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Review

Recent developments in the d-block metallo-supramolecular chemistry of polypyridyls

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Contents

Abstract

Polypyridyl ligand derivatives have been widely employed for the construction of metallo-supramolecular entities from the beginning of this contemporary area of research. Representative recent developments in the use of such ‘classical’ polypyridyl ligands combined with selected d-block metal ions to obtain supramolecular assemblies incorporating both the polypyridyl and the metal ion as structural elements are described.

In particular, helicates, metal-chain oligo-pyridylamido systems, grids as well as a range of other metallo-supramolecular structures are discussed.

Keywords: Polypyridyls; Metallo-supramolecular chemistry; Self-assembly; X-ray structures

1. Introduction

Polypyridyls and related ligand systems have been employed in metallo-supramolecular chemistry since the latter’s emergence as a widely studied area of chemistry about 35 years ago. Metallo systems within this general category have been featured

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in many reviews since that time and, except when directly relevant to the present discussion; earlier studies are not included in the present review. A monograph covering the general area by one of the present authors was published in 2000 [1] and the present work will largely focus on systems reported since around that time; however, where more recent reviews of individual structural categories exist, the material covered in these will not, in general, be rediscussed.

The continued popularity of polypyridyl-containing building blocks is perhaps not surprising when one considers that the simpler systems bipyridine and terpyridine, along with their parent pyridine, are all excellent metal coordinating agents and have been intensively studied from the early days of coordination chemistry. As a consequence, there is a very large amount of 'simple' metal ion coordination chemistry involving these ligands available in the literature. This has acted as a foundation upon which both the design and synthesis of new extended metallo systems incorporating di-, tri- and polypyridyl components has taken place.

The aim of the present review is to provide an overview of representative more recent studies in the metallo-supramolecular area involving linear (that is, non-branched) pyridyl-containing ligand derivatives; we have restricted our coverage to ligand systems incorporating a minimum of three pyridine groups. In this context, it is noted that reviews of aspects of the metal ion chemistry of terpyridine derivatives [2–4] and of molecules incorporating at least two 2,2′-bipyridine units [5] have appeared previously. Simple metal complexes of unsubstituted terpyridine and related ligands that fall outside the supramolecular realm are not included in the present coverage. The treatment has also been restricted to a discussion of selected discrete systems incorporating d-block metals. Interwoven systems such as rotaxanes [1,6,7], catenanes [1,6,8,9] and boromean rings [10] are also not discussed.

2. Helicates

2.1. General considerations

Transition metal helicates, many incorporating polypyridyl and related ligands [11–20] have been investigated for many years and have made a central contribution to the development of metallo-supramolecular chemistry. Clearly, the important role that self-assembled helical structures play in biology has provided both a motivation and inspiration for the study of synthetic systems of this type and aspects of chemistry and properties of helicates have been reviewed over recent years [21–28].

While emphasis in the present discussion is given to helical systems incorporating solely pyridyl donor groups, it is noted that a number of studies involving closely related pyridine–pyrazine derivatives have also received attention and, where appropriate, examples of these will also be discussed [29–31]. However, systems incorporating conjugated ligand systems incorporating five-membered nitrogen heteroatom rings linked to pyridyl rings, such as those described by Ward et al. [32] are not included.

While the vast majority of helical structures so far reported are linear in nature, less-common examples of circular helicates, in which the metal ions are arranged in a cyclic array (for example, to form a polygonal 'core' of the helix) are known [33–39].

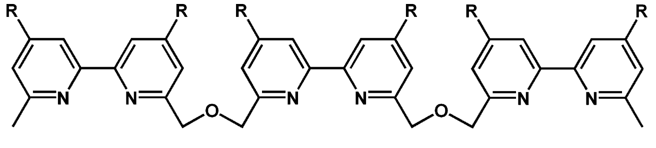
Helical metallo-structures ranging from simple single-stranded [40–48] structures through to four-stranded systems [49] are known. Typically, the single-stranded systems are mono- or dinuclear complex species incorporating a variety of ligand types.

Over the years, particular emphasis has been given to the synthesis and properties of double and triple helicates. Clearly, a number of design aspects need to be considered in order to successfully generate such arrangements [50]. For example, the number of ligand strands able to coordinate to a given metal centre is determined by the latter's potential coordination number and the 'dentate' nature of the individual metal binding domains along each strand. Four coordinate (tetrahedral) metal centres will be required to combine with bidentate domains to yield two-stranded helices (assuming that all sites are solely occupied by donors from the ligand domains) whereas six-coordinate metals will potentially yield three stranded systems with such a ligand type. If solely tridentate domains are present, then the use of an octahedral metal will generate a two-stranded system. For the above to occur, the ligand strands will normally need to be sufficiently flexible to allow strong metal-domain binding along each ligand's backbone but rigid enough to restrict conformations that may favour non-helicate arrangements.

For helicate formation each metal centre will adopt a similar screw sense; however, for symmetrical dinuclear metal helicates incorporating non-chiral ligand strands, a racemic mixture will normally result (the right-handed form being P and the left-handed one being M). The alternative situation where the optical activity of the metal centres is opposed corresponds to a *meso* (Δ,Λ) structure and, as implied above, this does not represent a true helicate.

2.2. Double and triple helicates

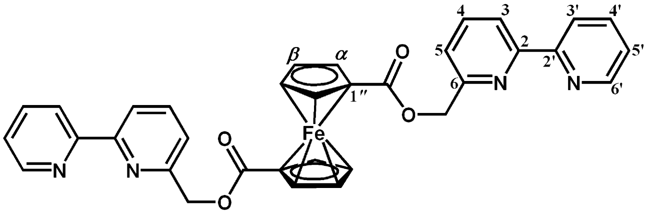
Following earlier studies on the mechanism of helicate formation, Lehn and co-workers [50,51] investigated the kinetic behaviour of double stranded helicate formation involving oligobipyridine ligands of type **1** and showed that products of type $[Cu_3L_2]^{2+}$ (L = **1**) form, with the kinetics of formation being strongly influenced by the nature of the substituents present. It was postulated that positive cooperativity occurs for metal binding in such cases leading ultimately to favourable near-tetrahedral coordination around each metal centre. However, it needs to be noted that subsequently it was shown that positive cooperativity does not occur for such helicate formation and that negative cooperativity in fact appears commonly to occur [27,28,52–59]. Thus, in 2003, Ercolani [59] observed that the previous methods employed to assess cooperativity in such helicate (and also ladder) self-assembly, namely the use of classical Scatchard and Hill plots, were inappropriate because they are only valid when intermolecular binding of a monovalent ligand occurs to a multivalent receptor—this condition is not met in the earlier analysis of helicate formation. Ercolani developed a procedure for the analysis of self-assembly of the above type which included both intermolecular and intramolecular aspects of the assembly process; no evidence for positive cooperativity was then obtained. The original criticism was further theoretically justified by Borkovec et al. using statistical mechanics [60]. In more recent work a non-linear (non-statistical) Scatchard-like procedure has been developed for describing metal-binding in the formation of double-stranded helicates [57]. Application of this new procedure to several polymetallic helicates revealed the presence of negative cooperative processes that were attributed mainly to arise from intermetallic repulsions. A procedure for the semi-quantitative estimation (and prediction) of the contribution of intermetallic repulsion to the total free energy of discrete polymetallic assembly in solution has also been the subject of a recent report [61].



1; L^1, R = $CONEt_2$ and L^2, R = CO_2Et

Thermodynamic and kinetic aspects of the self-assembly of an iron(II) triple-stranded helicate incorporating a bis(2,2′-bipyridine)diamide propyl-linked derivative have also been investigated in methanol using a combination of electrospray mass spectrometry, potentiometry, spectrophotometry and dissociation kinetics [20]. Three iron(II) complexes, one mononuclear $(FeL_2)^{2+}$ and two dinuclear $(Fe_2L_2)^{4+}$ and $(Fe_2L_3)^{4+}$, species were observed to occur in solution. Their respective structures were inferred from the (low) spin state of the iron(II) centres as well as from ^{1}H NMR measurements and molecular modelling. In the presence of excess ligand the mechanism for helicate formation was proposed to involve a stepwise wrapping of three bipyridine domains from different ligand strands around a single iron(II) followed by coordination of the second iron(II) to the three resulting pendant bipyridyl entities.

A 2:2 (Cu:L) helicate, where L is the ferrocene-based ligand **2** bearing two pendant 2,2′-bipyridine groups, forms in the presence of high reagent concentrations and with copper(I) present in excess. This product occurs in solution in equilibrium with the corresponding 1:1 and 1:2 species [54]. The lower solubility of the 2:2 helicate has enabled its crystallisation and subsequent X-ray structure determination [62]. The latter shows a six coordinate environment about each copper consisting of four nitrogen atoms provided by two bipyridine groups, each from a different ligand molecule, and two oxygen atoms from the linking ester functions. The results of electrochemical studies are in keeping with the dinuclear helicate dissociating in solution under the conditions employed to form mainly the 1:1 complex. There is no evidence for positive cooperativity in formation of the dimeric species which assemblies from the 1:1 complex with only a small thermodynamic driving force ($\Delta G^\circ = -3.5\,\mathrm{kJ\,mol^{-1}}$).



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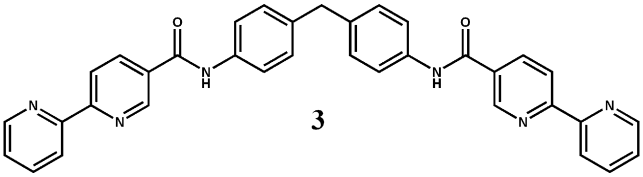
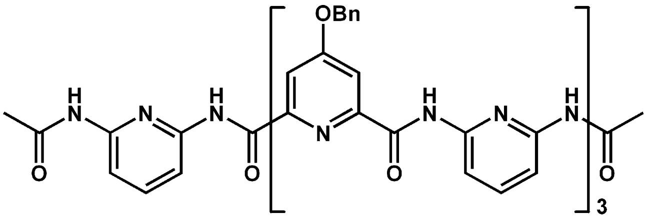
Reaction of the amide-containing bis-bipyridine ligands (of which the diphenylmethane bridged species **3** may be considered to be the parent derivative) with iron(II) yields dinuclear complexes of type $[Fe_2L_3]^{4+}$ containing two pseudo-C_3-symmetric 'amide hydrogen-surrounded' cavities between the metal centres [63]. ^{1}H NMR spectroscopy showed that the complexes exist as both *rac*-(helical) and *meso*-(non-helical) isomers in DMSO-d^6 at 298 K. In each case it was also demonstrated using ^{1}H NMR studies that each of the respective dinuclear complex types selectively binds chloride ion in a 2:1 (chloride:helicate) ratio, with the chloride ions occupying the respective pseudo-C_3-symmetric cavities. In each case the addition of chloride ion shifted the *rac*-/*meso*-species distribution from 1:2 in favour of the *meso*- to 100 percent in favour of the *rac*-isomer, demonstrating that the Cl^- ions promote the formation of the triple helicate species in DMSO-d^6 solution.



3

Extended helicates are known. For example, the solid-state structure of a copper(II) double helical structure incorporating two oligopyridine ligand strands of type **4** and six closely spaced copper(II) ions has been reported (Fig. 1) [64]. In this structure, deprotonation of six of the seven amide nitrogens on each ligand strand has occurred and six pyridine rings of each are involved in coordination to copper centres in this case.



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Similarly, extended linear arrays of silver(I) ions with Ag–Ag distances ranging from 2.78 to 4.42 Å are present in oligomeric double helicates containing ligand strands that incorporate pyridine/pyrimidine/hydrazone groups [65].

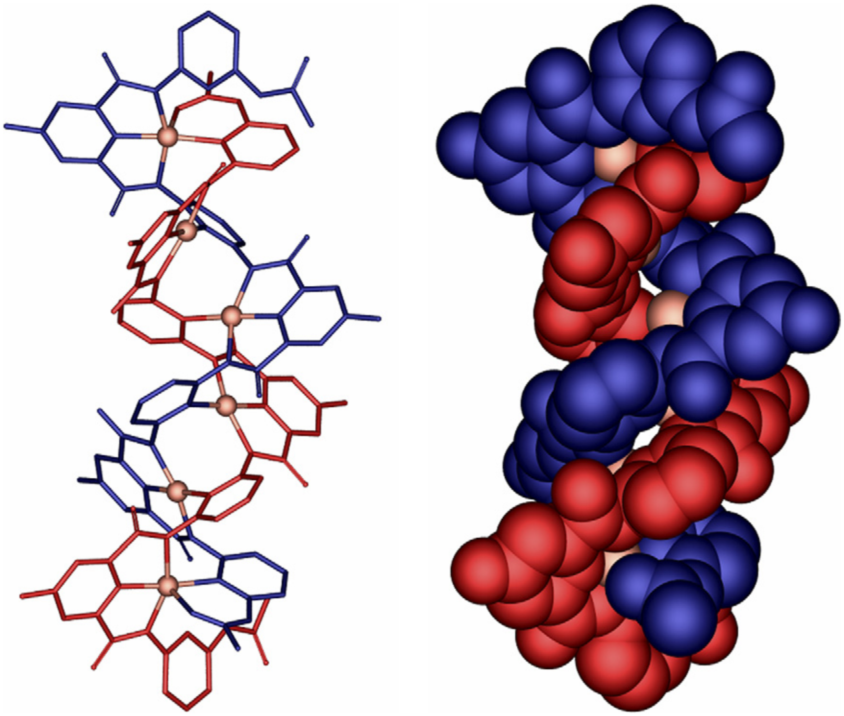
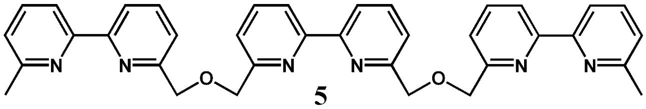


Fig. 1. Helical structure of the neutral $[Cu_6L_2]$ complex (L = **4**) [64].

An early investigation by Lehn and co-workers [66] demonstrated the occurrence of self-recognition in the assembly of helicates. This study showed that mixtures of oligo-2,2′-bipyridine ligands of different strand lengths failed to form heteroleptic double- and triple-stranded helicates with copper(I)—homoleptic assemblies were generated. Subsequently, there have been a considerable number of other studies also aimed at investigating self-recognition processes in the self-assembly of double- and triple-stranded helicates.

As expected, 'simple' homoleptic double stranded species were obtained when each of **5**–**8** were reacted with copper(I); namely, **5** and **6** each yielded $[Cu_3L_2]^{3+}$ complexes while **7** gave two complexes of this stoichiometry and **8** gave at least two complexes of type $[Cu_2L_2]^{2+}$ [67]. As might be predicted, the differences in the potential shifts obtained in electrochemical studies on a selection of these compounds were found to be in accord with the central copper(I) ions being bound more strongly than the terminal ions. NMR studies were employed to investigate the speciation that resulted when copper(I) was interacted with mixtures of the above ligands of different strand lengths. Interestingly, when a mixture of **7** with **5** or **6** was used for helicate synthesis, only homoleptic double-stranded species were formed in solution; whereas, when **5** was present with **6**, then the corresponding helicate distribution seemed to follow simple statistics. The reasons for the different behaviour in this latter case are not clear but likely have their origins in the presence of different inter-strand interactions occurring between the respective ligand systems.



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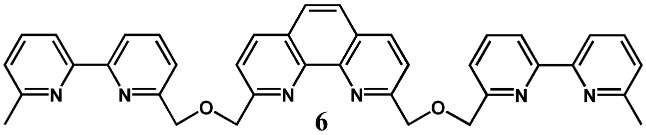

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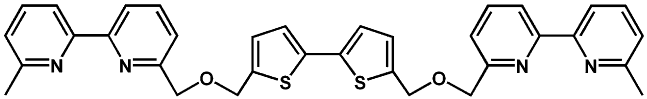

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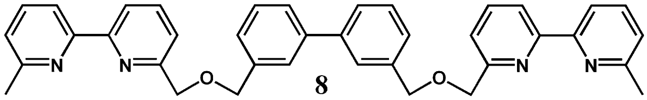

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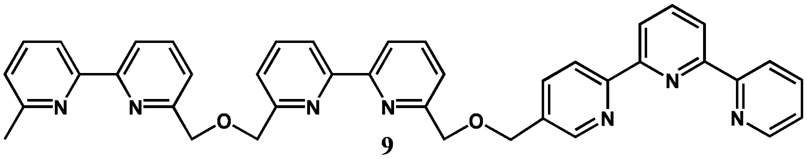
Combinations of tridentate (terpyridine, T) and bidentate (bipyridine, B) subunits have been incorporated in strands to give a set of tritopic ligands suitable for double helicate formation with appropriate metal ions. Four ligand strands BBB (**5**), BBT (**9**), TBT (**10**) and TTT (**11**), were synthesised [68]. These were used to form both homo- and heterostranded helicates incorporating both single- and mixed-domain metal binding sites, depending on the coordination properties of the metal employed. In general, these helicates were found to correspond to systems in which donor-site domain pairing occurred that corresponded to BB, BT, and TT pairs for tetra-, penta-, and hexacoordinate copper(I), copper(II) and zinc(II) cations, respectively. The study demonstrates how ligand and metal ion properties may be collectively employed to influence the nature of individual heterometallic helicates generated.



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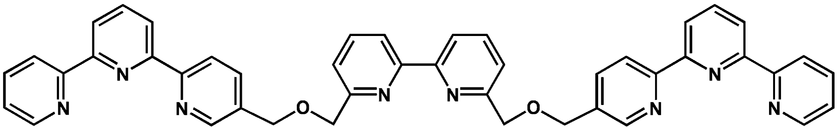

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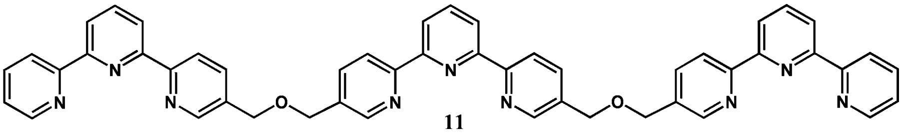

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^{1}H NMR diffusion spectroscopy (diffusion ordered spectroscopy, DOSY) experiments have been employed to probe the translational diffusion coefficients of homologous series of copper(I) and silver(I) double stranded helicates of type $[M_nL_2]^{n+}$ in acetonitrile solution (where n = 1–5 and L is a range of oxy-bridged polypyridyl ligands that includes **1**, **5** and **9** together with related derivatives of different strand lengths) [69]. An aim of these studies was to correlate the length and bulkiness (in some cases reflecting the presence of substituents on the periphery of the respective ligands) with the solution diffusion behaviour. The experiments were successful in yielding information concerning the dimensions of the respective helicates when present in solution both individually and as mixtures. With respect to the latter, it was confirmed that a mixture of helicates from the same series, but of different length and nuclearity, gave signals corresponding to homo-stranded helicates corresponding to each component. There was no evidence of "cross-binding" of ligands of different lengths under the conditions employed. Apart from the above, helicate formation by other linear ligands incorporating 2,9-substituted 1,10-phenanthroline moieties has also been reported [70–72].

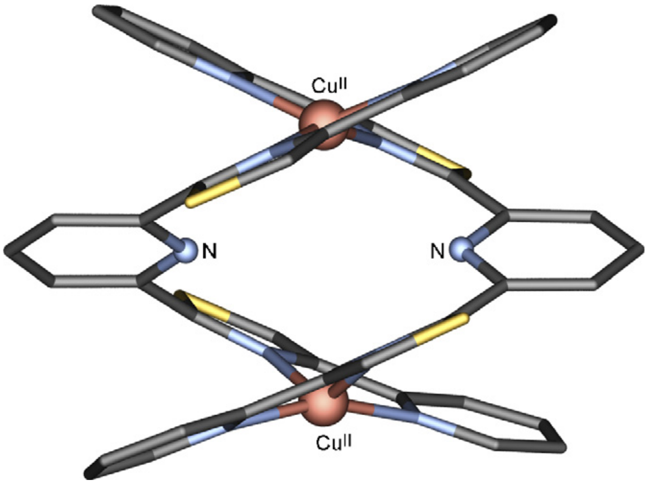
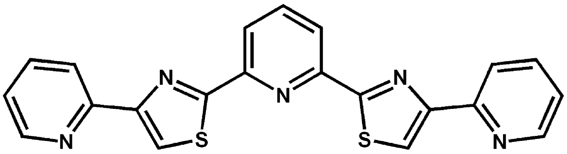


Fig. 2. View of the $[Cu_2L_2]^{4+}$ (L = **12**) cation showing the potentially two-coordinate cavity [73].

X-ray diffraction studies show that both the thiazole-containing ligands **12** and **13** readily form double helicates of type $[Cu_2(L^3)_2]^{4+}$ in which both ligands only use their two terminal bidentate (*N*,*N*-binding) domains for coordination to copper(II) [73]. In the case of **12** this results in two four-coordinate copper(II) centres, with two non-coordinated pyridyl residues present in the centre of each structure; these pyridyl residues are directed towards each other to give a potentially two-coordinate cavity between the metal ions in the centre of the helicate (Fig. 2). Similarly, in the corresponding structure derived from **13** the copper(II) ions are four-coordinate, with each ligand having its central bipyridyl unit uncoordinated. This in turn results in a potentially four-coordinate cavity between the two metal centres. While, in principle, the use of **13** could result in the formation of three potentially bidentate compartments and hence lead to a trinuclear double helicate with all three bidentate sites occupied, no such complex was able to be isolated. It was suggested by the authors that, in part, the trinuclear structure may be disfavoured due to the electrostatic barrier resulting from three dipositive metal ions being located close together. The Cu–Cu separation in the dinuclear helicate is 4.746 Å and insertion of an additional copper ion would result in very close metal–metal contacts.



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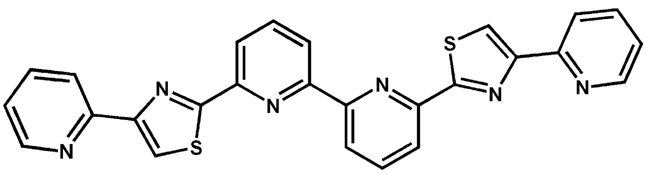

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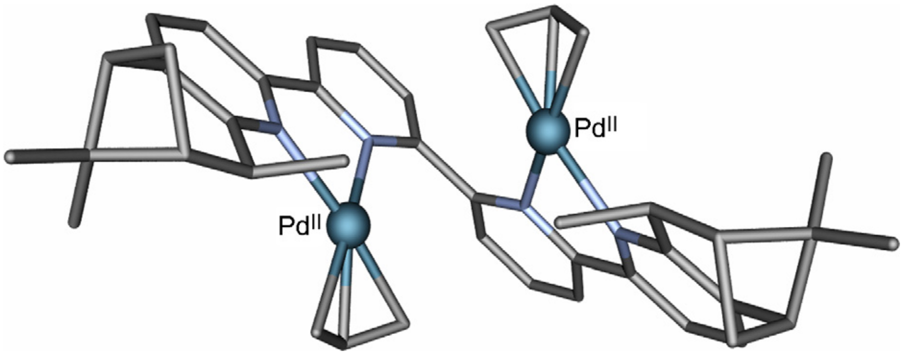
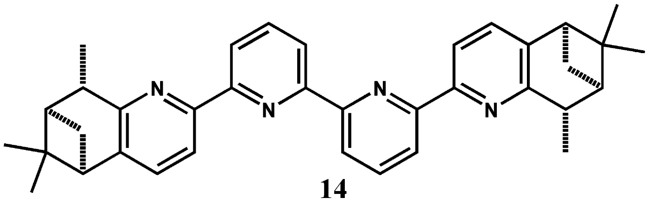


Fig. 3. X-ray structure of $[Pd_2(\eta_3\text{-}C_3H_5)_2(L)]^{2+}$ (L = **14**) showing the mono-helical arrangement [74].

2.3. Chiral considerations

As mentioned above, the use of achiral ligands for helicate formation normally leads to a racemic mixture of products. To generate enantiomeric (P or M) helicates, a chiral element (chiral auxiliary) normally needs to be present.

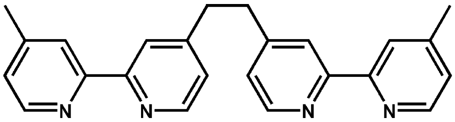
A single stranded helical system incorporating the chiral quaterpyridine ligand (**14**), has also been reported [74]. In this case, the chiral C_2-symmetric quaterpyridine derivative reacts stereoselectively with the allyl precursor, $[Pd(\eta_3\text{-}C_3H_5)Cl]_2$, to form a chiral single-stranded helical arrangement of type $[Pd_2(\eta_3\text{-}C_3H_5)_2(L)]^{2+}$.



14

The X-ray structure of this product (as its $[SbF_6]^{2-}$ salt) confirms that the cation has the single-handed helical structure shown in Fig. 3. A CD study provided evidence that the solid-state helical structure is maintained in solution. This product has been demonstrated to act as an effective catalyst for asymmetric allylic substitution, giving both excellent yields and an ee of up to 85%.

Provided the systems are sufficiently kinetically inert, it is sometimes possible to separate chiral isomers by conventional resolution procedures such as chromatography on a chiral column (or fractional crystallisation in the case of charged helicates after addition of a homochiral counter-ion). For example, the racemic dinuclear triple helicate $[Fe_2L_3]^{4+}$ (L = **15**) is readily resolved using the chiral tris(tetrachlorobenzenediolato)phosphate(V) TRISPHAT anion [75]. For charged helicates, the configuration adopted may in some cases be controlled through ion pair formation through the addition of a chiral counter-ion to the reaction solution. Thus, the TRISPHAT anion behaves as an efficient asymmetric directing unit that efficiently controls the configuration of a cationic dicobalt(II) triple helicate, $[Co_2L_3]^{4+}$ (where L is the tetradentate ligand, 1,2-bis[4-(4′-methyl-2,2′-bipyridyl)]ethane) yielding a de(diastereomeric excess) of up to 82% [76]. In a prior study [75] it was demonstrated that the enantiomeric purity of the analogous racemic helical $[Fe_2L_3]^{4+}$cation [77] can be efficiently measured using ^1H NMR by employing the TRISPHAT anion as a chiral shift reagent.



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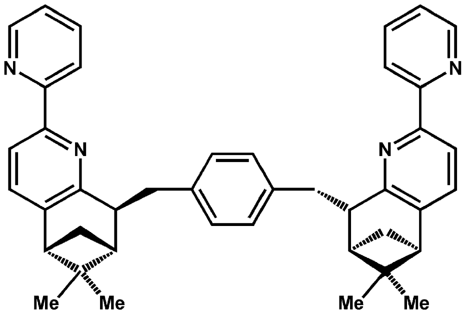
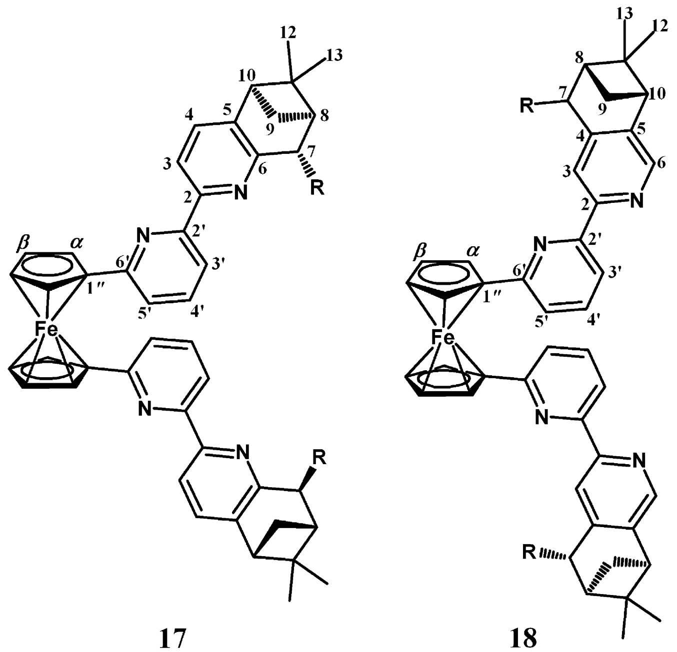
Of the above methods, the most common strategy for obtaining single-handed helicates has been to incorporate stereogenic elements in the backbones of the ligand strands employed for their synthesis. That is, the presence of one or more chiral centres in the ligand gives the prospect that selective, complementary aggregation of like handed ligands will occur during helicate assembly. Using such a strategy, the enantio-selective syntheses of a considerable range of chiral helicates have now been performed [78–80]. In particular, a large number of pyridine and bipyridine derivative ligands that are chiral through incorporation of structural fragments derived from enantiopure terpenes have been reported by von Zelewsky and co-workers and the use of such systems in metal ion studies was reviewed [81] in 2003; only selected examples from these extended studies are discussed here. Members of the above ligand family [82,83] have been named CHIRAGENs and have been employed for the synthesis of both linear and circular helicates with predetermined configurations. An example of this ligand type is given by **16** (5,6-CHIRAGEN[*p*-xylyl]). Similar ligands incorporating 4,5-CHIRAGEN frameworks have also been synthesised by this group. Series of related chiral species incorporating, for example, a central pyrazine ring connected to peripheral pyridine or bipyridine moieties, providing bipyridine- and terpyridine-like binding sites, have also been reported [84]. In early work the 4,5-CHIRAGEN analogue of **16** was shown to undergo an enantio-selective self-assembly process with tetrahedral copper[I] or silver[I] to yield circular hexanuclear (double stranded) helicates, each exhibiting C_6 symmetry axes [85]. CD spectroscopy confirmed that the configuration of the resulting helix was predetermined by the chiral pinene groups present in the ligands. The isomeric ligand (4,5-CHIRAGEN[*m*-xylyl]) was shown to interact with labile octahedral metals to yield dinuclear helicates of M_2L_3 stoichiometry [86].



16

More recently, von Zelewsky and co-workers [87] employed the optically pure (−)-L form of **16** for helicate formation. Reaction of a 1:1 mixture of this isomer with copper(I) led to the formation of corresponding hexanuclear circular P helicate, $[Cu_6(-)\text{-}L)_6]^{6+}$. An attempted scrambling experiment using a mixture of (+)-L and (−)-L with copper(I) yielded hexanuclear circular helicates which exhibited complete chiral recognition. The ^1H NMR spectrum showed resonances similar to those for $[Cu_6(-)\text{-}L)_6]^{6+}$ and CD spectroscopy revealed that the resulting product was a racemic mixture. Clearly, no mixing of the (+) and (−) ligands occurs upon complexation in this case. The corresponding *meso* ligand, which is composed of one (*RR*) and one (*SS*)-pinene-substituent, was also reacted with both copper(I) and silver(I). In contrast to the above, the self-assembly products from these reactions were polymeric products. This result exemplifies the dominating role that chiral centres may have on the nature of self-assembly processes of the present type.



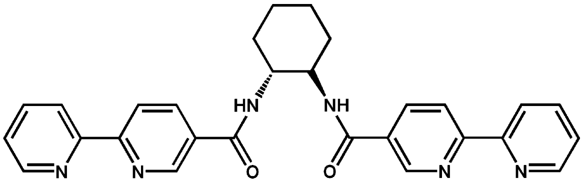
17 **18**

Fig. 4. Chiral ferrocene bridged quaterpyridine species: bis-(*RR*)-[4,5]-pinene-bipyridyl-6′-[ferrocene] L^2 (**17**) (R = H, methyl, isopropyl and benzyl groups) and bis-(*RR*)-[5,6]-pinene-bipyridyl-6′-[ferrocene] L^1 (**18**).

Ferrocene-bridged bis(bipyridine) ligands have also been synthesised and investigated by the above group [88,89]. Copper(I) helicates incorporating the ferrocene-bridged, enantiomerically pure, 5,6-pinene derivative quaterpyridines (**17**) and (**18**) shown in Fig. 4 were synthesised (the related bis-(*R*,*R*)-[4,5]-pinene-bipyridyl-6′-[ferrocene] derivative (L^3) was also employed) and the effects that the different appended diastereomeric pinene substituents had on the nature of the respective double helicate products were investigated [89]. A number of X-ray structures determined using crystals of the $[Cu_2L_2{}^1]^{2+}$ product obtained under different recrystallisation conditions revealed formation of both M and P-double-helices. However, the products obtained for copper(I) with L^2 and L^3 corresponded to P-double helices only (with Λ,Λ configurations at the copper centres). CD spectra revealed that in the case of L^1 the major product in solution, with a positive exciton couplet representing the Λ configuration, was thus the P-double helix. NMR studies indicated that the minor product, the corresponding M-helix (with Δ,Δ metal configurations), corresponded to the one that crystallised. Clearly, the conditions employed for crystallisation affect the observed chirality of the helicates in the solid state; in part, this may reflect different solubility influences. Use of zinc(II) with L^1 also resulted in a P-double helix while interestingly, for silver(I), the product is a M-double helix. It was suggested that the increased size of the silver(I) cation may affect the conformational geometry of the ferrocene bridge leading to the observed experimental outcome.

Constable and co-workers [90] have prepared chiral terpyridine derivatives incorporating enantiopure bornyloxy substituents in their 6-positions. These ligands once again react with copper(I) and silver(I) to yield double helices of type $[M_2L_2]^{2+}$. In the case of the copper derivatives good to high diastereo-selectivity was obtained. With silver(I), solvent-dependent reversible formation of both a mononuclear and dinuclear species was observed. With these non-symmetric ligands ‘head to head’ and ‘head to tail’ isomers are possible; in solution the latter is favoured (although solid-state interactions can overcome this tendency). Interestingly, in prior studies [91] it was found that chiral substituents at the 4′-position of terpyridine were ineffective for inducing selective homochiral helicate formation.

Fletcher and co-workers [92] have also synthesised enantiomerically pure ligands of type *R*,*R*-L and *S*,*S*-L (where L = *N*,*N*′-bis(-2,2′-bipyridyl-5-ylcarbonyl)-(1*S*/*R*,2*S*/*R*)-(+/−)-1,2-diaminocyclohexane) via linking two 2,2′-bipyridine units with a resolved (*R*,*R*)- or (*S*,*S*)-1,2-diaminocyclohexane unit (see **19**). The reaction of these ligands with iron(II), cobalt(III), zinc(II) and cadmium(II) gave dinuclear triple helicate complexes. CD spectroscopy indicated that the chiral diaminohexane unit gives rise to a dominant triple helicate diastereoisomer—with the *R*,*R*-ligand favouring P helicate formation, while the *S*,*S*-ligand favours the corresponding M helicate. Modelling studies indicate that the energy difference between the M and P forms is small. Both the zinc and the cadmium complexes undergo rapid ligand exchange in solution.



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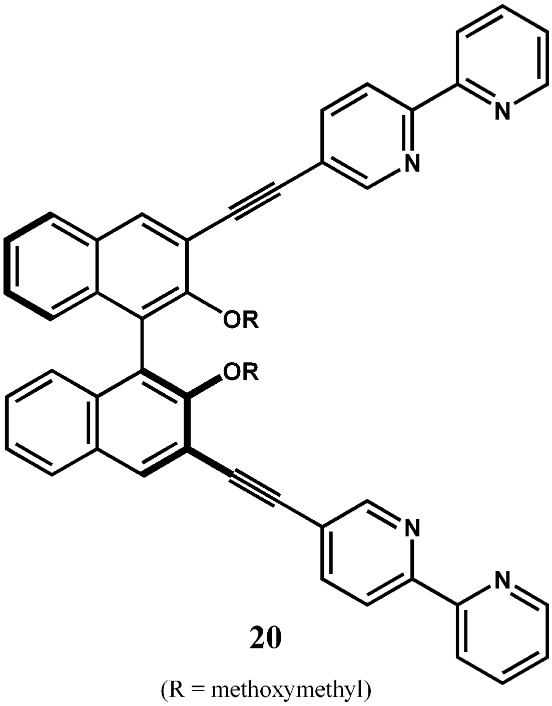
The above group has also reported a range of new helicate structures that are not accessible by traditional self-assembly procedures. These were obtained by utilising the kinetically inert tripodal metal complex building block, *fac*-tris(5-hydroxymethyl-2,2′-bipyridine)ruthenium(II), as a precursor for the stepwise incorporation of additional 2,2′-bipyridine chelating groups, followed by a second metal ion [93]. The procedure employed is illustrated in Scheme 1. By the introduction of the second metal ion in the final step, it is possible to achieve selective formation of a heterometallic helicate, despite two similar coordination environments being present in the final product.

In other studies, the individual ligand strands have been covalently linked by a chiral bridge so that the selective formation of either a P or M configured helicate is induced [94]. For example, complexation of **20** with $Zn(BF_4)_2$ yields a dinuclear triple stranded helicate whose X-ray structure is shown in Fig. 5 [95]. The latter corresponds to a D_3-symmetric, P-configured helicate of type (Δ,Δ)-$[Zn_2L_3]^{4+}$ (L = **20**).



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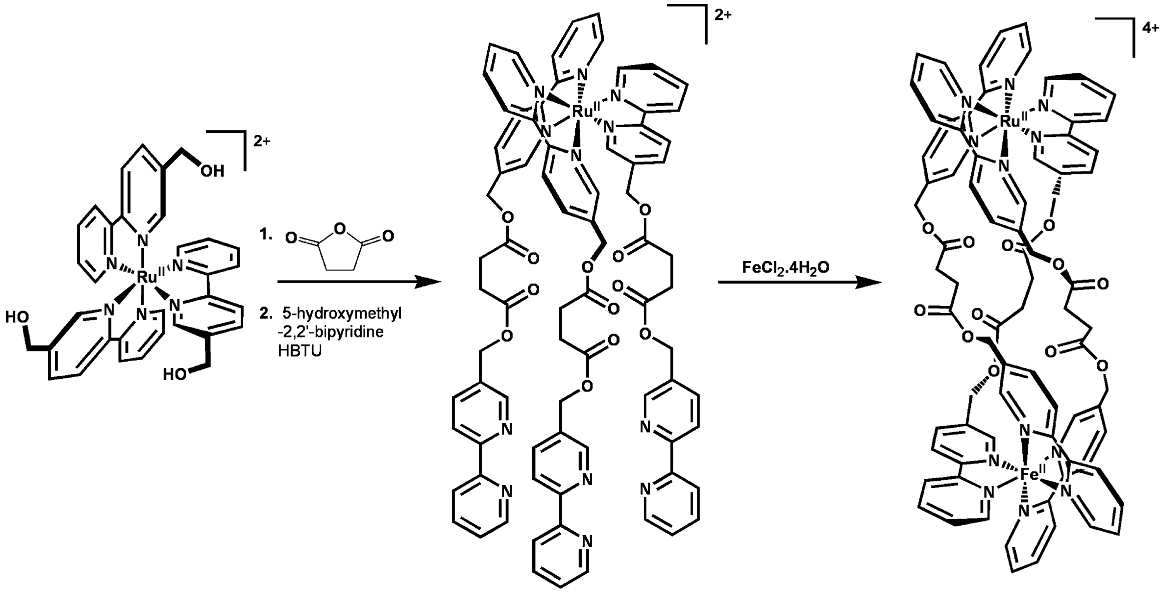
(R = methoxymethyl)

Pyridine-containing arylene/ethynylene strands connected to the 2- and 2′-positions of (*R*)- and (*S*)-1,1′-binaphthyl fragments (see **21**) undergo interaction with copper(I) or silver(I) to yield dinuclear double helicates, whose enantiopurity was established using CD spectroscopy [96]. Structure **22** is representative of the products generated; formation of a 2:1 (M:L.) ratio was confirmed for chloroform/dimethylformamide solution by means of CD titration studies. The CD exciton chirality method was employed to assign the sense of the chirality, the latter being consistent with the predictions from molecular modelling.



Scheme 1. Synthesis of the ruthenium(II), iron(II) heteronuclear helicate, where HBTU = (*O*-(1*H*-benzotriazol-1-yl)-*N*,*N*,*N*′,*N*′-tetramethyluronium hexafluorophosphate) [90].

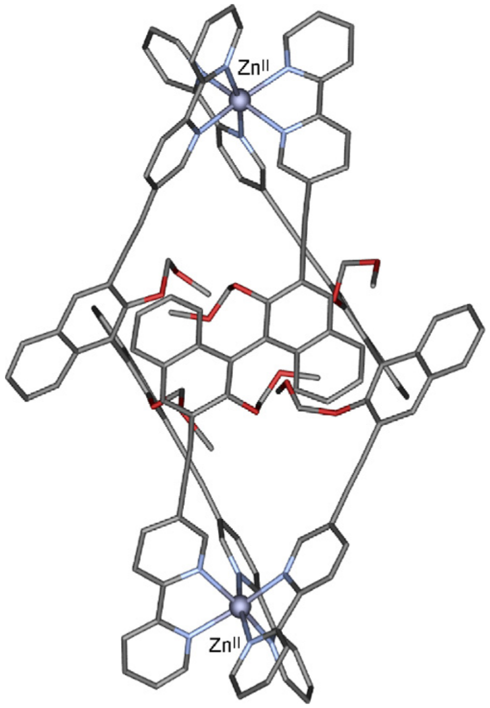
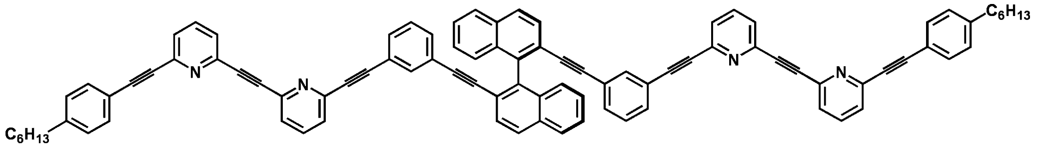


Fig. 5. X-ray structure of $[Zn_2L_3]^{4+}$ (L = **20**) [95].



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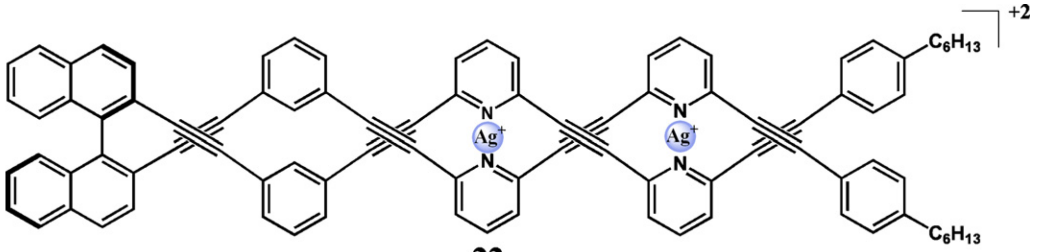

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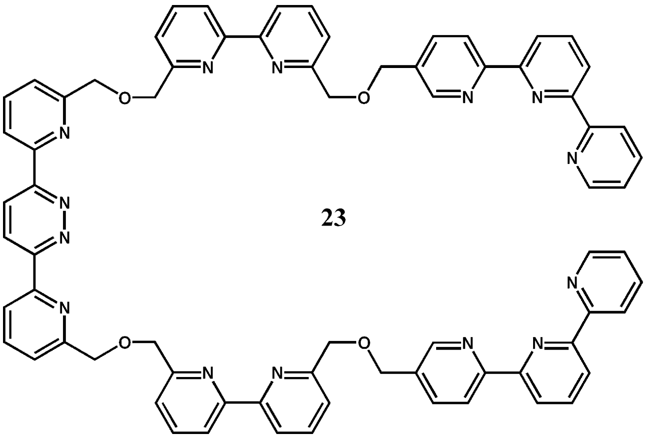
A study by Ueda and co-workers [97] investigated the interaction of oligo(2-ethynylpyridines) with copper(I) to yield tri-, tetra-, and pentanuclear triple-stranded helicates. When a chiral ligand was employed, the stereoselective assembly of a helicate exhibiting a single chirality was isolated. However, racemisation of the copper(I) helicate was observed in solution. A further report by this group [98] describes triple-stranded helicates possessing polyether side chains formed by reaction of oligo(ethynylpyridines) with copper(I).

Finally, in this section it is noted that double helix formation under solvent-free conditions has been achieved [99] by grinding chiral oligo(bipyridine) ligands with $[Cu(CH_3CN)_4]PF_6$ to yield products that matched those obtained previously by conventional solution synthesis [94,100].

2.4. Elaborated helical systems

Elaborated (hybrid) ligand systems incorporating potential helical domains have also been reported [101,102]. For example, **23** contains six metal ion binding domains of three different types [102]. Two of the latter are typical ‘helicate’ binding domains and both sets of these are separated by two fused binding sites that are typical grid-forming domains; namely, of the total of six sites, four are ‘coded’ for helicate formation and the remaining two (central) sites are coded for grid formation. Metal binding by this polytopic system was investigated to probe whether possible structural competitive behaviour on formation of the corresponding metallo-supramolecular assemblies might occur. Reaction of **23** with two equivalents of copper(II) or zinc(II) yielded coordinately unsaturated double helical products of type $Cu_4(L)_2(CF_3SO_3)_8$ and $Zn_4(L)_2(PF_6)_8$. The X-ray structures of these products show cyclic arrangements incorporating two bound double-helical domains linked by central (uncomplexed) pyridine–pyrazine–pyridine bridges (see Fig. 6); these helical arrangements are generated in preference to alternative grid-like structures. Mixed metal species were also prepared and were shown by ESMS to have the stoichiometries $Co_4Cu_8(L)_4(PF_6)_{16}$ and $Ni_4Cu_8(L)_4(PF_6)_{16}$. For these, symmetrical geometries were proposed in which all heteroatom donors of each ligand are bound to a metal and four di-copper-containing helical units radiate from a central tetranuclear (cobalt or nickel) cluster.



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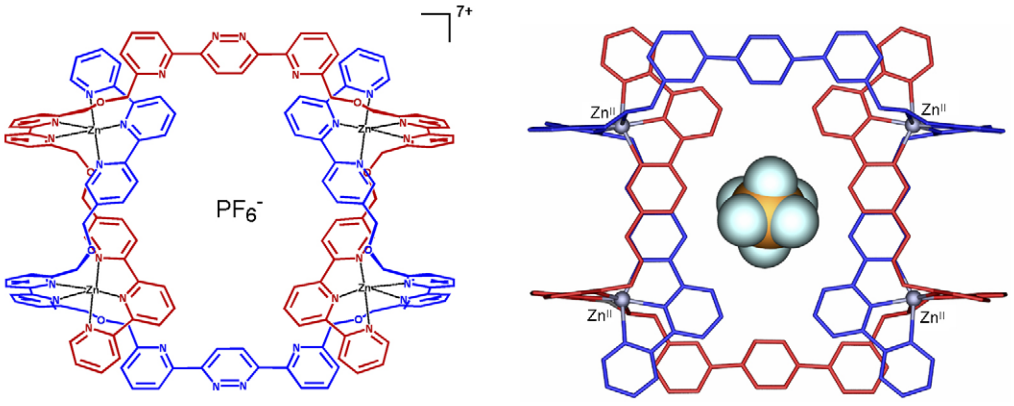
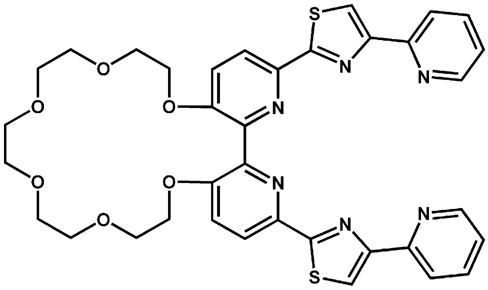


Fig. 6. The structure of the cation in $[Zn_4(L)_2{\subset}PF_6)](PF_6)_7$ (L = **23**) [102].

It is noted that other pyridyl-containing ligands related to those discussed above have also been employed for triple helicate formation with cobalt(II) [103].

The ditopic ligand **24** reacts with copper(II) to give a double helicate of type $[Cu_2L_2]^{4+}$ which is then further able to coordinate to s-block cations such as lithium, sodium and barium [104]. Coordination of the latter metal ions leads to a variation of the pitch of the attached helicate that depends on the size and charge of the guest cation.



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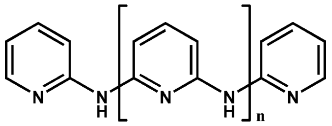
3. Metal-chain oligo-pyridylamido systems

The investigation of one-dimensional (1D) oligomers incorporating metal-chain backbones has received considerable attention over recent years [105–107]. In part, interest in such systems relates to their apparent suitability for investigating fundamental aspects of metal–metal interaction as well as their potential application as nanoscale analogues of conventional electric wires [108–112].

Metal-chain complexes with the deprotonated forms of oligo-pyridylamino ligands of type **25** of different lengths ($n = 0$, 1, 2) and chromium(II), cobalt(II), nickel(II), copper(II), ruthenium(II) and rhodium(II) have been synthesised [102]. For example, $Ni_3L_4Cl_2$ (where L is the deprotonated form of **25** ($n = 0$); usually abbreviated dpa = dipyridylamido) was first reported in 1968 [113], while its X-ray structure (Fig. 7) was not described until 1991 [114]. In this complex, the nickel ion in the inner section of the chain has a low-spin square planar coordination environment while the terminal nickel ions are five-coordinate and high spin.



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Subsequently the X-ray structure of a nona-nickel derivative, $[Ni_9L_4Cl_2]$ (L = deprotonated form of **25** with $n = 3$), was also reported [105]. The results of band structure calculations for infinite one-dimensional nickel(II) and chromium(II) chains based on this structure were also discussed. As occurs in the above structure, linear chains of nickel(II) ions bound by oligo-pyridylamido ligands and terminated at each end with monodentate ligands in axial sites results in systems in which the properties of the metal ions vary with their position in the chain. Metal-chain systems based on oligo-pyridylamido derivatives such as those of deprotonated **25** can be classified into two categories based on whether strong metal–metal bonding is present or not.

There have been a number of other computational studies to probe the nature of such systems [115–120]. DFT calculations

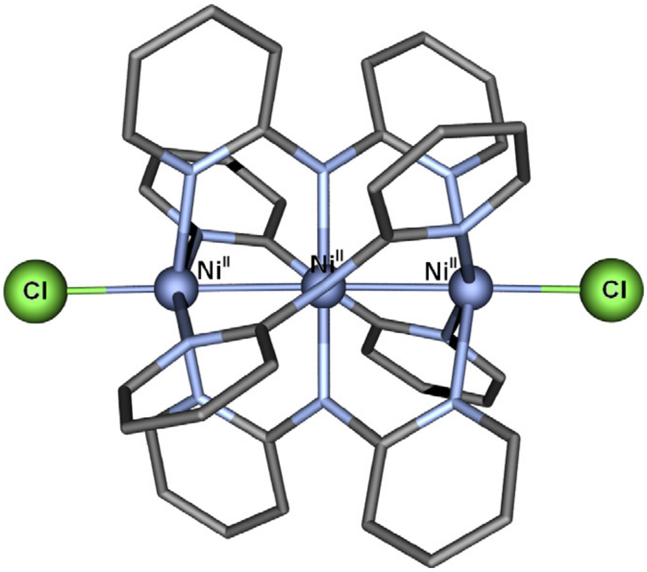
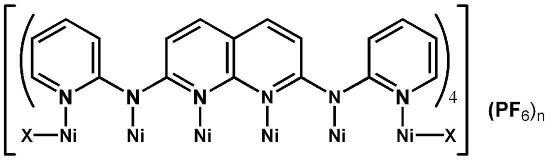


Fig. 7. Structure of $Ni_3L_4Cl_2$ (where L is the deprotonated form of **25** ($n = 0$)) [114].

for the model system $Ni_3L_4Cl_2$ (L = the deprotonated form of **25**, $n = 0$) have been carried out [120]. As mentioned above, in this complex the nickel ion in the inner section of the chain has a low-spin square planar coordination environment while the terminal nickel ions are five-coordinate and high spin. The latter high spin states gives rise to an antiferromagnetic interaction involving four electrons; coupling of the outer nickel ions via the central ion was proposed, with the interaction involving both direct magnetic exchange as well as superexchange (via the dipyridylamido ligands).

In other work, a STM study [121] of one-dimensional chains related to the above was undertaken in the context of their possible use as molecular wires.

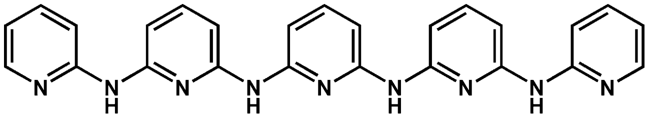
The preparation, magnetic properties and electrochemistry of the related linear (approximately D_4 symmetry) hexanuclear nickel complexes of type **26** ($n = 2$; X = Cl or NCS) incorporating four dianionic 2,7-bis(2-pyridylamino)-1,8-naphthyridine ligands have been reported [107]. The X-ray structure of $[Ni_6L_4(NCS)_2](BPh_4)_2$ was also obtained. Studies of the corresponding one electron reduction complexes, **26** ($n = 1$, X = Cl, NCS), were also carried out, with the X-ray structure of $[Ni_6L_4Cl_2]PF_6$ also being presented. Once again, in the non-reduced complexes the two terminal nickel ions have high-spin states ($S = 1$) and the four inner ones are low-spin ($S = 0$). Weak antiferromagnetic coupling between the terminal nickel ions (ca. $-5\,cm^{-1}$) is present in the complexes while partial metal–metal bonds (associated with a short Ni–Ni distance of 2.202 Å) occur in the one-electron reduction products. Magnetic results for the latter species are in agreement with a localized model, in which the two terminal nickel ions are in a spin state of $S = 1$ whereas this time the central Ni(3)–Ni(4) pair have a spin state of $S = 1/2$. Relatively strong antiferromagnetic coupling of around $60\,cm^{-1}$ occurs between the terminal and the central dinickel ions.



26 (X = Cl, NCS)

In a parallel study employing the same ligand system, related synthetic, magnetic, electrochemical and X-ray diffraction investigations on the corresponding hexacobalt(II) complexes and their one-electron reduced derivatives, namely, $[Co_6L_4(NCS)_2](PF_6)_n$ ($n = 1$ and 2) and $[Co_6L_4(OTf)_2](OTf)_n$ ($n = 1$ and 2), were performed [122].

Nickel(II) complexes involving a chain of three metal ions embraced by two interlocking heptadentate dianionic ligands (deprotonation of the secondary amines adjacent to the terminal pyridyl groups occurs) derived from **27** and the substituted derivatives, **28**, have been reported [106]. This type of extended metal chain differs from those discussed above in that the two ligands are arranged like opposed interlocking hairpins around the enclosed metal string. That is, the second ligand is introduced in a plane that is perpendicular to that of a first ligand but oppositely orientated. Four such compounds, all crystallographically characterised, were obtained in this case.



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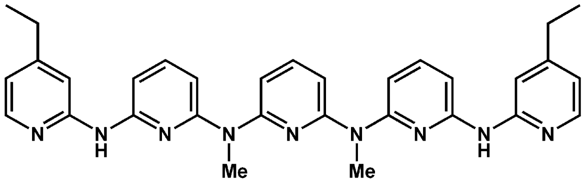

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4. Grids

4.1. General considerations

Metal-directed self-assembly has also allowed the efficient production of supramolecular entities with grid-like architectures. The intense current interest in such systems is driven largely by their potential for molecular scale information storage and processing. Lehn and co-workers have been major players in this area and a seminal review by this group [123] appeared in mid-2004, covering the preparation of individual systems, as well as mechanistic aspects of the self-assembly process and important grid properties. Twenty individual ligands or ligand types are listed in this review; all but one are polypyridyl systems which incorporate the equivalent of multi bipyridine-type or multi terpyridine-type entities by virtue of their bridging groups (aza- or polyaza aromatic rings or appropriate acyclic functionality). The present review will selectively address more recent developments, that is, literature from 2004 to the present.

Many of the studies outlined below have demonstrated that the grid complexes discussed exhibit interesting electrochemical and magnetic properties. In this connection it is noted that two recent reviews (in this journal) deal with the magnetic properties of grids and related polynuclear architectures [124,125] and hence these aspects will not be given emphasis in the present discussion.

4.2. Simple [2 × 2] grids

Further reports of simple [2 × 2] homometallic grid complexes continue to appear. Representative examples include copper(I), silver(I), and zinc(II) grid complexes of 4,6-bis(6-methylpyridin-2-yl)-2-phenylpyrimidine **29** (R = Ph, R′ = Me) [126] and copper(I) and silver(I) complexes of the related diethylamido ligand **27** (R = H, R′ = $CONEt_2$) [127]. The latter forms a zigzag polymeric chain with manganese(II) ions and had previously been shown [128] to afford octahedrally coordinated [2 × 2] grid complexes with iron(II), cobalt(II), and zinc(II).

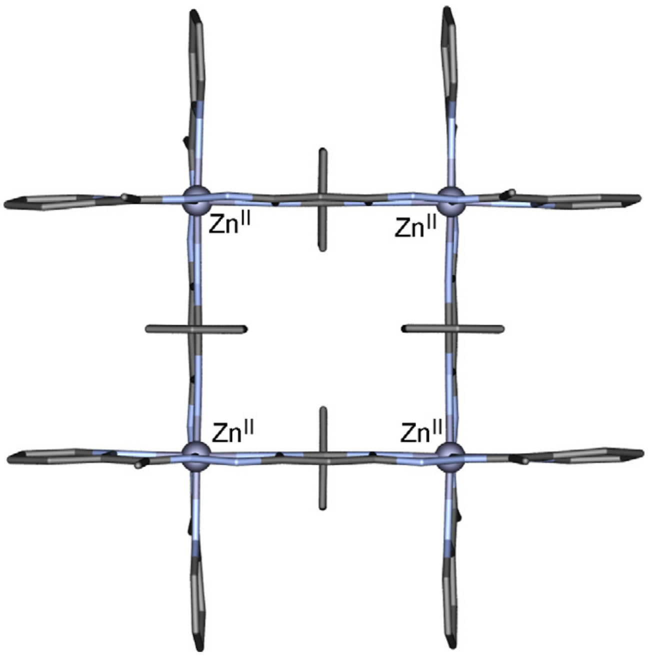
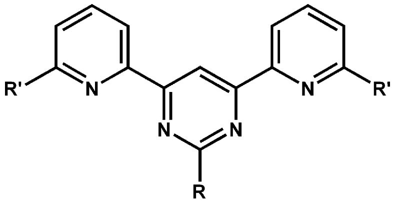


Fig. 8. X-ray structure of $[Zn_4L_4]^{8+}$ (L = **30**; R = Me, R′ = H) [129].



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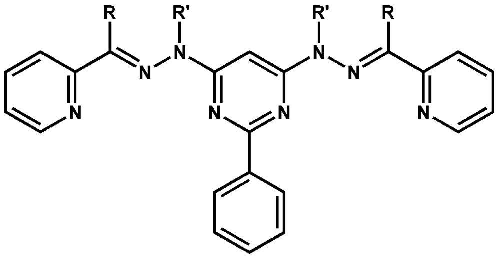
Zinc(II) [2 × 2] grid complexes derived from a family of symmetrical bis(hydrazone)pyrimidine ligands – exemplified by **30** (R = Me, R′ = H) – have also been reported [129]. In such complexes, π–π stacking between the phenyl ring and the hydrazone moieties of the perpendicular ligands leads to an almost perfectly orthogonal arrangement (Fig. 8), suitable for applications in self-organized metallo-upramolecular systems.



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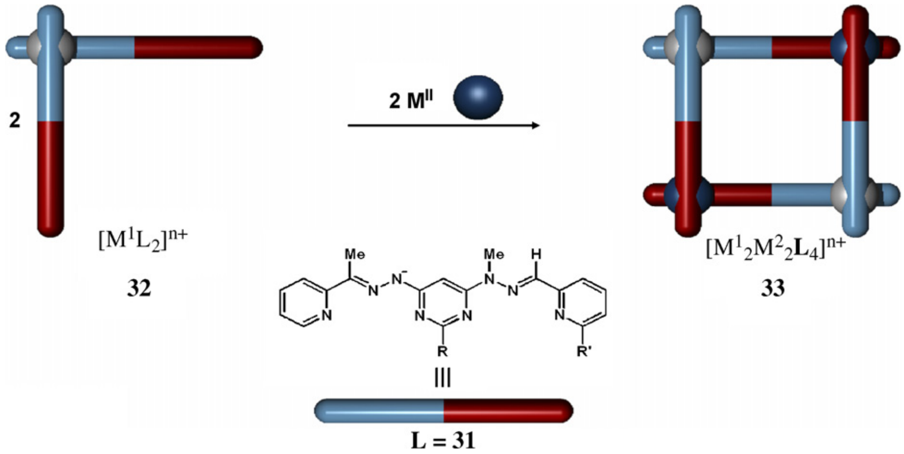
Interestingly, the parent bis-hydrazone **30** (R = R′ = H) affords different cobalt [2 × 2] grid complexes depending on the cobalt(II) counter-ion and solvent used for the self-assembly [130]. With $Co(BF_4)_2{\cdot}6H_2O$ in MeCN the paramagnetic $[Co_4^{II}L_4](BF_4)_8$ (L = **28**; R = R′ = H) grid complex is formed while with $Co(OAc)_2{\cdot}4H_2O$ in H_2O–MeOH the diamagnetic $[Co_4^{III}L'_4](PF_6)_4$ (where L′ is the doubly deprotonated form of **30**; R = R′ = H) grid complex was isolated on oxidation and precipitation of the product as the hexafluorophosphate salt. The cyclic voltammogram of the former complex shows a pair of two-electron ligand based reduction waves as well as a quasi-reversible four electron wave assigned to a Co(II)/Co(III) oxidation process.

4.3. Heterometallic grids

A novel three-tiered synthetic route [131] has been used to prepare an extended series of mixed-valence, mixed-spin-state, and heterometallic [2 × 2] grid like arrays based on heteroditopic hydrazone ligands **31** [132] (Scheme 2). Key to these syntheses is the controlled assembly of corner-type complexes **32** $[M^1L_2]^{n+}$ (M^1 = cobalt(III), $iron(II)_{LS}$; L = **31**) which in turn are reacted with a second metal ion (M^2 = cobalt(II), iron(II), zinc(II)) to afford the [2 × 2] grids **33** in a chiro- and toposelective assembly process. The 2-pyrimidine (R) and 6-pyridine (R′) substituents affect the overall complex geometry and influence both the electrochemical and magnetic properties of these systems. A case in point is the novel mixed-spin-state tetranuclear iron(II) grid $[(Fe_{LS})_2(Fe_{SC})_2L_4]^{4+}$ (L = **31**; R = H, R′ = Me]. Overall the grids act as electron



Scheme 2. Synthesis of heterometallic [2 × 2] grid-like arrays based on heteroditopic hydrazone ligands of type **31** [132].

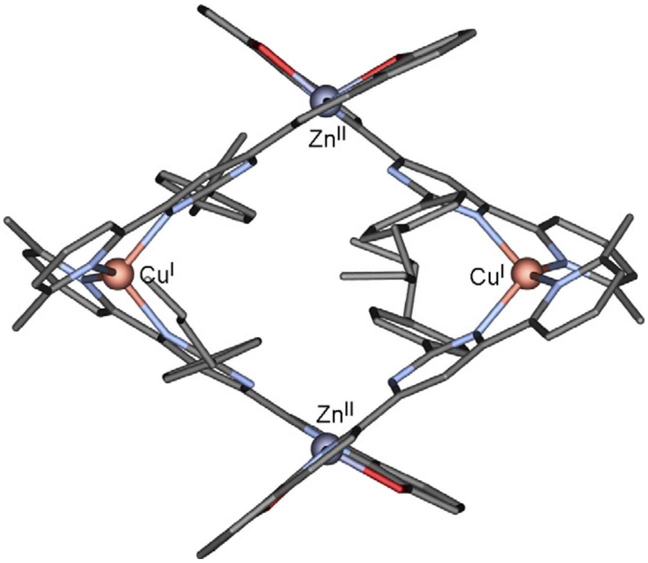
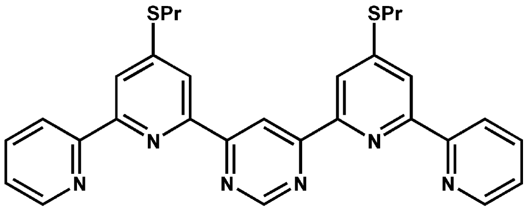


Fig. 9. X-ray structure of $[Zn_2Cu_2L_4]^{2+}$ (L = the deprotonated form of **35**) [135].

reservoirs and exhibit up to eight single-electron, reversible reductions. The latter generally occur in pairs and are assigned to ligand-based reductions as well as to the Co(III)/Co(II) couple.

An earlier approach to heterometallic [2 × 2] grids containing ruthenium(II), osmium(II) and iron(II) subunits involved either a sequential self-assembly process or a stepwise protection–deprotection procedure [133]. In both cases a “corner-type” mononuclear complex – derived from the pyrimidine linked bis-bipyridine ligand **34** – containing kinetically inert ruthenium(II) or osmium(II) was combined with a second metal ion of lower kinetic stability (iron(II), cobalt(II) or nickel(II)). The crystal structure [134] of the Ru_2Fe_2 grid complex confirms the *anti* topology of the ‘like’ metal ions and shows the presence of both possible enantiomers in the unit cell. The electrochemistry of these species is characterised by several metal-centred oxidation and ligand centred reduction steps, most of which are reversible [133]. The electronic interaction between particular subunits depends on their relative location and the oxidation states of the other components.

An alternative approach to the construction of heterometallic [2 × 2] grids involves the use of ligands with both bidentate and tridentate binding sites designed to accommodate metals of differing coordination geometry. Thus, the pyrimidine linked ligand **35** assembles with 0.5 equivalents each of Zn^{2+} and Cu^+ in the presence of tetramethylammonium hydroxide to give the heterometallic [2 × 2] grid $[Zn_2Cu_2L_4]^{2+}$ (L = the deprotonated form of **35**) [135]. The crystal structure of this cation (Fig. 9) clearly shows a diamond shaped tetrameric assembly with the two tetrahedrally coordinated copper(I) atoms on one diagonal and the two octahedrally coordinated zinc(II) atoms on the other. Preliminary mass spectral data indicate that copper(II) can replace zinc(II) in the above process.



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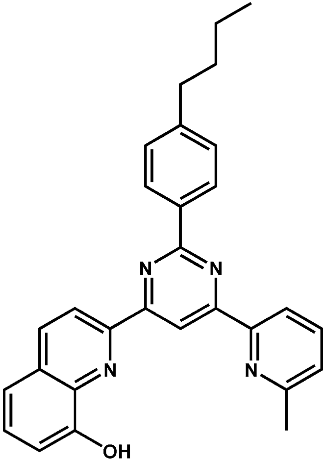

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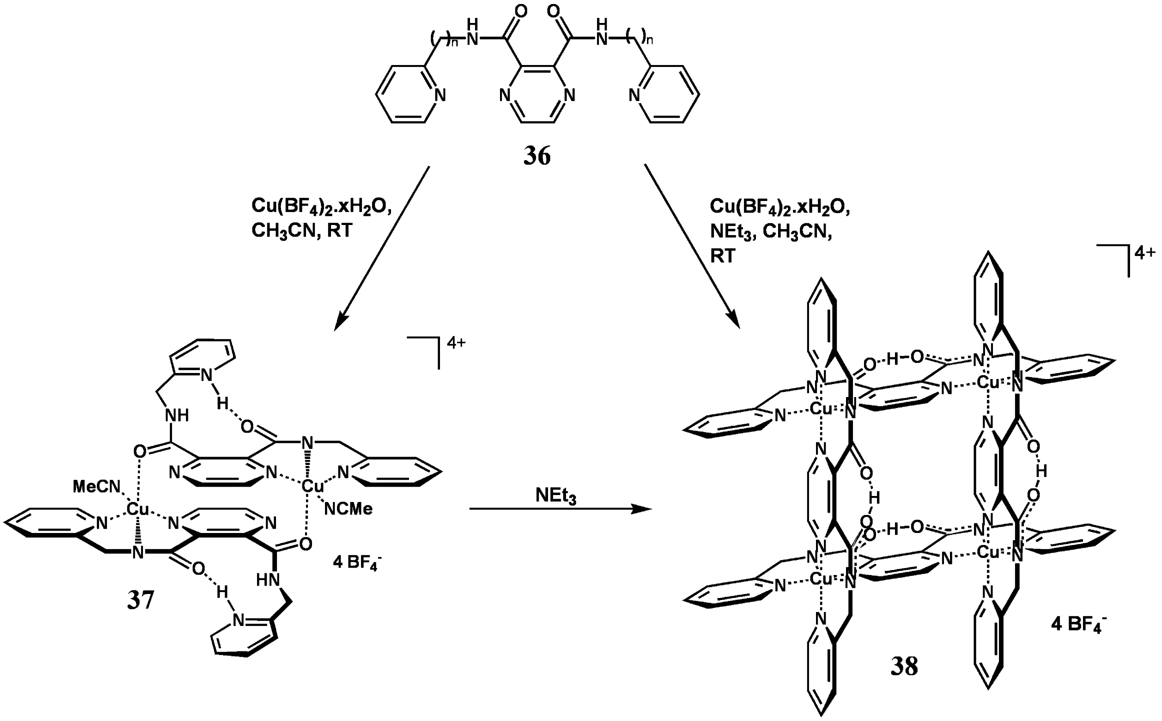
4.4. pH control of grid self-assembly

Studies involving the pyrazine-linked diamido ligands **36** ($n = 1, 2$) have provided opportunities to examine pH control of their self-assembly with appropriate metal ions. Reaction of the 2-pyridylmethyl compound **36** ($n = 1$) with $Cu(BF_4)_2 \cdot xH_2O$ (1:1 in MeCN) affords the dimeric copper(II) complex **37** of a zwitterionic form of the ligand (that is, two amide protons transferred to the two non-complexing pyridylmethyl side arms) (Scheme 3). Treatment of **37** with one equivalent of NEt_3 led to the symmetrical [2 × 2] grid complex **38** of the mono-deprotonated form of the ligand. This same complex was also formed in the (1:1:1) reaction of **36** ($n = 1$) with $Cu(BF_4)_2 \cdot xH_2O$ and Et_3N [136]. Similar results were described in a subsequent report by Stoekli-Evans and co-workers [137] except that added base was not required for formation of the copper(II) [2 × 2] grid complex (formed and isolated as the perchlorate salt) and the isolation of a nickel(II) [2 × 2] grid complex analogous to **38** was described.

Contrasting modes of self-assembly with cobalt ions were observed for the 2-pyridylethyl ligand **36** ($n = 2$) and its 2,5-substituted regioisomer **39** [138]. Reaction of **36** ($n = 2$) with one equivalent of $Co(BF_4)_2 \cdot 6H_2O$ in MeCN followed by air oxidation gave a mononuclear corner-type complex $[Co^{III}L]_2(BF_4)_3$ (L = **36**, $n = 2$) of the neutral ligand in a zwitterionic form. By contrast, similar reaction of **39**, most cleanly in the presence of two equivalents of NEt_3, afforded the [2 × 2] ‘grid-like’ complex $[Co^{III}{}_4L_4](BF_4)_4$ (L is the doubly deprotonated form of **39**) whose X-ray structure (Fig. 10) clearly shows the interwoven nature of the ligand strands.

A recent report [139] provides further details of the earlier studies discussed above and describes two subtly different square copper(II) complexes derived from different protonation



Scheme 3. Reaction of $Cu(BF_4)_2$ with **36** in the presence and absence of base [136].

states of ligand **36** ($n = 2$), together with a more conventional nickel(II) [2 × 2] grid complex of the mono-deprotonated version of the same ligand. These complexes display weak antiferromagnetic spin coupling.

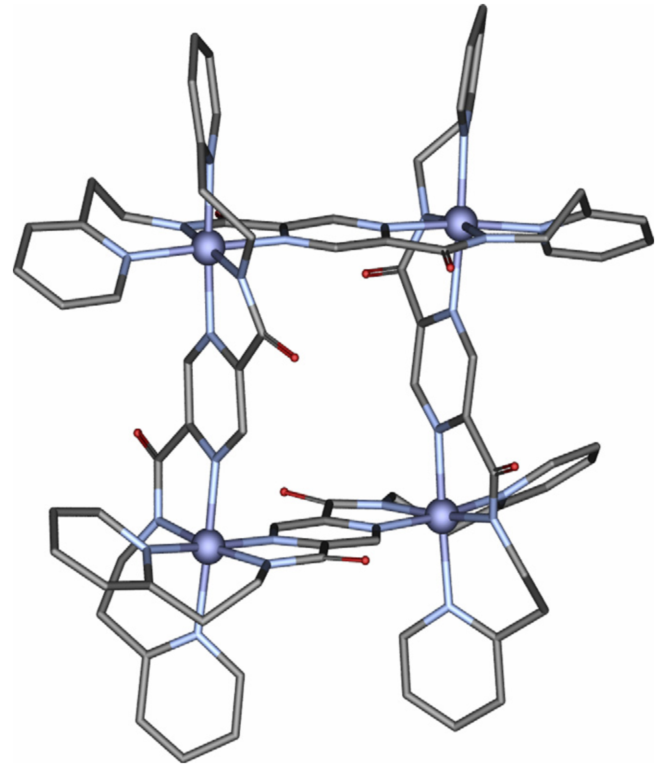
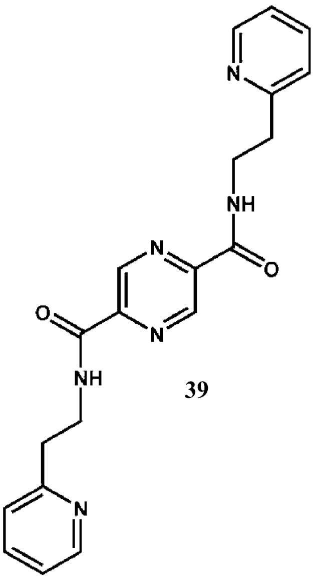


Fig. 10. X-ray structure of $[Co^{III}{}_4L_4](BF_4)_4$ (L is the doubly deprotonated form of **39**) [138].



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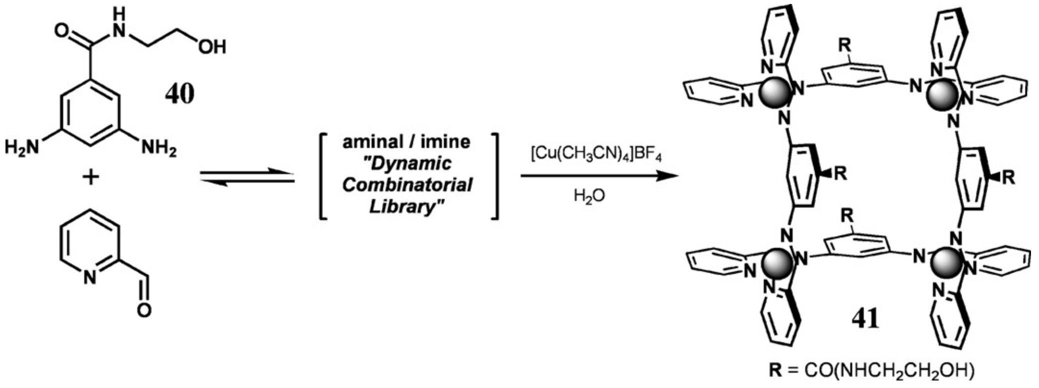
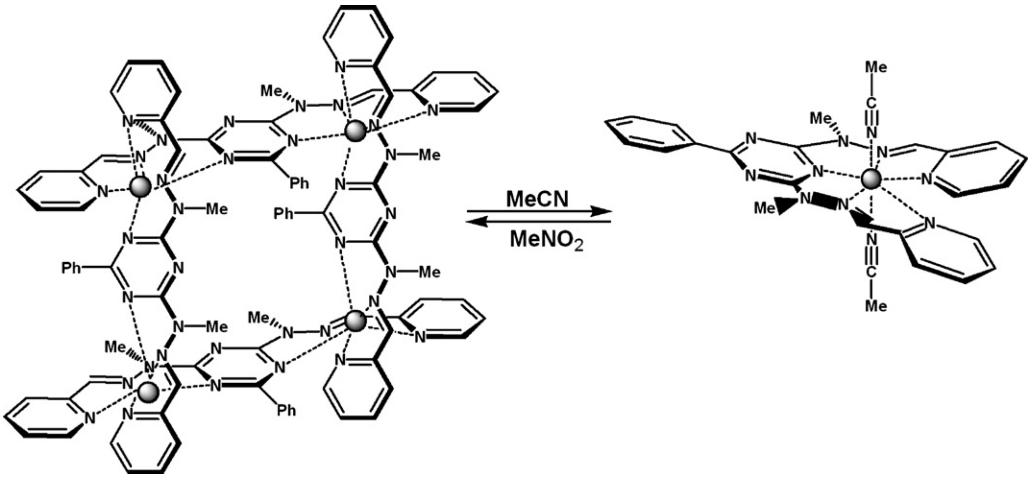
4.5. Dynamic processes involving grid complexes

A dynamic combinatorial aminal/imine library formed by reaction of diaminobenzamide **40** with pyridine-2-carboxaldehyde collapses uniquely in aqueous solution to the distorted [2 × 2] copper(I) grid **41** upon addition of $[Cu(CH_3CN)_4]BF_4$ (Scheme 4) [140]. This self-assembly process was not observed at all in other solvents, leading to the suggestion that the hydrophobic effect might play an essential role in the formation of **41**.

A recent communication [141] describes the solvent-mediated reversible conversion of a [2 × 2] grid into a pincer-like



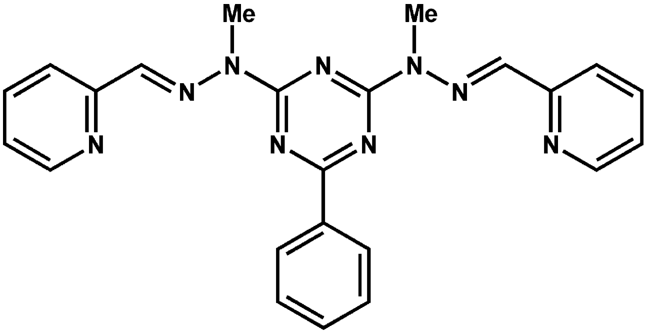
Scheme 4. Copper(I) mediated assembly of **41** [140].



Scheme 5. Solvent-mediated interconversion of grid and pincer-like complexes [141].

complex. This study involved the 1,3,5-triazine-linked bis-hydrazone **42**, which has the potential to provide separate double and single terpyridine-like binding sites. Reaction of **42** with $Co(BF_4)_2{\cdot}6H_2O$ in $MeNO_2$ and crystallisation by diffusion of $CHCl_3$ afforded the paramagnetic [2 × 2] grid complex $[Co_4L_4]^{8+}$ (L = **42**); by contrast, a similar reaction in acetonitrile produced the monomeric pincer-like cationic complex $[CoL(MeCN)_2]^{2+}$ (L = **42**) (Scheme 5). Interconversion between these complexes can be promoted by other species capable of coordinating to the axial sites of the pincer complex, in particular, primary amines and DMSO.

Constitutional dynamic libraries have been prepared by $Sc(OTf)_3$/microwave-assisted transimination of helical oligohydrazone strands related to **30**. Particular libraries are driven towards the production of specific [2 × 2] grid arrays by treatment with appropriate metal ions [142,143]. For example, the one-turn helical strand **43** (for clarity drawn as a linear strand) containing four hydrazone units affords a library with 26 characterised new components by reaction with the 3,4,5-trimethoxyphenylbis(hydrazine) **44** in the presence of 20 mol percent $Sc(OTf)_3$ in $CHCl_3$. In turn, this library leads to the previously characterised [2 × 2] grid complex $[Zn_4L_4]^{8+}$ (**30**, R = H, R′ = Me) as a major product from its treatment with one equivalent of Zn(OTf).



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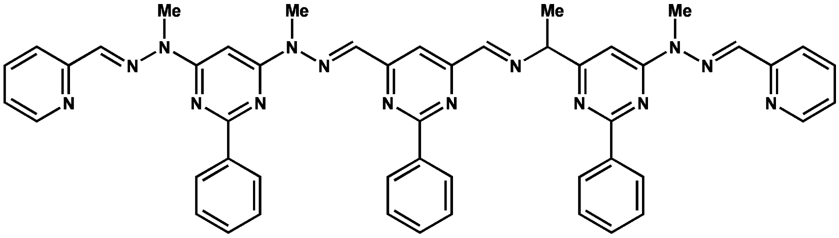
In a related study [144], a series of oligohydrazones related to **43** (containing two to ten hydrazone units) were shown to undergo helical unwinding promoted by complexation with metal ions such as zinc(II) or lead(II). The products from such complexation were generally linear rack-type complexes for the higher oligomers and grid and/or rack complexes for the lower members of the series, depending on the substitution pattern and the ligand:metal ion ratio. These interconversions between the helical free ligand and the extended ligand in the complexes lead to “nanomechanical” motions of large amplitude (extension factors of >500% in most cases).



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4.6. Functional assemblies

Some initial progress towards the incorporation of grid architectures into functional entities has been made recently. At a simple level, the hydrazone groups of ligands such as **30** (and regioisomers) have been decorated with biologically relevant functionality (for example, dipeptide moieties) and their ability to form [2 × 2] grids with metal ions such as zinc(II) and cobalt(II) examined [145]. These studies are seen as a first step towards the development of nano-biochips incorporated onto grid 'surfaces'. More ambitiously, bis-bipyridine ligands related to **34** have been elaborated to contain further pyrid-3- or 4-yl binding sites designed to promote hierarchial self-assembly of initially formed iron(II) [2 × 2] grids into more complex 1D and 2D architectures by subsequent reaction with an appropriate second metal ion. Thus, the iron(II) [2 × 2] grid complex derived from the bis-4-pyridyl substituted ligand **45** self assembles with silver(I) ions to afford the wall-like 2D complex $\{([\mathrm{Fe^{II}}_4\mathrm{L}_4](\mathrm{Ag^{I}})_4)^{12+}\}_n$ (where L = **45**), see Fig. 11, with consequent modulation of its magnetic properties [146]. An analogous reaction of the corresponding bis-3-pyridyl isomer, but with $\mathrm{La^{III}}$ in place of $\mathrm{Ag^{I}}$, affords a 1D columnar species.

Discrete [2 × 2] copper(I) grid complexes based on the 3,6-di(pyridine-2-yl)pyridazine moiety have been incorporated into star-shaped poly(ε-caprolactam) via a supramolecular variant of 'click' chemistry [147]. A related approach had previously been used to incorporate the same moieties into poly(L-lactide) by utilising a hydroxybutyl substituted pyridazine as a co-initiator in a controlled aluminium alkoxide-based polymerisation of L-lactide, followed by complexation with copper(I) ions [148]. Finally, early steps towards the integration of [2 × 2] grid-type complexes into functional materials have been taken. In particular, the 4,6-bis(2,2′-bipyrid-6-yl)-2-phenylpyrimidine ligand **46** and its [2 × 2] iron(II) grid complex have been adsorbed on highly ordered pyrolytic graphite (HOPG) and the resulting assemblies visualized by scanning tunneling microscopy (STM) at submolecular resolution [149]. The hexadecyl groups of **46** are designed to provide additional attractive forces with the HOPG surface. For the grid complex two stable orientations on the surface are observed—a flat and an edge-on assembly, of measured dimensions consistent with the known X-ray structure

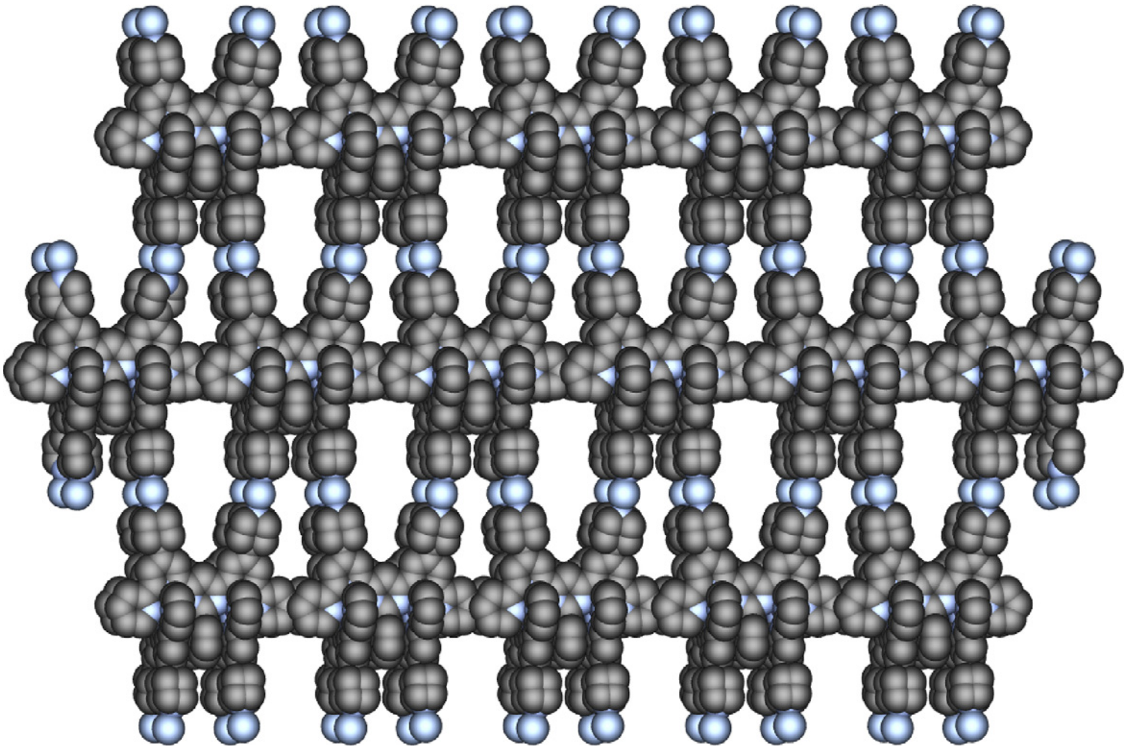
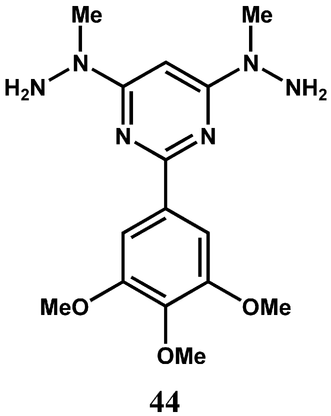


Fig. 11. X-ray structure of $\{([\mathrm{Fe^{II}}_4\mathrm{L}_4](\mathrm{Ag^{I}})_4)^{12+}\}_n$ (where L = **45**) [146].

of the free complex. In a further exciting development, current imaging tunneling spectroscopy (CITS) has been applied [150] to the direct imaging of the metal centres of a single molecule of a [2 × 2] Co_4^{II} grid complex (derived from the parent 4,6-bis(2,2′-bipyrid-6-yl)-2-phenylpyrimidine) within an ordered assembly, again on a HOPG surface.



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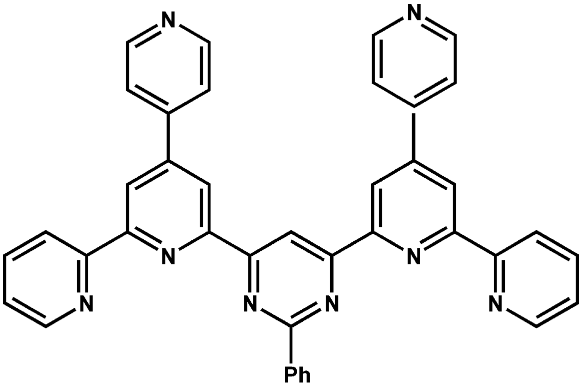

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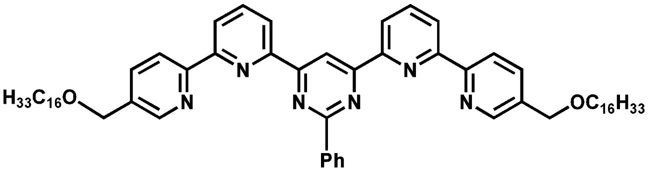

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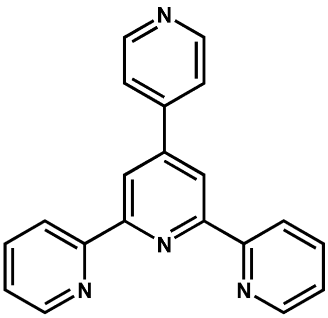


47

5. Other systems

5.1. Backbone-linked difunctional systems

Classical di- or tripyridine-containing ligands that are linked via their backbones to produce potential difunctional ligand derivatives, with sets of coordination donors that are unable to be directed towards a single metal centre, are known. For example, there are now a considerable number of studies involving the interaction of metal ions with ligands in which a terpyridine moiety has been linked via the 4-position of its central pyridyl ring to a further pyridyl or terpyridyl unit. Systems of this type have been the subject of recent timely reviews by Schubert and co-worker [151] and Constable [4], and only a few representative studies involving such systems will be discussed here.

The pyridyl–terpyridyl derivative **47** readily forms bis-ligand complexes with iron(II), copper(II), ruthenium(II) and osmium(II) of type $[ML_2]^{2+}$ in which metal binding occurs via the terpyridyl groups, leaving the pendant 4-pyridyl groups available for further reaction (including protonation, alkylation or coordination to an additional metal centre) [152–156].

In a typical metallo-supramolecular application, complexes of this type were demonstrated to act as the sides of discrete molecular squares by spanning the metal ions in 'corner' units of type $[Re(CO)_3Br]^+$ or $[Pd(dppf)]^{2+}$ (where dppf = 1,1′-bis(diphenylphosphino)ferrocene)—such that each corner metal centre changes its coordination number from four to six by *cis*-binding to two pyridyl groups from each of the adjacent side units forming the square [157,158].

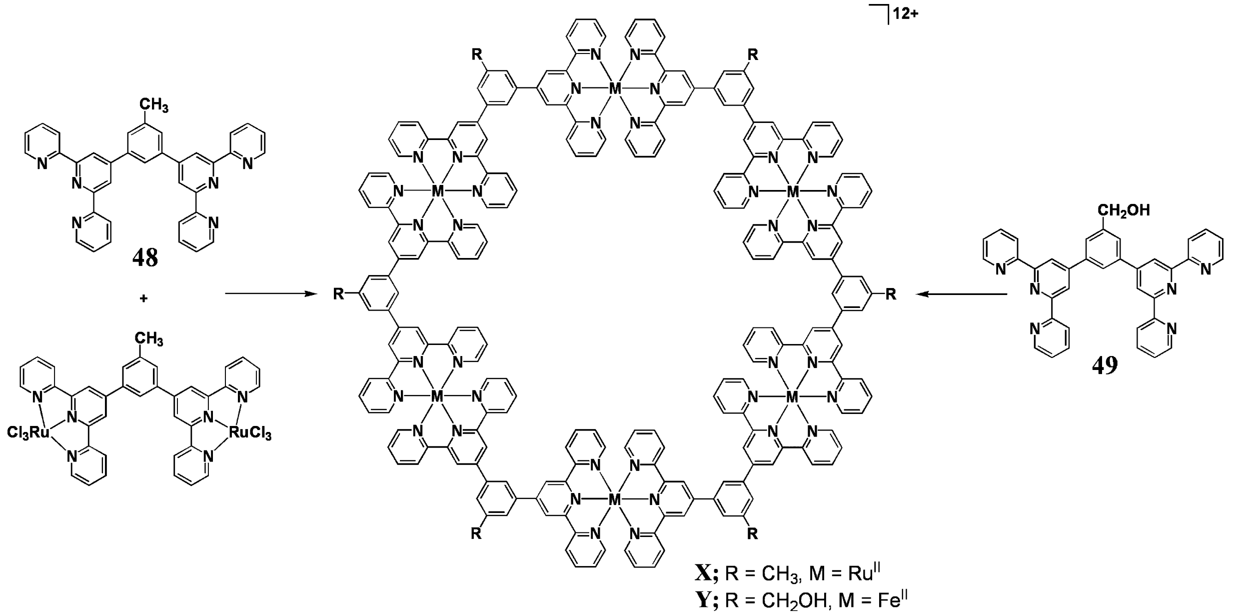
Reaction of the pendant pyridyl groups of $[RuL_2]^{2+}$ (L = **47**) with bis[4-(bromomethyl)phenyl]methane has been recently demonstrated to lead to formation of the corresponding [2 + 2] ruthenium(II) metallacycle [156].

As also found for the pyridyl–terpyridine ligand derivatives, prior work has demonstrated that bis(terpyridine) ligands (in which the two bipyridine fragments are linked via a range of linking groups at the 4-positions of the respective central pyridyl rings) yield both polymeric and discrete metallo-supramolecular species [4,159].

An interesting example of the formation of a discrete supramolecular structure is given by the self-assembly of hexaruthenium(II) or iron(II) metallacycles incorporating the bis-terpridine ligands **48** and **49** shown in Scheme 6. In the ruthenium case the assembly occurs via condensation of equimolar mixtures of bis-metallated and non-metallated bis(terpyridyl) monomers whereas, with iron(II), only a single (non-metallated) bis(terpyridyl) ligand is involved [160].

Other recent reports related to the above and involving discrete 4,4′-linked terpyridine systems include papers by Yam et al. [161], Newkome and co-workers [162–166], and Schemittel et al. [167].

Related studies to the above employing linked dipyridylamine (dpa) moieties, containing bridges connecting the central (aliphatic) amine sites of two dpa entities, have also been carried out. For example, such aryl-linked dpa derivatives in which the secondary nitrogen of each dpa is directly

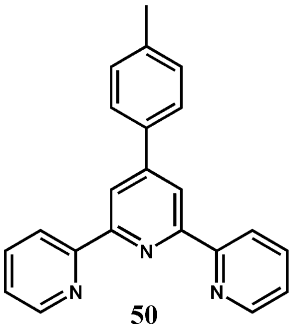


Scheme 6. Self-assembly of hexaruthenium(II) or iron(II) metallacycles incorporating bis-terpyridine ligands **48** and **49** [160].

bound to the aryl bridge have been employed in studies that range from metal coordination and supramolecular chemistry [168–175] to the synthesis of new luminescent materials [176–182]. Palladium(II) and platinum(II) complexes of such dpa derivatives have also been investigated as potential anticancer agents due to their structural similarity to *cis*-platin [183–187]. Linked di- (and tri-) dpa derivatives in which the linking groups between the dpa fragments are flexible have also been synthesised [186–188] and their complexes with copper(II) (as well as related mono-dpa derivatives of palladium(II) and platinum(II) [186,187]) together with silver(I) [189] have been reported. In the latter case a recent study [189] showed that the 2,2′-dipyridylamine derivatives, 1,2-bis(di-2-pyridylaminomethyl)benzene, 1,3-bis(di-2-pyridylaminomethyl)benzene, 2,6-bis(di-2-pyridylaminomethyl)pyridine and 1,4-bis(di-2-pyridylaminomethyl)benzene yield silver(I) complexes with varying coordination arrangements that include both discrete and polymeric species; this variation in the nature of the products largely appears to reflect both the substitution pattern at the aryl bridge as well as the inherent flexibility of the bridging groups in each case.

5.2. Miscellaneous structures

Isolated complexes of the tolyl-derivatised terpyridine ligand, 4′-*p*-tolyl-2,2′:6′,2″-terpyridine (**50**) and copper(II) [190–193] as well as other metal ions (as exemplified, for example, by reports by Zubieta and co-workers [192], McDonagh and co-workers [194] and Yin and co-workers [195]) have been synthesised. More recently [196], a new copper(II) complex of **50** and that of the isomeric and 6′-*p*-tolyl-2,2′:2″,4′-terpyridine derivative (**51**) have been prepared and characterised by X-ray diffraction. The first of these is a co-crystal of type [Cu(**50**)(NO$_3$)$_2$]·[Cu(**50**)(NO$_3$)(EtOH)]NO$_3$·MeOH while the second is a single complex of type [Cu(**51**)$_2$(NO$_3$)]NO$_3$·0.5MeOH·1.5H$_2$O. Crystallisation of a mixture of both these products from ethanol/methanol (1:1) yields an unusual co-crystalline product of stoichiometry [Cu(**51**)$_2$NO$_3$]$_2$[Cu(**50**)(NO$_3$)$_2$](NO$_3$)$_2$ whose structure was also confirmed by an X-ray structure determination.



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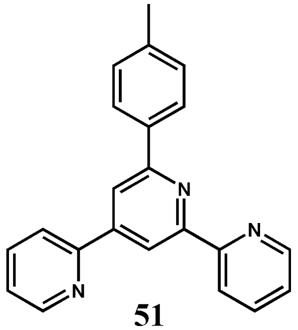

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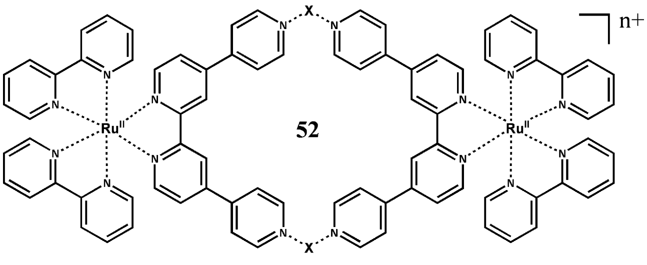
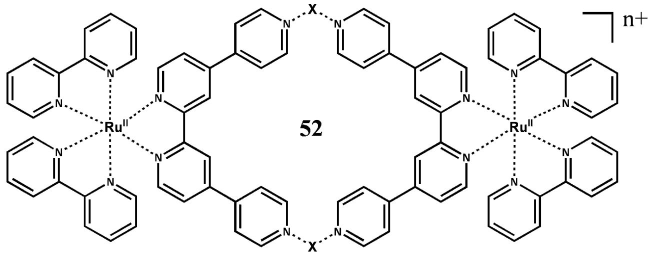


52

X = [Pd(en)]$^{2+}$; n = 8
X = [ReCl(CO)$_3$]$^{+}$; n = 4
X = [Pt(en)]$^{2+}$; n = 8

The use of a 'complex as ligand approach' has led to the metal-ion templated assembly of heterometallic tetranuclear metallacycles of type **52** containing (bound) 2,2′:4,4″:4′,4‴-quaterpyridyl and kinetically locked ruthenium centres [197].



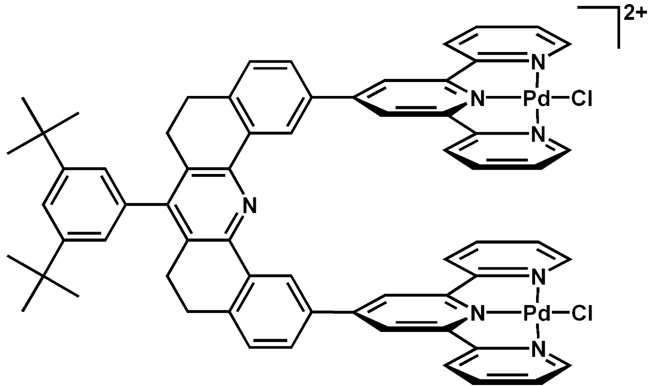
52

X = $[Pd(en)]^{2+}$; n = 8
X = $[ReCl(CO)_3]^{+}$; n = 4
X = $[Pt(en)]^{2+}$; n = 8

Fig. 12. The structures of the three metallacycles obtained by template synthesis from ruthenium(II) precursor complexes [197].

Three systems synthesised are shown in Fig. 12. Whether the product is kinetically labile or inert depends on the metal ion template employed. The kinetically inert ruthenium species display reversible RuII/III oxidation couples. Host–guest studies performed on the kinetically inert Ru_2Re_2 product in organic solvents demonstrated that the complex functions as a luminescent sensor for anions and that the binding affinity and luminescent modulation depends on the nature (including charge) of the guest anion. Computational DFT studies suggest that the observed guest-induced luminescence changes are most likely due to modulation of non-radiative decay processes.

Molecular receptors consisting of two parallel cofacially disposed terpyridyl-Pd-Cl$^+$ (see **53**) or terpyridyl-Pt-Cl$^+$ units, have been synthesised [198]. Concerted rotation of these units with respect to the spacer unit can alter their separation from 6.4 and 7.2 Å. Both neutral and anionic planar complexes of platinum(II) of type **54** were investigated as potential guests.



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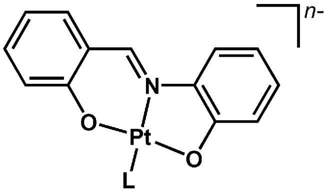
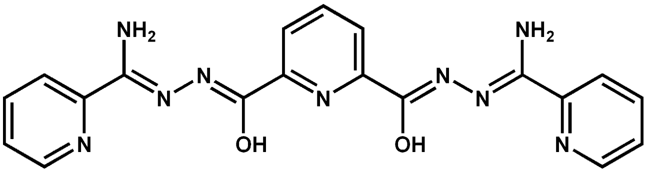


$[Pt(salap)L]^{n-}$
L = NH_3, Cl, CN
54

In an earlier study [199], bis-palladium(II) derivatives of the above general type were also shown to bind to aromatic hosts as well as to selected planar metal complexes. Moreover, reaction of two of the palladium-containing receptor units with two equivalents of 4,4′-bipyridine resulted in displacement of the labile chloride ligands to yield a large molecular rectangle.

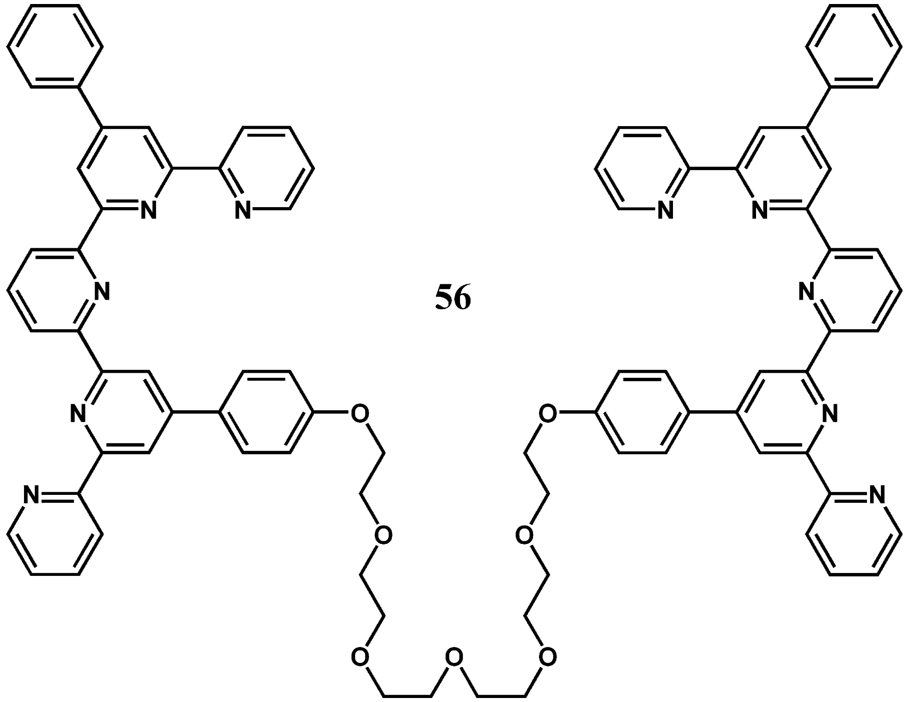
When a yellow acetonitrile solution of **54** ($L = NH_3$) was added to an acetonitrile solution of the yellow di-platinum receptor, a deep red brown colour formed and transitions assigned to a Pt–Pt interaction were observed. The structures of the host–(neutral) guest complexes in solution were assigned by ^1H NOESY spectra and a crystal structure of the solid di-platinum host–guest complex of **54** ($L = NH_3$) agreed with the structure found in solution and confirmed the presence of a Pt–Pt interaction. It was suggested that the metal–metal interactions contribute to molecular recognition in these systems.

The copper(II) cluster cation, $[Cu_8(L)_4(MeOH)_4(MeCN)_4]^{8+}$ (where L is the doubly deprotonated form of **55**), has an octanuclear 'pinwheel' structure, consisting of an alkoxide-bridged, $Cu_4(\mu\text{-}O)_4$ grid-like core with four additional peripheral copper(II) centres. The copper centres are weakly ferromagnetically coupled [200].



55

Ligand **56**, in which two polypyridyl metal binding domains are linked by a polyoxyethylene spacer, reacts with copper(II) salts to form dinuclear double helicates with a 'hairpin' structure [201]. The latter is formed regioselectively, confirmed by an X-ray diffraction study (see Fig. 13), as the head-to-tail stereoisomer.



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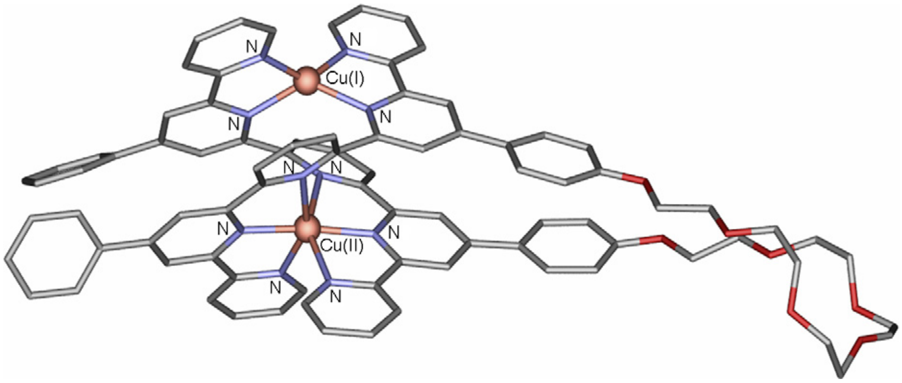
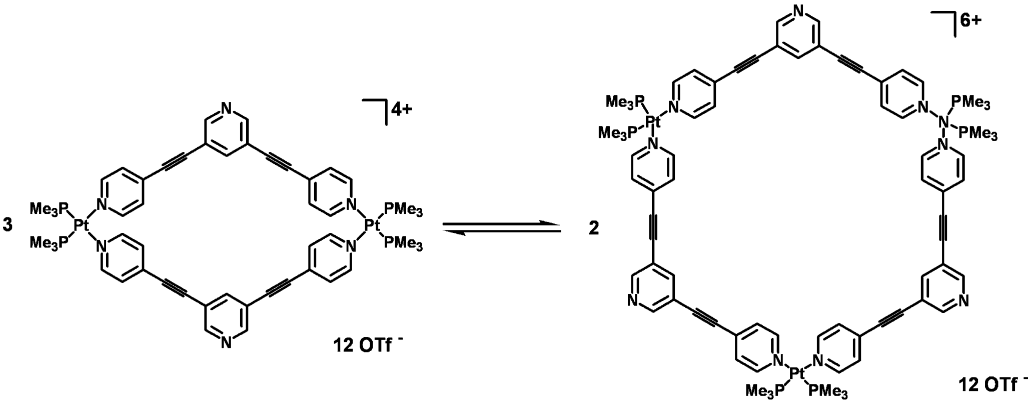


Fig. 13. X-ray structure of the cationic copper(II) dinuclear double helicate incorporating **56** showing its ‘hairpin’ structure [201].



Scheme 7. The equilibrium between rhomboidal and hexagonal structures [202].

The tripyridyl derivative, 3,5-bis(4-pyridylethynyl)pyridine, with its fixed 120° angle between the terminal pyridyl groups, interacts with *cis*-$(Me_3P)_2Pt(OTf)_2$ as a 90° 'corner' unit on loss of its two triflate ligands to yield both the rhomboidal structure (with convex sides) and its corresponding hexagonal counterpart (with concave sides) illustrated in Scheme 7 [202]. While corner units orientated at 60° and 120° clearly are the ideal for achieving these respective geometries, the present corner unit with inherent 90° directionality falls midway between these 'ideal' angles. As a consequence the assembly of the above systems relies on the flexibility of the ligand's acetylene links to achieve the respective observed arrangements. Indeed, both structures occur in dynamic equilibrium (Scheme 7) on mixing the ligand and corner unit in a 1:1 ratio in CD_3NO_2. No (NMR) evidence for participation of the central pyridine group of the ligand was observed under the conditions employed for the study. However, when a higher ratio of corner unit to ligand was employed, oligomer formation appeared to take place.

Although the 1:1 (ligand to corner) reaction leads to an equilibrium between the rhomboidal and hexagonal structures, crystals of the latter selectively form from the equilibrium solution. The hexagonal structure of this product was confirmed by an X-ray structure determination.

Although the 1:1 (ligand to corner) reaction leads to an equilibrium between the rhomboidal and hexagonal structures, crystals of the latter selectively form from the equilibrium solution. The hexagonal structure of this product was confirmed by an X-ray structure determination.

6. Concluding remarks

It is clear from the above discussion that the design of new metallo assemblies to achieve a desired structure is critically dependent on both the choice of metal ion and the organic component(s) employed. The self-assembly process requires that molecular recognition between the assembling components initially occurs and this in turn implies that these components be chosen such that steric and/or electronic complementarity occurs between them. An appreciation of the latent steric and electronic information inherent in both the molecular component(s) and the metal is thus central to the success of such an enterprise. Nevertheless, kinetic, thermodynamic, solvation and solubility factors may all influence the outcome of a given procedure. In view of this, the production of defined supramolecular architectures that incorporate metal ions as structural elements continues to be both a challenging as well as a creative area of chemical research.

Acknowledgement

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