

Supramolecular coordination compounds with chiral pyridine and polypyridine ligands derived from terpenes

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Abstract

This review summarizes the principles and the results in a special field of metallosupramolecular architectures. It deals with the stereochemical aspects of chiral assemblages that are formed using chiral derivatives of pyridine and polypyridine ligands. The modularity of the ligands that are discussed results in a variety of different structures that point in most cases to a high diastereoselectivity in the self-assembling process. Some aspects of solid state properties of such metallosupramolecular materials are discussed. Finally, the possibility of the stereoselective formation of topologically chiral organic molecules via metallosupramolecular architectures is presented.

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1. Introduction

Chiral¹ coordination species can be divided into two classes²: (i) metal complexes, where chirality disappears upon separation of the metal and the ligands, and (ii)

metal complexes where the free ligands (or the pro-ligands [1]), separated from the metal are still chiral objects, from the point of view of their molecular symmetry. The latter type of chirality has sometimes been designated to be due to “vicinal [chirality] elements” [1,2], a term, which has not found large acceptance. The prediction and the subsequent experimental realization of the former class of chiral coordination species, i.e. complexes where the chirality element is centered at the metal, was one of the main achievements of Alfred Werner after he had formulated the coordination theory [3–6]. Obviously, Werner was well aware of the interesting possibilities resulting from the

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¹ “Chiral” is used throughout this review as defined by Lord Kelvin [1].

² Other classification schemes will be introduced later in this article.

incorporation of chiral ligands into metal complexes, where the metal itself represents an element of chirality. One of the last collaborators of Alfred Werner, A.P. Smirnov [7] published in 1920 a very clearly formulated paper about the diastereoselective synthesis of platinum(IV) complexes using enantiomerically pure 1,2-diaminopropane. This publication can be considered to be the equivalent of E. Fischer's introduction of asymmetric synthesis in organic chemistry in 1894 [8]. We are presently repeating Smirnov's experiments, with the aim to reconstruct this important contribution to coordination chemistry and to complete these investigations using modern experimental methods. 1,2-Diaminopropane (**L1**), can be considered to be a “chiralized” derivative of 1,2-diaminoethane (**L2**), the classical en ligand, that was used by Alfred Werner in many cases in order to establish his coordination theory (Scheme 1).

Later, many other families of chelate ligands were introduced into coordination chemistry. Examples are the aminocarboxylic acids, like ethylene diamine tetra acetate (EDTA), nitrile triacetate (NTA), the enolates, catecholates, polypyridines etc. Most of them are achiral molecules. However, the chelate metal complexes, especially with the most frequently encountered octahedral coordination geometry, are often chiral species. From a systematic point of view, 144 different edge configurations exist for chelate complexes with octahedral geometry. Seventy four of these configurations are inherently chiral [9,10].

In all these ligand families chiral derivatives can, in principle, be obtained through judicious syntheses of suitable molecules. We have designated this as “chiralization” of a class of ligands and we have demonstrated this principle in detail for the pyridine and polypyridine ligands, a family of ligands that has shown to exhibit an extremely rich coordination chemistry. Several reviews dealing with this class of ligands have appeared [11–14].

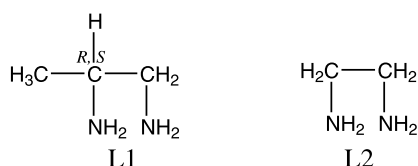
Here we restrict our interest to such pyridine and polypyridine molecules that are derived from terpenes, with special emphasis on their ability to form supramolecular coordination assemblies. The study of supramolecular coordination assemblies has become a subdomain of coordination chemistry during the past two decades [15–17]. Many supramolecular species that have been structurally characterized are intrinsically chiral, such as the large group of helicates [18,19]. Using the traditional achiral ligands, in all cases racemic mixtures of the chiral assemblies are obtained, except

in some cases, where chiral auxiliaries are used [20,21]. Diastereoselective supramolecular coordination assembling was one of our main motivations to search for a class of chiral ligands that could be obtained easily in enantiopure form. The *chiralized* pyridines and polypyridines fulfil this criterion in an almost ideal way. The concept could certainly be also applied to other classes of ligands, like e.g. the catecholates etc. The same type of ligands can, of course, also be useful for other purposes, such as the diastereoselective preparation of enantiopure mononuclear metal complexes [22–24]. For obtaining stereochemically stable chiral building blocks for polynuclear species [25], and last but not least for enantioselective catalysis [13,26–29].

2. Syntheses

The chiralization of pyridine and polypyridine through annellation with terpenes, especially with pinene, was achieved for both, the 4,5-pinene pyridine and the 5,6-pinene pyridine for the first time in 1992 through a Kröhnke type synthesis [11,30]. Since then, about 200 different *chiralized* ligands [31] of this family have been synthesized, mostly through variation of the original methods. Experimental details are given in the original publications [32–36]. It is not trivial, yet possible, to scale up the synthetic procedures. For many of these ligands synthesis on the gram or even kilogram scale is, therefore, feasible. The most outstanding property of the pinene annellated pyridine ligands is the acidity of the CH₂ group that is neighboring the pyridine ring. The two diastereotopic protons of these groups can be stereoselectively deprotonated by strong bases. This type of reactivity opens the field for the synthesis of the so called CHIRAGEN type of ligands [32,37]. Through this preparative scheme, an unlimited number of different polypyridine ligands becomes accessible.

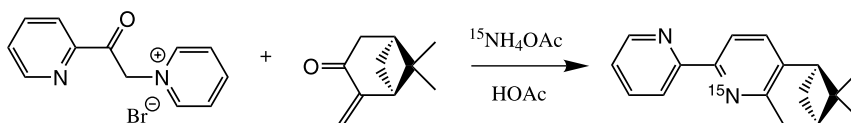
An interesting feature of the Kröhnke type synthesis is the fact that the nitrogen atom of the pyridine ring that is formed, stems from a simple ammonium ion. It is, therefore, very easy and relatively cheap to synthesize ¹⁵N enriched samples of any of the ligands. In the case of bipyridine only one of the two nitrogen donor atoms is labeled specifically through this method (Scheme 2). Since ¹⁵N has very useful properties in NMR spectroscopy through its nuclear spin of I = 1/2, a wealth of structural information can be obtained by the use of these isotopically labeled ligands [38].



Scheme 1.

3. Results and discussion

Several definitions have been applied to the concept of supramolecular chemistry since the term was coined



Scheme 2.

by J.M. Lehn in 1987. Lehn [39] himself defined the field as:

“Beyond molecular chemistry based on the covalent bond there lies the field of supramolecular chemistry, whose goal it is to gain control over the intermolecular bond”.

Since the bond between metal ions and ligands cannot, in general, be unambiguously defined as covalent or not covalent, it is sometimes a matter of taste, whether a coordination species is considered just as a polynuclear metal complex or a supramolecular assembly. In the following, we will show that a continuous transition exists between different situations. The “supramolecular” species is either formed through a step-wise synthesis resembling the traditional fabrication of molecules, or relatively large, but discrete species are formed in rapid reactions leading to one or few assemblages where compositions and structures are thermodynamically determined. Finally “infinite” coordination polymers can be formed in the solid state. All this we want to consider for cases where chirality is an essential structural feature.

3.1. Building stereochemically well defined polynuclear species

Several years ago, we were confronted with the problem of fabricating polynuclear coordination species in an effort of studying photoinduced interactions between metal centers in a collaboration with the Bologna group of V. Balzani [40]. The typical environments of the metal centers in these systems were of the $\text{M}(\text{bpy})_3$ -type, where $\text{M} = \text{Ru}(\text{II/III})$ and $\text{Os}(\text{II/III})$. Since each of these coordination centers represents a Δ/Λ -type chiral element in racemic abundance, combination of several such units leads to a combinatorial set of stereo isomers, in most cases with statistical abun-

dance distribution. Except in a few cases [41,42] these isomers cannot be separated in an efficient way. That means that the prepared multicenter systems represent isomeric mixtures, which are difficult to characterize. It was therefore our aim to solve the problem in a modular way, where building blocks with well defined and stable stereochemistry are used for the construction of the larger units. An example for such a building block is the uncharged Ru-complex $\Delta\text{-Ru}(4,5\text{-CHIRAGEN}[m\text{-xyl}])\text{Cl}_2$ (Fig. 1).

The *m*-xylene bridge, which is anchored on both ends at the stereogenic center of the pinene moiety of the 4,5-pinenebpy unit with identical absolute configuration, determines in an unambiguous way the helical chirality at the metal center. Two important points concerning this building block should be mentioned: (i) since terpenes in general and pinene in particular, occur in nature in both enantiomeric forms (but not as racemates!), both enantiomers of the CHIRAGEN ligands are equally accessible. This gives the possibility of using them for the construction of both pure enantiomers ($\Delta\Delta$ and $\Lambda\Lambda$) of, e.g. a dinuclear complex, as well as of its *meso*-form ($\Delta\Lambda$). (ii) The building blocks cannot isomerize

An example of a stereochemically unique (one single isomer) trinuclear complex that has been prepared using an enantiomerically pure building block has been described (Fig. 2), where three units are docked to a CHIRAGEN ligand offering three bidentate sites [43].

3.2. The self assembly of helicates with CHIRAGEN-type and related ligands

CHIRAGEN ligands were first used in a trial and error way in order to produce self assembled supramolecular coordination species. In the first attempts, 4,5-CHIRAGEN ligands (Scheme 3) were combined with labile metal ions that normally coordinate in octahedral coordination geometry.

Model considerations showed that triple helices are to be expected with the ligand 4,5-CHIRAGEN[*m*-xyl], the same as that discussed in Section 3.1 for the construction of the chiral building block. Indeed, $\text{Cd}(\text{II})$, $\text{Zn}(\text{II})$, and $\text{Fe}(\text{II})$ all form in rapid reactions only complexes of $\text{M:L} = 2:3$ stoichiometry [44]. NMR-, CD-, and MS-spectra indicate the formation of triple helices with homochiral metal centers according to Scheme 4.

Despite the fact that no solid state characterizations were possible, all experimental evidence points to a completely stereoselective formation of the triple helices.

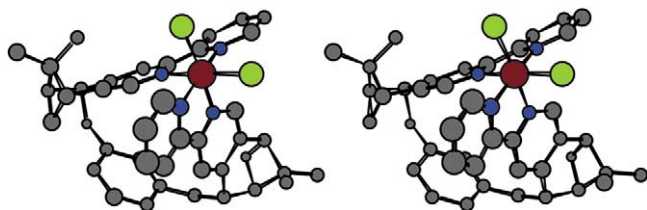


Fig. 1. A stereopair of the enantiomerically pure chiral building block $\text{Ru}(\text{CHIRAGEN}[m\text{-xyl}])\text{Cl}_2$.

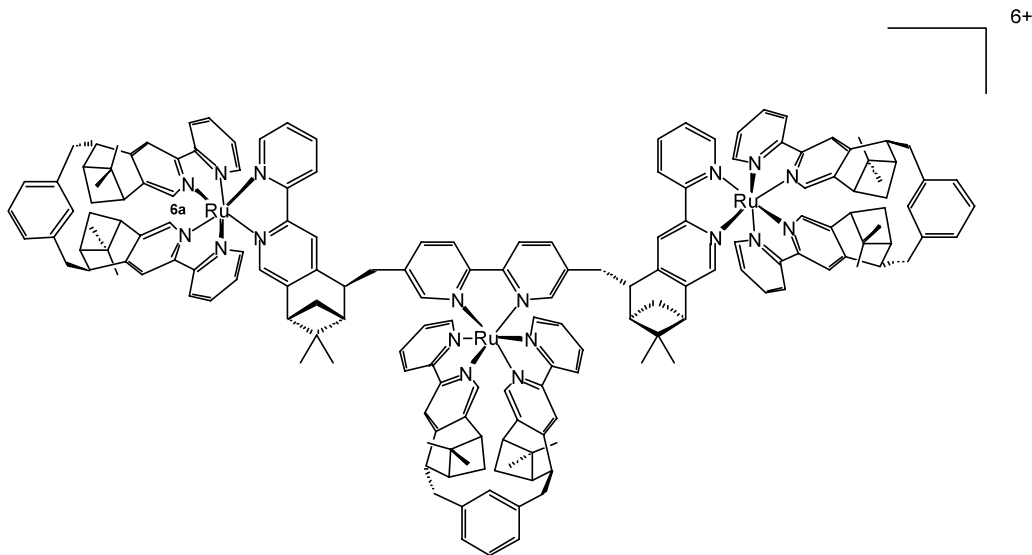


Fig. 2. Schematic representation of the trinuclear complex $\{(\text{RuCHIRAGEN}[m\text{-xyl}])_3\text{CHIRAGEN}[5,5'\text{-bpy}]\}^{6+}$, containing 27 elements of chirality. One pure isomer can be prepared.

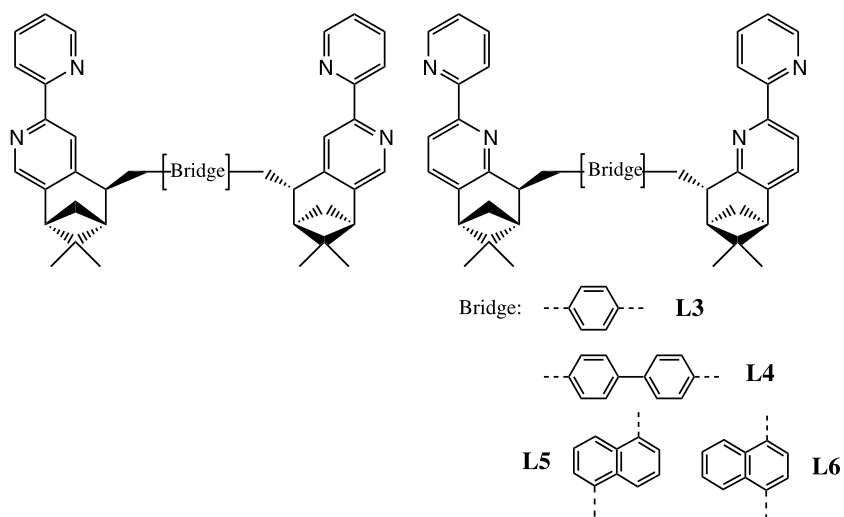
5,6-CHIRAGEN-type ligands (Scheme 3) do not form any well defined assemblies with metals that coordinate in octahedral geometry. This is due to a strong steric crowding near the nitrogen donor atom of the pyridine, which bears the pinene moiety. Therefore, the tetrahedrally coordinating ions Cu(I) and Ag(I) were tested for their ability to form supramolecular assemblies. After testing several different 5,6-CHIRAGEN ligands, a species with high symmetry, according to NMR-spectroscopy, was found when either Cu(I) or Ag(I) was mixed with 5,6-CHIRAGEN[*p*-xyl] (**L3**, see Scheme 3) in an equimolar ratio.

It is evident from ^1H -NMR spectra that the species formed has a high symmetry, i.e. the C_2 symmetry of the ligand is preserved in the assembly. Fortunately, crystals

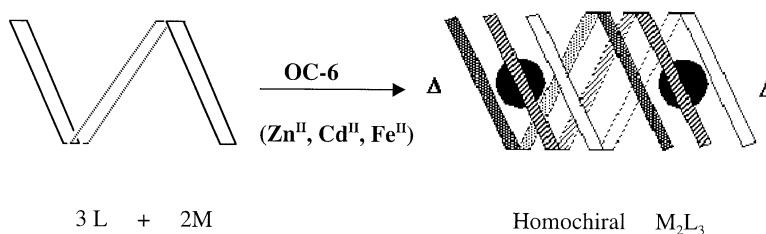
can be obtained from these solutions. The crystals containing Ag(I) or Cu(I) ions are isostructural. The solid contains hexamers that can be interpreted as a circular mono helical structure. The symmetry in the crystal is C_6 , i.e. the sixfold rotation axis is polar [45].

Fig. 3 shows a simplified picture of this supramolecular structure together with the packing in the solid.

This hexagon represents a supramolecular structure with nanometric dimensions. The outside diameter is ca. 3 nm and its thickness about 1.4 nm. The inner part of the chiral disk is almost closely packed with the 12 pinene moieties of the six CHIRAGEN ligands. The crystal packing is remarkably loose. The planes formed by the supramolecular disks are separated by anions (PF_6^-) and some solvent molecules (diethyl ether),



Scheme 3. CHIRAGEN type ligands.

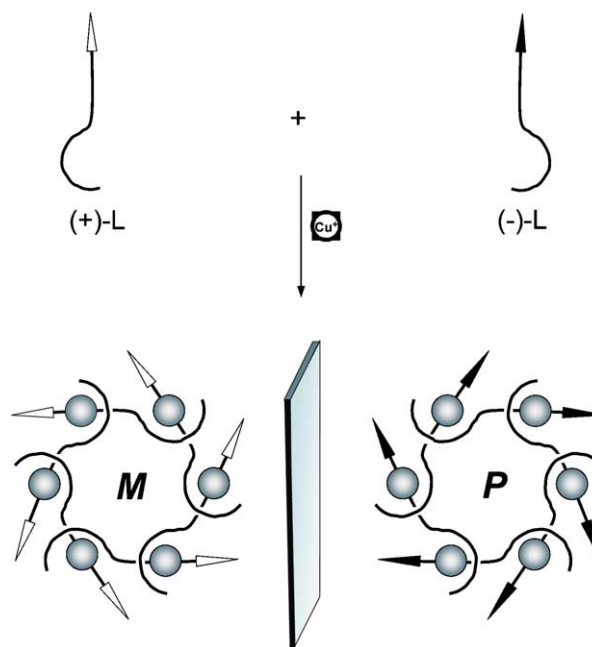


Scheme 4.

forming a layered structure. It can be considered to be a blown up equivalent of the graphite lattice. The mechanical strength of the crystals is accordingly very low. They have to be handled with utmost care because they easily split along the gliding planes. The solution properties of these species has been investigated with several spectroscopic methods, including ^{109}Ag -NMR and ^1H -NMR at variable pressure and temperature [46]. It was found that an equilibrium between the hexameric and a tetrameric species exists, which is shifted to the hexamer at increasing temperature and decreasing pressure. The hexamer is largely dominant at ambient temperature and pressure.

Since, again, both enantiomers of the ligand are easily accessible, studies concerning the enantio-self-recognition could be carried out. It was found that there is complete mutual recognition of the configuration of the ligands within a supramolecular assemblage with Cu(I) (Scheme 5) [47].

If an artificial racemate of the two enantiomeric ligands is used for complex formation, a racemate of hexameric supramolecular species is formed. That means that no polynuclear complexes are formed where both enantiomers of the ligand are present in one species. A similar ligand (**L4**) containing a longer bridge (two phenyl units instead of one) has been found to form with Ag (I) (molar ratio ligand to metal of 1:1) a highly symmetrical species in solution [48]. We tested the self-recognition between these two ligands when complexation with Ag(I) occurs. The ^1H -NMR spectrum of the mixture ($\text{L3:L4:Ag}^I = 1:1:2$) shows essentially the peaks corresponding to pure “homoligand” complexes.



Scheme 5. Chiral recognition between ligands (+)-L3 and (–)-L3.

A ligand that was especially designed for the formation of a configurationally predetermined assemblage with D_4 symmetry is discussed in the following paragraph. Ligand **L8** (Scheme 6) had been used by J.A. Osborn et al. [49] in a self-assembly reaction with Cu(I) leading to a grid-like structure 1 (Fig. 4). 1 shows D_{2d} symmetry and it is accordingly achiral. Ligand **L7**, later used by Lehn et al. [50] yields also D_{2d} grids with octahedral coordination centers. The design of a new

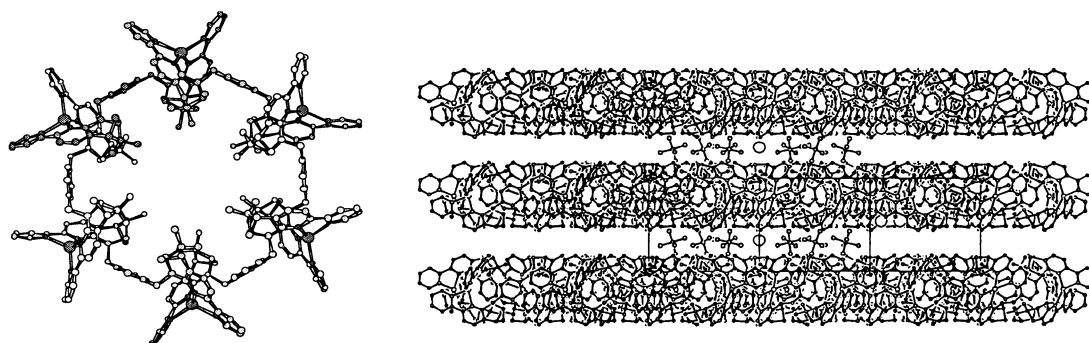
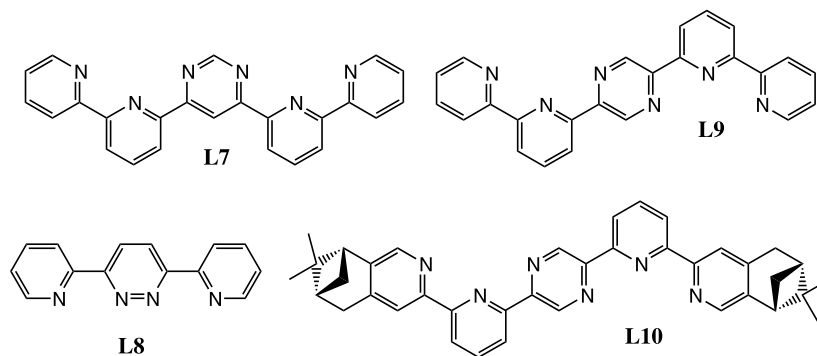


Fig. 3. Self assembled hexagonal circular helix with predetermined configuration. Crystal packing (right) showing the loosely layered structure.



Scheme 6.

ligand **L9**, [51] where the binding vectors of the two terpy-subunits are anti parallel and not parallel as in **L7** led with some metal ions (Co(II), Ni(II), Cu(II), and Zn(II)) to the formation of a chiral assemblage with symmetry D_4 (Fig. 4).

Other metal ions like Mn(II), Pb(II), and Cd(II) yield coordination polymers. Of course, the complexes show-

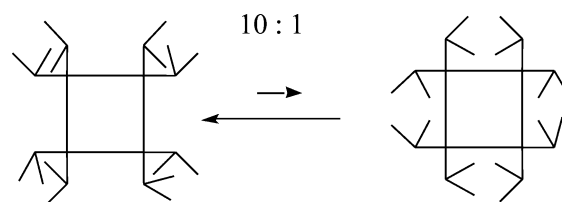
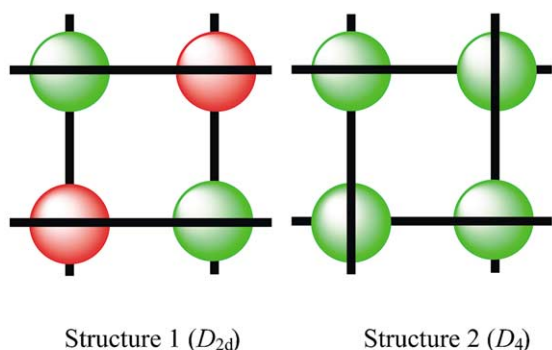
Scheme 7. Diastereoisomeric assemblies with **L10**.

Fig. 4

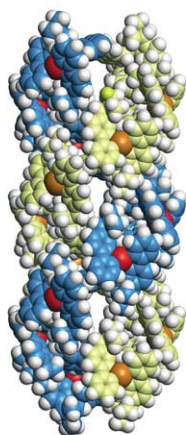


Fig. 5

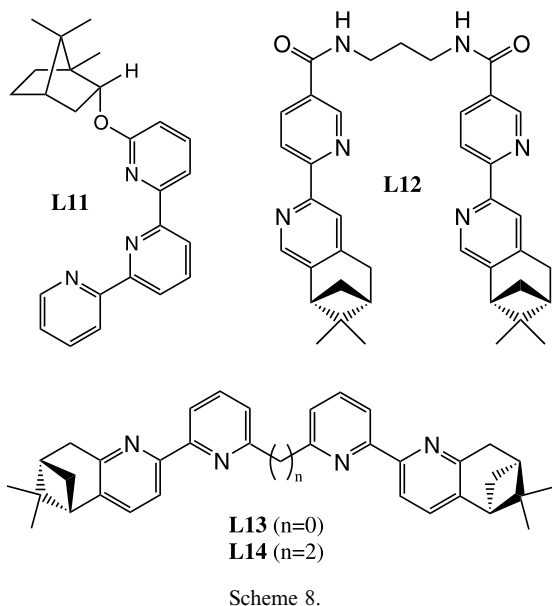
Fig. 4. Two different types of square grids. Left the achiral assemblage of ligands with parallel coordinating sites, right the chiral one with anti parallel coordinating sites.

Fig. 5. Polymer double helix formed in the solid state from **L5** ligand and Ag^+ through a self assembly reaction.

ing structure 2 are formed as racemates. The *chiralization* of **L9**, which was achieved by the synthesis of **L10** (Scheme 6), leads to the formation of two diastereomeric assemblies, both having D_4 symmetry. From equilibrium measurements, a value of $\Delta G^\circ = 2.7 \text{ kJ mol}^{-1}$ could be determined, which gives a 10:1 ratio of the two stereoisomers at room temperature (Scheme 7) [51]. The more stable form is that where the pinene groups of the *chiralized* ligands are clustered, in analogy to the hexagon discussed earlier.

A chiral 6-bornyloxy functionalized terpy type ligand **L11** (Scheme 8) forms with Cu(I) double stranded helicates [52]. Because of the unsymmetrical ligand isomers of the type *HT* (head to tail) or *HH* (head to head) could be envisaged. However, the reaction is completely stereoselective with respect to this type of stereoisomers: only the *HT* isomer is observed as well as with respect to the helicity. A *P* helicate is obtained if the (1*R*)-*endo*-bornyloxy- chiral auxiliary is used and a *M* helicate when the chiral substituent is the enantiomer (1*S*)-*endo*-bornyloxy.

The bis-didentate ligands **L12** and **L13** lead diastereoselectively to dinuclear *P* helicates with Fe(II) [53] and Ag(I) [36,54], respectively. The introduction of a diethylene bridge in the 6 position of the bipyridine moieties in the case of the ligand **L14** preserves the capacity to form, as in the case of **L13**, *P* dinuclear double stranded helicates with Ag(I). Curiously, the distereoselective discrimination is lost when Cu(I) is used. A pseudo-racemic mixture of dinuclear and trinuclear cyclic helicates is obtained [55].



3.3. Ordered polymers in the solid state

Variations in the bridging group of the CHIRAGEN ligands can lead to quite fundamental changes in the structures of the assembled species. Particularly interesting examples are the three CHIRAGEN ligands **L3**, **L5**, and **L6**. **L3** is the ligand that forms the hexagon given in Fig. 3. Introducing the derivatives of 1,5 (**L5**) and 1,4 dimethylnaphthalene (**L6**) as bridges causes the following changes.

L6, where the two bpy units are laterally displaced forms, according to spectroscopic indications, again hexameric circular species in solution. In the solid state, however, an ordered polymer is formed, with parallel columns formed of double stranded helices (Fig. 5) [56]. All helices are homochiral.

Analysis of the solid state structure shows that there is no specific interaction between the two strands within a single double helix. However, the columns are packed very densely, giving close contacts between one given column and its six surrounding neighbors. These close contacts lead to 12 π - π interaction per pitch of one helix

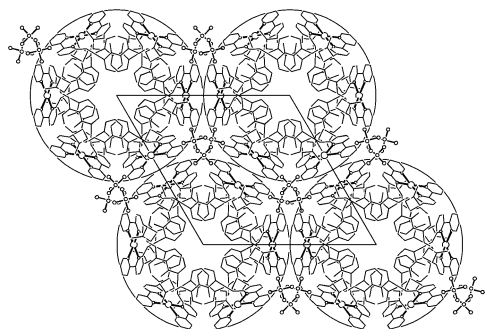


Fig. 6. Packing of the double helices in the crystal. View along the axes of the homochiral helices.

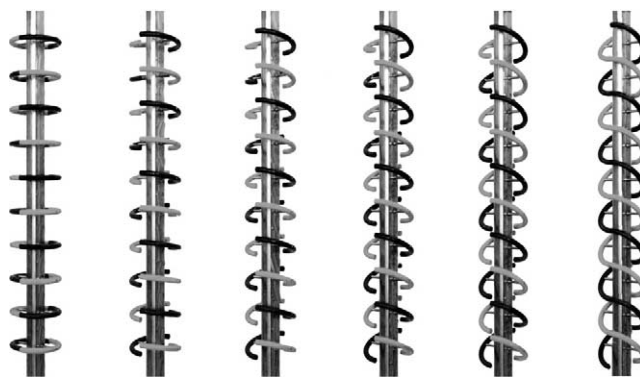
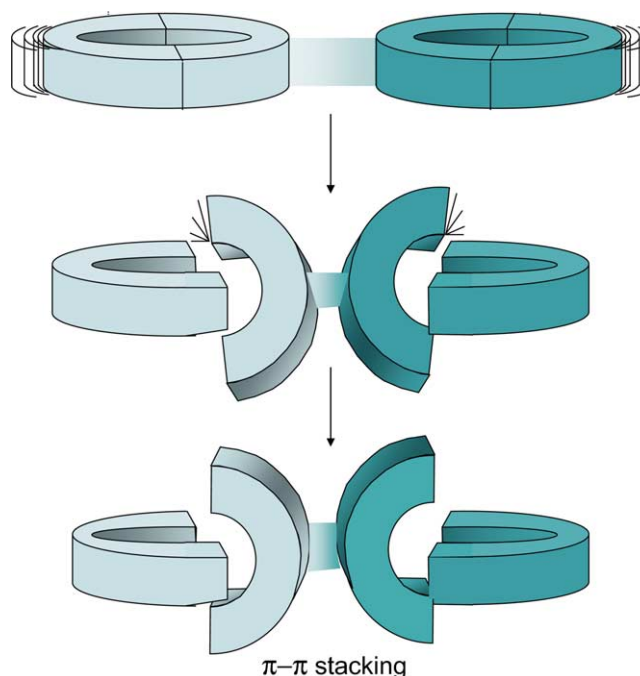


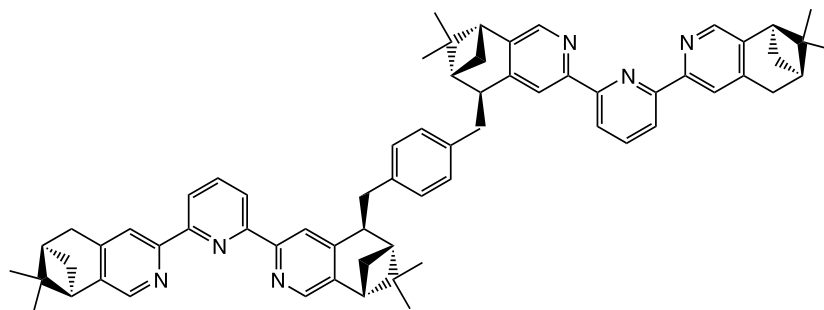
Fig. 7. Mechanical model showing a possible way of formation of a double helix from a circular structure upon crystallization.

(Fig. 6). The anions occupy the narrow channels of threefold symmetry, which are left between the columns.

No solvent molecules are included in the structure. Consequently, the crystals behave mechanically in a very different way, as compared with the pseudo-graphite structure described above for the hexagon. They are quite sturdy and not easy to split, whereas the latter are extremely fragile. How can the circular assemblages in solution turn into a double helix in the solid? Considering the lability of the coordination centers, which leads to rapid equilibria as discussed above, opening of a cyclic assembly is a process that can occur needing only very little activation energy. On this basis, we have developed a simple topological model that describes the transition, which occurs upon crystallization. It is depicted in Fig. 7. As can be seen, a double helix can be formed from a circular structure by consecutive ring-



Scheme 9. Mechanism of helix formation.

Ligand **L15**Scheme 10. Ligand **L15**.

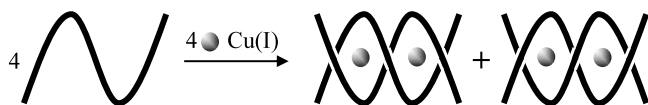
opening steps. Since the circular structures have a polar axis, the senses of the two possible rotations that open the circles are diastereomeric. Therefore, one opening process occurs more facilely as compared with the other and consequently a double helix of defined configuration results. The driving force for the formation is, as discussed above, the π – π interaction between the strands of two adjacent helices. The primary step for the formation of the supramolecular crystal lattice could, therefore, be a meta-supramolecular interaction of two cyclic structures in solution through π – π stacking, followed by a ring-opening step as described above (Scheme 9).

Ligand **L6** (Scheme 3) forms a polymeric *P* single stranded helix in the solid state with five Ag**L6** coordination units per helical pitch. It shows extensive intra helical π – π stacking interactions [57].

The pinene terpyridine type ligands have been shown to form diastereoselectively mononuclear complexes with d (Rh(III), Ru(II), metal to ligand ratio = 1:2) [33] and f metals (metal to ligand ratio = 1:3), [58] the latter complexes having interesting luminescent properties. The connection of two terpyridine units in a similar way as for the bis-didentate CHIRAGEN ligands leads to a bis-tridentate ligand **L15** (see Scheme 10), which forms chiral coordination polymers in reaction with Fe(II) [59]. These polymers form highly ordered domains on Highly Ordered Pyrolytic Graphite (HOPG), as observed by STM. Their homochirality was confirmed by CD studies and subsequent calculations.

3.4. Topologically chiral molecules

The overwhelming number of chiral molecules occurring in nature or those synthesized by chemists are topologically achiral. That means that one enantiomeric



Scheme 11. Schematic representation of the formation of the double stranded helicates, the precursor of a trefoil knot.

form can be transformed into its non-equivalent mirror image by a continuous transformation of its structure, without ever breaking a chemical bond. However, molecules are known, where this process is not possible. Such structures are consequently topologically chiral [60–62].

A particularly interesting topologically chiral structure has been synthesized using supramolecular assemblages [63,64]. A racemic mixture of the two topological enantiomers of a trefoil knot was synthesized from a precursor double helix (Scheme 11). The enantiomers were obtained in pure form by resolution of the racemate [65].

If, through the use of appropriately chosen ligands, the formation of the precursor helix can be rendered diastereoselective, the resulting molecular knot would be formed in a preferred configuration. We are presently working on this project in a collaborative effort with the Sauvage group [CERC3 program].

4. Conclusions and outlook

Supramolecular coordination chemistry is a promising field for future developments of new molecular functions, like nanoelectronics, nanomechanics and in general also materials sciences. Even today, coordination chemists often seem to neglect the fact that many structural elements in supramolecular coordination chemistry are intrinsically chiral. There are still papers published, even in respected journals, where the fabrication of new molecules is described, without even mentioning the fact that stereoisomers occur due to elements of chirality present in such assemblages. In contrast, organic chemists are almost always aware of the presence of chiral elements in a molecule. As bioorganic chemistry shows, chirality is a key concept in all living systems. With the advent of supramolecular coordination chemistry, inorganic chemists should develop a culture, where chirality plays an important role in the design of new functional systems. *Chiralization* of ligand systems is, therefore, not only of basic impor-

tance for enantioselective catalysis, but also in supramolecular coordination chemistry. In the present review, this has been exemplified for the family of pyridine and polypyridine ligands.

Acknowledgements

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