategies attempted. ESI-mass spectrometry revealed no peaks corresponding to the reduced rotaxane.



Scheme 1: Synthesis of ligand **L1S$_2$** and formation of pentacoordinate complex [**L0"L1S$_2$**Zn](ClO$_4$)$_2$. Reagents and conditions: a) N-bromosuccinimide, AIBN, benzene, hλ, 4 h, 52%, b) NaH, **S**, DMF, reflux, 10 h, 46%, c) 1,10-decoxybis(4-benzylamine) and 2,6-diformylpyridine, Zn(ClO$_4$)$_2$·6H$_2$O, CH$_2$Cl$_2$/MeOH, RT, 2 h, d) NaH$_4$, MeOH, 120 min.

The Threading Approach - 1

In the threading and capping approach the unstoppered ligand **L1** and N,N'-2,6-dimethylpyridyl[(1,10-decoxybis(4-benzylamine)], **L0**, underwent complexation with zinc(II)perchlorate giving what is commonly known as a pseudo-rotaxane, (**Scheme 2**, a.).



Scheme 2: Formation of pentacoordinate pseudo-rotaxane [**L0L1**Zn](ClO$_4$)$_2$ and *capping* reaction. Reagents and conditions: a) **L1**, Zn(ClO$_4$)$_2$·6H$_2$O, CH$_2$Cl$_2$/MeOH, 2 h, 99%, b) NaH, **S**, DMF, reflux, 2 h.

Partial ^{1}NMR spectra (400 MHz, $CDCl_3$, 298 K) of i) free macrocycle, ii) pseudo-rotaxane and iii) ligand **L1** are shown in **Figure 8**. Comparison between the three clearly points to metal coordination and threading, confirming the formation of the pseudo-rotaxane: the pyridine protons, H_A and H_B, are shifted downfield. The broadening of the bipyridyl resonances, H_a H_b and H_c , suggests rapid exchange between free and complexed form. Shielding of the benzylic aromatic rings (H_E and H_F) as well as of the bipyridyl protons is indicative of extensive intercomponent π-stacking due to the threaded architecture in solution. The singlets due to the benzylic protons of the macrocycle, H_C and H_D, present a downfield shift of almost 0.5 ppm because of the deshielding environment caused by the nearby positively charged metal.

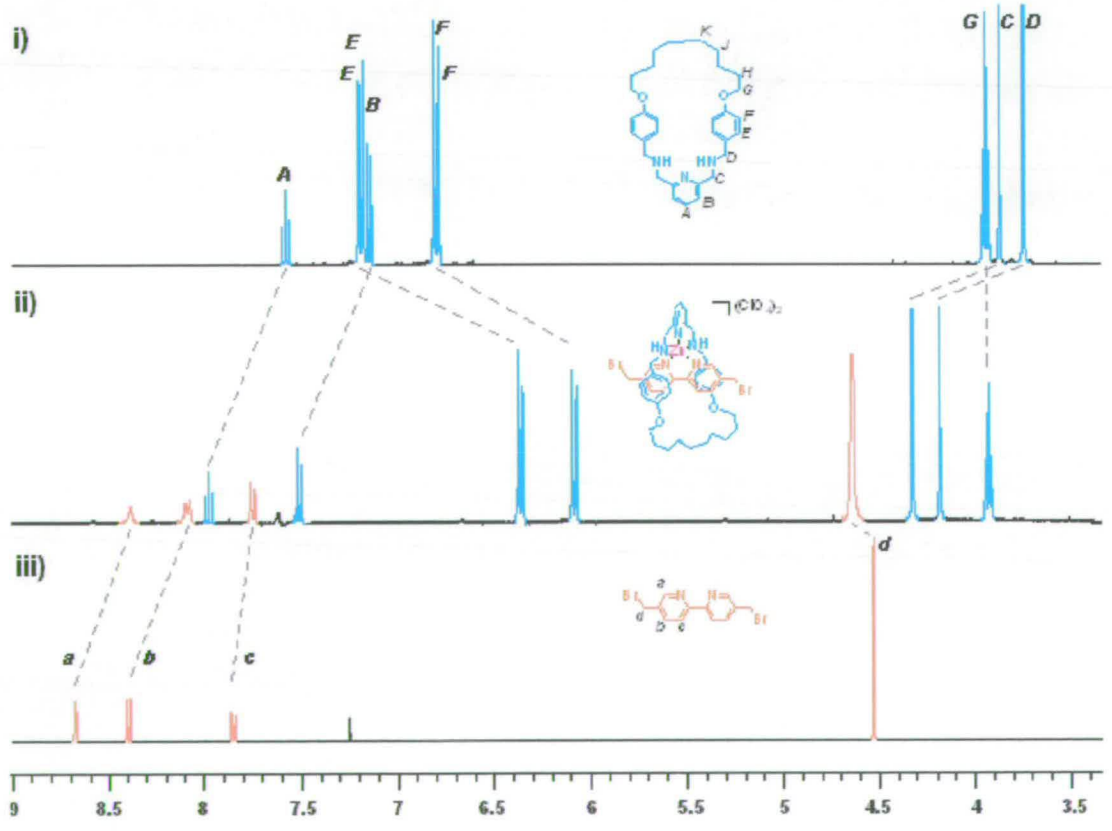


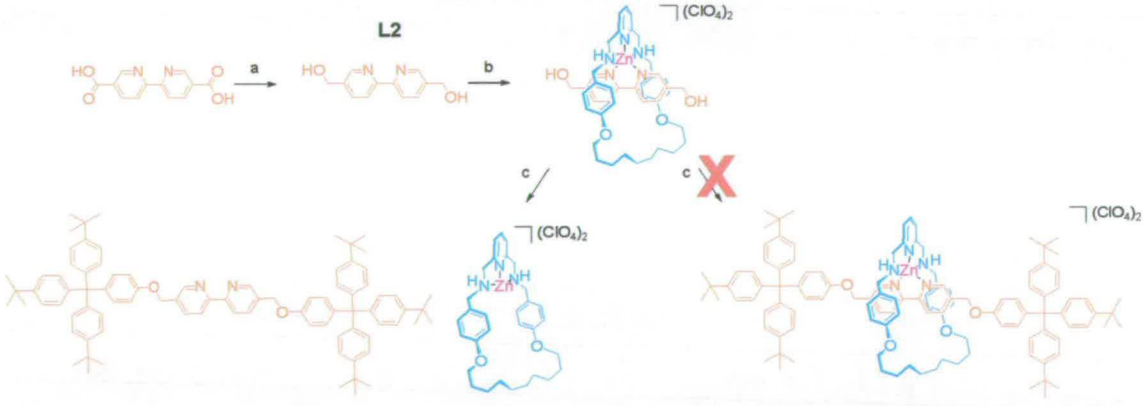
Figure 8: Partial ^{1}NMR spectra (400 MHz, $CDCl_3$, 298 K) of i) macrocycle, ii) pseudo-rotaxane [**L0L1**Zn]$(ClO_4)_2$ and iii) **L1.**

The capping reaction was attempted on the pseudo-rotaxane following the procedure utilised to deliver the free thread, i.e. reacting the phenol stopper **S** with sodium hydride in refluxing dimethylformamide; unfortunately the reaction conditions necessary to perform the substitution proved too harsh and detrimental leading to the decomposition of both complex and macrocycle (**Scheme 2**, b.).

4.3.2. Thread *L2S*$_2$

The Threading Approach – 2.

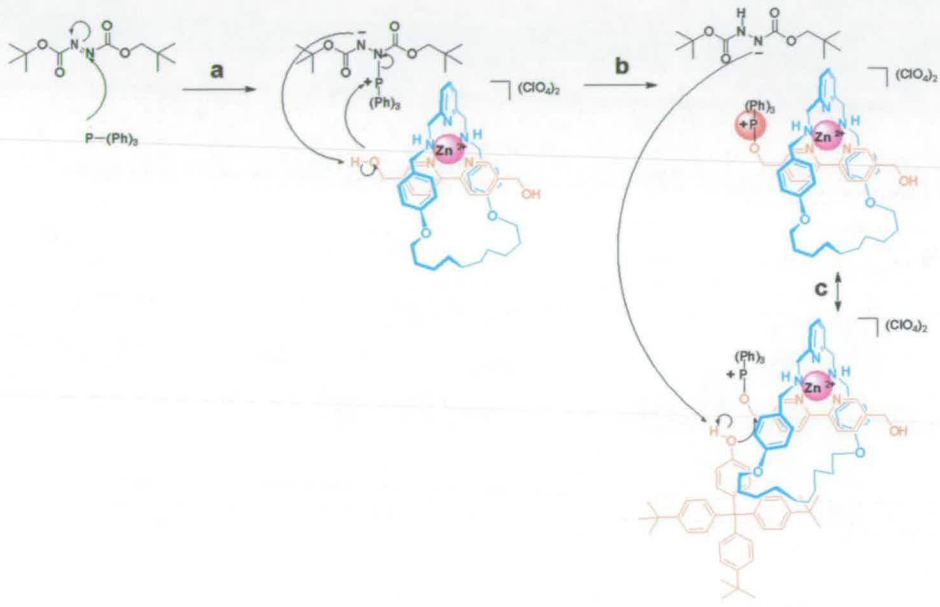
A Mitsunobu reaction was thought to be a milder route to the stoppering of the pseudo-rotaxane. Ligand **L1** was replaced with 5,5'-Bis-hydroxymethyl-[2,2']bipyridyl, **L2**, obtained from esterification of [2,2']bipyridinyl-5,5'-dicarboxylic acid with ethanol[10] followed by sodium borohydride reduction in methanol (**Scheme 3**, a.).[11] Reaction with the macrocycle and the metal gave quantitative conversion to the precursor complex. Reacting the pseudo-rotaxane with an excess of phenol stopper **S**, this time using diisopropyl azodicarboxylate, DIAD, and triphenylphosphine, PPh_3, in tetrahydrofuran, failed to deliver the desired rotaxane. Rather than the rotaxane, thread **L2S$_2$** was isolated in 43% yield, leading to the conclusion that the Mitsunobu displacement takes place with the free "unthreaded" ligand 5,5'-Bis-hydroxymethyl-[2,2']bipyridyl.



Scheme 3: Formation of pentacoordinate pseudo-rotaxane [**L0L2**Zn]$(ClO_4)_2$ and *capping* reaction yielding the free thread. Reagents and conditions: a) i. EtOH, H_2SO_4, reflux, 2 h, 76%, b) **L1**, $Zn(ClO_4)_2{\cdot}6H_2O$, CH_2Cl_2/MeOH, 2 h, 99%, c) **S**, DIAD, PPh_3, THF, 0 °C to RT, 15 h.

One rationale to this observation is that the alcohols reside in close proximity with the doubly positively charged zinc. It is conceivable then that the oxygen is less prone to

undergo nucleophilic attack on the phosphonium salt to generate an extra positively charged species (**Scheme 4**, b.). An alternative interpretation accounts for the fact that, once inserted in the macrocycle through the metal complex, the alcohols are hidden and sterically hindered. Even though the phosphorous derivative of the alcohol is formed the presence of the ring might inhibit the final S_N2 attack of the nucleophile (**Scheme 4**, c.).



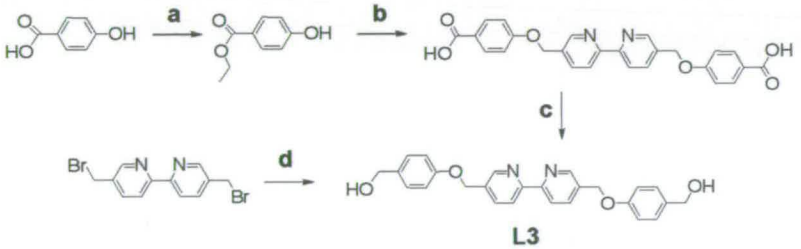
Scheme 4: Mitsunobu reaction mechanism: a) Phosphine adds to the weak N=N π bond to give anion stabilised by one of the adjacent ester groups; b) i. The anion produced is acidic enough to deprotonate the alcohol, ii. The strong affinity between O and P drives the S_N2 reaction on the positively charged phosphorous, displacing a second nitrogen anion; c) i. The second basic nitrogen removes the proton from the phenolyc stopper, ii. The nucleophilic phenoxide attacks the P derivative of the alcohol in a S_N2 at carbon with the phosphine oxide as leaving group.

If either of these two speculations was correct, it was anticipated that the lengthening of the unstoppered threading ligand might have solved the problem by moving the alcohol groups away from the sterically hindered site and thus allowing the Mitsunobu reaction to take place.

4.3.3. Thread *L3S₂*

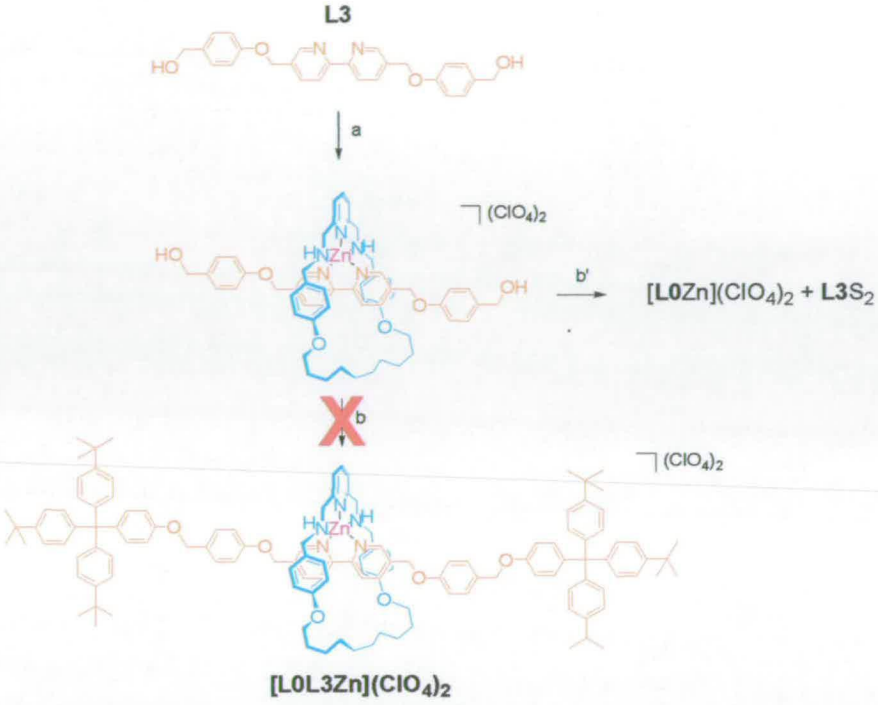
The Threading Approach – 3.

The extended ligand **L3** was conveniently prepared in one step from **L1** (**Scheme 5**, d.). Due to the poor reactivity of the bromide as a leaving group in this specific system, as previously reported in the reaction with the phenol derivative stopper,[9] the substitution required sodium hydride as base and high temperature and was low yielding. Under these conditions the deprotonation of the hydroxy group in 4-hydroxymethyl-phenol enables nucleophilic attack from both sides of the molecule and a variety of oligomers can be generated by reaction with 5,5'-bis-bromomethyl-[2,2']bipyridine. This type of molecule had been made in four steps from 4-hydroxy-benzoic acid: protection of the carboxyl group via esterification with ethanol was followed by reaction with 5,5'-bis-bromomethyl-[2,2']bipyridine to yield the diethyl ester derivative.[12] Reduction of the esters with sodium borohydride gave the desired diol (**Scheme 5**).



Scheme 5: Synthesis of ligand L3 via esterification, a., substitution, b., and reduction, c., or via dibenzo-18-crown-6 assisted substitution. Reagents and conditions: a) H_2SO_4, MeOH, b) 5,5'-bis-bromomethyl-[2,2']bipyridine, NaH, DMF, c) $NaBH_4$, MeOH, d) 4-hydroxymethyl-phenol, dibenzo-18-crown-6, dicholoromethane, 36 h, 86%.

In our method starting with 5,5'-bis-bromomethyl-[2,2']bipyridine the substitution took place in one step at 40 °C in dicholoromethane using potassium carbonate as base. One equivalent of dibenzo-18-crown-6 while complexing the potassium atoms mediated the dissolution and dissociation of the salt rendering the anionic carbonate more available (**Scheme 5**, d.). Ligand **L3** was isolated as a white solid.

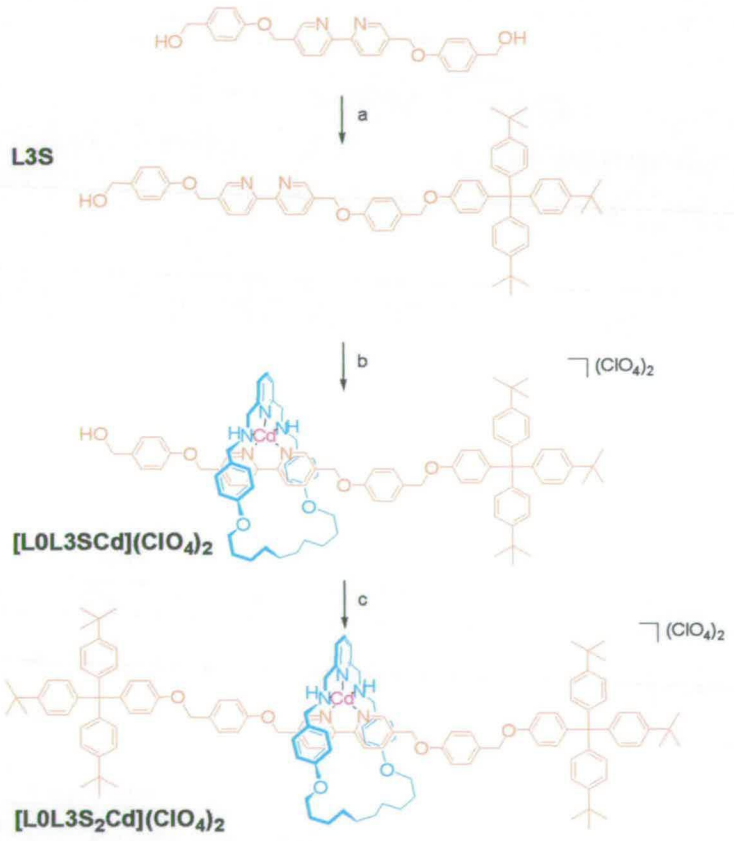


Scheme 6: Synthesis of ligand **L3** and formation of pentacoordinate pseudo-rotaxane complex $[\mathbf{L0L3}Zn](ClO_4)_2$. Formation of the free thread, c', as opposed of the desired rotaxane, c. Reagents and conditions: a) **L1**, $Zn(ClO_4)_2 \cdot 6H_2O$, CH_2Cl_2/MeOH, 12 h, 92%, b) **S**, DIAD, PPh_3, THF, 0 °C to RT, 15 h.

L3 was characterised by very poor solubility and the complexation could be accomplished in tetrahydrofuran over a period of 12 hours. To our disappointment, the Mitsunobu reaction between the pseudo-rotaxane and the phenol stoppers once again gave solely the formation of the free thread as opposed to the desired rotaxane (**Scheme 6**).

To interpret this lack of success in generating rotaxanes via this threading and capping method, the nature of the metal was taken in account. Zinc(II) is characterised by fast ligand exchange which means that the bipyridyl is rapidly moving in and out the macrocycle. In order to slow down this complexation/decomplexation reaction and create a more stable complex, zinc(II) was replaced with cadmium(II). Cadmium(II),

known to form more inert complexes with slower ligand exchange rate than zinc. Analysis of the literature[13] suggested improvements for the Mitsunobu reaction: 1,1'-(azodicarbonyl)dipiperidine, ADDP, and tributylphosphine, PBu_3, were used to replace respectively DIAD and PPh_3. Finally, to simplify the last reaction on the psuedo-rotaxane and hopefully improve the yield, ligand **L3** was replaced with the monostoppered thread **L3S** (**Scheme 7**, a.): only one Mitsunobu being now required to deliver the pentacoordinate mechanically interlocked system (**Scheme 7**, c.). These modifications proved appropriate and NMR and FAB-mass spectrometry (m/z = 2025) confirmed the formation of rotaxane $[\mathbf{L0L3S_2}Cd](ClO_4)_2$.



Scheme 7: Synthesis of ligand **L3S,** formation of pentacoordinate pseudo-rotaxane complex $[\mathbf{L0L3S}Cd](ClO_4)_2$ and final capping Mitsunobu reaction. Reagents and

conditions: a) **S**, ADDP, PBu_3, THF, 0 °C to RT, 15 h, 43%, b) **L1**, $Cd(ClO_4)_2 \cdot nH_2O$, CH_2Cl_2/MeOH, 24 h, 94%, c) **S**, ADDP, PBu_3, THF, 0 °C to RT, 15 h, 23%.

Partial ^{1}H NMR spectra of macrocycle, rotaxane [**L0L3S**Cd]$(ClO_4)_2$ and thread are shown in **Figure 9.** Comparison between the three compounds reveals many of the pattern observed in the pseudo-rotaxane illustrated in **Figure 8**. A downfield shift of about 0.5 ppm corresponding to protons H_A and H_B is distinctive of the coordination of the macrocycle to the metal. The π–stacking between the macrocycle aromatic rings (H_E and H_F) and the bipyridine, H_a, H_b and H_c, corroborates the intertwined structure. Not surprisingly, the aromatic hydrogens corresponding to the phenoxide spacer, H_f and H_e, and the stopper, H_h, H_i, H_j, and H_k, are not affected and show virtually identical resonances.

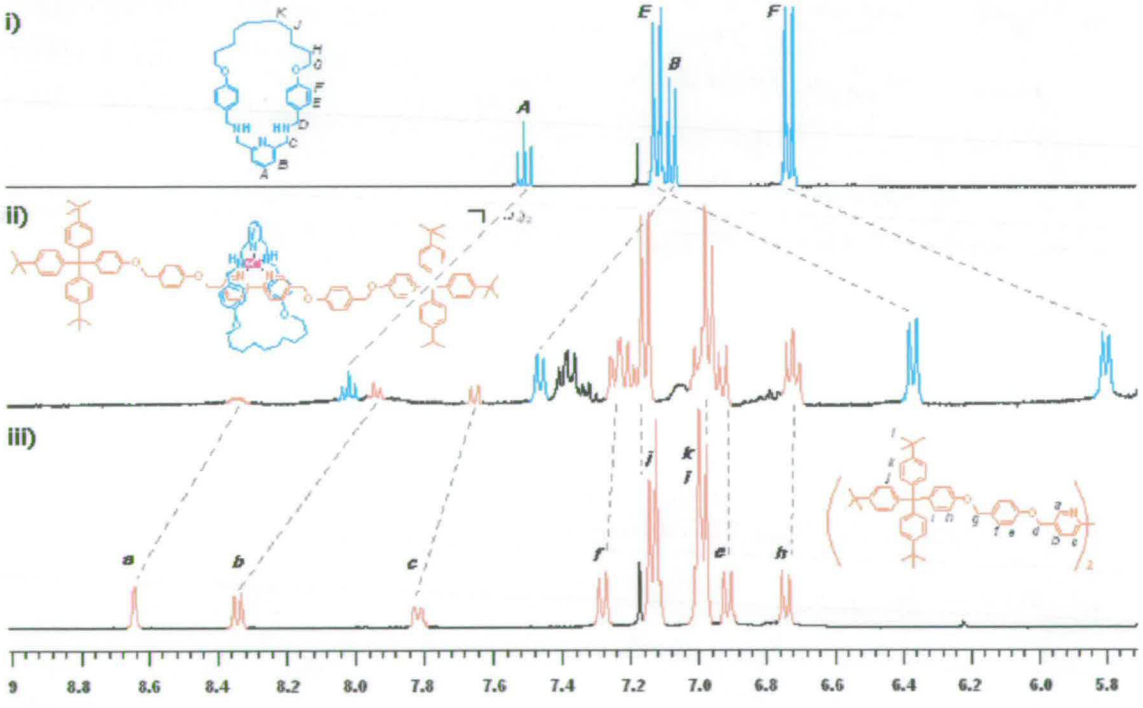
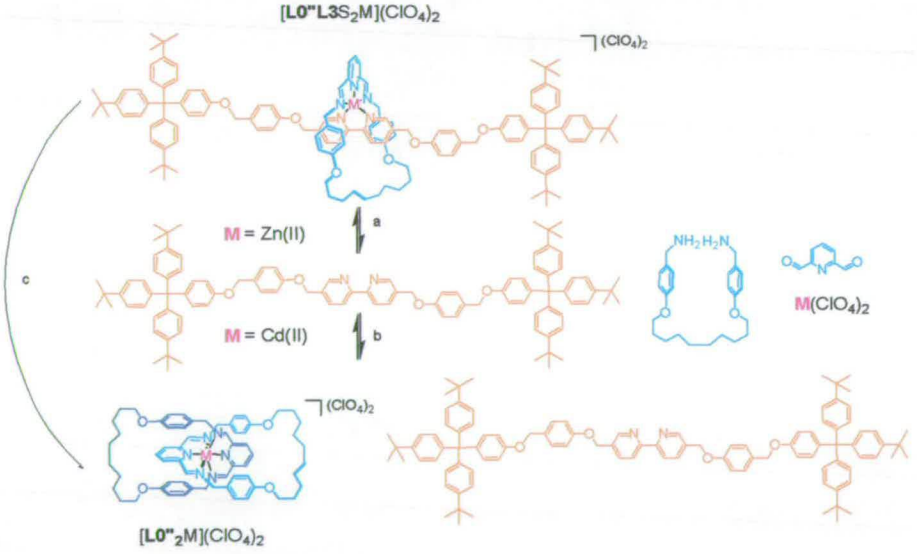


Figure 9: Partial ^{1}NMR spectra (400 MHz, $CDCl_3$, 298 K) of i) free macrocycle, ii) rotaxane [**L0L3S**Cd]$(ClO_4)_2$ and iii) free thread.

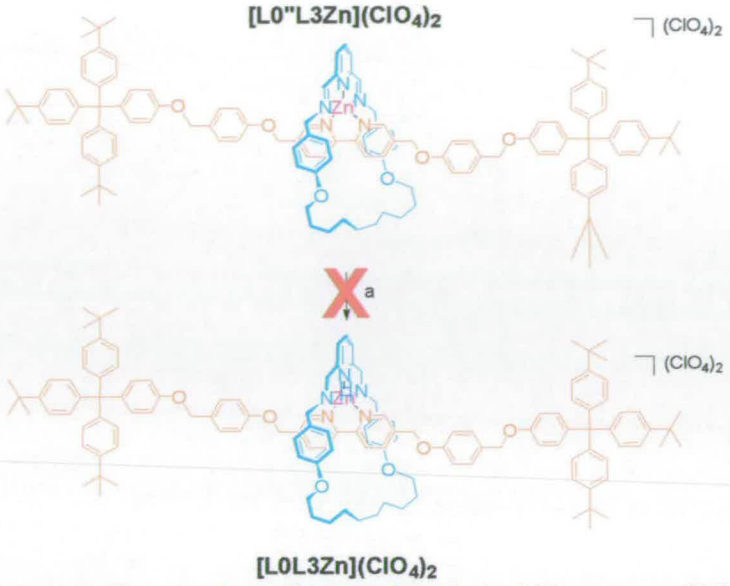
The Clipping Approach – 4.

The success with the threading approach renewed the interest in the clipping one. Thread **L3S$_2$** was reacted with cadmium(II) perchlorate, the diamine and the dialdehyde compounds in a mixture of methanol and dichloromethane, monitoring the reaction via ESI-mass spectrometry. After a few hours no rotaxane formation was detectable, (**Scheme 8**, a.) while the peak corresponding to the [2]catenate [**L0"$_2$**Cd](ClO$_4$)$_2$, (*m/z* = 1179) (**Scheme 8**, b.) was clearly present and increasing over time,. The reaction was repeated under identical conditions with zinc perchlorate: after thirty minutes ESI-mass spectrometry revealed the formation of both [2]rotaxane [**L0"L3**Zn](ClO$_4$)$_2$ and catenate. Over a period of twelve hours the pentacoordinate rotaxane converted quantitatively into hexacoordinate catenate, (**Scheme 8**, c.).



Scheme 8: Self-assembling of macrocycle via Schiff base condensation around divalent metals in the presence of a bipyridyl ligand. a) Formation of kinetic product 5-coordinate [2]rotaxane in the presence of Zn(II); b) Formation of thermodynamic product 6-coordinate [2]catenate in the presence of Cd(II); c) Convertion of the Zn(II) rotaxane into catenate over a period of 12 hours. Reagents and conditions: a) $Zn(ClO_4)_2 \cdot 6H_2O$, CH_2Cl_2/MeOH, RT; b), $Cd(ClO_4)_2 \cdot nH_2O$, CH_2Cl_2/MeOH, RT; c) time, CH_2Cl_2/MeOH, RT.

The reasons for such different behaviours rely on arguments involving the nature of the formed interlocked complex as well as the characteristics of the metal. The [2]rotaxane is a pentacoordinate species promptly given by condensation reactions generating two imine bonds while the [2]catenate has an octahedral geometry with coordination number six for which four Schiff bases need to be formed. While pentacoordinate complexes are possible both with zinc and cadmium, hexacoordinate are more stable because they saturate the metals coordination sphere. Furthermore, the chelation of two rings in the catenate complex provides a stabilising contribution due to a double macrocyclic effect. Finally, bipyridyl ligands fall earlier than imine ones in the spectrochemical series of increasing ligand field strength, therefore two imine nitrogen provide more stabilisation than two bipyridyl ones.[14] In conclusion, upon reaction of fast ligand exchanging zinc(II) with the bipyridyl thread and the macrocycle precursors, the first compound formed was the kinetic product which assembled faster because it required the formation of only two imine bonds about a pre-existing bipyridine unit; over a period of time the equilibrium shifted towards the most stable complex, catenate $[\mathbf{L0''}_2Zn](ClO_4)_2$, the thermodynamic product. The complexation with cadmium(II) took place in a slower manner selectively yielding the thermodynamic product.



Scheme 9: Attempted reduction of imine bonds in [2]rotaxane [**L0"L3**Zn]$(ClO_4)_2$. Reagents and conditions: a) $NaBH_4$, MeOH, 2 h.

Isolation of zinc(II) rotaxane was not achieved in the imine form, therefore reduction was attempted with sodium borohydride in methanol. Similarly to the results obtained with rotaxane [**L0"L1**Zn]$(ClO_4)_2$ full conversion to amine was achieved but the clean desired compound could not be isolated (**Scheme 9**).

4.4. Conclusions

The synthesis of [2]rotaxanes by template directed synthesis about a pentacoordinate metal was investigated. A thread derivatised with a bipyridyl group as the coordinative unit and hydroxybenzylic spacers to distance the capping reaction site was suitable for the formation of the rotaxane via *threading* approach about a preformed tridentate macrocycle. Cadmium(II) perchlorate was used as template to form the pseudo-rotaxane which was then stoppered following a Mitsunobu protocol. Zinc(II) proved inadequate failing to provide sufficient stability to the pseudo-rotaxane and therefore enabling the capping reaction to take place on the unthreaded diol generating free thread.

The *clipping* approach afforded the formation of different types of complexes depending on the metal used. Zinc(II) perchlorate first assembled into the kinetic product the pentacoordinate [2]rotaxane to convert quantitatively into the thermodynamic one over a period of twelve hours. Under identical conditions cadmium(II) perchlorate complexes directly into the hexacoordinate [2]catenate.

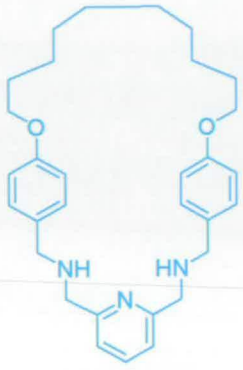
4.5. Experimental Section

4.5.1. *General*

Unless stated otherwise, all reagents were purchased and techniques were carried out as specified in the previous chapters.

N,N'-2,6-dimethylpyridyl[(1,10-decoxybis(4-benzylamine)]

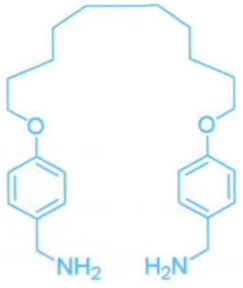
L0



$C_{31}H_{41}N_3O_2$
Mol. Wt.: 487.7

This compound was prepared as described in chapter 2 and showed identical spectroscopycal data to those reported therein.

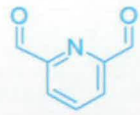
1,10-decoxybis(4-benzylamine)



$C_{24}H_{36}N_2O_2$
Mol. Wt.: 384.6

This compound was prepared as described in chapter 2 and showed identical spectroscopycal data to those reported therein.

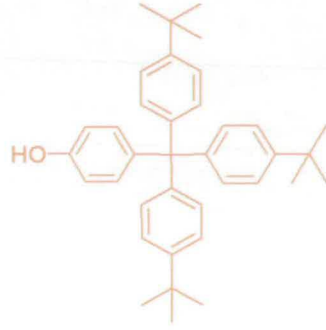
2,6-diformylpyridine



$C_7H_5NO_2$
Mol. Wt.: 135.1

This compound was prepared as described in A. L. Vance, N. W. Alcock, J. A. Heppert, D. A. Bush, *Inorg.. Chem*, **1998**, 37, 6912 – 6920 and showed identical spectroscopycal data to those reported therein.

4-[Tris-(4-*tert*-butyl-phenyl)-methyl]-phenol

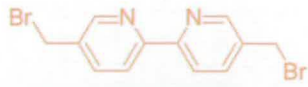


S
$C_{37}H_{44}O$
Mol. Wt.: 504.7

This compound was prepared as described in H. W. Gibson, S. H. Lee, P. T. Engen, P. Lecavalier, J. Sze, Y. X. Shen, M. Bheda, *J. Org. Chem*, **1993**, *58*, 3748 – 3756 and showed identical spectroscopycal data to those reported therein.

5,5'-Bis-bromomethyl-[2,2']bipyridyl

L1

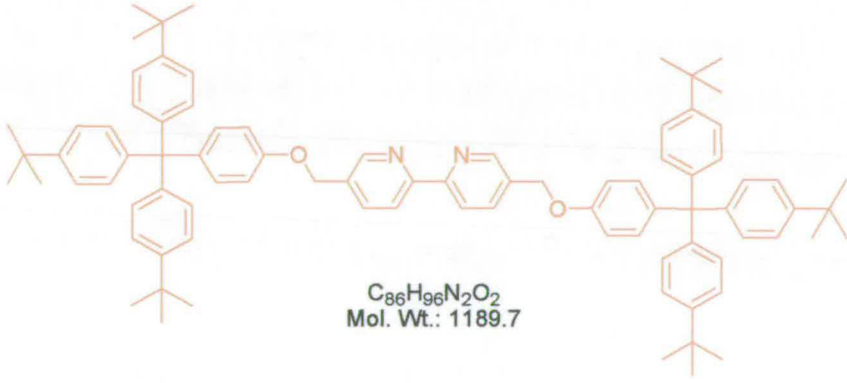


$C_{12}H_{10}Br_2N_2$
Mol. Wt.: 342.0

This compound was prepared as described in P. M. Windscheif, F. Vőgtle, *Synthesis*, **1994**, 87-92 and showed identical spectroscopycal data to those reported therein.

5,5'-Bis-{4-[tris-(4-*tert*-butyl-phenyl)-methyl]-phenoxymethyl}-[2,2']bipyridyl

$L1S_2$



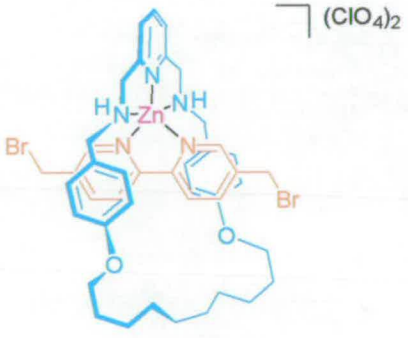
$C_{86}H_{96}N_2O_2$
Mol. Wt.: 1189.7

To a solution 5,5'-Bis-bromomethyl-[2,2']bipyridine (0.34 g, 1.00 mmol) and 4-[Tris-(4-*tert*-butyl-phenyl)-methyl]-phenol (1.11 g, 2.20 mmol) in N,N'-dimethylformamide (250 mL) under an atmosphere of nitrogen was added NaH (0.80 g, 0.020 mol). The reaction was refluxed for 10 hours then it was filtered under gravity. The solvent was removed under reduced pressure, the crude residue purified by column chromatography (Silica gel, 1:5 EtOAc/CH_2Cl_2) and then recrystallised from n-hexane to yield the title compound as a colorless solid (0.54 g, yield = 46%). m.p. 171-176 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293K): δ = 1.30 (s, 54H, $C(CH_3)_3$), 5.11 (s, 4H, ArOC$\underline{H}_2$Pyr), 6.86 (d, J=9.1 Hz, 4H, ArH), 7.08 (d, J=8.6 Hz, 12H, ArH), 7.12 (d, J=9.1 Hz, 4H, ArH), 7.23 (d, J=8.6 Hz, 12H, ArH), 7.90 (d, J=7.7 Hz, 2H, pyridyl-H), 8.42 (d, J=7.7 Hz, 2H,

pyridyl-H), 8.73 (s, 2H, pyridyl-H); ^{13}C NMR (100 MHz, $CDCl_3$, 293K): δ = 31.4, 34.2, 63.0, 69.7, 113.3, 115.0. 129.4, 130.7, 132.4, 139.8, 144.0, 144.2, 147.9, 148.3, 157.6, 158.2 ; LRFAB-MS (3-NOBA matrix): m/z = 189 $[M]^+$, HRFAB-MS (3-NOBA matrix): m/z = 1189.75511 (calcd. for $C_{86}H_{97}N_2O_2$, 1189.75500).

[5,5'-Bis-bromomethyl-[2,2']bipyridyl]-[N,N'-2,6-dimethylpyridyl[(1,10-decoxybis(4-benzylamine)]zinc(II) perchlorate

[L0L1Zn](ClO$_4$)$_2$

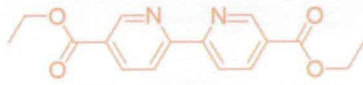


[L0L1Zn](ClO$_4$)$_2$
$C_{43}H_{49}Br_2Cl_2N_5O_{10}Zn$
Exact Mass: 1087.1
Mol. Wt.: 1092.0

To **L0** (0.098 g, 0.200 mmol) in anhydrous dichloromethane (20 mL) was added zinc perchlorate hexahydrate (0.074 g, 0.200 mmol) in anhydrous methanol (10 mL). The reaction was stirred at room temperature under an atmosphere of nitrogen for 60 minutes and then **L1** (0.068 g, 0.200 mmol) was added to it and stirred for 4 hours. The solvent was removed under reduced pressure to yield the title compound as a pale yellow solid (0.216 g, yield = 99%). m.p. 251 °C (dec); ^{1}H NMR (400 MHz, $CDCl_3$, 293K): δ = 1.23-1.33 (m, 8H, Alkyl-H), 1.38-1.46 (m, 4H, Alkyl-H), 1.98-2.02 (m, 4H, J = 6.7 Hz, Alkyl-H), 3.91 (t, 4H, J = 6.3 Hz, OC$\underline{H_2}$ CH_2), 4.23 (s, 4H, PyrC$\underline{H_2}$NH), 4.45 (s, 4H, ArC$\underline{H_2}$NH), 4.69 (s, 4H, BrC$\underline{H_2}$Pyr), 5.92 (d, J=8.8 Hz, 4H, ArH), 6.39 (d, J=8.8 Hz,

4H, ArH), 7.50 (d, *J*=7.8 Hz, 2H, pyridyl-H), 7.72 (d, *J*=8.1 Hz, 2H, pyridyl-H), 7.98 (t, *J*=7.8 Hz, 1H, pyridyl-H), 8.15 (d, *J*=8.1 Hz, 2H, pyridyl-H), 8.38 (br s, 2H, pyridyl-H); ^{13}C NMR (100 MHz, Acetone-d_6, 293K): δ = 25.9, 28.4, 28.9, 29.0, 53.5, 54.6, 66.1, 67.9, 110.2, 114.9, 121.0, 129.3, 129.9, 132.3, 135.6, 137.2, 145.7, 158.6, 155.1, 159.4 - LRESI-MS: *m/z* = 895 $[\mathbf{L0L1Zn}]^{2+}$, 994 $[\mathbf{L0L1Zn}]\mathbf{ClO_4}]^{+}$.

[2,2']bipyridinyl-5,5'-dicarboxylic acid diethyl ester

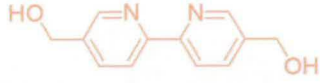


$C_{16}H_{16}N_2O_4$
Mol. Wt.: 300.3

This compound was prepared as described in C. M. Elliott and E. J. Hershenhart, *J. Amer. Chem. Soc.*, **1982**, *104*, 7519 - 7526 and showed identical spectroscopycal data to those reported therein.

5,5'-Bis-hydroxymethyl-[2,2']bipyridyl

L2

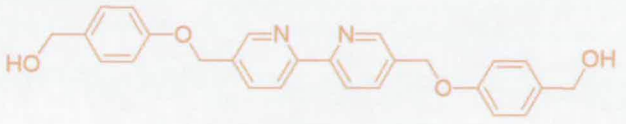


L2
$C_{12}H_{12}N_2O_2$
Mol. Wt.: 216.2

This compound was prepared as described in W. Geoffrey and D. Fitzgerald, *J. Phys. Chem. B.*, **1999**, *103*, 8070 - 8075 and G. Shane, G. Bernardinelli, A. F. Williams, *Dalt. Trans.* B, **2003,** *3*, 435 - 440 and showed identical spectroscopycal data to those reported therein.

{4-[5'-(4-Hydroxymethyl-phenoxymethyl)-[2,2']bipyridinyl-5-ylmethoxy]-phenyl}-methanol

L3

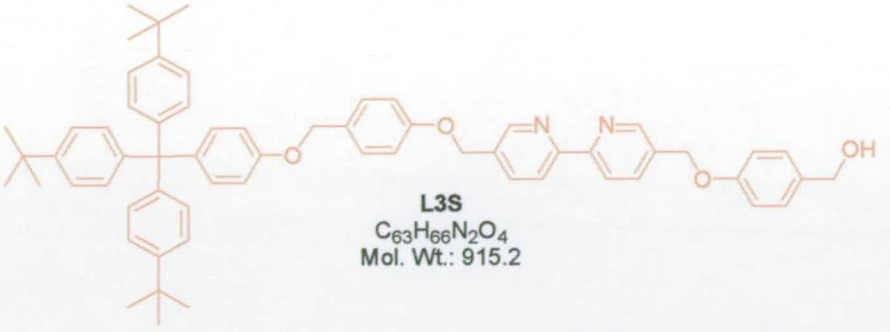


L3
$C_{26}H_{24}N_2O_4$
Mol. Wt.: 428.5

To a solution 5,5'-Bis-bromomethyl-[2,2']bipyridine (0.342 g, 1.000 mmol), 4-hydroxymethyl-phenol (0.272 g, 2.200 mmol) and dibenzo-18-crown-6 (0.790 g, 2.200 mmol) in dichloromethane (250 mL) under an atmosphere of nitrogen was added potassium carbonate (2.76 g, 0.020 mmol). The reaction was stirred at 40 °C for 36 hours then it was filtered under gravity. A layer of water (250 mL) was added on top of the dimethylchloride solution and left over night: the title compound was isolated as a pale cream solid formed at the interphase between aqueous and organic layer (0.368 g, yield = 86%). m.p. 160 (dec); ^{1}H NMR (400 MHz, CD_3SO, 293K): δ = 4.16 (s, 4H, ArC$\underline{H_2}$OH), 4.96 (s, 4H, ArOC$\underline{H_2}$Pyr), 6.76 (d, J=8.5 Hz, 4H, ArH), 7.00 (d, J=8.5 Hz, 4H, ArH), 7.77 (d, J=7.8 Hz, 2H, pyridyl-H), 8.16 (d, J=7.8 Hz, 2H, pyridyl-H), 8.51 (s, 2H, pyridyl-H); ^{13}C NMR (100 MHz, CD_3SO, 293K): δ = 62.4, 66.6, 114.4, 120.2, 127.9, 133.2, 135.0, 136.7, 148.6, 154.5, 156.8 - LRFAB-MS (3-NOBA matrix): m/z = 429 $[MH]^+$; HRFAB-MS (3-NOBA matrix): m/z = 429.18143 (calcd. for $C_{26}H_{25}N_2O_4$, 429.18130).

{4-[5'-(4-{4-[Tris-(4-*tert*-butyl-phenyl)-methyl]-phenoxymethyl}-phenoxymethyl)-[2,2']bipyridinyl-5-ylmethoxy]-phenyl}-methanol

L3S

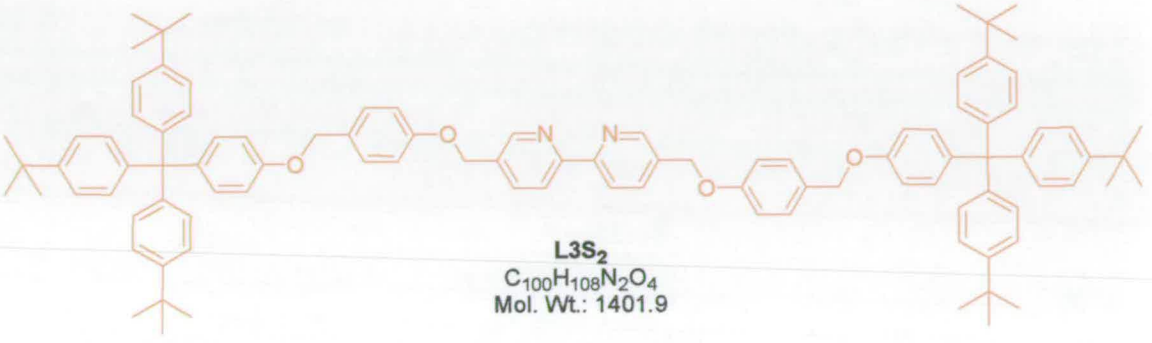


L3S
$C_{63}H_{66}N_2O_4$
Mol. Wt.: 915.2

To **L3** (0.086 g, 0.200 mmol), 4-[tris-(4-*tert*-butyl-phenyl)-methyl]-phenol (0.101 g, 0.200 mmol), and tributylphosphine (0.045 g, 0.220 mmol) in anhydrous tetrahydrofuran (50 mL) at 0 °C was added 1,1'-(azodicarbonyl)dipiperidine (0.055 g, 0.220 mmol). The reaction was stirred at 0 °C under an atmosphere of nitrogen for 20 minutes and then was allowed to warm to room temperature and stirred for 4 hours. A colour change from yellow to colourless was observed. The solvent was removed under reduced pressure; the residue was stirred in methanol and filtered. The solution obtained was purified by column chromatography (Silica gel, 1:25 MeOH/CH_2Cl_2) to yield the title compound as a colorless solid (0.115 g, yield = 43%). m.p. 169-173 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293K): δ = 1.29 (s, 27H, $C(CH_3)_3$), 4.64 (s, 2H, ArCH_2OH), 4.96 (s, 2H, ArCH_2OS), 5.16 (s, 4H, ArOCH_2Pyr), 6.84 (d, *J*=8.8 Hz, 2H, ArH), 6.99 (d, *J*=8.3 Hz, 2H, ArH), 7.01 (d, *J*=8.6 Hz, 2H, ArH), 7.06 -7.11 (m, 8H, ArH), 7.23 (d, *J*=8.3 Hz, 6H, ArH), 7.32 (d, *J*=8.3 Hz, 2H, ArH), 7.38 (d, *J*=8.6 Hz, 2H, ArH), 7.91 (d, *J*=8.5 Hz, 2H, pyridyl-H), 8.44 (d, *J*=8.5 Hz, 2H, pyridyl-H), 8.74 (s, 2H, pyridyl-H); ^{13}C NMR (100 MHz, $CDCl_3$, 293K): δ = 29.7, 34.3, 63.0, 65.0, 67.5, 69.6, 113.2, 113.7, 114.9, 121.0, 124.0, 125.5, 128.7, 129.4, 130.0, 130.7, 132.3, 132.6, 133.9, 139.8, 144.1, 148.3, 148.4, 156.7, 157.6, 157.7, 158.2 - LRFAB-MS (3-NOBA matrix): *m/z* = 915 $[MH]^+$, 411 $[M\text{-}SO]^+$, HRFAB-MS (3-NOBA matrix): *m/z* = 915.50943 (calcd. for $C_{63}H_{67}N_2O_4$, 915.51008).

5,5'-Bis-(4-{4-[tris-(4-*tert*-butyl-phenyl)-methyl]-phenoxymethyl}-phenoxymethyl)-[2,2']bipyridinyl

$L3S_2$

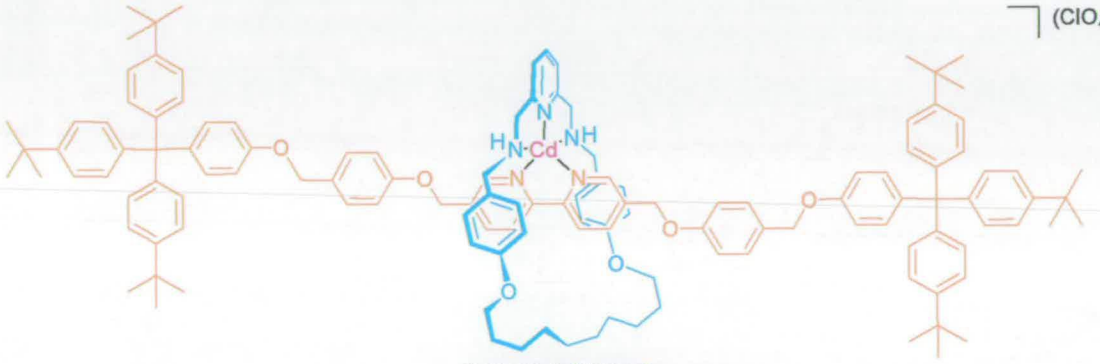


$L3S_2$
$C_{100}H_{108}N_2O_4$
Mol. Wt.: 1401.9

To **L3** (0.086 g, 0.200 mmol), 4-[tris-(4-*tert*-butyl-phenyl)-methyl]-phenol (0.222 g, 0.440 mmol), and tributylphosphine (0.090 g, 0.440 mmol) in anhydrous tetrahydrofuran (50 mL) at 0 °C was added 1,1'-(azodicarbonyl)dipiperidine (0.110 g, 0.440 mmol). The reaction was stirred at 0 °C under an atmosphere of nitrogen for 20 minutes and then was allowed to warm to room temperature and stirred for 4 hours. A colour change from yellow to colourless was observed. The solvent was removed under reduced pressure and the residue was purified by column chromatography (Silica gel, 1:25 MeOH/CH_2Cl_2) to yield the title compound as a colorless solid (0.199 g, yield = 71%). m.p. 180 °C (dec); ^{1}H NMR (400 MHz, $CDCl_3$, 293K): δ = 1.29 (s, 54H, $C(CH_3)_3$), 4.95 (s, 4H, Ar$\underline{CH_2}$OS), 5.15 (s, 4H, ArO$\underline{CH_2}$Pyr), 6.83 (d, *J*=8.8 Hz, 4H, ArH), 7.00 (d, *J*=8.6 Hz, 4H, ArH), 7.07 (d, *J*=8.3 Hz, 16H, ArH), 7.22 (d, *J*=8.3 Hz, 12H, ArH), 7.37 (d, *J*=8.6 Hz, 4H, ArH), 7.91 (d, *J*=8.1 Hz, 2H, pyridyl-H), 8.43 (d, *J*=8.1 Hz, 2H, pyridyl-H), 8.73 (s, 2H, pyridyl-H); ^{13}C NMR (100 MHz, $CDCl_3$, 293K): δ = 31.4, 34.3, 63.0, 67.4, 69.6, 113.2, 114.9, 115.3, 124.0, 129.4, 130.1, 130.5, 130.7, 132.3, 139.8, 144.1, 144.6, 147.9, 148.3, 156.6, 157.8, 158.1 - LRFAB-MS (3-NOBA matrix): *m/z* = 1402 $[MH]^+$, HRFAB-MS (3-NOBA matrix): *m/z* = 1402.84245 (calcd. for $C_{100}H_{109}N_2O_4$, 1402.84209).

[5,5'-Bis-(4-{4-[tris-(4-*tert*-butyl-phenyl)-methyl]-phenoxymethyl}-phenoxymethyl)-[2,2']bipyridinyl]-[N,N'-2,6-dimethylpyridyl[(1,10-decoxybis(4-benzylamine)cadmium(II) perchlorate

$[L1L3Cd](ClO_4)_2$



$[L0L3S_2Cd](ClO_4)_2$
$C_{131}H_{149}CdN_5O_6$ Mol. Wt.: 2002.0
$C_{131}H_{149}CdClN_5O_{10}$ Mol. Wt.: 2101.5
$C_{131}H_{149}CdCl_2N_5O_{14}$ Mol. Wt.: 2200.9

To **L0** (0.098 g, 0.200 mmol) in anhydrous dichloromethane (20 mL) was added cadmium perchlorate hydrate (0.062 g, 0.200 mmol) in anhydrous methanol (10 mL). The reaction was stirred at room temperature under an atmosphere of nitrogen for 60 minutes and then **L3S** (0.183 g, 0.200 mmol) was added to it and stirred for 4 hours. The solvent was removed under reduced pressure and the residue was dissolved in anhydrous tetrahydrofuran (20 mL). 4-[tris-(4-*tert*-butyl-phenyl)-methyl]-phenol, **S**, (0.111 g, 0.220 mmol), and tributylphosphine (0.045 g, 0.220 mmol) in anhydrous tetrahydrofuran (50 mL) were added to the residue and the solution was cooled to 0 °C. 1,1'-(azodicarbonyl)dipiperidine (0.055 g, 0.220 mmol) was then added and the reaction was stirred at 0 °C under an atmosphere of nitrogen for 20 minutes and then was allowed to warm to room temperature and stirred for 4 hours. A colour change from bright orange-yellow to pale yellow was observed. The solvent was removed under reduced pressure and the solid obtained was purified by column chromatography (Silica gel, gradient 1:100- 20:100 MeOH/CH_2Cl_2) to yield the title compound as a pale yellow

solid (0.070 g, yield = 16%). m.p. 278°C (dec); ^{1}H NMR (400 MHz, $CDCl_3$, 293K): δ = 1.29 (s, 54H, $C(CH_3)_3$), 1.23-1.33 (m, 8H, Alkyl-H), 1.38-1.46 (m, 4H, Alkyl-H), 1.98-2.02 (m, 4H, J = 6.7 Hz, Alkyl-H), 3.91 (t, 4H, J = 6.3 Hz, $OC\underline{H_2}$ CH_2), 4.23 (s, 4H, $PyrC\underline{H_2}NH$), 4.45 (s, 4H, $ArC\underline{H_2}NH$), 4.95 (s, 4H, $ArC\underline{H_2}OS$), 5.31 (s, 4H, $ArOC\underline{H_2}Pyr$), 5.90 (d, J=8.8 Hz, 4H, ArH), 6.36 (d, J=8.8 Hz, 4H, ArH),6.74 (d, J=8.8 Hz, 4H, ArH), 6.91 (d, J=8.6 Hz, 4H, ArH), 6.96-7.05 (m, 16H, ArH), 7.22 (d, J=8.3 Hz, 12H, ArH), 7.46 (d, J=7.8 Hz, 2H, pyridyl-H), 7.66 (d, J=8.1 Hz, 2H, pyridyl-H), 7.94 (d, J=8.1 Hz, 2H, pyridyl-H), 8.12 (t, J=7.8 Hz, 1H, pyridyl-H), 8.35 (br s, 2H, pyridyl-H); ^{3}C NMR (100 MHz, Acetone-d_6, 293K): δ = 25.9, 28.4, 28.9, 29.0, 31.4, 34.3, 50.5, 51.5, 61.0, 65.4, 67.9, 69.6, 110.1, 113.7, 114.9, 115.3, 121.0, 123.5, 124.0, 124.2, 129.4, 129.7, 130.1, 130.5, 130.7, 136.7, 139.3, 144.1, 144.6, 145.2, 148.3, 152.7, 156.6, 158.1, 159.6, 161.3 - LRFAB-MS (3-NOBA matrix): m/z = 2100 $[\mathbf{L0L3S_2}Cd]ClO_4^+$, HRFAB-MS (3-NOBA matrix): m/z = 2023. 04797 (calcd. for $C_{131}H_{146}CdN_5NaO_6$, 1421.56550) $[\mathbf{L0L3S_2}Cd]Na^+$.

4.6. References

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Reprints of Publications

"Creativity is...seeing something that doesn't exist already. You need to find out how you can bring it into being and that way be a playmate with God"
Michele Shea

.... And that's what I enjoyed the most in a Synthetic Lab.!
Ale: Thoughts on my PhD work (2001-2004)

A Journal of the Gesellschaft Deutscher Chemiker

Angewandte International Edition Chemie

Rotaxanes

A Simple General Ligand System for Assembling Octahedral Metal–Rotaxane Complexes

Full Metal Jacket: Simple stirring of a five component mixture at room temperature is sufficient to assemble a wide range of octahedrally coordinated [2]metallorotaxanes under thermodynamic control (see picture).

L. Hogg, D. A. Leigh,* P. J. Lusby, A. Morelli, S. Parsons, J. K. Y. Wong

Keywords: coordination modes · rotaxanes · self-assembly · template synthesis · thermodynamic control

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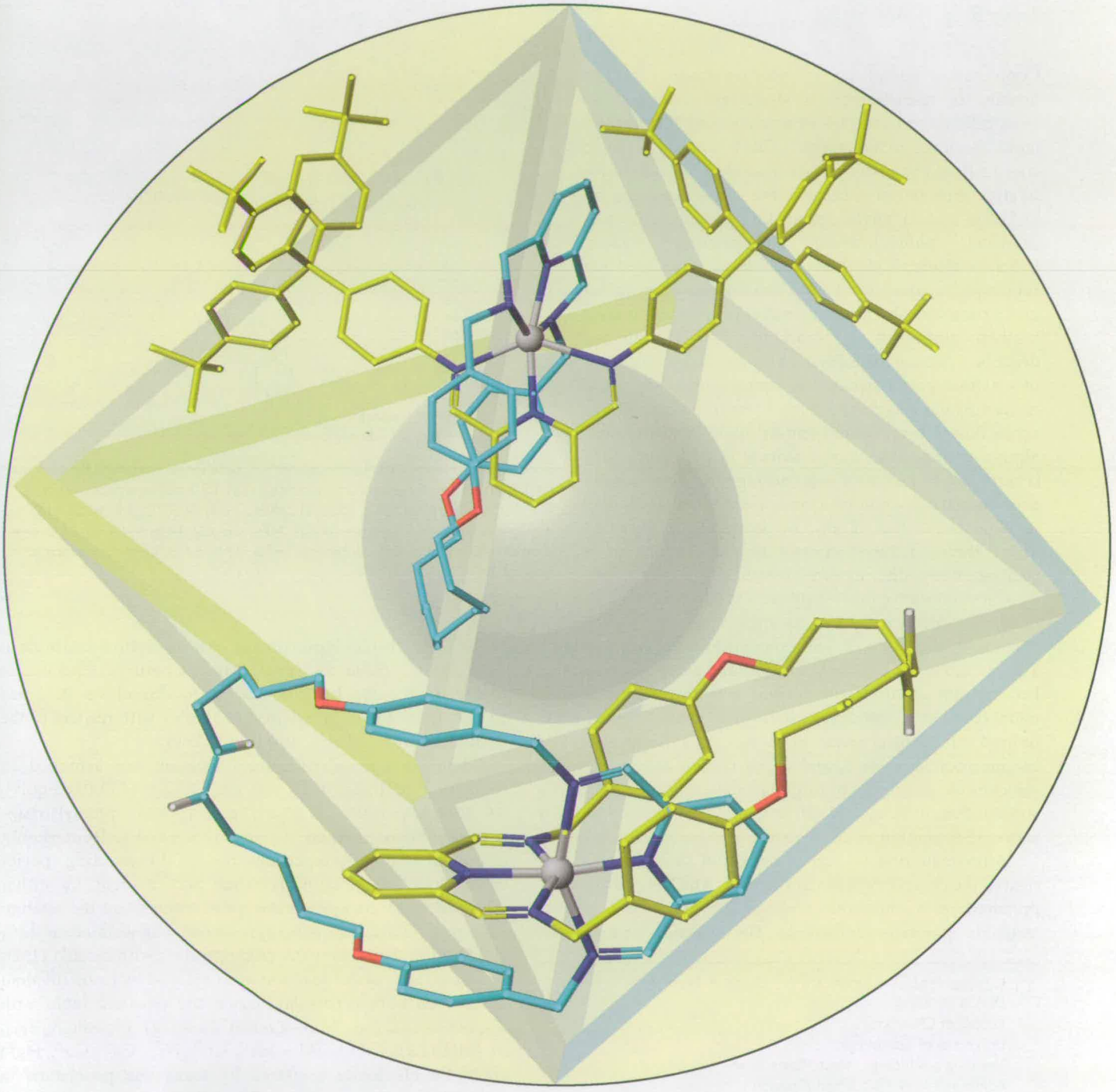
Communications



In their Communication on the following pages, D. A. Leigh and co-workers describe a general ligand system for rotaxane complexes of transition-metal ions that prefer octahedral coordination—a rare coordination mode for rotaxanes. Simple mixing of the components at room temperature is sufficient to assemble a broad range of octahedrally coordinated [2]metallorotaxanes in high yields.

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Rotaxanes

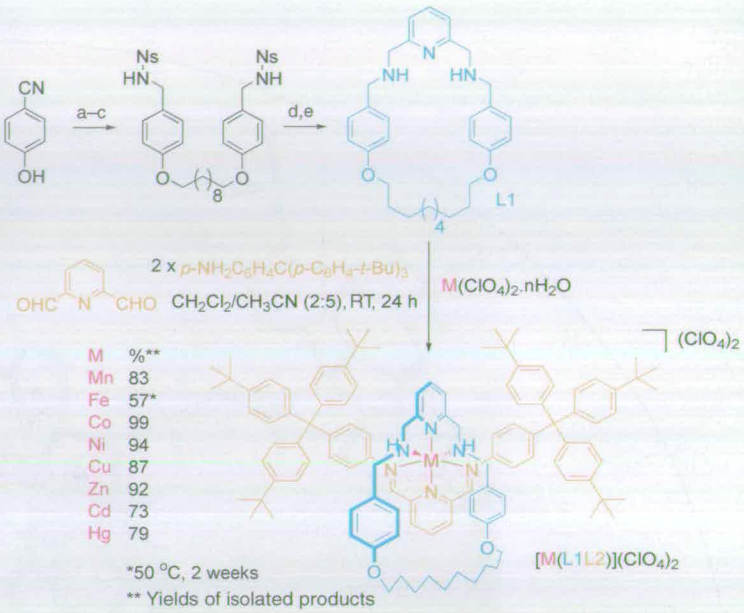
A Simple General Ligand System for Assembling Octahedral Metal–Rotaxane Complexes**

Louise Hogg, David A. Leigh, Paul J. Lusby, Alessandra Morelli, Simon Parsons, and Jenny K. Y. Wong*

Coordination complexes in which rotaxanes act as ligands for transition-metal atoms are amongst the most celebrated examples of mechanically interlocked molecular level architectures.[1] This is not only because coordination chemistry makes possible a rich diversity of structures, but also because the metal atom can be locked in unusual environments for subsequent electrochemical,[2] photochemical[3] and catalysis[4] studies. Efficient synthetic methods have been developed for rotaxanes based on tetrahedral and trigonal-bipyrimidal metal complexes by using the metal-bis-phenanthroline synthon pioneered in Strasbourg.[1a,b,5] Herein we describe a general ligand system for rotaxane complexes of ions that prefer octahedral coordination—the commonest ligand geometry amongst transition metals, but up to now a rare[6] coordination mode for rotaxanes. Simple mixing of the components at room temperature is sufficient to assemble a broad range of octahedrally coordinated [2]metallorotaxanes in excellent yields. The reactions have few, if any, by-products and proceed under thermodynamic control in the absence of a catalyst or any other external reagents.

Catenanes have previously been synthesized around octahedral metal templates by employing macrocycles containing tridentate 2,6-diiminopyridine chelating units.[7] This system is not well-suited to forming rotaxanes, however, because thread–thread–metal and macrocycle–macrocycle–metal (catenate) complexes can form in competition with the desired thread–macrocycle–metal assembly. Replacement of the macrocycle imine ligand set by nonlabile amine groups removes the possibility of forming catenates and introduces a structural asymmetry that can potentially be tailored to favor rotaxane formation under dynamic exchange conditions.[8]

After exploring several unsuccessful designs, we investigated the chemistry of macrocycle **L1**, which is conveniently prepared on a multigram scale in five steps from readily available materials (Scheme 1). The key step to **L1** is the macrocyclization of a bis-2-nitrobenzenesulfonamide (NsNH) derivative with 2,6-dibromomethylpyridine to give the protected macrocycle in 67% yield. Cyclization of the analogous Boc-protected diamine proceeded with a low yield



Scheme 1. Five-component self-assembly of octahedral metal(II)[2]rotaxanes, [M(**L1L2**)](ClO$_4$)$_2$. Reagents and conditions: a) 1,10-dibromodecane, K_2CO_3, NaI, butanone, reflux, 18 h, 83%, b) $LiAlH_4$, THF, 0–60 °C, 3 h, 92%, c) 2-nitrobenzenesulfonyl chloride (NsCl), NEt_3, CH_2Cl_2, 18 h, 93%, d) 2,6-dibromomethylpyridine, K_2CO_3, butanone, reflux, 18 h, 67%, e) mercaptoacetic acid, LiOH, DMF, 24 h, 80%.

(< 20%) and routes based on ring-closing olefin metathesis to form the C_{10} chain also proved uncompetitive. The use of aniline, rather than benzylamine, in the thread was designed to destabilize the dithread–metal complex with respect to the desired interlocked structure (see below).

Octahedral metal–rotaxane formation was achieved by sequential treatment of **L1** with Zn(ClO$_4$)$_2$·6H$_2$O (0.8 equiv), 2,6-diformylpyridine (1 equiv) and (*p*-aminophenyl)tris(*p*-*tert*-butylphenyl)methane (2 equiv), Scheme 1. Remarkably, after 24 h at room temperature no metal-containing species other than the zinc(II)[2]rotaxane was evident by either ^{1}H NMR or electrospray mass spectrometry and the analytically pure [Zn(**L1L2**)](ClO$_4$)$_2$ rotaxane was isolated in 92% yield by simply washing the crude product with diethyl ether. The generality of the reaction was explored by using divalent metal ions both across and down the periodic table with respect to zinc (i.e., Mn←Zn and Zn→Hg). Pleasingly, each of [M(**L1L2**)](ClO$_4$)$_2$ (M = Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, Cd^{II}, Hg^{II}) could be efficiently prepared by using the procedure in isolated yields ranging from 73 to 99% (Scheme 1). In all cases no other metal-containing species could be detected[9] after 24 h, which suggests near-quantitative formation of the interlocked metal-rotaxane complex. Formation of [Fe(**L1L2**)](ClO$_4$)$_2$ required a longer reaction time and gentle heating (CH_2Cl_2/CH_3CN, N_2, 40 °C, 2 weeks) and

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resulted in a lower yield of rotaxane (57%). The sluggish rate of reaction is characteristic of the slow rate of ligand exchange of low spin d^6 metal complexes, but a potentially useful feature of the slower dynamics is that Fe^{II} therefore locks the rotaxane architecture in a particularly kinetically stable form.

The nonparamagnetic metal–rotaxane complexes all have similar ^{1}H NMR spectra; those of the zinc(II)[2]rotaxane $[Zn(\mathbf{L1L2})](ClO_4)_2$ and macrocycle **L1** are shown in Figure 1.[10] The shielding of the H_C and H_D protons of the benzyl rings of the macrocycle and several protons of the thread indicate that extensive intercomponent π stacking occurs in solution. Single crystals of $[Cd(\mathbf{L1L2})](ClO_4)_2$ suitable for investigation by X-ray crystallography were obtained by slow vapor diffusion of diethyl ether into a solution of the rotaxane in acetonitrile.[11] The crystal structure (Figure 2) confirms the interlocked molecular architecture, the pseudooctahedral geometry of the cadmium(II) ion, and shows π stacking of both the macrocycle benzylic rings with the pyridyl unit and an imine group of the thread.

The mechanism of the rotaxane-forming reaction provides insight into the reasons for the effectiveness of the ligand assembly. When **L1** is treated with $Zn(ClO_4)_2{\cdot}6H_2O$ (CH_2Cl_2/CH_3CN, room temperature) followed by the preformed thread, **L2**, electrospray mass spectrometry shows that within 10 minutes the thread has extracted the zinc(II) ion from the macrocycle to form the dithread complex, $[Zn(\mathbf{L2})_2](ClO_4)_2$ in >95% yield (Scheme 2). The $[Zn(\mathbf{L2})_2](ClO_4)_2$ species is then quantitatively converted to the rotaxane $[Zn(\mathbf{L1L2})](ClO_4)_2$ over 24 h.[12] Whilst the

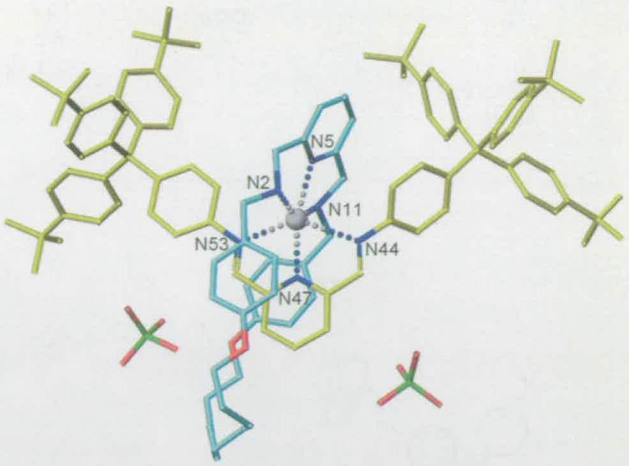


Figure 2. X-ray crystal structure of $[Cd(\mathbf{L1L2})](ClO_4)_2$.[11] Carbon atoms of the macrocycle, **L1**, are shown in light blue and those of the thread, **L2**, in yellow; oxygen atoms are red; nitrogen dark blue; chlorine green; cadmium grey. Hydrogen atoms and a molecule of acetonitrile are omitted for clarity. Selected bond lengths [Å]: Cd-N2 2.40, Cd-N5 2.30, Cd-N11 2.40, Cd-N44 2.52, Cd-N47 2.26, Cd-N53 2.38; other selected interatomic distances [Å]: N2-N11 4.52, N5-N47 4.52, N44-N53 4.59; ligand bite angles [°]: N2-Cd-N11 141.5, N44-Cd-N53 139.2.

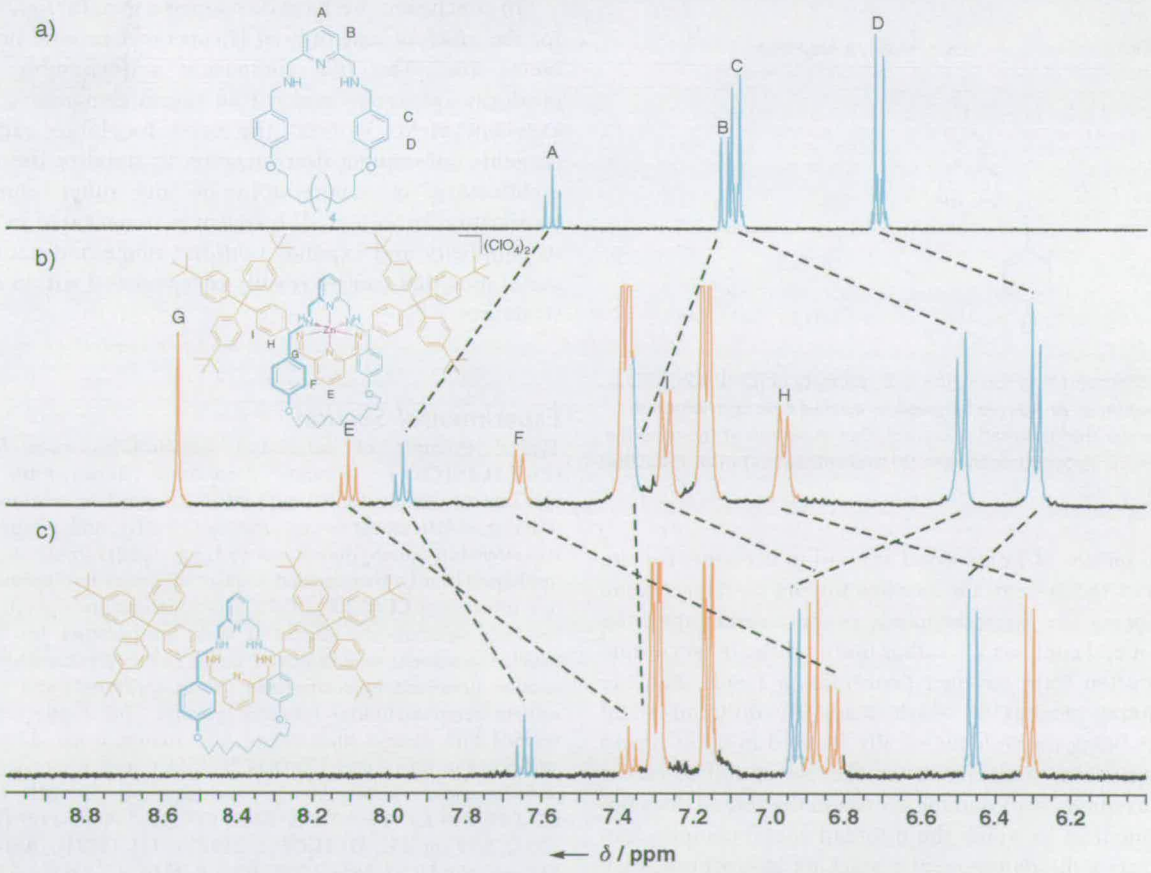
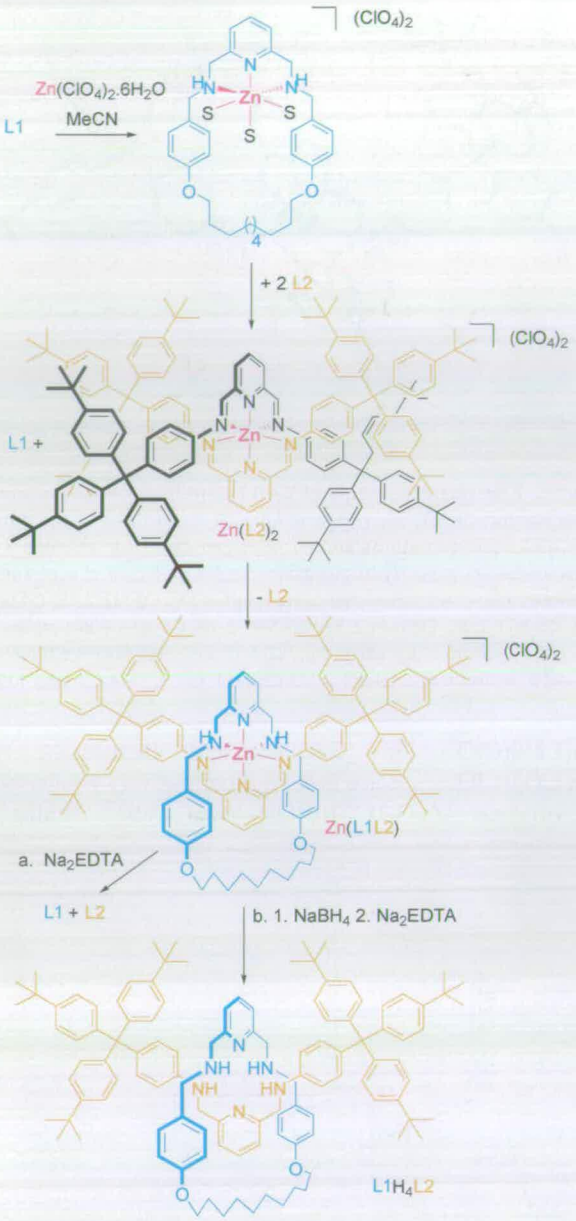


Figure 1. Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 298 K) of a) macrocycle **L1** b) zinc(II)[2]rotaxane $[Zn(\mathbf{L1L2})](ClO_4)_2$ c) demetallated, reduced, rotaxane $\mathbf{L1}H_4\mathbf{L2}$.



Scheme 2. Mechanism of formation and reactivity of $[Zn(\mathbf{L1L2})](ClO_4)_2$. Rapid formation of $Zn(\mathbf{L2})_2$ is followed by quantitative conversion to $Zn(\mathbf{L1L2})$ under thermodynamic control. Demetallation of the rotaxane by using Na_2EDTA occurs both with (b) and without (a) prior reduction of the imine groups.

reversible nature of imine bond formation accounts for the dynamics of the system, the reasons for the metal–rotaxane complex being the thermodynamic product rather than the dithread–metal complex are rather more subtle. In fact, imine N donors often form stronger coordination bonds than the corresponding amines,[13] which leads to dithread–metal complexes being thermodynamically favored in other ligand systems we investigated. However, the use of aniline rather than, for example, benzylamine groups in the thread does not allow geometries in which the dithread–metal complex can form attractive intercomponent π-stacking interactions, such as those observed in the rotaxane between the benzyl groups of the macrocycle and the extended π system of the thread in both solution (NMR spectroscopy) and the solid state (X-ray crystal studies). We believe these favorable secondary interactions are important for the thermodynamic stability of the rotaxane over the other possible products of the reaction.

The 2,6-diminopyridyl motif imparts high kinetic stability in metal-coordinated interlocked structures. Tetraimine metal(II) catenates are not demetallated by Na_2EDTA (EDTA = ethylenediaminetetracetate), which required reduction to the more labile tetraamine catenates for the metal atom to be extracted.[7] The $[M(\mathbf{L1L2})](ClO_4)_2$ rotaxanes, which contain a combination of imine and amine N donors, do react with excess Na_2EDTA when heated (10 equiv, CH_3CN/MeOH, 60 °C, 0.5 h) to remove the metal. However, without the stabilization provided by metal coordination the rotaxane decomposes through imine bond exchange and only free macrocycle and thread are observed experimentally (Scheme 2, path a). If the rotaxane imine bonds are reduced beforehand ($[Zn(\mathbf{L1L2})](ClO_4)_2$, 10 equiv $NaBH_4$, CH_3CN/MeOH, Δ, 1.5 h), however, treatment with Na_2EDTA (10 equiv, CH_3CN/MeOH, 60 °C, 0.5 h) gives the demetallated, reduced, rotaxane $\mathbf{L1}H_4\mathbf{L2}$ (88% yield) with no evidence of dethreading (Scheme 2, path b). The ^1H NMR of $\mathbf{L1}H_4\mathbf{L2}$ is shown in Figure 1c. The downfield shift in the resonances of the benzyl groups with respect to $[Zn(\mathbf{L1L2})](ClO_4)_2$ indicates that π stacking with the thread is less pronounced in the demetallated rotaxane in which there are no coordination bonds to organize the geometry of the components.

In conclusion, we have developed a general ligand system for the efficient assembly of [2]rotaxanes around octahedral metal ions. The five component self-assembly reaction produces rotaxanes under true thermodynamic control in excellent yields without the need for large excesses of reagents, subsequent derivatization to stabilize the rotaxane architecture, chromatography or any other complicated purification processes. The system is remarkable in terms of its simplicity and expands both the range and geometry of metal ions that can be readily encapsulated within rotaxane structures.

Experimental Section

Typical example of octahedral metal(II)[2]rotaxane formation, $[Zn(\mathbf{L1L2})](ClO_4)_2$: Zinc(II) perchlorate hexahydrate (0.127 g, 0.342 mmol) in acetonitrile (5 mL), 2,6-pyridinedicarboxaldehyde (0.055 g, 0.410 mmol) in acetonitrile (10 mL), and *p*-aminophenyltris(*p*-*tert*-butylphenyl)methane (0.413 g, 0.820 mmol) in dichloromethane (10 mL) were added sequentially over five-minute periods to a solution of **L1** (0.200 g, 0.410 mmol) in acetonitrile (10 mL). The resulting solution was stirred at room temperature for 24 h, after which the solvent was removed under reduced pressure, the crude residue dissolved in acetonitrile (30 mL), filtered, and finally the solvent removed under reduced pressure. The crude residue was washed with diethyl ether (30 mL) for 10 min, isolated by filtration and dried in air to give $[Zn(\mathbf{L1L2})](ClO_4)_2$ as a bright yellow solid (0.582 g, yield = 92%). Mp 266 °C (decomp). ^1H NMR (400 MHz, CD_3CN, 298 K): $\delta = 1.32$ (s, 54H, $C(CH_3)_3$), 1.48–1.68 (bm, 12H, alkyl), 1.79 (m, 4H, OCH_2CH_2), 3.84 (br, 4H, OCH_2), 4.06–4.55 (br, 8H, pyCH_2NHCH_2Ar; py = pyridyl), 6.29 (d, $J = 8.6$ Hz, 4H, macrocycle ArH), 6.49 (d, $J = 8.6$ Hz, 4H, macrocycle ArH), 6.96 (d, $J = 8.6$ Hz, 4H, thread ArH), 7.16 (d, $J = 8.6$ Hz, 12H, thread ArH), 7.27

(d, $J = 8.6$ Hz, 4H, thread ArH), 7.37 (m, 14H, thread ArH plus macrocycle pyridyl H), 7.65 (d, $J = 7.8$ Hz, 2H, thread pyridyl H), 7.96 (t, $J = 7.8$ Hz, 1H, macrocycle pyridyl H), 8.11 (t, $J = 7.8$ Hz, 1H, thread pyridyl H), 8.57 ppm (s, 2H, thread HC=N); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): $\delta = 25.6$, 28.4, 28.5, 29.4, 31.5, 34.5, 52.2, 55.3, 63.9, 67.4, 114.1, 120.8, 123.0, 124.1, 124.3, 124.6, 127.0, 128.5, 130.6, 141.5, 141.9, 143.3, 143.4, 145.9, 148.9, 149.0, 155.0, 158.2, 158.7 ppm; IR (KBr pressed pellet): $\tilde{\nu} = 3465$, 2960, 2865, 1611, 1582, 1513, 1464, 1395, 1363, 1251, 1180, 1109, 1089, 1017, 840, 823, 637, 625, 582 cm^{-1}; LRESI-MS: $m/z = 830$ $[Zn(\mathbf{L1L2})]^{2+}$, 1759 $[Zn(\mathbf{L1L2})](ClO_4)^+$; HRFAB-MS (3-NOBA matrix): $m/z =$ 1657.97065 (calcd for $^{12}C_{111}{}^{13}CH_{132}N_6O_2{}^{64}Zn$ $[(\mathbf{L1L2})Zn]$, 1657.97363).

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[9] Reactions were monitored by electrospray mass spectrometry in all cases and by ^{1}H NMR spectroscopy for systems not containing paramagnetic metals.

[10] The **L1** and **L2** resonances in $[Zn(\mathbf{L1L2})](ClO_4)_2]$ were distinguished by a combination of COSY and ROESY experiments.

[11] $[Cd(\mathbf{L1L2})](ClO_4)_2 \cdot 2\,MeCN \cdot 1.5\,Et_2O$: $C_{124}H_{153}CdCl_2N_8O_{11.5}$, $M_r = 2098.82$, yellow block, crystal size $0.15 \times 0.12 \times 0.10$ mm, monoclinic Cc, $a = 31.636(2)$, $b = 22.4269(14)$, $c = 22.2668(15)$ Å, $\beta = 133.7570(10)°$, $V = 11410.8(13)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.222$ Mg m^{-3}; $Mo_{K\alpha}$ radiation (graphite monochromator, $\lambda = 0.71073$ Å), $\mu = 0.300$ mm^{-1}, $T = 150(2)$ K. 36017 data (22989 unique, $R_{int} = 0.03170$, $1.27 < \theta < 28.96°$), were collected on a Bruker SMARTApex CCD diffractometer by using narrow frames (0.3° in ω), and were corrected semiempirically for absorption and incident beam decay. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 values of all data (G. M. Sheldrick, SHELXTL manual, Siemens Analytical X-ray Instruments, Madison WI, USA, **1994**, version 5) to give $wR = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2} = 0.1536$, conventional $R = 0.0627$ for F values of 22989 reflections with $F_o^2 > 2\sigma F_o^2$), $S = 1.048$ for 1371 parameters. Residual electron density extremes were 1.12 and -0.89 e Å^{-3}. Hydrogens were added in calculated positions and constrained to a Riding model. CCDC-224059 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[12] Under identical experimental conditions the reduced thread, $H_4\mathbf{L2}$, does not afford $[Zn(\mathbf{L1}H_4\mathbf{L2})](ClO_4)_2$, thus precluding the possibility of a "slippage" mechanism.

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