Chem. Rev. **2001,** *101,* 3457−3497

“Let’s Twist Again”—Double-Stranded, Triple-Stranded, and Circular Helicates

Markus Albrecht

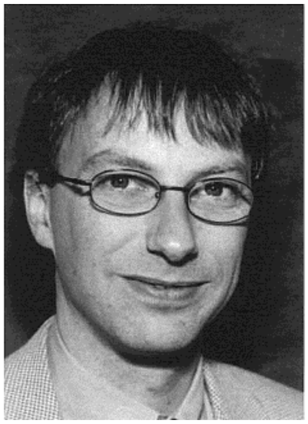
Institut für Organische Chemie, Universität Karlsruhe, Richard-Willstätter-Allee, D-76131 Karlsruhe, Germany

Received May 18, 2001

Contents

I. Introduction

A helix is a geometric motif which is found in natural as well as in artificial structures. Helicity can be observed in the spiral arms of galaxies or in microscopic structures such as right- or left-handed quartz[1] as well as in human art and architecture.



Markus Albrecht was born in 1964 and studied Chemistry in Würzburg and Münster. He obtained his Dr. rer. nat. degree in 1992 for his work on organometallic planar-tetracoordinate carbon compounds (research group of Professor Gerhard Erker). After one year as a postdoctoral fellow in the laboratories of Professor Kenneth N. Raymond in Berkeley (bioinorganic chemistry), he moved to the Institute of Organic Chemistry of the University of Karlsruhe and received his habilitation in 1997. His work on the metal-directed self-assembly of metallo-supramolecular aggregates was honored with the “ADUC-Jahrespreis für Habilitanden”, and he obtained a Heisenberg Fellowship from the DFG.

In chemistry or biochemistry helicity is present in various systems.[2] α-Amylose is a macromolecule with a helical structure that contains about six glucose units per helical turn.[3] Deoxyribonucleic acid (DNA) exists as a double helix in which the two strands are connected by hydrogen bonding between complementary bases.[4] It stores and transmits our genetic make up and therefore is essential for life. Peptides can adopt an α-helical structure or form larger helical arrays as, for example, found in the collagene triple helices.[5]

In artificial supramolecular architectures, helicity can be introduced by conformational restrictions of macromolecules,[6] inter- or intramolecular hydrogen bonds,[7] or coordination to metal ions.[8,9]

In this context, a class of unnatural double- and triple-stranded helical oligonuclear coordination compounds, which are formed in metal-directed self-assembly processes, recently was investigated thoroughly.[10−16] In 1987 J.-M. Lehn introduced the term “helicate” for metal complexes that contain one or more ligand strands and two or more metal centers.[17] The most common of such coordination compounds, which are the focus of this article, are the double-stranded and triple-stranded helicates. The challenge of helicate chemistry is not only to understand fundamental principles of recognition and (self)-

10.1021/cr0103672 CCC: $36.00

assembly processes, but also to search for new supramolecular functional devices.[18] Questions on the influence of noncovalent interactions on supramolecular stereo- or regiochemistry can be studied by using helicates as simple model systems.[19]

The 1987 publication by Lehn[17] marked the beginning of some excellent work regarding the self-assembly, the structures, the properties, and the functions of helicates. Many investigations have already been done, but the future will show what else we can learn and achieve by studying this fascinating topic of metallo-supramolecular chemistry.

In 1997 helicate chemistry was already reviewed thoroughly with the focus on not only structures but also the investigation of helicates and helicate formation by mass spectrometry and crystallography.[11] The number of publications on helicate chemistry more than doubled since this review appeared, so that it seems to be about time for a new overview taking the novel results into account.

Thus, the chemistry on double- and triple-stranded helicates will be the topic of this review article with a focus on the literature since 1997 including the rapidly developing chemistry of circular helicates[20] and the recent extensive use of helicates as templates for the synthesis of topologically interesting derivatives such as molecular knots and related compounds.[21] Furthermore, concepts to control ligand self-recognition during the self-assembly of helicates will be presented. Single-stranded helicates[11] will not be discussed in this article, and helicate-type compounds in which the ligand strands are connected by spacers[22] are also excluded.

In contrast to the earlier review,[11] the helicates will be discussed due to the kind of donor ligand which is used for their formation.

1. Helicates: Supramolecular Coordination Compounds

The formation of helicates depends on the nature of the metal and ligands and sometimes on additional information which can be introduced by appropriate templates or reaction conditions.[11]

The chiral information which leads to the formation of the helical structure very often is embedded in the preferred coordination geometry at the metal ions.[23,24]

Bidentate chelating ligands in combination with tetrahedrally (**B**) or octahedrally (**C**) coordinated metal ions lead to mononuclear complexes which already possess a helical twist and therefore are ideal building blocks for double- or triple-stranded helicates.[13,25] Tridentate ligands on the other hand can form double-stranded complexes with octahedral (**A**) or triple-stranded systems with a tricapped trigonal prismatic geometry at the metal (**D**). “Linear combination” of two such complex units leads either to the double- (**H**) or triple-stranded (**I**) helicate (both complex units possess the same configuration) or the corresponding meso-form (**J**, **K**; opposite configuration at the metal centers): the meso-helicate[26] (side-by-side complex,[27] mesocate[28]).

Complex units such as **E**−**G** do not possess a helical twist. However, oligonuclear coordination compounds possessing two or more such complex units can adopt a helicate (or meso-helicate) type structure, if the chiral information is introduced by the ligand.[29]

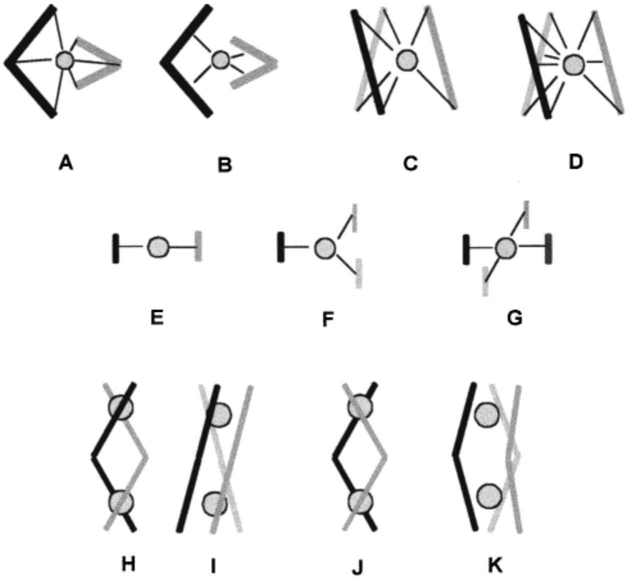


Figure 1.

2. Double- and Triple-Stranded Helicates before 1987—Historical Introduction

Some examples of helical double- or triple-stranded dinuclear complexes were already known when the term helicate was introduced in the 1987. In 1976 it was reported that doubly deprotonated octaethylformylbiliverdine (**1**) forms a mononuclear pentacoordinated zinc complex $[Zn\mathbf{1}(H_2O)]$ which under acidic conditions rearranges to the dinuclear complex $[Zn_2\mathbf{1}_2]$. Both complex units possess a pseudotetrahedral coordination geometry, and the two ligands are wrapping around the metal ions to form a double-stranded helix (Figure 3).[30]

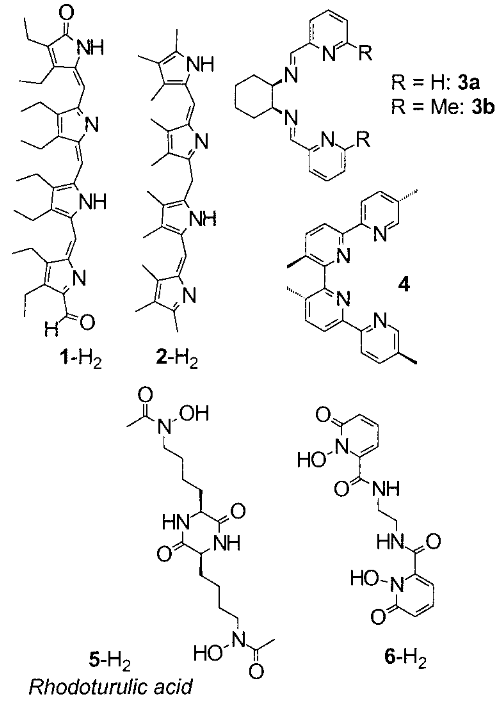


Figure 2.

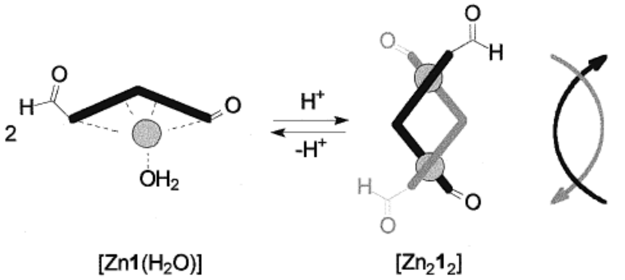


Figure 3.

Ligand **1** is a directional ligand due to the presence of a lactame unit at one end of the molecule and a formyl moiety at the other. The X-ray structure of [Zn$_2$**1**$_2$] clearly demonstrates that the two directional ligand strands are orientated in an antiparallel ("head to tail") fashion.[30] The analogous symmetrical decamethylbiladiene derivative (**2**-H$_4$) also forms a dinuclear double-stranded helical zinc(II) complex [Zn$_2$**2**$_2$].[31]

In 1980 the imino/bipyridine ligands **3a** and **3b** were used to obtain dinuclear coordination compounds [M$_2$**3**$_2$]$^{2+}$ with silver(I) (**a, b**) and copper(I) ions (**b**). The X-ray structure of [Ag$_2$**3a**$_2$]$^{2+}$ shows the presence of a double-stranded helix in the solid state, while NMR studies indicate the same structural motif in solution.[32] With the tetramethyl-substituted 2,2′:6′,2′′:6′′,2′′′-quaterpyridine **4**, a dinuclear double-stranded helical copper(I) complex [Cu$_2$**4**$_2$]$^{2+}$ was obtained and characterized by X-ray diffraction.[33]

Triple-stranded helical coordination compounds have also been known since the 1970s. *Rhodoturulic acid* **5**-H$_2$ is a naturally occurring siderophore which was isolated from low iron cultures of *Rhodotorula pilimanae* and related yeasts.[34] As a siderophore it is important for the control of the iron uptake in microorganisms.[35] In 1978 Raymond described the formation of dinuclear complexes of *Rhodoturulic acid* with iron(III) as well as with chromium(III) and aluminum(III). Dinuclear triple-stranded coordination compounds [M$_2$**5**$_3$] (M = Fe, Cr, Al) were isolated, and it was shown by circular dichroism (CD) studies that both complex units possess the same configuration Δ. Therefore, the compounds exist as triple-stranded (*P*)-helicates. Up to now the diiron complex of *Rhodoturulic acid* [Fe$_2$**5**$_3$] was the only helicate which was found to exist in nature.[36] In 1985 Raymond presented the bis(hydroxypyridinone) derivative **6**-H$_2$ as an unnatural analogue of *Rhodoturulic acid*. Both ligands have two hydroxamic acid binding sites for the coordination of metal ions. From **6**-H$_2$ a triple-stranded dinuclear complex [Fe$_2$**6**$_3$] is formed with iron(III) ions, which in the solid state adopts a helical structure and encapsulates one molecule of water in its interior.[37]

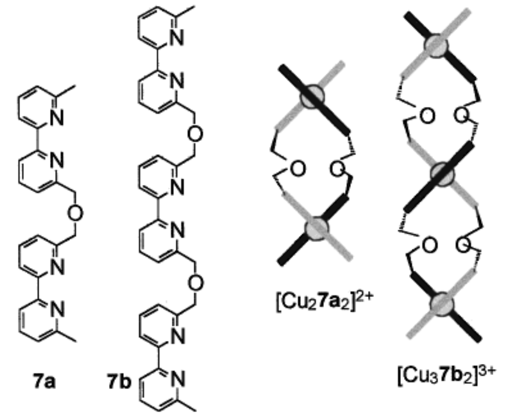


Figure 4.

In 1987 Lehn introduced the term *double-stranded helicate* for inorganic double helices in which two linear organic ligand strands are wrapping around two or more metal centers. Bis(bipyridine) ligand **7a** and tris(bipyridine) ligand **7b** (Figure 4) were used to form dinuclear [Cu$_2$**7a**$_2$]$^{2+}$ or trinuclear [Cu$_3$**7b**$_2$]$^{3+}$ complexes with copper(I) ions. For [Cu$_3$**7b**$_2$]$^{3+}$, the structure of a double helix was shown by X-ray crystallography. It was assumed that to some extent π-stacking interactions might contribute to the stabilization of the trinuclear double-stranded helix and favor its spontaneous self-assembly from the five components: two ligands and three metal ions.[17]

II. Linear Oligonitrogen Donors as Ligands for Double- and Triple-Stranded Helicates

1. Bipyridine Derivatives

Nitrogen-donor molecules play an important role in the chemistry of helicates. The reason for this might be that nitrogen, which is sp^2-hybridized and is embedded in an aromatic or any other unsaturated system, is an excellent donor for the coordination to metal ions.[38] Therefore, over the years numerous pyridine and oligopyridine derivatives were used for the assembly of helicates. 2,2′-Bipyridine (or the related phenanthroline) is a bidentate ligand which is an excellent building block for helicating ligands. Here, the substitution pattern at the ligand is important for the outcome in a coordination study. For example, 2,2′-bipyridines which bear substituents in the 6- and/or 6′-positions are ideal to form pseudotetrahedral 2:1 metal complexes with appropriate metal ions. Octahedral 3:1 complexes on the other hand cannot be formed due to the steric interaction of the substituents in the 6-position.[33] Therefore, 6,6′-substituted derivatives are potential ligands for double-stranded but not triple-stranded helicates. Triple-stranded systems however can be obtained from 2,2′-bipyridine derivatives, which bear substituents (for example, the spacer) in the 4- or 5-position of the pyridine units. With such ligands octahedral metal complexes can be obtained leading to triple-stranded helicates.[39]

As discussed before, the ether-linked oligo(bipyridine) derivatives **7a** and **7b** form dinuclear and trinuclear double-stranded helicates [Cu$_2$**7a**$_2$]$^{2+}$ and [Cu$_3$**7b**$_2$]$^{3+}$ in metal-directed self-assembly processes (Figure 5).[17] Similar tetra- and pentanuclear derivatives [Cu$_m$**7**$_2$]$^{m+}$ (m = 4 **c**, 5 **d**) are obtained with the extended linear ligands **7c** and **7d**.[40] Using silver(I) instead of copper(I) as the metal which directs the self-assembly of the helicates leads to the analogous silver complexes [Ag$_m$**7**$_2$]$^{m+}$ (m = 3, **b**; m = 4, **c**; m = 5, **d**).[41] In all complexes formed from ligands **7** and copper(I) or silver(I) ions the metal centers adopt a

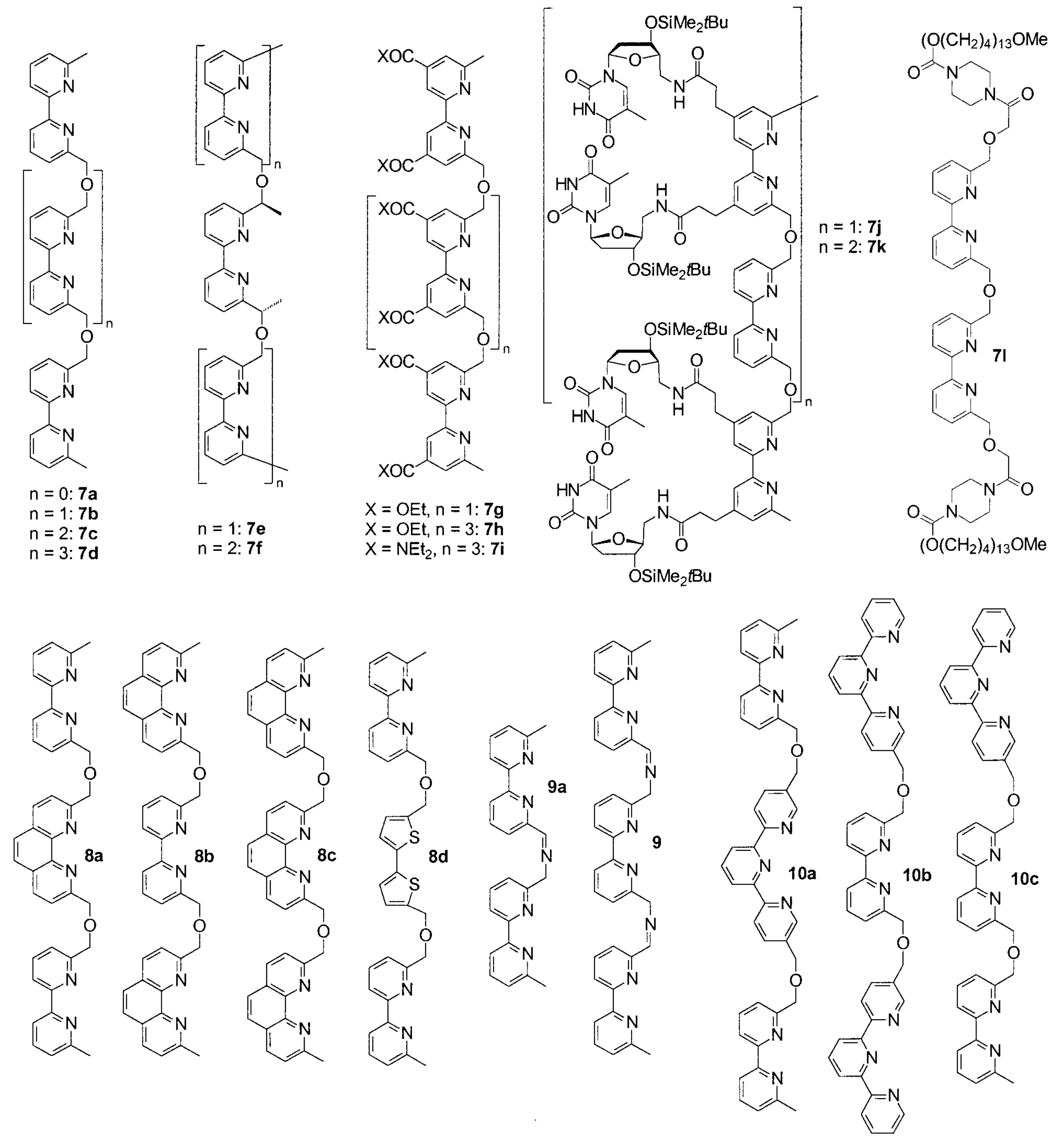


Figure 5.

pseudotetrahedral coordination geometry. Linear linkage of the tetrahedra by the flexible CH_2OCH_2 spacers leads to a helical arrangement. In the case of the pentanuclear species $[Cu_5\mathbf{7d}_2]^{5+}$, the complex shows more than two turns of the helix.[40]

In 1987 it was already determined that racemization of the helix (inversion of the right-handed helix into the left-handed and vice versa) could be measured by ^1H NMR (200 MHz). However, upon heating a sample of $[Cu_2\mathbf{7a}_2]^{2+}$ in d_5-nitrobenzene, no coalescence of the diastereotopic protons of the CH_2 groups could be observed up to 393 K. A racemization barrier of at least 21 kcal/mol was estimated. Even higher barriers are expected for complexes with higher nuclearity.[17]

Derivatives **7e** and **7f** have three and five bipyridine units connected by ether linkages. Here, the central ligand unit bears a methyl group in the benzylic positions with an (*S*)-configuration. The chiral information which is introduced into the ligand strand of **7e** leads, upon complex formation, to diastereomerically and thus enantiomerically pure double-stranded helicates. By NMR spectroscopy only one diastereomer can be detected for complexes $[M_3\mathbf{7e}_2]^{2+}$ (M = Cu, Ag). CD spectroscopy shows that the right-handed helix (*P*) is induced by the (*S*,*S*)-configured ligand.[27]

By titration experiments of ligand **7g** with copper(I) ions it could be shown that the formation of the trinuclear helicate $[Cu_3\mathbf{7g}_2]^{3+}$ proceeds with positive cooperativity,[42] and thus, it is an example of strict self-assembly.[43] This means that the formation of the final helicate is highly favored over every single step in the process of formation, and thus, only the final product and no intermediates can be observed.[44]

Following the reaction of the penta(bipyridine) ligands **7h,i** with copper(I) ions by ES MS (electrospray mass spectrometry) leads to the observation of $[Cu_2\mathbf{7i}]^{2+}$ and $[Cu_3\mathbf{7i}]^{3+}$ as intermediates in the assembly of $[Cu_5\mathbf{7i}_2]^{5+}$. Therefore, metal ions are bound successively to a single ligand strand **7i** until three copper(I) ions are coordinated. Here, the ligand is able to adopt a loop-type conformation and generate a saturated tetrahedral environment at each metal center. In the final step two intermediates $[Cu_2\mathbf{7i}]^{2+}$ and $[Cu_3\mathbf{7i}]^{3+}$ have to combine to form the final pentanuclear helicate $[Cu_5\mathbf{7i}_2]^{5+}$.[45]

The simplicity and effectiveness of the self-assembly of oligonuclear helicates from the bipyridines **7** makes them interesting candidates to introduce some properties by functionalization. The thymidine-substituted ligands **7j,k** were synthesized[46] and used for helicate formation to obtain the deoxyribonucleohelicates (DNH) $[Cu_3\mathbf{7j}_2]^{3+}$ and $[Cu_5\mathbf{7k}_2]^{5+}$, which were characterized by 2D NMR spectroscopy and FAB mass spectrometry. The thymidine residues of the DNHs are attached to the periphery of the double helix. This is contrary to the structure of DNA, which bears the nucleobases in its interior to connect two complementary strands by hydrogen bonding. Due to its substituents, the DNHs should have the potential to interact with DNA via hydrogen bonding.[47] Experiments which would show such an interaction were not reported.[47] However, it was found that the unsubstituted helicates $[Cu_n(\mathbf{7a}-\mathbf{d})_2]^{n+}$ ($n = 2-5$) bind to double-stranded DNA. An important driving force for this interaction is the electrostatic attraction of the positively charged helicate by the negatively charged DNA backbone.[48]

Complexation of the polymer-substituted bis(bipyridine) **7l** with copper(I) forms a dinuclear double-stranded helicate $[Cu_2\mathbf{7l}_2]^{2+}$, which is covalently linked to linear macromolecules and induces a helical twist in the polymer chain.[49] An inverted helicate in which ether-linked bicyclic guanidinium dimers or tetramers wrap around sulfate anions is also described.[50]

2,10-Phenanthroline is a chelating ligand that possesses coordination features that are very similar to those of 2,2′-bipyridine.[38] Ligand strands **8** are analogous to the tris(bipyridine) derivative **7b** with at least one bipyridine unit substituted by phenanthroline (or in **8d** bithiophene).[51−54] All of ligands **8** form trinuclear double-stranded helicates $[Cu_3\mathbf{8}_2]^{3+}$ with copper(I) ions. Complex $[Cu_3\mathbf{8a}_2]^{3+}$ could be characterized by X-ray structural analysis.[52] The compound with the bis(bipyridine)−dithiophene ligand $[Cu_3\mathbf{8d}_2]^{3+}$ is very labile but can be studied by NMR spectroscopy and electrochemistry.[51]

With ligand **8a** the silver(I) complex $[Ag_3\mathbf{8a}_2]^{3+}$ and the zinc(II) complex $[Zn_3\mathbf{8a}_2]^{6+}$ are obtained.[52] The bis(phenanthroline)/bipyridine derivative **8b** forms the corresponding silver(I) helicate $[Ag_3\mathbf{8b}_2]^{3+}$, while the analogous silver(I) tris(phenanthroline) helicate $[Ag_3\mathbf{8c}_2]^{3+}$ is only stable in solution in the presence of an excess of silver(I) ions. This is attributed to the increased steric hindrance of the phenanthroline compared to the bipyridine units.[51,53]

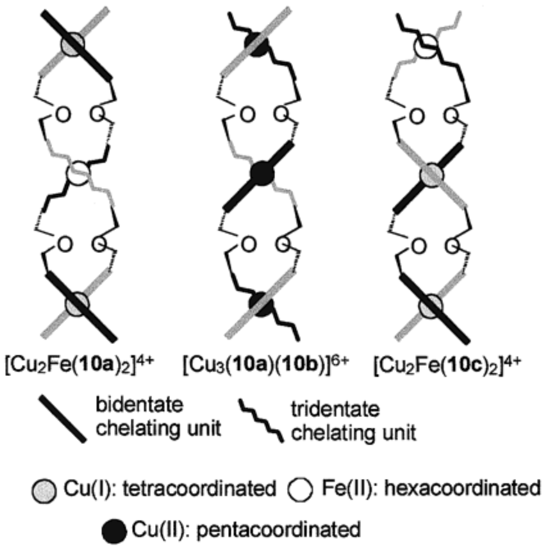


Figure 6.

The flexibility of the spacer which connects the chelating metal binding sites is reduced in derivatives **9**. Here the ether linkage CH_2OCH_2 of ligands such as **7** is substituted by an imine-unit, $-CH{=}N-CH_2-$. However, with copper(I) as well as silver(I) ions dinuclear and trinuclear double-stranded helicates $[M_2\mathbf{9a}_2]^{2+}$ and $[M_3\mathbf{9b}_2]^{3+}$ ($M = Cu, Ag$) are obtained.[55]

As discussed above, double-stranded helicates can be formed from ligands with bidentate chelating units and tetrahedrally coordinated metal ions. An alternative is the combination of tridentate binding sites with octahedrally coordinated metal centers. In derivatives **10**, bidentate and tridentate units are combined and therefore should be able to form helicates which incorporate both tetrahedral and octahedral complex moieties.

With the bis(bipyridine)/monoterpyridine ligands **10a** and **10c** heterotrinuclear Cu(I)/Fe(II) complexes $[Cu_2Fe\mathbf{10a}_2]^{4+}$ and $[Cu_2Fe\mathbf{10c}_2]^{4+}$ are obtained in which the copper(I) ions are binding to two bipyridine units, exhibiting a pseudotetrahedral environment, while iron(II) is located at the tridentate binding site of the ligands having a pseudooctahedral coordination geometry (Figure 6). The heteroleptic helicate with two different ligand strands $[Cu_3(\mathbf{10a})(\mathbf{10b})]^{6+}$ is obtained if the two ligands **10a** and **10b**, which possess an “opposite sequence” of the binding sites, are mixed and copper(II) ions are added. In $[Cu_3(\mathbf{10a})(\mathbf{10b})]^{6+}$ copper(II) is pentacoordinated and binds to one bipyridine and one terpyridine unit, leading to the heteroleptic double-stranded system incorporating two different (“complementary”) ligand strands.[56]

Ligands **11a**−**c** possess two bipyridine units which are bridged by CH_2OCH_2-linked aromatic systems of different sizes (Figure 7). With zinc(II) ions all of them form double-stranded complexes $[Zn_2(\mathbf{11a}-\mathbf{c})_2]^{4+}$. The X-ray structure of $[Zn_2\mathbf{11a}_2]^{4+}$ shows that it is not the double-stranded helicate that is formed but the achiral meso-form, the meso-helicate, which

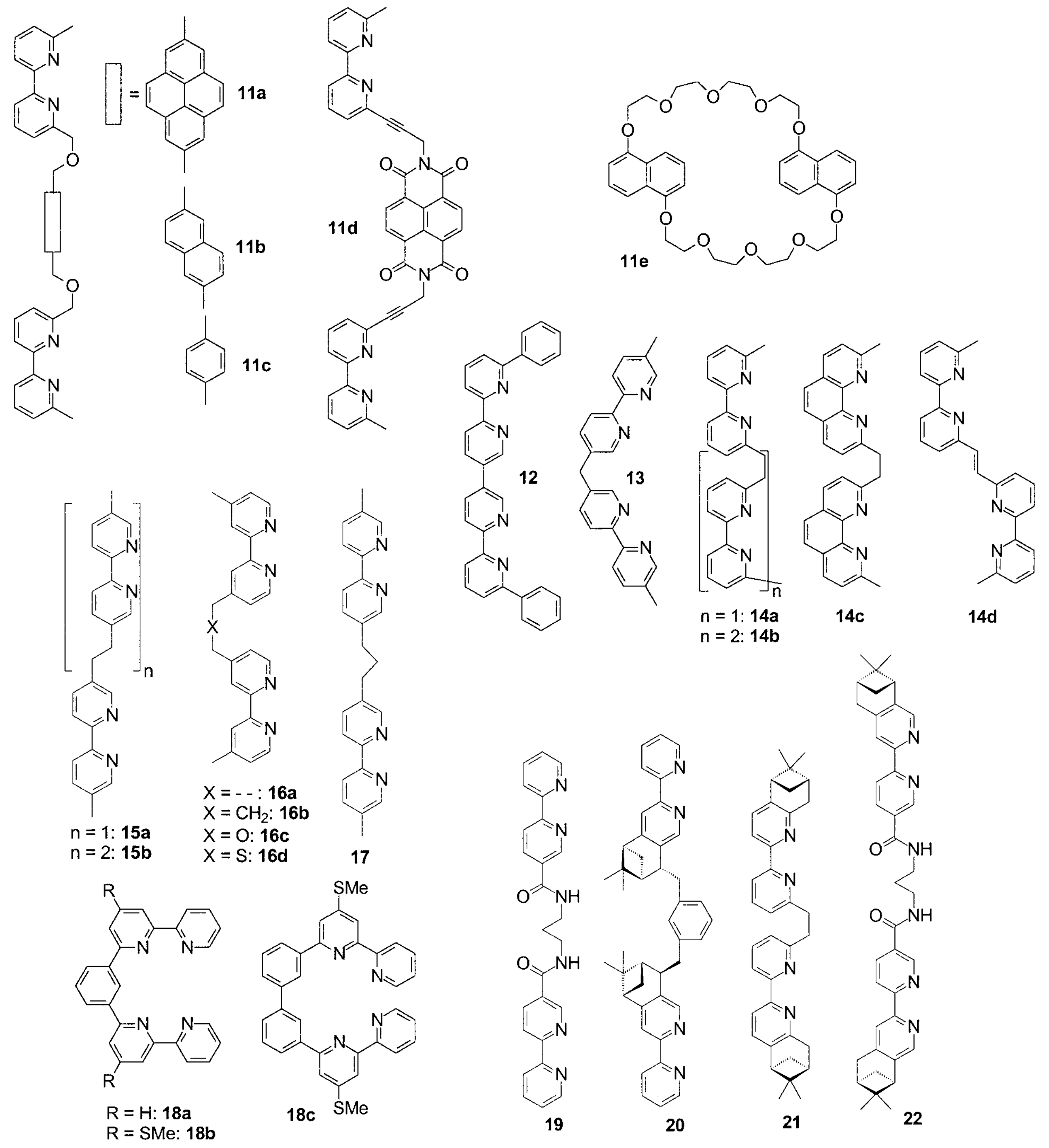
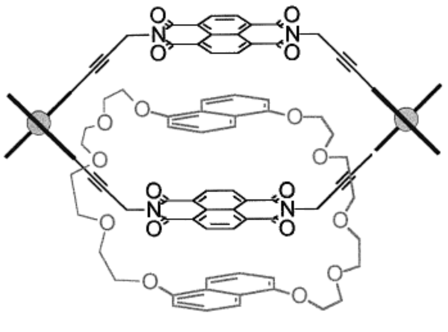


Figure 7.

possesses different a configuration at the two complex units. The coordination geometry at the zinc centers can be described best as pseudooctahedral with binding of the metal to the bipyridine units as well as to the ether oxygen atoms of the ligand. NMR spectroscopy in CD_3OD and CD_3CN shows that the nonhelical isomer of $[Zn_2\mathbf{11a}_2]^{4+}$ is the major species in solution (>98%). For complexes $[Zn_2\mathbf{11b}_2]^{4+}$ and $[Zn_2\mathbf{11c}_2]^{4+}$, both helical and nonhelical isomers can be observed by NMR.[57] In addition, the nickel(II) complex $[Ni_2\mathbf{11b}_2]^{4+}$ could be crystallized and the X-ray structure shows a similar structure as that found for $[Zn_2\mathbf{11a}_2]^{4+}$ with a meso relation of the complex units and N_4O_2-hexacoordination at the metal centers.[58]

When the related ligand **11d** is used in coordination studies with zinc(II) ions, no specific complexes can be found. NMR spectroscopy shows undefined spectra which suggest the presence of oligomeric or polymeric material. However, addition of appropriate templates leads to the specific formation of well-defined double-helical dinuclear complexes $[\text{guest}\subset\{Zn_2\mathbf{11d}_2\}]^{4+}$. X-ray structures of the complex in the presence of veratrole (1,2-dimethoxybenzene) and 1,2,4,5-tetramethoxybenzene could be obtained and show the double-helical structure of the zinc complex $[Zn_2\mathbf{11d}_2]^{4+}$ which encapsulates the electron-rich aromatics by $\pi-\pi$ interaction with the two central electron-poor units of ligand **11d**.[59]



[{**11e**}{Zn$_2$**11d**$_2$}]$^{4+}$

Figure 8.

The template-directed self-assembly of [guest⊂{Zn$_2$**11d**$_2$}]$^{4+}$ is a very nice example for the principle of dynamic combinatorial chemistry. Here, first a library of compounds is formed in which all components are in a dynamic equilibrium and can transform into each other. Upon addition of a template, a stable complex is formed between the template and the component of the library, which is the best receptor for this template. The binding of the guest shifts the equilibrium between the species of the mixture and results in one well-defined host−guest complex.[15,60,61] In the case of ligand **11d**, this principle could be used to obtain the [2]catenane [{**11e**}-{Zn$_2$**11d**$_2$}]$^{4+}$ from an equilibrating mixture of complexes in the presence of **11e** (Figure 8).[62]

Formation of a mixture of complexes and not of only one coordination compound is also observed by reaction of the bis(bipyridine) ligand **12** with copper(I). ES mass spectrometry shows that dinuclear, trinuclear, as well as tetranuclear species [Cu$_n$**12**$_n$]$^{n+}$ (n = 2, 3, 4) are formed. However, by crystallization the dinuclear double-stranded helicate [Cu$_2$**12**$_2$]$^{2+}$ is obtained and can be characterized by X-ray structural analysis. The rigidly linked bipyridine units are tilted at the σ-bond connecting the two chelating units. This leads to the double-helical arrangement of the ligands in [Cu$_2$**12**$_2$]$^{2+}$.[63]

Ligand **13** is made up from two bipyridine units which are connected by a methylene spacer in the 5-position. This ligand forms the dinuclear complex [Fe$_2$**13**$_3$]$^{4+}$ with iron(II) ions. NMR spectroscopy shows that the complex adopts an achiral structure with one metal complex unit Λ- and the other Δ-configured. The stereochemistry is deduced from the NMR signal of the methylene spacer. In the case of a helical conformation, the two protons would be homotopic (leading to one singlet), while in the case of the meso-form, the two diastereotopic protons should lead to two doublets. Two signals are observed for the spacer of [Fe$_2$**13**$_3$]$^{4+}$, indicating the formation of a meso-helicate. This species is made up from two similar building blocks (the metal complex units) which possess opposite helicity.[24]

Ligands **14** have ethylene (or ethene) spacers attached in the 6-position of the bipyridine (phenanthroline) units. Therefore, they are candidates for the self-assembly of double-stranded oligonuclear complexes. **14a**, **14b**, and **14c** form double-stranded complexes [Cu$_2$**14a**$_2$]$^{2+}$, [Cu$_3$**14b**$_2$]$^{2+}$, and [Cu$_2$**14c**$_2$]$^{2+}$ with copper(I) ions.[64−66] X-ray analysis of [Cu$_2$**14a**$_2$]$^{2+}$ reveals the double-helical structure of the complex, while with **14c** and cobalt(II) the mononuclear complex [Co**14c**][CF$_3$SO$_3$]$_2$ could be structurally characterized.[65] The very similar but more rigid ethene-bridged ligand **14d** does not form defined coordination compounds, but mixtures of different copper(I) complexes are observed.[64]

Ligands **14** are ideal for the formation of double helicates. Shifting the spacer from the 6- to 5-position leads to derivatives such as **15** which should be good candidates for the formation of triple-stranded helicates. The bis(bipyridine) **15a** and **15b** forms dinuclear and trinuclear triple-stranded helicates with iron(II).[65,67] The corresponding helical nickel(II) complex [Ni$_3$**15b**$_3$]$^{6+}$ crystallizes with separation of the enantiomeric helices and was structurally characterized.[39]

Further shifting of the ethylene spacer from the 5- to 4-position of the bipyridines still enables the formation of triple-stranded helical complexes. Ligands **16a** and **16b** form helicates [Fe$_2$**16a**$_3$]$^{4+}$ and [Fe$_2$**16b**$_3$]$^{4+}$ with iron(II) ions, as could be shown by X-ray diffraction. The (CH$_2$)$_2$ as well as the (CH$_2$)$_3$ spacer of **16a/b** lead to helical metal complexes.[68,69] The enantiomeric helicates (M)-[Fe$_2$**16a**$_3$]$^{4+}$ and (P)-[Fe$_2$**16a**$_3$]$^{4+}$ can be separated by asymmetric extraction/precipitation. Extraction of a [Fe$_2$**16a**$_3$]$^{4+}$ containing water phase with a dichloromethane solution of [cinchonidinium][Δ-tris(tetrachlorobenzenediolato)phosphate(V)] (Δ-TRISPHAT$^-$) leads to the complex salt (P)-[Fe$_2$**16a**$_3$][Δ-TRISPHAT]$_4$ in the organic phase (50% yield, de > 97%) and (M)-[Fe$_2$**16a**$_3$][Δ-TRISPHAT]$_4$ as a precipitate (48%, de > 97%). In solution, (P)-[Fe$_2$**16a**$_3$][Δ-TRISPHAT]$_4$ rapidly epimerizes at 80 °C. Observation of free ligand **16a** by NMR at elevated temperatures suggests that this epimerization process proceeds via a dissociative mechanism.[70] Heterodinuclear ruthenium(II)/iron(II) complexes [RuFe**16**$_2$]$^{4+}$ are obtained, and energy transfer between the ruthenium and the iron centers can be studied.[69]

With the (CH$_2$)$_3$-linked bipyridine **17**, no helicate but instead a triple-stranded meso-helicate [Fe$_2$**17**$_3$]$^{4+}$ is obtained. NMR spectroscopic investigations show two distinct signals for the diasterotopic protons of the central methylene unit of the spacer. In the case of a helical structure, the protons should be homotopic.[71] Thus, **17** exhibits a high analogy to ligand **13**, which shows the same connectivity as **17** but possesses only one methylene group in the spacer. **13** also forms the meso-helicate [Fe$_2$**13**$_3$]$^{4+}$. With the related ligands **15** (with (CH$_2$)$_2$ linkage) the helicates (e.g., [Ni$_3$**15b**$_3$]$^{6+}$)[39] are observed exclusively. The reason for the high but different stereoselectivity in the self-assembly process of ligands **13**, **15**, and **17** is the different nature of the spacers. The 5-positions of the bipyridine units are connected by alkyl chains. However, the length of the spacer varies from one to three methylene units with the diastereoselectivity of the complex formation depending on the number of CH$_2$ groups. An odd number of methylene units (n = 1, 3) leads to the achiral meso-helicate. Alkyl chains prefer a zigzag structure as the energetically favored conformation. In the case of an odd number

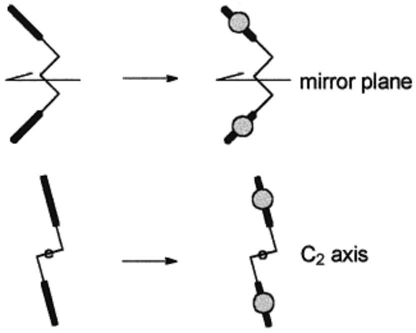


Figure 9.

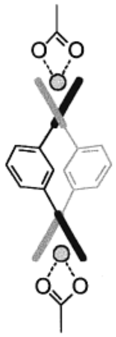


Figure 10.

of methylene units, this yields a molecule with an internal mirror plane. If this conformation is conserved during the formation of a dinuclear metal complex, it consequently will lead to the meso-form, which also exhibits this internal mirror plane. In the case of an even number of methylene units, the favored conformation possesses a C_2 axis which upon complex formation will lead to the chiral helicate. Thus, the stereoselective formation of complexes from linear alkyl-bridged ligands such as **13**, **15**, and **17** highly depends on the preferred conformation of the spacer. Simple "addition" or "removal" of one methylene unit results in a switch from the chiral helicate to the achiral meso-helicate or vice versa (Figure 9).[12,26]

Ligands **18** represent bis(bipyridine) derivatives which bear aromatic spacers connecting the ligand units. In **18a** and **18b** a single aromatic ring possesses two bipyridines attached in the 1- and 3-positions, while in **18c** biphenyl carries the bipyridines in the 3- and 3′-positions. All of ligands **18** form dinuclear double-stranded helicates $[M_2\mathbf{18}_2]^{2+}$ with copper(I) and silver(I) ions. $[Cu_2\mathbf{18c}_2]^{2+}$ could be characterized by X-ray diffraction, showing the helical arrangement of the two ligands which are wrapping around the copper(I) centers.[72]

From nickel(II) and **18** dinuclear double-stranded helicates are formed. However, due to the preference of nickel for an octahedral coordination geometry additional co-ligands have to be present. The helicates were obtained as $[Ni_2\mathbf{18}_2(OAc)_2]^{2+}$. X-ray structural analyses of $[Ni_2\mathbf{18b}_2(OAc)_2]^{2+}$ and $[Ni_2\mathbf{18c}_2(OAc)_2]^{2+}$ show the double-helical arrangement of the two ligand strands with two acetates coordinating to the nickel(II) ions at the termini of the helicate (Figure 10).[72]

In ligand **19** two bipyridine units are connected by a $(CH_2)_3$ linker which, through amide groups, is attached to the 5-position of the ligands. With iron(II) ions a dinuclear triple-stranded helicate $[Fe_2\mathbf{19}_3]^{4+}$ is obtained.[73] The X-ray structure shows the presence of the helical and not of the meso-form. The helicate is formed, although an odd number of methylene units is present in the spacer. This is due to the amide groups which are tilted at the CH_2-NH σ-bonds, leading to a distortion of the zigzag conformation of the alkyl chain.[26] ^1H NMR shows only one multiplet for the protons of the central methylene unit, indicating the presence of the helical stereoisomer of $[Fe_2\mathbf{19}_3]^{4+}$ not only in the solid state but also in solution.[73]

Helicates usually are formed as a racemic mixture of the two enantiomers. As mentioned before, it is possible to obtain only one of the helical isomers by spontaneous separation during crystallization.[39] On the other hand, it is possible to induce a particular twist by chiral substituents at the ligand. The chiral ligands **7e** and **7f** and the *Rhodoturulic acid* **5**-H_2 were already mentioned.[27,36,74] In addition, ligands **20**−**22** which bear pinene-derived units as substituents at the bipyridines were synthesized. Derivatives **20** and **22** form triple-stranded helicates (*P*)-$[M_2\mathbf{20}_3]^{4+}$ (M = Cd, Zn, Fe)[75] and (*P*)-$[Fe_2\mathbf{22}_3]^{4+}$. The (*P*)-sense of the helical turn was shown by CD spectroscopic investigations. An X-ray structural investigation of (*P*)-$[Fe_2\mathbf{22}_3]^{4+}$ supports the stereochemical assignment.[76]

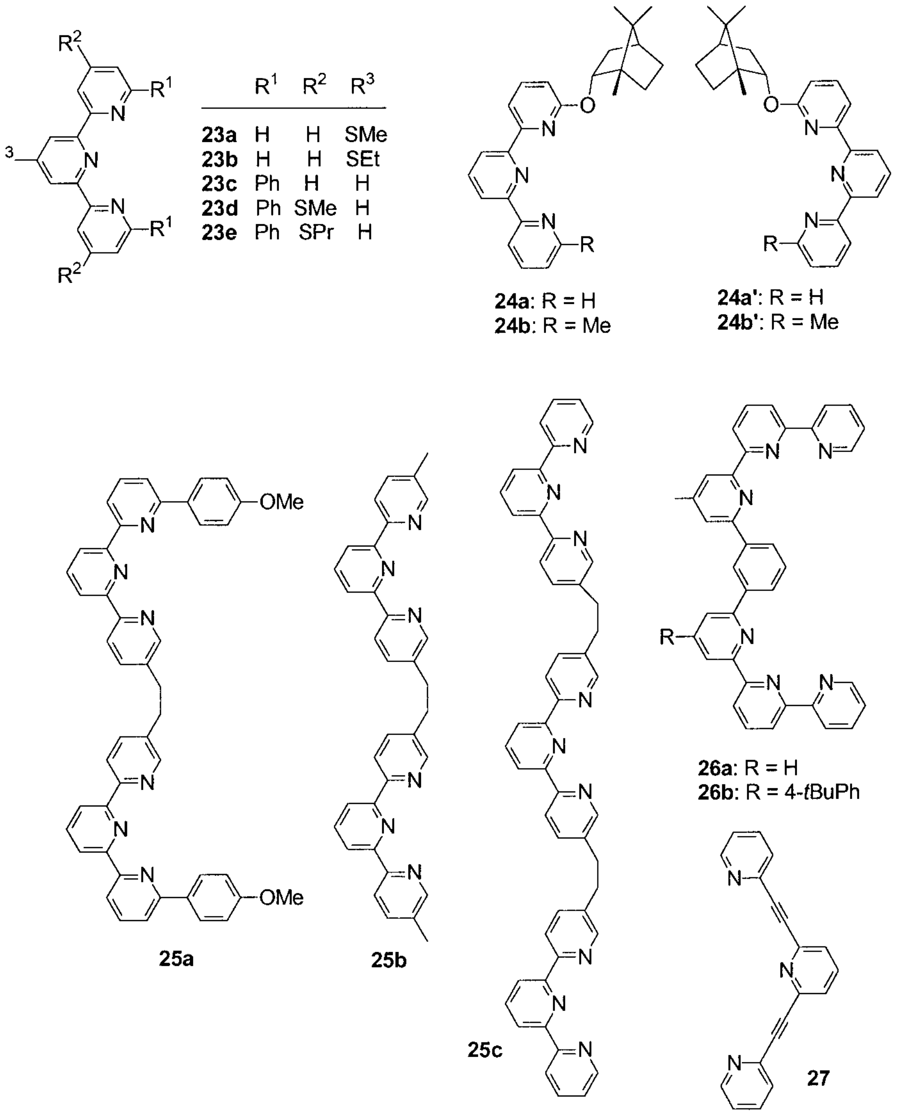
Due to its substitution pattern at the aromatic units, **21** is more appropriate for the formation of double- than triple-stranded helicates. With copper(I) ions in methanol, a mixture of two species (ratio 10:7) is formed. Crystallization yields the dinuclear double-stranded helicate $[Cu_2\mathbf{21}_2]^{2+}$, and the X-ray structure analysis shows that the (*R*,*R*)-configured ligand induces a (*P*)-helix while (*S*,*S*)-**21** leads to the corresponding (*M*)-helix.[77]

2. Terpyridine Derivatives

Ligands **10** were discussed before, in which a terpyridine unit is introduced into ligand strands containing bipyridines.[56] However, 2,2′:6,2″-terpyridine itself and ligand strands containing several terpyridine units are able to form helicates.

A number of different 2,2′:6′,2″-terpyridine derivatives **23**−**26** (Figure 11) were synthesized[78] and used for the formation of double-stranded helicates. Ligand **23b** forms double-stranded helicates with copper(I) as well as with cadmium(II) ions which possess the structure of "molecular boxes". Complexes $[Cu_2\mathbf{23b}_2(MeCN)_2]^{2+}$ and $[Cd_2\mathbf{23b}_2(AcO)_2(MeOH)_2]^{2+}$ were characterized by X-ray analysis. Each of ligands **23b** binds with two of its pyridine units to one of the metal centers and with the third one to the other, filling three coordination sites at each metal. In addition, co-ligands bind to the metals and fill up their coordination sphere (**I**) (Figure 12).[79]

Ligands **23a,c**−**e** form dinuclear double-stranded helicates $[Cu_2\mathbf{23a,c-e}_2]^{2+}$ without any co-ligands present. The solid-state structure of $[Cu_2\mathbf{23d}_2]^{2+}$ shows that one copper ion is tetracoordinated, binding to two pyridines of each ligand **23d**, while the



	R^1	R^2	R^3
23a	H	H	SMe
23b	H	H	SEt
23c	Ph	H	H
23d	Ph	SMe	H
23e	Ph	SPr	H

Figure 11.

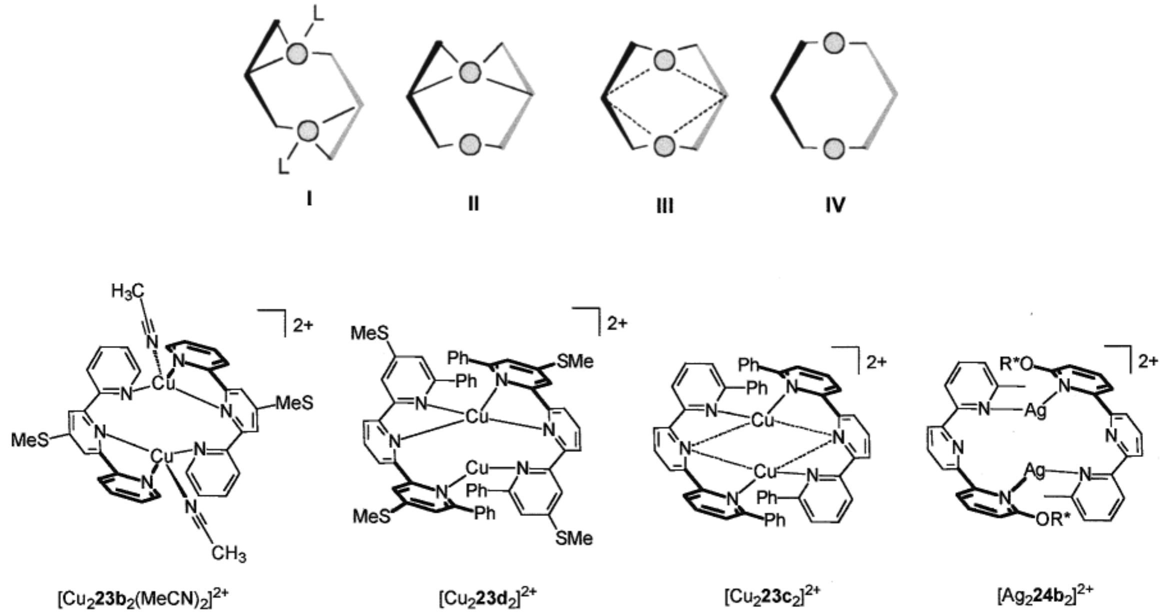


Figure 12.

second copper ion is bound to the two remaining pyridines (**II**). However, NMR studies at −80 °C show that in solution the more symmetric structure **III** is probably present. Two copper(I) centers are tetracoordinated, and the central pyridine units of the ligands are bridging between the metals.[80] A structure **III**, as it was proposed for $[Cu_2\mathbf{23d}_2]^{2+}$ in solution, is observed for the double-stranded helicate $[Cu_2\mathbf{23c}_2]^{2+}$ in the solid state.[81]

Ligands **24** are highly sophisticated examples of terpyridine derivatives. On the one hand, they bear chiral substituents which can induce a preferred twist in the helix; on the other hand, they are directional due to the unsymmetric substitution pattern and can adopt a parallel or an antiparallel orientation. That means that the termini of the ligand which bear the chiral substituents can either be bound to the same (parallel) or to different metal centers (antiparallel). Derivatives **24** form complexes with silver(I) and copper(I) ions. Crystallization of the silver(I) complex of **24a** from acetonitrile yields a mononuclear species $[Ag\mathbf{24a}(NCMe)]^{+}$ with the tridentate ligand **24a** and one molecule of acetonitrile coordinating to the metal in a distorted square planar coordination geometry.[82] On the other hand, crystallization of silver complexes of **24a** and **24b** from methanol and acetone, respectively, affords the dinuclear double-stranded helicates $[Ag_2\mathbf{24}_2]^{2+}$.[82,83] The X-ray crystal structures of the complexes show that the chiral ligands **24** induce an (*M*)-configuration at the helix. With the enantiomeric ligands **24a′,b′** the (*P*)-helix is obtained. However, two different structures are observed for $[Ag_2\mathbf{24a}_2]^{2+}$ or $[Ag_2\mathbf{24b}_2]^{2+}$ in the solid state. The coordination geometry at the silver in both complexes can be described best as linear dicoordinated. The two silver(I) ions are only binding to the terminal pyridine units of the terpyridine ligand (**IV**). Ligand strands of $[Ag_2\mathbf{24a}_2]^{2+}$ are orientated parallel with the two chiral and sterically demanding units at one terminus of the helicate and with the unsubstituted terminus interacting with the unsubstituted terminus of a second complex by π-stacking. In the solid state this leads to a tetranuclear arrangement $[\{Ag_2\mathbf{24a}_2\}_2]^{4+}$. Ligand **24b** bears an additional methyl substituent which suppresses the $\pi-\pi$ interaction in the solid state. Here the X-ray structure of the dinuclear antiparallel isomer of $[Ag_2\mathbf{24b}_2]^{2+}$ is obtained. Copper(I) ions form the structurally very similar complex $[Cu_2\mathbf{24b}_2]^{2+}$ with an antiparallel orientation of the two strands. In solution two different species are observed for $[Cu_2\mathbf{24b}_2]^{2+}$ (ratio 13:2). It is supposed that this isomerism is due to two different stereoisomers with a different turn of the helix and not to different regioisomers with parallel and antiparallel ligand orientations.[82−84]

Connection of two terpyridine units by appropriate spacers leads to extended ligands which bear two (or more) tridentate binding sites for metal ions. Therefore, they are ideal to form double-stranded helicates with metal centers that prefer an octahedral coordination geometry.

Thus, the ethylene-linked bis(terpyridine) derivative **25a** forms double-stranded helicates $[M_2\mathbf{25a}_2]^{4+}$ with iron(II) or ruthenium(II) as the metal. A poor X-ray structure of the ruthenium complex $[Ru_2\mathbf{25a}_2]^{4+}$ shows the helical arrangement of the ligands.[85] The two enantiomeric forms of the analogous iron(II) helicate $[Fe_2\mathbf{25b}_2]^{4+}$ could be separated chromatographically by chiral resolution with tartrate. X-ray structural analysis allows the assignment of the absolute configuration of the helix. The helical arrangement at the iron(II) centers in $[Fe_2\mathbf{25b}_2]^{4+}$ leads to an extraordinarily high optical rotation of $[\alpha]_D = -2015$ for the (*P*)-enantiomer and $+2070$ for the (*M*)-enantiomer.[86] The trinuclear double-stranded helicate $[Fe_3\mathbf{25c}_2]^{6+}$ was resolved in a similar manner, and the resulting enantiomerically pure helicates were investigated by CD spectroscopy.[87]

The bis(terpyridine) ligands **26** form dinuclear double-stranded helicates $[Ag_2\mathbf{26}_2]^{2+}$ and $[Cu_2\mathbf{26}_2]^{4+}$ with silver(I) or copper(II) ions. X-ray structural analyses of $[Ag_2\mathbf{26b}_2]^{2+}$ and $[Cu_2\mathbf{26b}_2]^{4+}$ show that the silver(I) ions are pentacoordinated, leaving one pyridine unit at each ligand strand **26b** uncoordinated. The copper(II) ions on the other hand adopt a hexacoordinated distorted octahedral geometry.[88]

Ligand **27** represents an "extended terpyridine" in which the direct connections between the pyridines were substituted by rigid alkyne spacers. This ligand forms a trinuclear triple-stranded helicate $[Cu_3\mathbf{27}_3]^{3+}$ with copper(I) ions. The X-ray structure analysis shows a trigonal-planar coordination geometry at the copper(I) centers.[89]

3. Quater-, Quinque-, Sexi-, Septi-, and Novipyridine Derivatives

Oligopyridines which are connected in the 2- and 6-positions of the pyridine units can be extended to obtain quater-, quinque-, sexi-, septi-, or novipyridines **28**−**35** and **37**−**39** as helicating ligands (Figure 13).[78]

2,2′:6′,2″:6″,2‴-Quaterpyridine consists of two bipyridine units.[33] Connection of the didentate units at the 6-position favors the formation of double-stranded over triple-stranded complexes. Consequently, double-stranded helicates are formed from the symmetric ligands **28** with copper(I) or silver(I) ions. The X-ray structures of $[Cu_2\mathbf{28a,b}_2]^{2+}$ and $[Ag_2\mathbf{28a}_2]^{2+}$ reveal the double-helical structures of the dinuclear coordination compounds.[90] $[Cu_2\mathbf{28b}_2]^{2+}$ was used as a molecular switch which gives a structural response on an electrochemical signal (Figure 14). Oxidation of the copper(I) centers of $[Cu_2\mathbf{28b}_2]^{2+}$ leads to the rearrangement of the dinuclear complex to form the mononuclear species $[Cu\mathbf{28b}(solvent)]^{2+}$. Reduction regenerates the helicate $[Cu_2\mathbf{28b}_2]^{2+}$.[91]

Derivatives **29** represent a class of directional quaterpyridine ligands which all form double-stranded dinuclear helicates with copper(I) $[Cu_2\mathbf{29}_2]^{2+}$. In general, it is found that a parallel orientation of the strands is favored over an antiparallel one. However, complexes with antiparallel ligands are also observed. The relative orientation of the two ligand strands depends on the size of the substituents. With the small methyl group in the 4-position of the terminal pyridine ring (ligand **29h**), the dinuclear

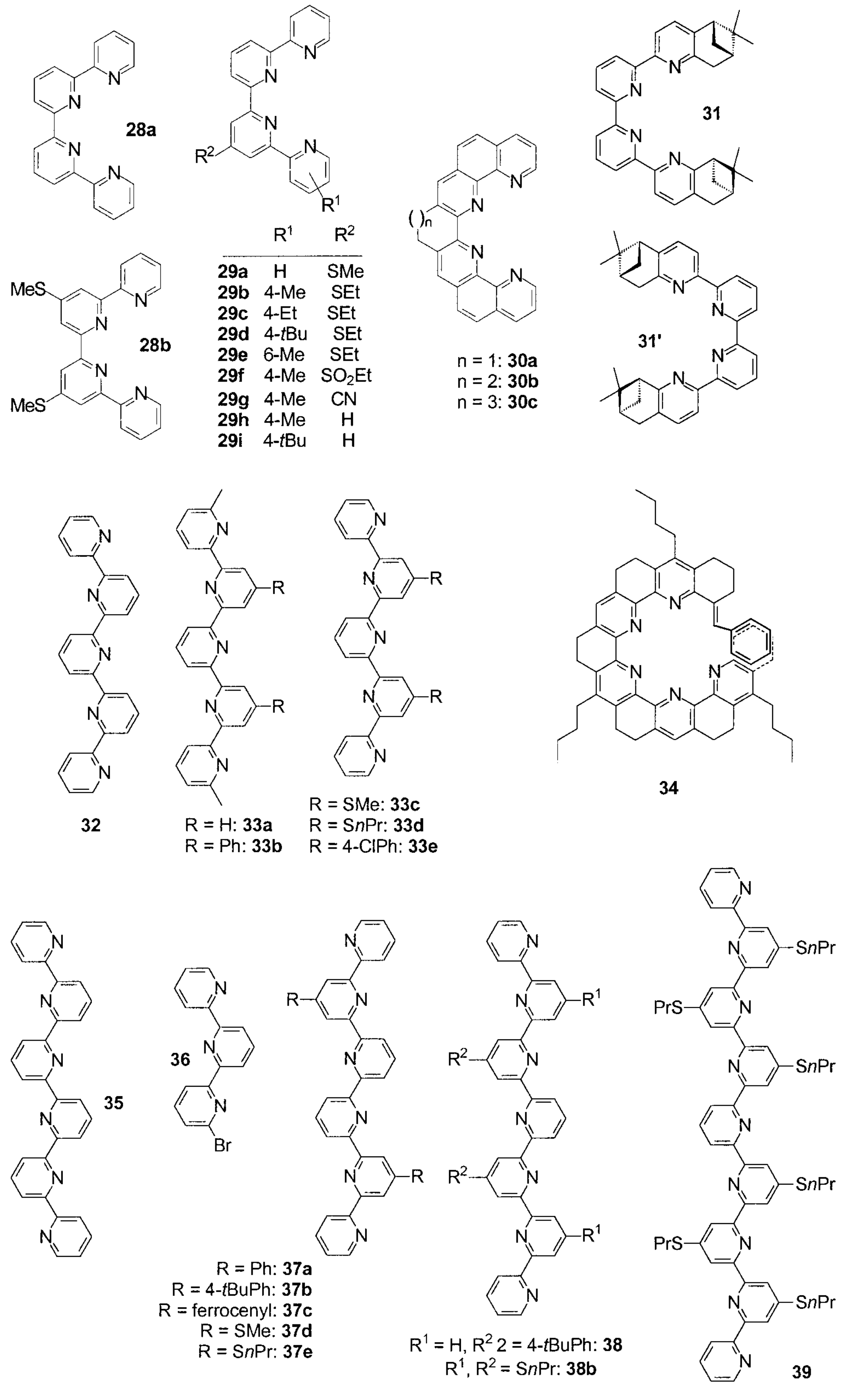
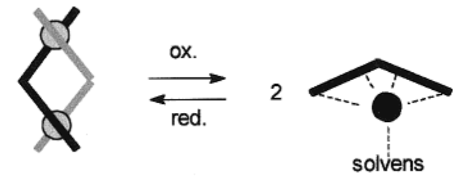


Figure 13.

complex $[Cu_2\mathbf{29h}_2]^{2+}$ exists in solution as a mixture of the two regioisomers in a 1:1 ratio. In contrast, ligand **29i** with a bulky *tert*-butyl group in the same position exclusively forms one isomer of $[Cu_2\mathbf{29i}_2]^{2+}$ which, by crystallization and X-ray structural studies, was shown to be the one with parallel ligand strands.[92]

The quaterpyridine substructure is hidden in compounds **30**. Additional alkyl linkages are introduced in the backbone of the ligand, making it more rigid. With the most flexible derivative **30c** a copper(I) complex $[Cu_2\mathbf{30c}_2]^{2+}$ is obtained. The solid-state structure shows the double-helical arrangement of the ligand strands.[93]



$[Cu_2\mathbf{28b}_2]^{2+}$ $[Cu\mathbf{28b}(solvens)]^{2+}$

Figure 14.

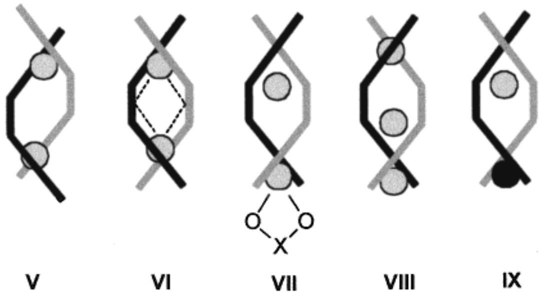


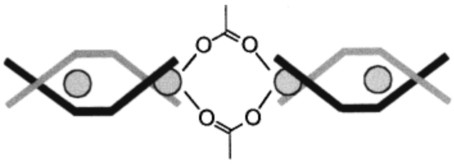
Figure 15.

Introduction of chiral groups at the terminus of 2,2′:6′,2″:6″,2‴-quaterpyridine leads to chiral induction during the formation of dinuclear double-stranded silver(I) and copper(I) helicates $[M_2\mathbf{31}_2]^{2+}$ from ligands **31** and **31′**. Although one major and one minor stereoisomer are obtained initially, crystallization enables the isolation of the enantio- and diastereomerically pure double-stranded helicates. X-ray structural investigations in combination with CD spectroscopy show that ligand **31** favors the formation of (*P*)-$[M_2\mathbf{31}_2]^{2+}$ (M = Cu, Ag), while **31′** leads to the (*M*)-isomer as the major product. The helical complexes show an extraordinarily high optical rotation of $[\alpha]_D = +1128°$ for (*P*)-$[Ag_2\mathbf{31}_2]^{2+}$ and $[\alpha]_D = +2126°$ for (*P*)-$[Cu_2\mathbf{31}_2]^{2+}$.[94]

2,2′:6′,2″:6″,2‴:6‴,2⁗-Quinquepyridine undergoes a variable coordination chemistry. In principle, it can be segmented into different ligand units leading to a variety of different coordination modes **V**−**IX** in double-stranded helicates (Figure 15).

From a formal point of view, quinquepyridines can act as linear oligopyridine ligands with (i) one bipyridine and one terpyridine unit (**V**, **IX**), (ii) two bipyridines bridged by a pyridine (**VI**), or (iii) two bipyridines with a terminal pyridine (**VII**, **VIII**).[95]

Simple unsubstituted 2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine **32** forms a dinuclear double-stranded helicate $[Pd_2\mathbf{32}_2]^{4+}$ with palladium(II). This complex exhibits coordination mode **V**, in which the ligand acts as a segmental bipyridine/terpyridine derivative. Each of the palladium centers shows pentacoordination, binding to the bipyridine unit of the one and to the terpyridine unit of the other ligand strand **32**.[96] Silver(I) ions and **32** form a mononuclear complex $[Ag\mathbf{32}]^+$. However, the dinuclear double-stranded structure **V** is found in the solid state for the silver(I) complex $[Ag_2\mathbf{33a}_2]^{2+}$ of ligand **33a**. The methyl groups at the termini of **33a** disfavor a mononuclear species by steric interaction.[97] Introduction of phenyl groups in the 4-position of the second and fourth pyridine unit results in ligand **33b** which is related to **33a**. However, the coordination mode of the silver(I) complex $[Ag_2\mathbf{33b}_2]^{2+}$ changes compared to $[Ag_2\mathbf{33a}_2]^{2+}$. The two silver ions are coordinating to the terminal bipyridine units of the ligand, and the central pyridine units act as bridging ligands. As a result, a highly distorted octahedral coordination geometry is observed at the metals.[97]



$\{[Co_2\mathbf{33e}_2(OAc)]_2\}^{6+}$

Figure 16.

Trinuclear complexes $[Cu_3\mathbf{33c,d}_2]^{3+}$ which probably possess a structure like **VIII** result from the reaction of copper(I) with the quinquepyridines **33c** and **33d**. Oxidation of the copper(I) centers to copper(II) results in the removal of one of the copper ions and a dinuclear complex $[Cu_2\mathbf{33c,d}_2]^{4+}$ is obtained. X-ray structural analysis of $[Cu_2\mathbf{33c}_2]^{4+}$ shows that one of the copper(II) metals is tetra- and the other hexacoordinated (similar to **IX**). In the presence of acetate, complex $[Cu_2\mathbf{33c}_2(OAc)]^{6+}$ is formed. In this complex of type **VII** both copper(II) ions are hexacoordinated with one metal binding to the terpyridine domains of the two ligand strands and the other to the bipyridine units. The latter additionally coordinates an acetate as a bidentate ligand.[91] Structure **VII** is also present in the helicates $[M_2(\mathbf{32/33c,d})_2(OAc)]^{3+}$ (M = Fe, Co, Ni, Zn)[98] and $[Ru_2\mathbf{32}_2(oxalate)]^{2+}$.[99] Cobalt(II) ions and **33e** result in the related complex $\{[Co_2\mathbf{33e}_2(OAc)]_2\}^{6+}$ (Figure 16). In this compound two acetates bridge the two dinuclear helicate moieties which are oppositely configured, leading to a tetranuclear meso-complex.[100]

The unique feature of quinquepyridine **32** and its derivatives opens up a way to the systematic synthesis of heterodinuclear double-stranded helicates. Binding of a metal ion that prefers hexacoordination to two terpyridine domains and one that prefers tetracoordination to two bipyridine units leads to heterodinuclear complexes of the type **IX**. Experimentally this is realized by simple mixing of mononuclear complexes $[Co\mathbf{32}(MeOH)_2]^{2+}$ and $[Ag\mathbf{32}]^+$. X-ray analysis of the resulting double-stranded helicate $[CoAg\mathbf{32}_2]^{3+}$ shows the proposed heterodinuclear structure **IX** with silver occupying the tetrahedral and cobalt the octahedral binding sites.[101] Reaction of $[Co\mathbf{32}(MeOH)_2]^{2+}$ with copper(I) or silver(I) salts also enables the isolation of the heterodinuclear complexes $[CoM\mathbf{32}_2]^{3+}$ (M = Ag, Cu).[102] Another method for the generation of type **IX** heterodinuclear helicates is the redistribution reaction of two homodinuclear helicates. Thus, $[Ni_2\mathbf{33c}_2(NO_3)]^{3+}$, which possesses a structure like **VII**, forms the heterodinuclear double-stranded helicate $[NiCu\mathbf{32c}_2]^{3+}$ by reaction with $[Cu_2\mathbf{33c}_2]^{2+}$, which could be characterized by X-ray diffraction.[103]

The very rigid helicene-type quinquepyridine derivative **34** is ideally preorganized for the complexation of sodium. Here, a mononuclear complex $[Na\mathbf{34}]^+$ can be generated in solution and transformed into

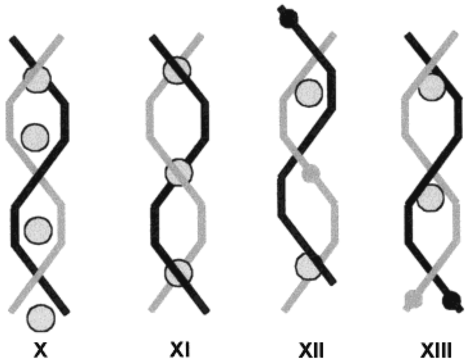


Figure 17.

the corresponding dinuclear complex $[Na_2\mathbf{34}_2]^+$. Thorough 2D NMR spectroscopic investigations show that the dinuclear complex $[Na_2\mathbf{34}_2]^+$ adopts a structure in which the two directional ligands **34** are antiparallel orientated.[104,105]

2,2′:6′,2″:6″,2‴:6‴,2⁗:6⁗,2⁗′-Sexipyridine **35** and its derivatives **37** usually act either as a tris(bipyridine) or a bis(terpyridine) ligand. For example, **35** can be synthesized by homocoupling reaction of two terpyridine derivatives **36** with nickel(II) salts in the presence of triphenylphosphane and zinc. Initially the double-stranded dinuclear helicate $[Ni_2\mathbf{35}_2]^{4+}$ is formed, which by reaction with CN^- releases ligand **35**.[106] The related dinuclear compounds $[M_2\mathbf{35}_2]^{4+}$ (M = Mn, Fe, Co, Zn, Cd, Hg), $[M_2\mathbf{37a-c}_2]^{4+}$ (M = Fe, Co, Ni, Zn), and $[M_2\mathbf{37d,e}_2]^{4+}$ (M = Fe, Co, Ni, Cu) are obtained by coordination of an appropriate metal(II) salt with the corresponding free ligand.[98,107−109] X-ray structures of $[Zn_2\mathbf{37a}_2]^{4+}$,[109] $[Ni_2\mathbf{37d}_2]^{4+}$, and $[Cu_2\mathbf{37d}_2]^{4+}$ [98] show the double-helical structure with both metal centers pseudooctahedrally coordinated. Trinuclear helicates $[M_3\mathbf{35}_2]^{3+}$ (M = Cu, Ag) and $[Cu_3\mathbf{37d,e}_2]^{3+}$ are obtained with copper(I) or silver(I) ions.[98,107] The solid-state structure of $[Cu_3\mathbf{35}_2]^{3+}$ shows the three tetracoordinated copper centers with the two ligand strands wrapping around them.[107]

2,2′:6′,2″:6″,2‴:6‴,2⁗:6⁗,2⁗′:6⁗′,2⁗″-Septipyridine possesses various possibilities to form helicate-type complexes. However, very few coordination studies have been performed with this ligand system. The septipyridine derivative **38b** forms a tetranuclear helicate $[Cu_4\mathbf{38b}_2]^{4+}$ with copper(I) ions. It is supposed that three of the copper centers possess a pseudotetrahedral and one terminal a linear dicoordination geometry (**X**) (Figure 17). The mixed-valent species $[Cu^{II}Cu^{I}_2\mathbf{38b}_2]^{4+}$ is assumed to possess one hexacoordinated copper(II) and two tetracoordinated copper(I) centers **XI**. With copper(II) a dinuclear species $[Cu_2\mathbf{38b}_2]^{4+}$ is obtained. The X-ray structure of the corresponding cobalt complex $[Co_2\mathbf{38b}_2]^{4+}$ reveals two hexacoordinated metal centers. The terminal pyridine unit of the one ligand strand and the central unit of the other do not participate in the binding to the metals (**XII**).[110]

In the solid-state structure of $[Zn_2\mathbf{38a}_2]^{4+}$ it is observed that one pyridine of each strand, which are both located at the same terminus of the helicate **XIII**, is not coordinating to the zinc(II) ions.[111]

Oligonuclear coordination compounds of the nonipyridine **39** are only detected by FAB mass spectrometry. Thus, the pentanuclear complexes $[Cu_5\mathbf{39}_2]^{5+}$ and $[M_3\mathbf{39}_2]^{6+}$ (M = Co^{II}, Cu^{II}) could be observed. For the latter it is assumed that the metals occupy pseudooctahedral coordination sites, with ligands **39** acting as tris(terpyridine) derivatives.[112]

4. Imine-Based Ligand Strands

Imine-based ligands are very easy to synthesize and—as Hannon pointed out[113]—are inexpensive. This means that they are easily available in large amounts to do coordination studies and to investigate the properties of supramolecular metal complexes.

The simple ligand **40**, which is obtained by imine condensation of 2-pyridinecarbaldehyde and ethylenediamine, forms a dinuclear double-stranded helicate $[Ag_2\mathbf{40}_2]^{2+}$ with silver(I) ions (Figure 18). X-ray characterization shows the double-helical structure with the two silver ions being tetracoordinated.[114] The analogous ligand **41a** is similar to the meso-configured derivatives **3a,b**,[32] which yield double-stranded helicates $[Ag_2\mathbf{3}_2]^{2+}$. **41a** does not form discrete dinuclear complexes with silver(I), but a polymeric structure $[Ag_n\mathbf{41a}_n]^{n+}$ is observed in the solid state.[114] However, **41a** and its bromo-substituted analogue **41b** yield dinuclear double-stranded helicates $[Cu_2\mathbf{41}_2]^{2+}$. An X-ray structure of $[Cu_2(R,R\text{-}\mathbf{41b})_2]^{2+}$ shows that the *R*,*R*-configuration in the ligand backbone induces an (*M*)-configuration of the helicate. The self-assembly of the dinuclear complexes proceeds with chiral self-recognition if a racemic mixture of *R*,*R*- and *S*,*S*-**41a,b** is used for the complexation studies (vide infra).[115]

The bipyridine (or phenanthroline) derivatives **42**, which possess either a bipyridine-type or two iminopyridine binding sites for metal ions, were used for the formation of dinuclear double-stranded helicates. All ligands **42** lead to helical complexes $[Cu_2\mathbf{42}_2]^{2+}$. For $[Cu_2\mathbf{42b}_2]^{2+}$ [116] and $[Cu_2\mathbf{42e}_2]^{2+}$,[117] it was found for the first time that phenanthroline does not act as a chelating but as a bridging unit. The potential thioether donors of **42e** do not participate in the binding to the copper(I) centers.[117] However, due to the presence of the bipyridine unit, which is an excellent bidentate binding site for metals, the formation of the dinuclear complexes is not cooperative. This means that in the presence of an excess of ligand **42** the formation of a mononuclear species $[Cu\mathbf{42}_2]^+$ (**XIV**) is favored over the dinuclear complex $[Cu_2\mathbf{42}_2]^{2+}$ (**XV**) (Figure 19).[116]

Liquid crystalline behavior was observed for $[Cu_2\mathbf{42d}_2][BF_4]_2$ (Figure 20). The complex undergoes a first-order phase transition at 25 °C to form a columnar mesophase and melts at 181 °C into the isotropic liquid.[118]

With the naphthyridine derivative **43** a dinuclear double-stranded helicate $[Cu_2\mathbf{43}_2]^{2+}$ is formed and structurally characterized. Solution ES-MS and competition studies show that the compound is partly dissociated in solution, and thus, noncooperative binding of the two metal centers can be concluded. It is supposed that this is due to the close spatial contact of the two cationic centers and the resulting electrostatic repulsion.[119]

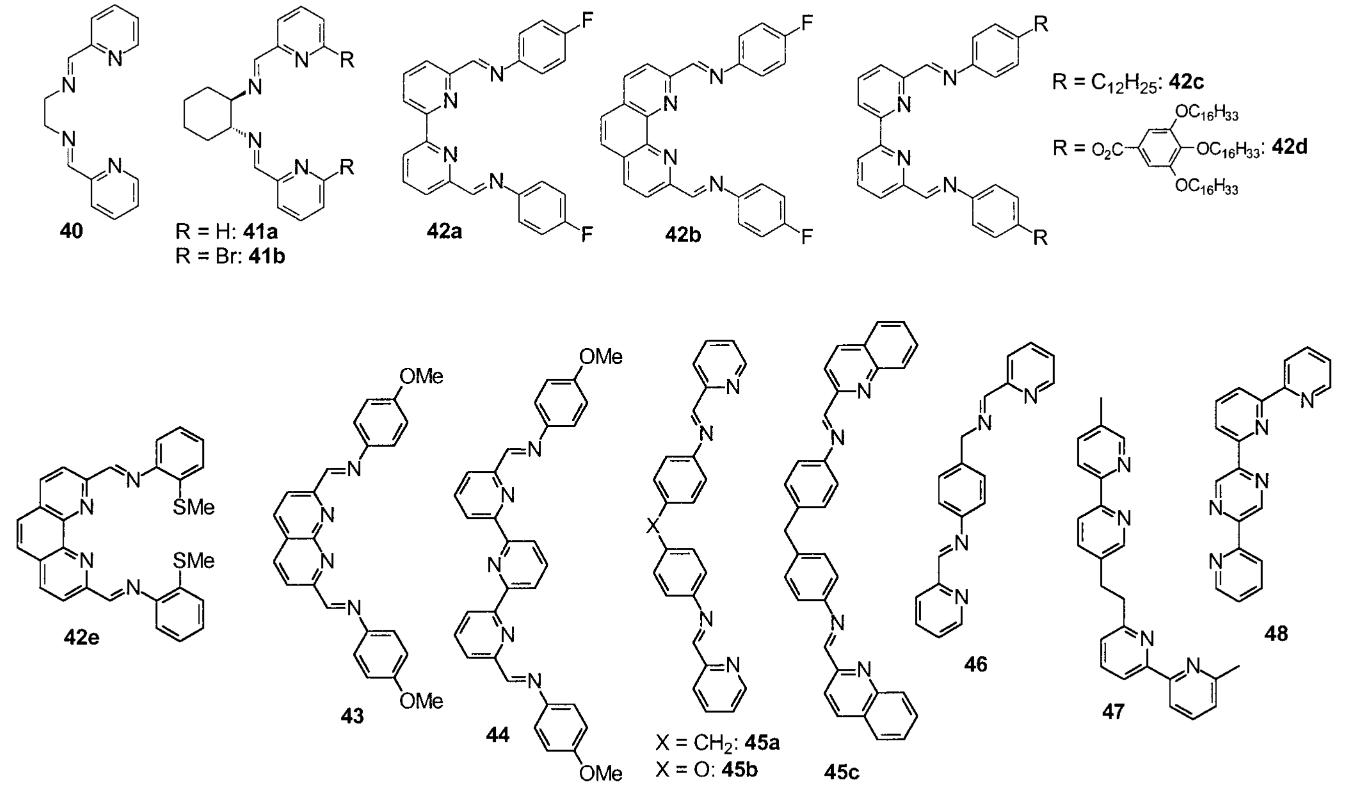


Figure 18.

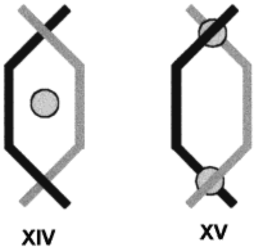


Figure 19.

The dinuclear copper(I) helicate $[Cu_2\mathbf{44}_2]^{2+}$ is obtained in a noncooperative process (Figure 21). X-ray structural investigations show that each copper(I) is bound to three pyridine ligands and one imino-nitrogen atom, leaving two imines uncoordinated. NMR and IR spectroscopy indicate symmetrical complexes, which is attributed to a fluctional behavior of $[Cu_2\mathbf{44}_2]^{2+}$ in solution.[120]

Copper(I) complex $[Cu_2\mathbf{44}_2]^{2+}$ can be oxidized successively, initially yielding the mixed-valent copper(I)/copper(II) species $[Cu_2\mathbf{44}_2]^{3+}$ which after formation should possess a tetracoordinated copper(I) and a pentacoordinated copper(II) center with one uncoordinated imine moiety. However, the X-ray structure analysis shows a dinuclear complex $[Cu_2\mathbf{44}_2]^{3+}$ with one hexacoordinated and one tetracoordinated copper atom in the solid state. Further oxidation of $[Cu_2\mathbf{44}_2]^{3+}$ leads to the dinuclear copper(II) helicate $[Cu_2\mathbf{44}_2]^{4+}$ with two pentacoordinated copper(II) centers.[120]

The imine/pyridine derivatives **45a,b** form triple-stranded helicates $[Ni_2\mathbf{45a,b}_3]^{4+}$ [113,121] and $[Co_2\mathbf{45b}_3]^{4+}$ [121] which were characterized in the solid state. However, the diaryl ether derivative **45b** possesses two O−C_{aryl} bonds with a high conformational flexibility. Therefore, **45b** should be able to form not only helical but also nonhelical complexes. Indeed, the double-stranded complex $[Ag_2\mathbf{45b}_2]^{2+}$ adopts the meso-structure in the solid state.[121]

Ligand **45c** bears a quinoline group instead of the pyridine of **45a**. **45c** forms a dinuclear double-

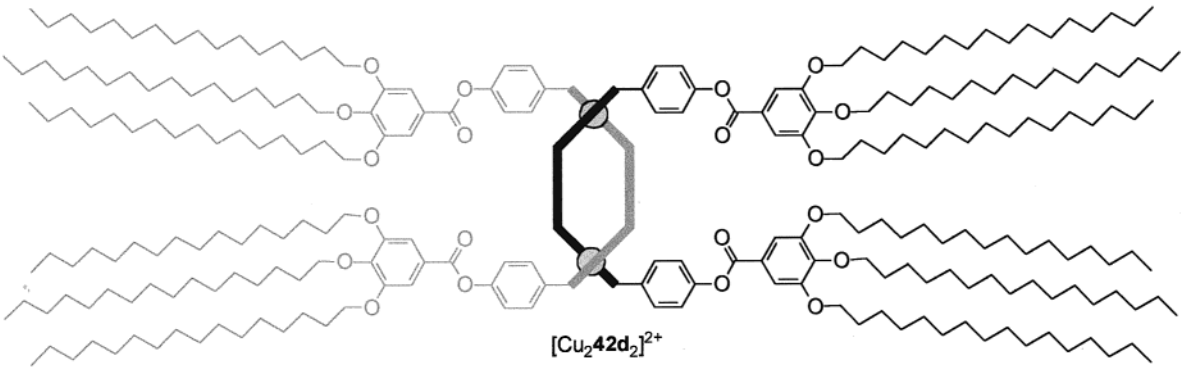


Figure 20.

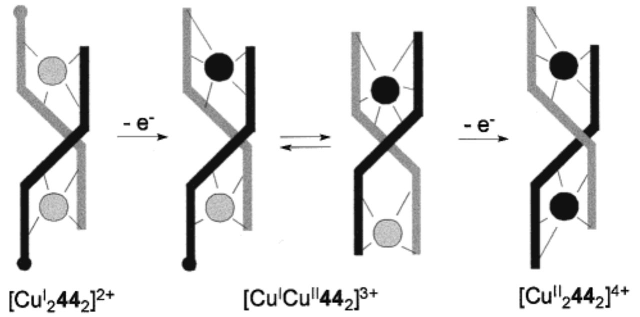


Figure 21.

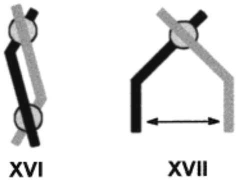


Figure 22.

stranded silver(I) helicate $[Ag_2\mathbf{45c}_2]^{2+}$. X-ray analysis shows that this helicate adopts a bent structure, forming a major and a minor groove as observed for double-stranded DNA. In the solid state one molecule of benzene is intercalated in the major groove of $[Ag_2\mathbf{45c}_2]^{2+}$.[122]

The directional ("unsymmetric") ligand **46** yields an antiparallel double-stranded helicate $[Ag_2\mathbf{46}_2]^{2+}$ with silver(I) ions. The antiparallel orientation **XVI** of the ligand strands is enforced due to the special steric constraints of **46** (Figure 22). A dinuclear complex with parallel orientation cannot be formed because of the unfavorable spatial orientation of the two ligands after complexation of the first metal ion (**XVII**).[123]

The structural situation **XVI** which is found for $[Ag_2\mathbf{46}_2]^{2+}$ is very similar to the one observed for the double-stranded helicates $[Ag_2\mathbf{47}_2]^{2+}$[124] and $[Cu_2\mathbf{48}_2]^{2+}$.[125] In ligands **47** and **48** the dissymmetry is generated by linking of two bipyridine-type ligands at the 5- and 6-positions, either by a direct bond (**48**) or by an ethylene group (**47**).

5. Ligand Strands Containing Five-Membered Azaheterocycles as Donors

Five-membered aza-heterocycles of the pyrrole-, pyrazole-, imidazole-, 1,3-oxazoline-, or 1,3-thiazole-type can act as N-donor ligands for the complexation of metal ions. The self-assembly of double-stranded helicates $[Zn_2\mathbf{1}_2]$ and $[Zn_2\mathbf{2}_2]$ from ligands **1** or **2** in the presence of zinc(II) ions was already discussed in the introductory part of this article.[30,31]

The 10-oxo-5,15-biladiene derivative **49**-H_2 (Figure 23) forms double-stranded dinuclear helicates $[M_2\mathbf{49}_2]$ with zinc(II) as well as cadmium(II) and mercury(II) ions. The cadmium complex $[Cd_2\mathbf{49}_2]$ was characterized by X-ray structural analysis, and it was shown that the metal possesses a pentacoordinated environment, binding to four pyrrol-nitrogen donors and one carbonyl oxygen atom.[126]

Double-stranded helicates are also obtained from the oligo-pyrrol ligands **50**. Derivatives **50a**−**c** differ in the length of the spacer bridging the second and third pyrrol unit. For **50a**-H_2, with a direct connection between those two pyrroles, the double-stranded helicate $[Zn_2\mathbf{50a}_2]$ is formed and structurally characterized. Ligand **50b** with a methylene unit as a spacer allowed the isolation and characterization of $[Co_2\mathbf{50b}_2]$. The analogous dinuclear complex $[Co_2\mathbf{50c}_2]$ with the ethylene-linked ligand **50c** as well as the trinuclear double-stranded complex $[Zn_3\mathbf{50d}_2]$ could be characterized by ES mass spectrometry.[127]

Bis(dipyrromethane) ligands **50e**−**i**-H_2 with the spacer in the β- and β'-positions form double-stranded helicates with copper(I), zinc(II), and cobalt(II) ions. Complexes $[Zn_2\mathbf{50e}_2]$, $[Zn_2\mathbf{50f}_2]$, $[Zn_2\mathbf{50g}_2]$, and $[Co_2\mathbf{50f}_2]$ were characterized by X-ray structural analysis.[128] Helicate $[Zn_2\mathbf{50e}_2]$ of ligand **50e**-H_2 with a short CH_2 spacer was characterized by NMR spectroscopy using lanthanide shift reagents. **50j**-H_2 with six methylene units in the spacer does not form dinuclear double-stranded but mononuclear complexes $[M\mathbf{50j}]$ ($M = Zn^{II}, Co^{II}$).[129]

The simple pyrazole/pyridine ligand **51**-H forms a pentametallic triple-stranded diruthenium helicate $[Ru_2Cu_3\mathbf{51}_6]^+$ with bridging copper(I) atoms as components of the spacer (Figure 24). Two hexacoordinated ruthenium(II) centers are bridged by three linear ligand strands $[\mathbf{51}\text{-}Cu\text{-}\mathbf{51}]^-$.[130]

Compounds **52** consist of two terminal pyrrazole and one central pyridine unit. With copper(I) ligands **52** form double-stranded dinuclear helicates $[Cu_2\mathbf{52}_2]^{2+}$. However, three different coordination modes **II**, **III**, and **XVIII** are found, depending on the substituents at the ligand (Figure 25). Structures of types **II** and **III** were already discussed for dinuclear complexes of terpyridine/derivatives.[131]

The most simple ligand of this series, **52a**, which bears hydrogen atoms as substituents in the 5-positions of the pyrazoles, forms a copper(I) complex $[Cu_2\mathbf{52a}_2]^{2+}$ which in the solid state possesses a structure like **II**. The two copper centers are bound to the terminal pyrazol units of **52a**, while the central pyridines are additionally bridging the two metals. Introduction of a mesityl group at the 5-position of pyrazole (ligand **52b**) leads to an unsymmetric solid-state structure of the parent complex $[Cu_2\mathbf{52b}_2]^{2+}$ with one di- and one tetracoordinated copper(I) ion (**III**). Ligand **52c** with a *tert*-butyl group in the 5-position forms a complex $[Cu_2\mathbf{52c}_2]^{2+}$ that possesses two tricoordinated copper centers as shown in **XVIII**.[131]

The bis(imidazole)/bipyrimidine ligand **53** forms a very similar dinuclear complex $[Cu_2\mathbf{53}_2]^{2+}$ which adopts a structure with two linearly dicoordinated copper centers **IV**. In the solid state this complex staples to form an infinite helical architecture.[132]

The structural motif **IV** is also found for the dinuclear double-stranded copper(I) complexes derived from ligands **54** and **55** and for the analogous silver(I) complexes of **56**.[133−135] However, complex $[Cu_2\mathbf{54a}_2]^{2+}$ possesses a planar nonhelical structure in the solid state.[133] On the other hand, the corresponding pyridine derivative **55a** forms a double-stranded dinuclear helicate $[Cu_2\mathbf{55a}_2]^{2+}$, as shown by X-ray diffraction. The introduction of a 3,5-dimethoxybenzyl group at the 3-positions of the benzimid-

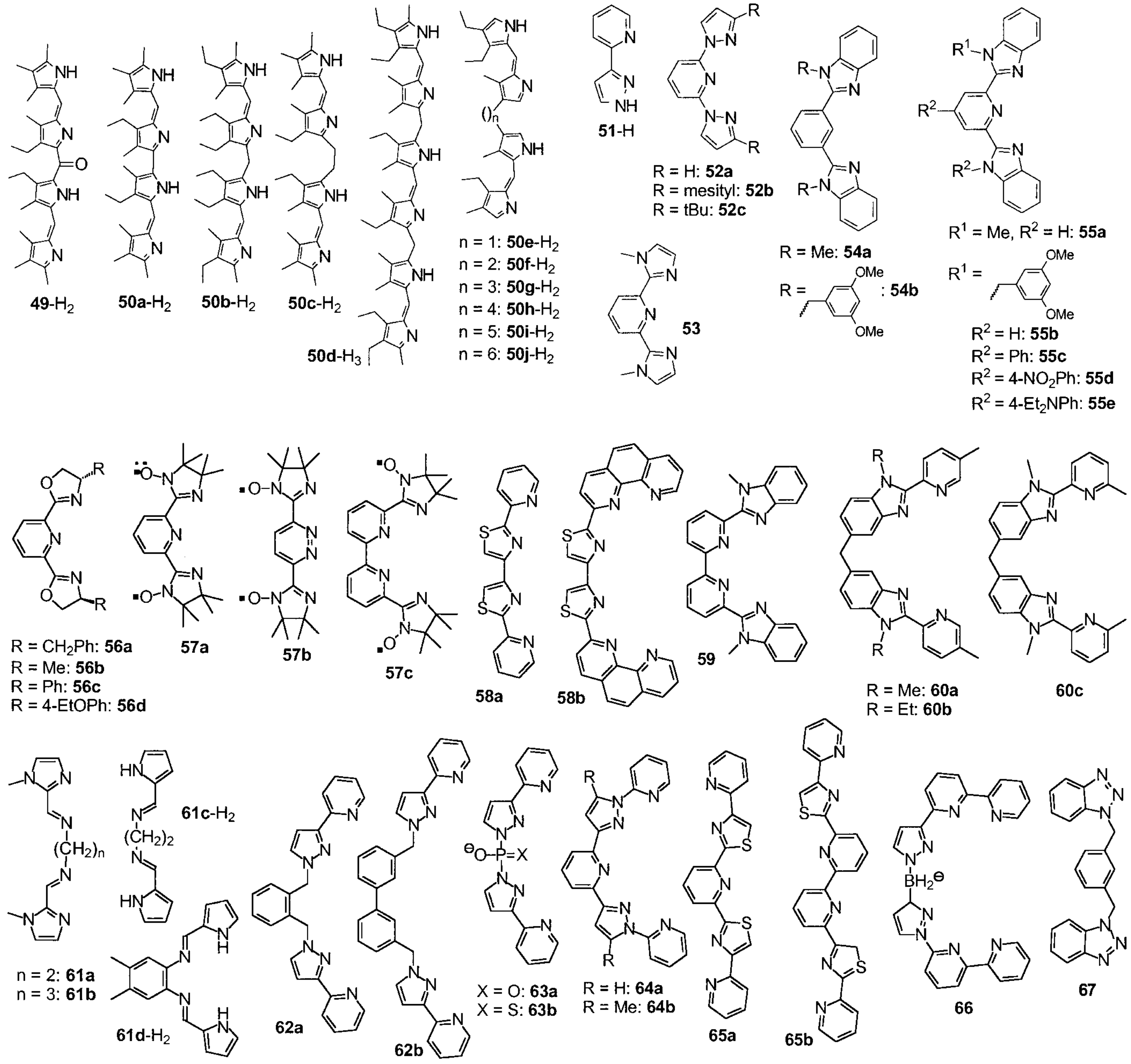
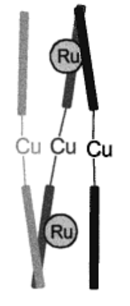


Figure 23.



$[Ru_2Cu_3\mathbf{51}_6]^+$

Figure 24.

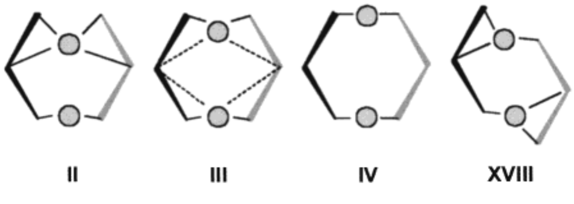


Figure 25.

azoles of derivatives **55** allows the NMR spectroscopic study of the inversion (“racemization”) of the helicate in solution (Figure 26). Here, the diastereotopic protons in benzylic position act as a stereochemical probe. From the coalescence temperature which is observed for the signals of the benzylic protons, a barrier for racemization of the helical complexes $[Cu_2(\mathbf{55b}-\mathbf{e})_2]^{2+}$ of $\Delta G^{\ddagger}_{298} = 50-77$ kJ/mol can be calculated. This energy barrier is solvent-dependent.[134]

The pyridine/bis-1,3-oxazoline ligands **56** form dinuclear helicates $[Ag_2\mathbf{56}_2]^{2+}$ as well as trinuclear complexes $[Ag_3\mathbf{56}_3]^{3+}$. In solution the two species are in equilibrium with the ratio depending on the solvent, concentration, and ability of the substituents in the 4-position of the 1,3-oxazoline ring to undergo π-stacking interactions.[135]

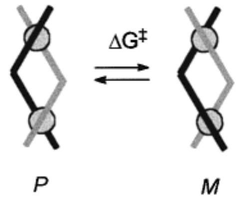


Figure 26.

Ligand systems which are related to the imidazole derivatives **55** are the imino nitroxyl diradicals **57**. **57a,b** form dinuclear double-stranded helicates $[Ag_2\mathbf{57a}-\mathbf{c}_2]^{2+}$. X-ray structural analysis reveals a structure of type **II** for $[Ag_2\mathbf{57a}_2]^{2+}$. One of the silver(I) ions is tetracoordinated, binding to two imidazoline and two pyridine units, while the second one is dicoordinated interacting with two imidazoline moieties.[136] Derivatives **57b** and **57c** represent tetradentate ligands and thus can form double-stranded dinuclear helicates $[Ag_2\mathbf{57b,c}_2]^{2+}$ with a pseudotetrahedral coordination geometry at the silver(I) centers.[137] The bipyridine unit of $[Ag_2\mathbf{57c}_2]^{2+}$ acts as a bridging and not as a chelating moiety, as discussed earlier for ligand **42**.[116]

A bis-1,3-thiazole is the central part of ligand **58a**, which bears two terminal pyridines. With copper(I) a double-stranded dinuclear helicate $[Cu_2\mathbf{58a}_2]^{2+}$ is obtained. Each of the tetracoordinated copper centers is bound to two pyridine-nitrogen and two thiazole-nitrogen atoms. The sulfur atoms do not participate in the coordination to the metal.[138] The same ligand **58a** with zinc(II) or copper(II) forms the triple-stranded helicates $[Zn_2\mathbf{58a}_3]^{4+}$ and $[Cu_2\mathbf{58a}_3]^{4+}$.[139]

In **58b** three chelating binding sites are present, two phenanthroline and one bisthiazole unit. With copper(I) ions a double-stranded trinuclear helicate $[Cu_3\mathbf{58b}_2]^{3+}$ is formed. Here the two terminal copper ions are coordinating to the phenanthrolines while the central copper is bound by two bisthiazole moieties.[138] With copper(II) or zinc(II) ions dinuclear double-stranded helicates $[M_2\mathbf{58b}_2]^{4+}$ (M = Cu, Zn) are formed. In those complexes the metal ions adopt a pseudooctahedral coordination geometry.[139]

Reaction of the bis(benzimidazole)-substituted bipyridine **59** with platinum(II) ions yields a double-stranded dinuclear helicate $[Pt_2\mathbf{59}_2]^{4+}$. The platinum centers show a distorted square-planar geometry with each platinum binding to a bipyridine and a benzimidazole of the one ligand and one benzimidazole of the other.[140]

The methylene-linked bis(benzimidazole/pyridine) derivatives **60** represent tetradentate ligands with two distinct bidentate binding sites for metal ions. Ligand **60** yields dinuclear triple-stranded helicates $[M_2\mathbf{60}_3]^{4+}$ with metal ions which prefer an octahedral coordination geometry (e.g., cobalt(II) or iron(II)). For example, ligand **60a** forms the labile dinuclear complex $[Co_2\mathbf{60a}_3]^{4+}$ with cobalt(II) ions (Figure 27).[141] Upon oxidation with bromine, the corresponding cobalt(III) complex $[Co_2\mathbf{60a}_3]^{6+}$ is obtained. This complex is kinetically inert, and the two enantiomeric helices (*P*)-$[Co_2\mathbf{60a}_3]^{6+}$ and (*M*)-$[Co_2\mathbf{60a}_3]^{6+}$ can be separated chromatographically by chiral resolution on Sephadex in the presence of tartrate. Reduction of the enantiomer (*P*)-$[Co_2\mathbf{60a}_3]^{6+}$ produces the enantiomerically pure labile dinuclear cobalt(II) helicate (*P*)-$[Co_2\mathbf{60a}_3]^{4+}$, and its racemization can be followed by CD spectroscopy. Racemization of the labile helicate (*P*)-$[Co_2\mathbf{60a}_3]^{4+}$ proceeds surprisingly slow ($k = 1.4 \times 10^{-5}\ s^{-1}$ at 298 K) compared to related mononuclear species. This behavior is attributed to a cooperative behavior of the two cobalt(II) centers.[142]

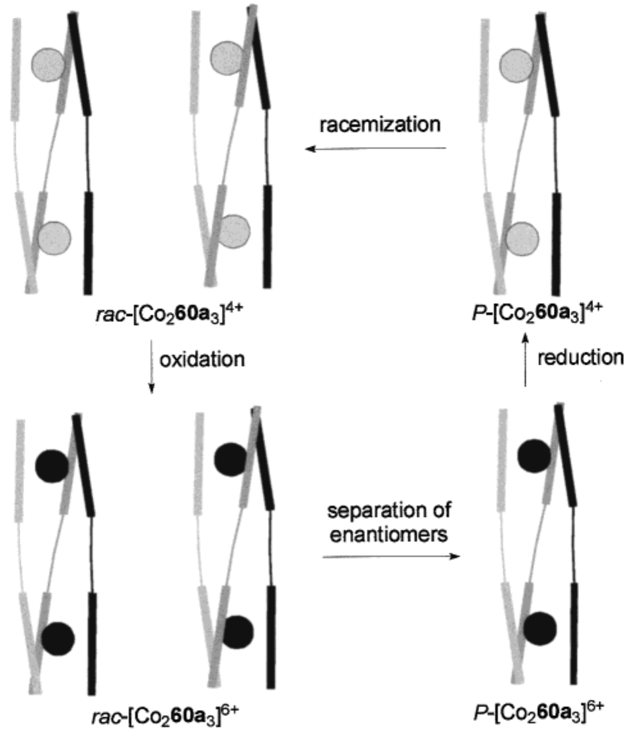


Figure 27.

Racemization of the dinuclear complex (*P*)-$[Co_2\mathbf{60a}_3]^{4+}$ is pressure dependent, indicating a dissociative mechanism for this process. This mechanism also is supported by ligand exchange experiments of $[Co_2\mathbf{60a}_3]^{4+}$ with **60b**.[143] In addition, the iron(II) complexes $[Fe_2\mathbf{60a}-\mathbf{c}_3]^{4+}$ were prepared, characterized, and used for magneto- and electrochemical investigations.[144]

The imidazole/imine derivatives **61** form different kinds of silver complexes. With an ethylene spacer in ligand **61a**, the dinuclear double-stranded silver(I) helicate $[Ag_2\mathbf{61a}_2]^{2+}$ was obtained and could be structurally characterized. Ligand **61b** with a propylene spacer leads to oligonuclear complexes $[Ag_3\mathbf{61b}_3]^{3+}$, $[Ag_6\mathbf{61b}_6]^{6+}$, and $[Ag_7\mathbf{61b}_7]^{7+}$.[145]

The imino-pyrrole ligands **61c**-H_2 and **61d**-H_2 form neutral double-stranded dinuclear $[Mn_2\mathbf{61c/d}_2]$ helicates with manganese(II) ions with pseudotetrahedrally coordinated metal centers. The helicates in THF solution react with molecular oxygen under H-abstraction from the solvent to form a neutral mixed-valent species $[Mn^{II/III}{}_2(\mu\text{-}O_2H)\mathbf{61c/d}_2]$. Here, the geometry of the complex has to change and ligands **61c/d** adopt a nonhelical arrangement in $[Mn^{II/III}{}_2(\mu\text{-}O_2H)\mathbf{61c/d}_2]$.[146]

Ligands **62** and **63** possess two bidentate pyrazol/pyridine units. The binding sites of **62** are separated by aromatic moieties, while in **63** a PO_2^- or a POS^- unit acts as the spacer. **62a** forms a double-stranded

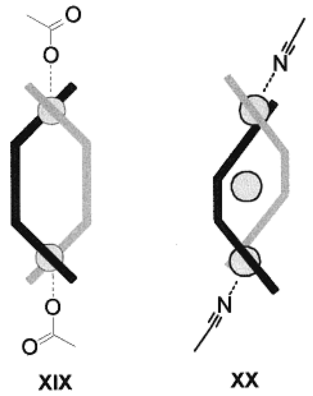


Figure 28.

dinuclear helicate $[Cu_2\mathbf{62a}_2]^{2+}$ with copper(I) ions,[147] and a similar silver(I) complex $[Ag_2\mathbf{62b}_2]^{2+}$ is observed by ES-MS for ligand **62b**.[148] In addition, ligand **62b** yields a double-stranded helicate $[Cu_2\mathbf{62b}_2(OAc)_2]^{2+}$ with copper(II). The two copper(II) centers are pentacoordinated, binding to two pyrrazole/bipyridine units and one acetate ligand. Thus, a structure of type **XIX** is observed (Figure 28).[148]

For ligands **63** the situation is different. Here the spacer contains functionalities which in addition to the N-donors can interact with metal ions. Both ligands **63** form dinuclear double-stranded helicates $[Cu_2\mathbf{63}_2]^{2+}$ with copper(I) ions. However, X-ray structural analyses reveal that the two complexes $[Cu_2\mathbf{63a}_2]^{2+}$ and $[Cu_2\mathbf{63b}_2]^{2+}$ are fundamentally different. In the case of the oxygen-substituted ligand **63a**, the tetracoordinated copper(I) ions bind to a pyrazole/pyridine unit of each strand. The oxygen atoms do not interfere with the binding to the metal. On the other hand, ligand **63b** binds in an unsymmetric fashion to the metal centers. Each copper is coordinating to a dinitrogen donor site of a ligand strand and to a pyrazole/sulfur chelate of the other. Therefore, one pyridine group of each ligand does not contribute to metal coordination.[149]

The pentadentate pyridine–pyrrazole–pyridine–pyrrazole–pyridine ligands **64** form trinuclear double-stranded helicates $[Cu_3\mathbf{64}_2(NCMe)_2]^{3+}$. X-ray structural analysis of $[Cu_3\mathbf{64b}_2(NCMe)_2]^{3+}$ shows two different binding modes for the copper(I) ions. All copper(I) ions possess a distorted tetrahedral coordination geometry. One of them is bound to the central part of each ligand strand coordinating to the central pyridine units and to two pyrrazoles. The other two copper centers are binding to the terminal pyridine units and to one pyrrazole moiety. The coordination sphere at the metals is completed by two acetonitrile molecules binding to the termini of the helicate (see structure **XX**).[150]

Derivatives **65** possess two pyridyl/thiazole chelating units which are bridged by pyridine (**65a**) or bipyridine (**65b**). With copper(II) ions both ligands form dinuclear double-stranded helicates $[Cu_2\mathbf{65}_2]^{4+}$ with the copper ions coordinating to the terminal chelating units of the strand, resulting in a highly distorted geometry at the metals. Uncoordinated pyridine and bipyridine units are present which have the potential to bind small guests by hydrogen bonding.[139]

The negatively charged hexadentate ligand **66** forms double-stranded dinuclear helicates $[Cu_2\mathbf{66}_2]^{2+}$ and $[K_2\mathbf{66}_2]$. The metal centers in the two complexes are pseudooctahedrally coordinated.[151] The latter one is a rare example in which an s-block element acts as the metal ion which induces the self-assembly of a double-stranded helicate.[105]

Bis(benzotriazole) **67** forms a triple-stranded dinuclear helicate $[Ag_2\mathbf{67}_3]^{2+}$ with silver(I) ions. The silver centers are bound to the nitrogen donors in the 3-position of the benzotriazole units in a trigonal planar fashion, and the helical twist is introduced by ligand **67**.[152]

6. "Piguet" System for the Complexation of f-Block Elements

Up to now helicates have been discussed which contain either transition metal or main group elements as the metal centers. In very elegant studies, Piguet and co-workers developed a ligand system which is able to form helicates with f-block or both f- and d-block metals **68**–**73** (Figure 29).[153,154]

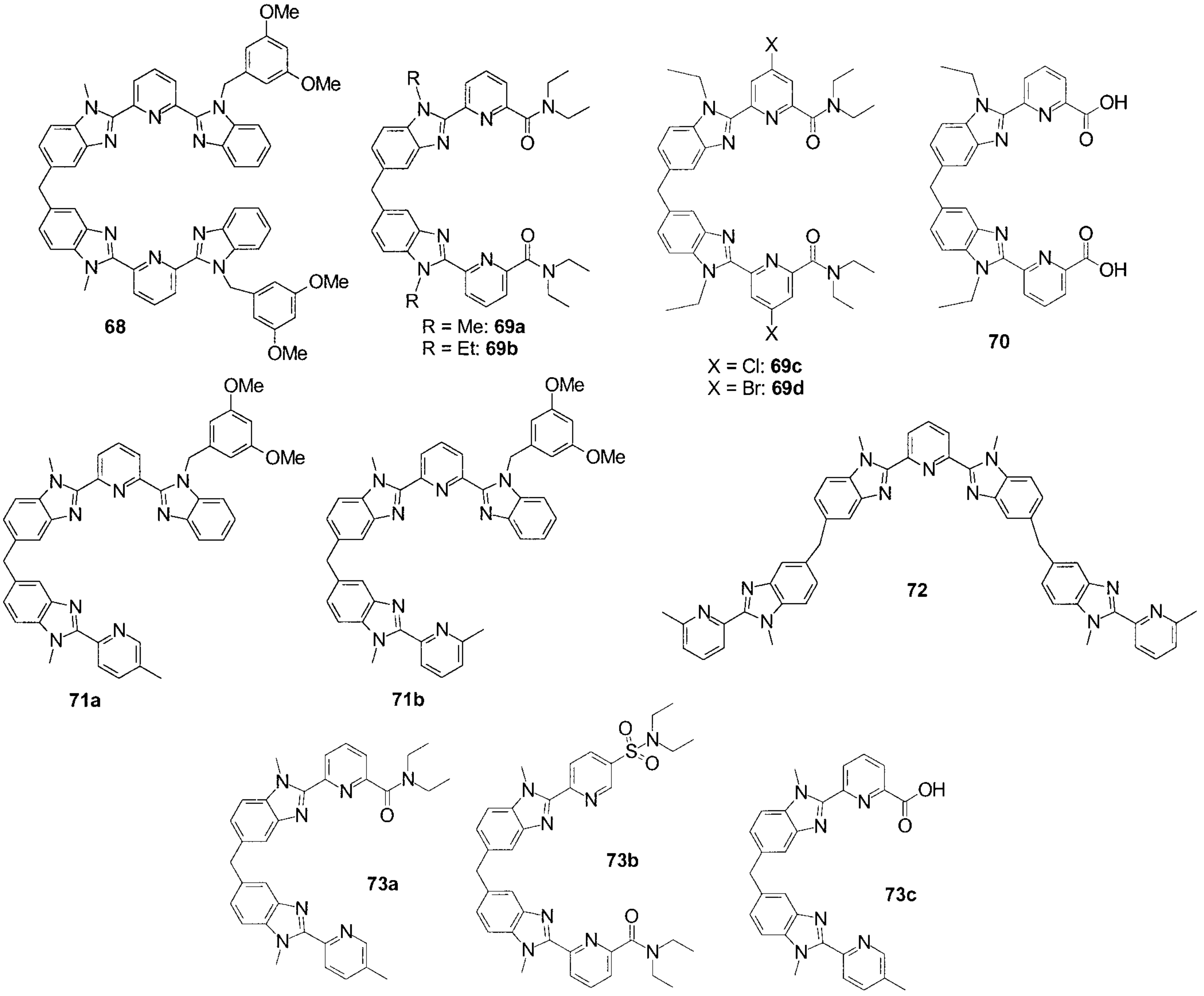
Here, derivatives **68**–**70** bear two tridentate ligand moieties. With lanthanide(III) ions they form triple-stranded dinuclear helicates $[Ln_2(\mathbf{68}-\mathbf{70})_3]^{6+}$. Each metal is binding to three chelating units, resulting in a nonacoordination at the metals. X-ray structural analysis of $[Eu_2\mathbf{68}_3]^{6+}$ shows the helical arrangement of the three ligands which are wrapping around the two europium centers.[155,156] Similar X-ray structures were obtained for $[Tb_2\mathbf{69b}_3]^{6+}$ [157] and $[M_2\mathbf{70}_3]^{6+}$ (M = Eu, Tb, Yb).[158] The compounds are highly luminescent, and the photophysical properties were studied. Doping the terbium complex $[Tb_2\mathbf{68}_3]^{6+}$ with europium(III) leads to heterodinuclear complexes $[EuTb\mathbf{68}_3]^{6+}$ with a fixed separation of the two metal centers. In complex $[EuTb\mathbf{68}_3]^{6+}$ the energy transfer from terbium to europium was investigated.[156] Introduction of substituents at the periphery of the ligands allows a fine-tuning of the photophysical properties, as demonstrated for the halogen-substituted ligands **69c** and **69d**.[159]

With the bisamide-substituted ligand **69b** a dinuclear double-stranded meso-complex $[Eu_2\mathbf{69b}_2][CF_3SO_3]_6$ is obtained, which possesses a structure of type **XXI** (Figure 30).[157]

Each europium(III) ion is coordinated to a tridentate binding site of each ligand strand **69b**. Two trifluoromethylsulfonates and one water molecule are filling up the coordination sphere at the metal centers which thus are nine-coordinate. In addition, water molecules are fixed by hydrogen bonding in the interior of this meso-complex.[157]

Complexes $[M_2\mathbf{70}_3]^{6+}$ (M = La, Pr, Nd, Gd, Tb, Tm, Yb, Lu) of the carboxylic acid derivative **70** self-assemble even in water and were shown to be very stable in this solvent. Again, highly luminescent complexes are obtained. X-ray structures show that each metal center is coordinated by a tridentate benzimidazole/pyridine–carboxylate unit leading to the triple-stranded helicates $[M_2\mathbf{70}_3]^{6+}$ (M = Eu, Tb, Yb).[158]

Ligands **71**–**73** possess tri- as well as bidentate binding sites for metal ions. The ligands form either



68

R = Me: **69a**
R = Et: **69b**

X = Cl: **69c**
X = Br: **69d**

70

71a

71b

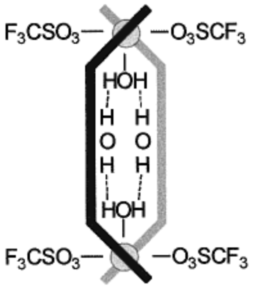
72

73a

73b

73c

Figure 29.



XXI

Figure 30.

double- or triple-stranded helicates with d-, f-, or a combination of d- and f-block elements.[154]

The segmental ligands **71** and **73** have a directionality due to the sequence of di- and tridentate ligand units.[160] This allows the formation of a variety of different double- or triple-stranded helicates with a parallel or an antiparallel orientation of the ligand strands.[154]

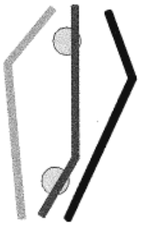
Mixing of ligand **71a** with zinc(II) ions leads, in a stepwise reaction, initially to the mononuclear species $[Zn\mathbf{71a}_2]^{2+}$ with one octahedrally coordinated zinc center. In a second step, another zinc(II) ion is coordinated, occupying the remaining tetrahedral coordination site. Thus, a double-stranded helicate $[Zn_2\mathbf{71a}_2]^{4+}$ of type **XXII** with parallel orientation (head to head = HH) of the ligands is formed (Figure 31). This parallel orientation of the ligands seems to be due to the successive formation of the dinuclear complex.[161] With ligands **73a,b** a mixture of zinc(II) helicates $[Zn_2\mathbf{73a,b}_2]^{4+}$ and $[Zn_2\mathbf{73a,b}_3]^{4+}$ is formed which contains as one component a complex of type **XIII** with an antiparallel (head to tail = HT) orientation of the ligands. The reason for this behavior is the enhanced lability of the tridentate binding sites of **73a,b** which possesses an amide or sulfonamide oxygen atom as the donor.[162−165]

Iron(III) and cobalt(II) form dinuclear double-stranded complexes $[M_2\mathbf{71b}_2]^{4+}$ (M = Fe, Co) with **71b**. They are assumed to possess a structure **XXII** similar to the corresponding zinc complex $[Zn_2\mathbf{71b}_2]^{4+}$.[166] Reaction of ligand **71b** with iron(II) and silver(I) ions leads, with strict self-assembly, to the heterodinuclear double-stranded helicate $[FeAg\mathbf{71b}_2]^{3+}$. NMR spectroscopic investigations reveal that the iron is hexacoordinated while silver

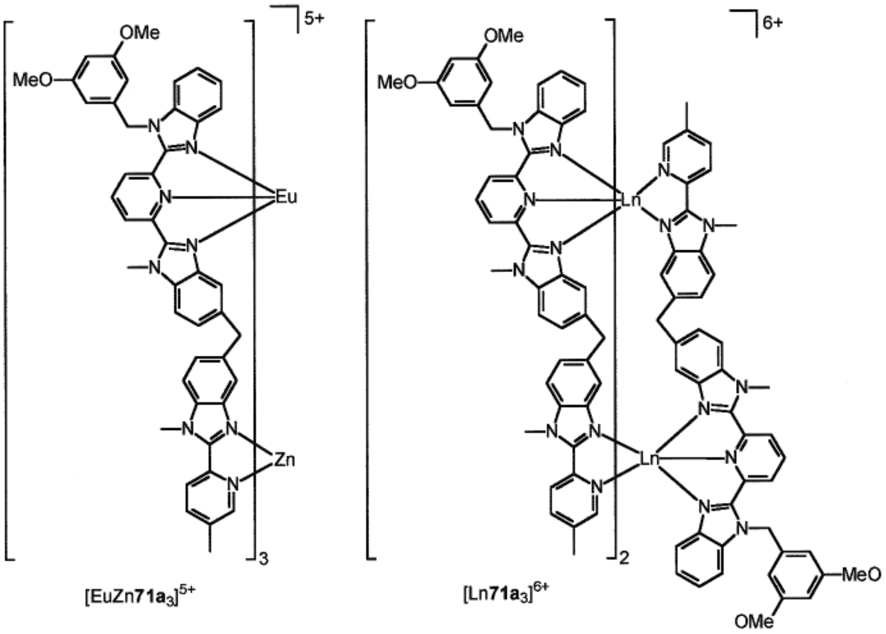
XXII

XXIII

XXIV



XXV



$[EuZn\mathbf{71a}_3]^{5+}$ $[Ln\mathbf{71a}_3]^{6+}$

Figure 31.

$[Ag_2Fe\mathbf{72}_2]^{4+}$

Figure 32.

possesses a pseudotetrahedral coordination environment.[166] Ligand **72** with two bidentate and one tridentate coordination sites does not form a trinuclear Ag_2Fe helicate but a trinuclear catenate $[Ag_2Fe\mathbf{72}_2]^{4+}$ (Figure 32).[167]

The segmental ligands **71** and **73** form triple-stranded helicates $[Ln_2(\mathbf{71})_3]^{6+}$ and $[Ln_2(\mathbf{73})_3]^{6+}$ with lanthanum(III) ions. The ligands of the complexes adopt an antiparallel (head to head to tail = HHT) orientation **XXV**. Thus, one of the lanthanide(III) ions is seven coordinate, binding to two bidentate and one tridentate chelating units, while the second one is octacoordinated with two tridentate and one bidentate binding sites as ligands. The reason for the specific formation of the unsymmetric antiparallel helicate is that the two similar metal centers try to adopt a coordination geometry which is as similar as possible. This is only the case if an antiparallel orientation of the ligands is present in the metal complexes.[165,168,169]

In addition to the homodinuclear helicates, the segmental ligands **71** and **73** open up an entry to heterodinuclear d−f-block complexes. The two different binding sites of the ligand can discriminate between d- (octahedral binding site) and f-block (tricapped trigonal prismatic binding site) elements. This leads to triple-stranded helicates with a parallel orientation of all three ligand strands **XXIV**, giving the d-element a hexa- and the f-element a nonacoordinate geometry. Some of the triple-stranded heterodinuclear helicates (e.g., $[EuZn\mathbf{71a}_3]^{5+}$, $[LaCo\mathbf{73a}_3]^{6+}$, $[EuZn\mathbf{73a}_3]^{5+}$, $[LaFe\mathbf{71a}_3]^{5+}$, $[EuZn\mathbf{73b}_3]^{5+}$) were characterized by X-ray structural analysis, showing the presence of structures such as **XXIV** in the solid state.[163,164,168,170,171] In addition, an NMR spectroscopic method was developed which enables the characterization of the complexes by paramagnetic NMR in solution,[172] and the luminescence properties[163,170] of the dinuclear d−f-element helicates were studied.

7. Circular Helicates

Circular helicates are oligonuclear complexes with a cyclic arrangement of metal ions[173] and several bridging ligands wrapping around the metal cen-

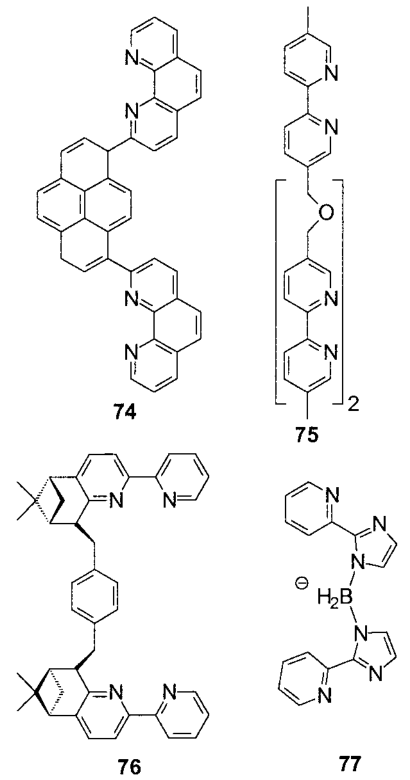


Figure 33.

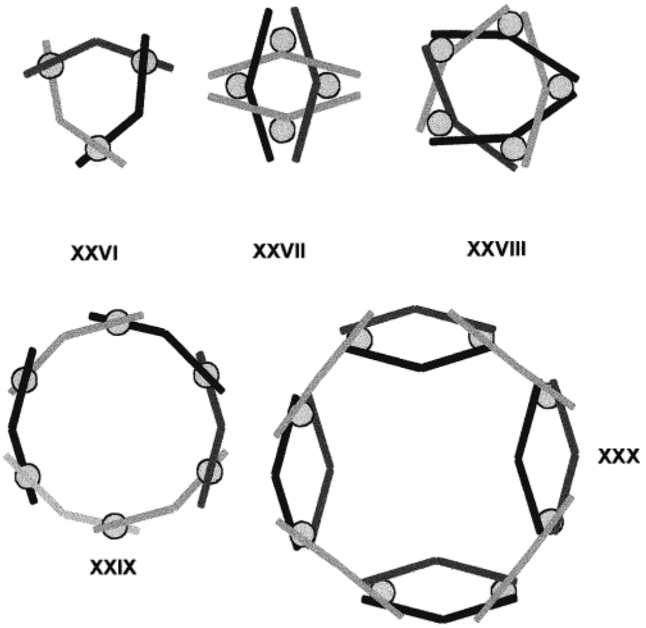


Figure 34.

ters.[20] Recently some circular helicates were formed by self-assembly, and it was shown that the formation of such complexes may depend on templating of guest molecules (Figure 33).[15]

It was already mentioned before that the bisoxazoline ligands **56** form a mixture of double-stranded helicates $[Ag_2\mathbf{56}_2]^{2+}$ and trinuclear complexes $[Ag_3\mathbf{56}_3]^{3+}$ in solution. X-ray structural analysis of $[Ag_3\mathbf{56c}_3]^{3+}$ shows the presence of a trinuclear circular helicate **XXVI** (Figure 34). The three silver(I) centers of $[Ag_3\mathbf{56c}_3]^{3+}$ are dicoordinated, and a helical twist is introduced by the ligands. An enantiomerically pure circular helicate is obtained due to the chiral ligands.[135]

A structure like **XXVI** also can be formed from bis(bidentate) ligands with tetrahedrally coordinated metal ions, which is documented for the trinuclear copper(I) complex $[Cu_3\mathbf{74}_3]^{3+}$.[174] A similar enantiomerically pure trinuclear circular helicate $[Cu_3\mathbf{21}_3]^{3+}$ of type **XXVI** is obtained from the chiral bis(bipyridine) ligand **21**. Here the metal centers are tetracoordinated with each copper binding to two bipyridine units.[77]

The ether-linked tris(bipyridine) ligand **75** forms a tetranuclear circular helicate $[Fe_4\mathbf{75}_4]^{8+}$ with iron(II) ions. Each of the metal ions possesses a pseudo-octahedral coordination geometry and binds to two terminal and one central bipyridine unit of three different ligand strands **75** resulting in a structure like **XXVII**.[175]

Ligand **15b** was already discussed to form a trinuclear triple-stranded helicate $[Ni_3\mathbf{15b}_3]^{6+}$ which could be structurally characterized.[39] With iron(II) ions a similar helicate $[Fe_3\mathbf{15b}_3]^{6+}$ is obtained initially. However, it was found that the triple-stranded helicate is the product of kinetic control of complex formation. Under thermodynamic control, pentanuclear $[Fe_5\mathbf{15b}_5]^{10+}$ or hexanuclear circular helicates $[Fe_6\mathbf{15b}_6]^{12+}$ are obtained.[67] Here, the nuclearity depends on the nature of the counteranions. Those can act as templates and support the formation of a defined macrocyclic helicate. The pentanuclear coordination compound $[Cl\subset\{Fe_5\mathbf{15b}_5\}]^{9+}$ is formed in the presence of chloride anions. X-ray structural analysis shows that one chloride ion is bound in the interior of the complex which possesses a structure like **XXVIII**. The coordination geometry at the iron centers is very similar to that described for $[Fe_4\mathbf{75}_4]^{8+}$ with each iron binding to two terminal and one central bipyridine of three different ligands. With the bigger bromide anion a mixture of pentanuclear and hexanuclear complexes is observed by ES mass spectrometry and the large anions BF_4^-, SO_4^{2-}, and SiF_6^{2-} support the formation of the hexanuclear circular helicate $[Fe_6\mathbf{15b}_6]^{12+}$.[20,175]

The control of the structure of the circular helicates by templates is a very nice example for dynamic combinatorial chemistry. Selection of one species from a dynamic mixture or a “virtual” mixture proceeds by binding of the guest anions to the most appropriate host. Thus, the equilibrium between noncovalently linked components is shifted to form only one product species.[61]

$[Fe_6\mathbf{15b}_6]^{12+}$ possesses six hexacoordinated iron centers arranged as a hexagon with ligands **15b** wrapping around those centers. This complex could not be characterized by X-ray diffraction.[175] However, another hexanuclear circular helicate $[Ag_6\mathbf{76}_6]^{6+}$ was crystallized and structurally characterized. The six silver ions are pseudotetrahedrally coordinated by bipyridine units, and the six ligands **76** have a helical arrangement around the hexagon of metal ions (**XXIX**). Due to the chirality at ligand **76**, an enantiomerically pure circular helicate (P)-$[Ag_6\mathbf{76}_6]^{6+}$ is obtained.[176] In solution the hexanuclear circular helicate $[Ag_6\mathbf{76}_6]^{6+}$ is in equilibrium with the corresponding tetranuclear species $[Ag_4\mathbf{76}_4]^{4+}$. This equilibrium was shown to be pressure dependent.[16]

The octanuclear cobalt(II) complex $[Co_8\mathbf{77}_{12}]^{4+}$ is related to the circular helicates although this coordination compound adopts the nonhelical structure **XXX**.[177]

Up to now very few circular helicates have been found, but they are interesting self-assembled complexes due to their ability to form host/guest complexes. Functionalization at the ligand units might lead to a broad chemistry, as found for other ring compounds which can bind guest species (e.g., cyclodextrines).[178]

8. Molecular Knots

When helicates are formed, the linear ligand strands are fixed in a very special spatial arrangement. This can be used to synthesize topologically interesting molecules by coupling reactions with functionalized helicates. The strategy that leads to molecular knots is outlined in Figure 35.[21,179]

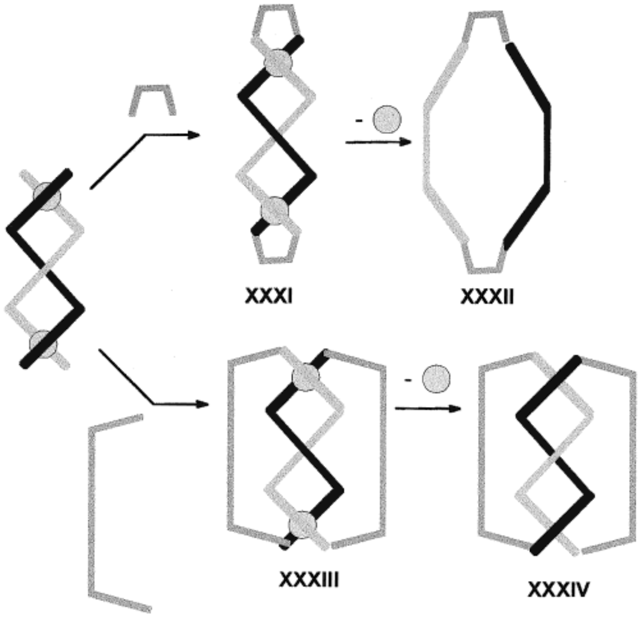


Figure 35.

A double-stranded helicate which is functionalized at the termini of the ligands can undergo coupling reactions with appropriate bifunctional derivatives. One possibility is that this derivative forms bonds to the ends of the two ligands at the same terminus of the helicate. A dinuclear helicate-type complex **XXXI** is obtained which after removal of the metal ions yields a macrocyclic molecule **XXXII**. Another possibility is that the bifunctional molecule connects the two ligand strands at different termini of the helicate. Complex **XXXIII** is formed which after demetalation leads to the molecular knot **XXXIV**. Sauvage, Dietrich-Buchecker, and co-workers were able to use this concept and achieve the synthesis of molecular knots templated by the metal ions.[21,179]

The bis(phenanthroline) and bis(terpyridine) ligands **78** were used for the preparation of helicates and in subsequent reaction steps of molecular knots. **78a** forms a mixture of the double-stranded helicates (*P*/*M*)-$[Cu_2\mathbf{78a}_2]^{2+}$ and the meso-form Δ,Λ-$[Cu_2\mathbf{78a}_2]^{2+}$ (Figure 36). Upon reaction of the mixture of the diastereomeric complexes with $ICH_2(CH_2OCH_2)_5CH_2I$, a mixture of two different dinuclear compounds is obtained in a Williamson ether synthesis. The complex formed from Δ,Λ-$[Cu_2\mathbf{78a}_2]^{2+}$ bears two macrocyclic ligands, while the one obtained from the dinuclear helicate $[Cu_2\mathbf{79a}]^{2+}$ has the structure of a doubly metal ion-bridged molecular knot with a double-helical domain at the two copper centers. An X-ray structural investigation of $[Cu_2\mathbf{79a}]^{2+}$ shows this unusual topological arrangement. The copper ions can be removed by reaction with cyanide to obtain the free knot **79a**.[180] The knotted helicates $[Cu_2\mathbf{79b,c}]^{2+}$ are also formed by Williamson ether linkage of the helicates $[Cu_2\mathbf{78b,c}]^{2+}$, and the free knots **79b,c** are obtained by demetalation reaction.[181] The two enantiomers of $[Cu_2\mathbf{79c}]^{2+}$ could be resolved by crystallization of the diastereomeric salts (*M*)- and (*P*)-$[Cu_2\mathbf{79c}][S\text{-}(2,2'\text{-biphenolate})PO_2]_2$. The copper-substituted knots $[Cu_2\mathbf{79c}]^{2+}$ show an optical rotation of $[\alpha]_D = \pm 7000$, while the demetalated knot **79** possesses $[\alpha]_D = \pm 2000$.[182]

The yields of the Williamson ether synthesis are low, although they are still high for the preparation of such unusual knotted systems. A more convenient approach was found by ring-closing metathesis with the Grubbs ruthenium catalyst. The bis(phenanthroline) ligand **78d** forms a double-stranded helicate $[Cu_2\mathbf{78d}_2]^{2+}$ with copper(I) ions,[183] while from the bis(terpyridine) ligand **78e** a double-stranded iron(II) helicate $[Fe_2\mathbf{78e}_2]^{4+}$ can be synthesized. Both helicates possess four pendant oligo-ether substituents with terminal vinyl groups. Ring-closing metathesis connects pairs of two such vinyl groups, and subsequent hydrogenation of the resulting mixture of *E*- and *Z*-alkenes leads to the knotted complexes $[Cu_2\mathbf{79d}]^{2+}$ and $[Fe_2\mathbf{79e}]^{4+}$. Again, the metal ions can be removed to yield the corresponding free trefoil knots **79d** and **79e**.[183,184]

A mixture of the linear and the macrocyclic ligands **80a** and **80b** leads to a trinuclear helicate-type complex $[Cu_3(\mathbf{80a})(\mathbf{80b})]^{3+}$, and upon Williamson ether synthesis with $ICH_2(CH_2OCH_2)_6CH_2I$ the doubly interlocked catenate $[Cu_3\mathbf{80b}_2]^{3+}$ is formed which possesses the structure **XXXV** (Figure 37).[185] Ligand **80c** enables the synthesis of a similar doubly interlocked catenate **XXXV** by metathesis reaction. Here, a trinuclear lithium(I) helicate $[Li_3\mathbf{80c}_2]^{3+}$ could be isolated as an intermediate which possesses a remarkably high stability.[186] The oligoether-linked tetra(bipyridine) derivative **81** forms a mixture of dinuclear helicate-type complexes $[Cu_2\mathbf{81}]^{2+}$ in the ratio 1:7 (**XXXVI**:**XXXVII**). The compounds bear terminal alkynes, and the performance of a Glaser coupling reaction on the mixture of isomers yields tetranuclear complexes **XXXVIII**, **XXXIX**, and **XL**.[187]

The synthetic studies with helicates as preorganized building blocks show the value of this class of coordination compounds for the preparation of topologically challenging molecular targets.

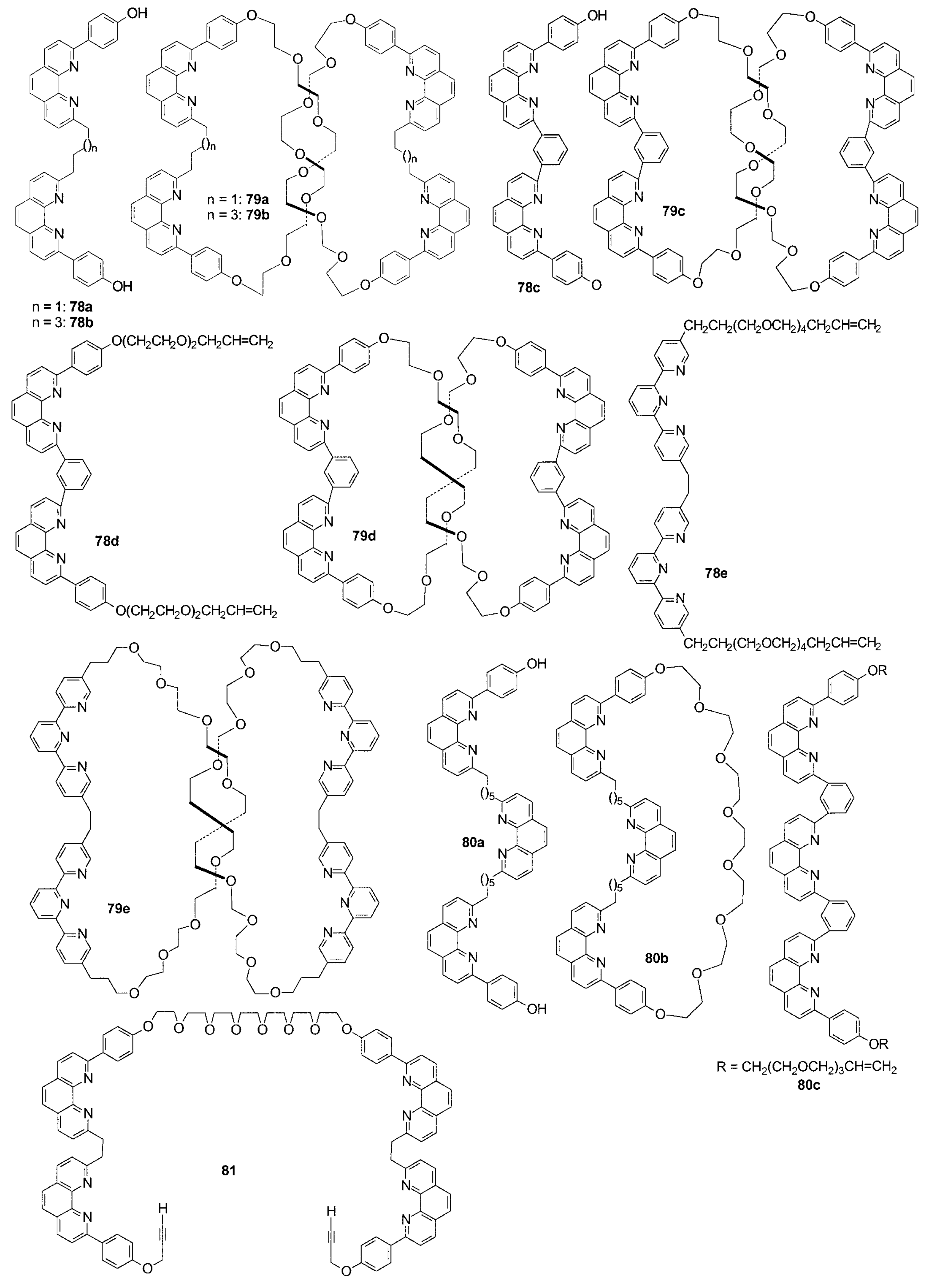

n = 1: **78a**
n = 3: **78b**
n = 1: **79a**
n = 3: **79b**
78c
79c
$O(CH_2CH_2O)_2CH_2CH{=}CH_2$
78d
79d
$CH_2CH_2(CH_2OCH_2)_4CH_2CH{=}CH_2$
78e
79e
80a
80b
R = $CH_2(CH_2OCH_2)_3CH{=}CH_2$
80c
81

Figure 36.

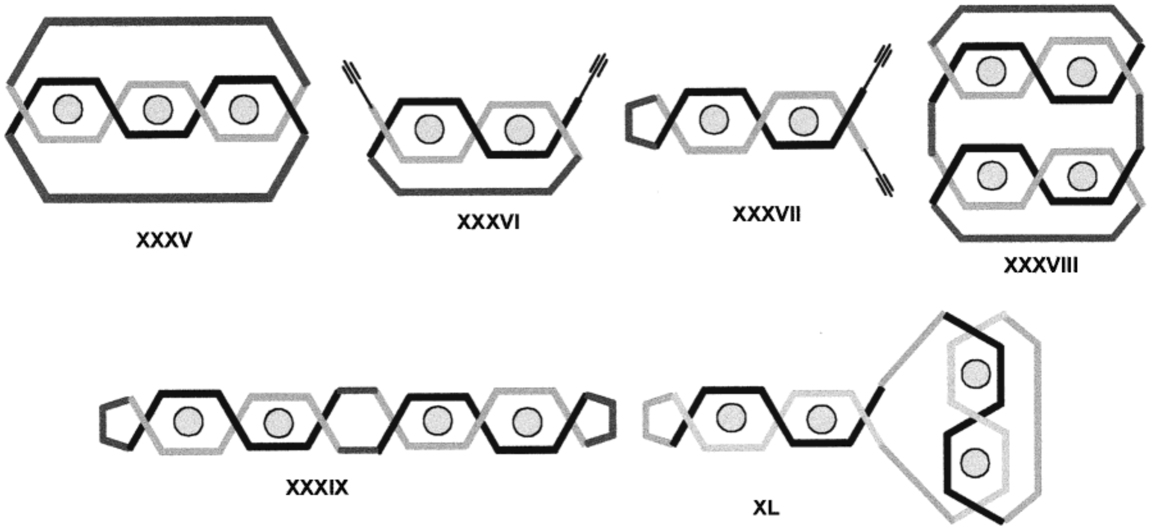


Figure 37.

III. Linear Oligooxygen Donors as Ligands for (Double- and) Triple-Stranded Helicates

Nitrogen donors were and still are the dominating ligand systems in investigations toward the self-assembly, structure, and properties of helicates. This is to some extent surprising due to the fact that the only natural product which in vivo is known to form a triple-stranded helicate $[Fe_2\mathbf{5}_3]$ is *Rhodoturulic acid* $\mathbf{5}$-H_2. In $[Fe_2\mathbf{5}_3]$, three ligand strands are bridging the two iron(III) centers.[36] For *Alcaligin*—another bis(hydroxamic acid) siderophore—again a dinuclear iron complex is obtained. However, here only one Alcaligin is bridging the two metals with the two other ligands acting as tetradentate ligands, each binding to one metal center.[188]

The dinuclear complex $[Fe_2\mathbf{6}_3]$, which was described in the Introduction, represents the first triple-stranded helicate of a hydroxamic acid oxygen-donor ligand, which was structurally characterized.[37]

The bis(pyridinone) **82** (Figure 38) forms a dinuclear triple-stranded complex $[M_2\mathbf{82}_3(NO_3)_6]$ with promethium(III), neodymium(III), samarium(III), and erbium(III). The neodymium complex $[Nd_2\mathbf{82}_3(NO_3)_6]$ was characterized by X-ray diffraction. The other complexes were shown to be isostructural by powder diffraction. Three ligands **82** are bridging the two metal centers and act as a monodentate ligand. Additionally, three nitrate ions are binding to each of the metals.[189]

Ligand **83**-H_4 was designed to form a titanium(IV) complex which could act as a chiral Lewis acid catalyst. However, a trinuclear triple-stranded helicate $[Ti_3\mathbf{83}_3]$ was obtained which did not show any Lewis acid activity. X-ray structure analysis reveals that two of the titanium(IV) ions are bound to one phenolate and one alkanolate while the central alkoholates bridge to a third titanium, encapsulating this ion in the interior of the helicate. Due to the chiral ligand **83**, the complex is formed in enantiomerically pure form as (M)-$[Ti_3\mathbf{83}_3]$ possessing $[\alpha]_D = -854$ ($c = 0.2$, CH_2Cl_2).[190]

The oxygen donors which were used most for the assembly of helicates are 1,3-dicarbonyl and catechol derivatives.[12]

1. Bis(1,3-dicarbonyl) Derivatives

Acetylacetone is a versatile bidentate chelating ligand which in its deprotonated form leads to coordination compounds with many different metal ions.[191]

m-Xylylenebis(acetylacetone) **84**-H_2 forms double-stranded complexes with vanadium(I) as well as with vanadium(II) ions. With vanadium(III) the dinuclear double-stranded complex $[V_2\mathbf{84}_2(THF)_2]^{2+}$ is obtained and structurally characterized. The metals are pentacoordinated with two acetylacetonate and one THF binding to each of them. In the case of the vanadium(II) complex $[V_2\mathbf{84}_2(TMEDA)_2]$, a similar structure is observed with hexacoordination at the metals. In both cases not the helicate but the nonhelical meso-form is present. With copper(II) ions the double-stranded linear complex $[Cu_2\mathbf{84}_2]$ is obtained which possesses a square-planar coordination geometry at the metals.[192]

Derivatives **85a** and **85b** are linear bis(β-diketonate) ligands with a m-phenylene spacer. The helicates $[M_2\mathbf{85a}_3]$ ($M = Ti^{III}$, V^{III}, Mn^{III}, Fe^{III}) are obtained with ligand **85a** and were structurally characterized. The complexes possess the structure of a triple-stranded helicate **XLI** (Figure 39).[193]

The triple-stranded helicate structure is observed in the solid state for $[Fe_2\mathbf{85b}_3]$.[194] The related ligands **85c**-H_2 and **85d**-H_2 possess a pyridine unit in the spacer.[194,195] Therefore, those ligands contain an additional binding site for metal ions. With iron(III) neutral triple-stranded dinuclear complexes $[Fe_2\mathbf{85c}_3]$[195] and $[Fe_2\mathbf{85d}_3]$[194] are formed which are able to encapsulate cations in their interior. For the potassium cryptate $[K\subset\{Fe_2\mathbf{85d}_3\}]^+$ the meso-helicate **XLII** is found by X-ray structural investigations, while $[(H_2O)Sr\subset\{Fe_2\mathbf{85d}_3\}]^{2+}$ and $[(H_2O)(THF)La\subset\{Fe_2\mathbf{85c}_3\}]^{3+}$ possess the helical structures **XLIII** and **XLIV** in the solid state.[195] This is attributed to the different sizes of the cationic guests. For an optimized

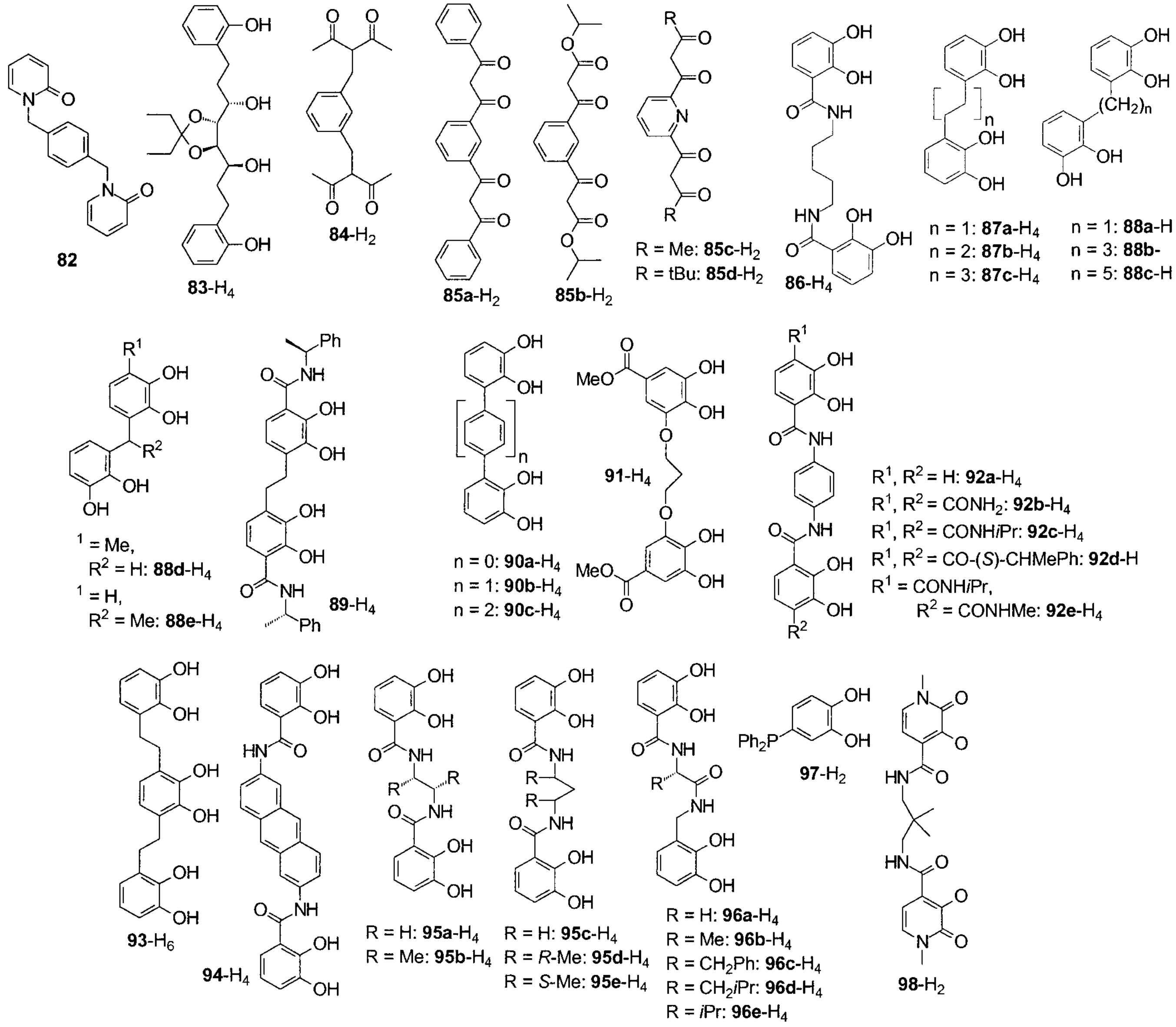


Figure 38.

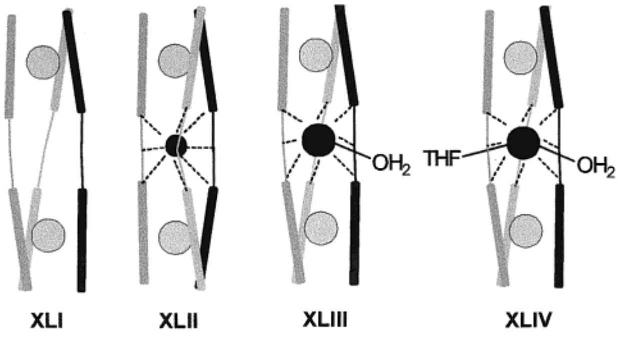


Figure 39.

binding of the small potassium cation, the cryptand-type triple-stranded complex has to adopt the more compressed meso-helicate structure.[26] For the larger strontium(II) and lanthanum(III) ions, a larger cavity is needed and the stretched helicate structure is observed. In $[K\subset\{Fe_2\mathbf{85d}_3\}]^+$ the nine-coordinated alkaline metal binds to the internal oxygen atoms of the β-ketonate moieties and to the pyridine units of the spacer. For $[(H_2O)Sr\subset\{Fe_2\mathbf{85d}_3\}]^{2+}$ and $[(H_2O)(THF)La\subset\{Fe_2\mathbf{85c}_3\}]^{3+}$, additional binding of the encapsulated metal occurs to water or to water and THF, respectively. X-ray structural analysis of $[Fe_2(\mathbf{85d}\text{-}H)_3]^{3+}$ shows the presence of a triple-stranded helicate with three protonated pyridine units.[195]

2. Linear Oligo(catechol) Ligands

The biscatecholamide **86**-H_4 with a $(CH_2)_5$ spacer linking the two bidentate units is a siderophore analogue which forms a double-stranded helical complex $[(MoO_2)_2\mathbf{86}_2]^{4-}$ with two *cis*-molybdenum(VI) dioxo units. Molybdenum complexes such as $[(MoO_2)_2\mathbf{86}_2]^{4-}$ possess some relevance for the understanding of MoO_2 coordination to siderophores, which is proposed to occur in nature.[196]

Alkyl-bridged dicatechol ligands **87**−**89** can be synthesized via different "classical" organic or more modern organometallic coupling procedures.[197,198] Ligands **87**−**89** form dinuclear triple-stranded complexes with titanium(IV) ions, but coordination com-

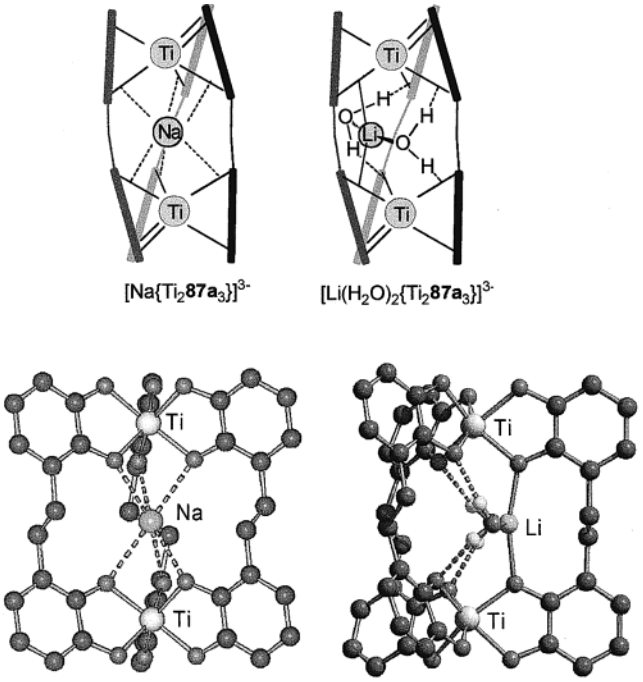


Figure 40.

pounds with other metals such as vanadium(IV), iron(III), aluminum(III), or gallium(III) also can be obtained in metal-directed self-assembly processes.[12]

The ethylene-linked dicatechol ligand **87a**-H_2 forms a dinuclear triple-stranded helicate $[Ti_2\mathbf{87a}_3]^{4-}$ in the presence of appropriate cations (Li, Na, K, Rb, Cs, NH_4). The X-ray structures of $[(H_2O)_2Li\subset\{Ti_2\mathbf{87a}_3\}]^{3-}$ [199] and $[Na\subset\{Ti_2\mathbf{87a}_3\}]^{3-}$ [200] were obtained and show the presence of a helicate $[Ti_2\mathbf{87a}_3]^{4-}$ which encapsulates one of the four alkaline metal countercations in its interior. In $[Na\subset\{Ti_2\mathbf{87a}_3\}]^{3-}$ the sodium ion binds to the six internal oxygen atoms of ligand strands **87a**, and thus, a structure like **XLII** results. However, only one broad signal ($\nu_{1/2} = 308$ Hz) is observed at $\delta_{Na} = -3.5$ by ^{23}Na NMR spectroscopy of $Na_4[Ti_2\mathbf{87a}_3]$ in methanol-d_4 at room temperature. Cooling the sample to 188 K results in splitting of the signal ($T_{coal.} = 193-198$ K) into one dominating resonance at $\delta_{Na} = -0.9$ for "free" (solvated) sodium cations and one minor signal at $\delta_{Na} = -15.5$.[201] The latter is found in a similar region to that observed for the sodium complex of [2.2.2]-cryptand ($\delta_{Na} = -11.4$)[202] and is assigned to the sodium ion which is encapsulated in the helical metallacryptand $[Ti_2\mathbf{87a}_3]^{4-}$. Competition experiments at room temperature in D_2O/H_2O show that $[Ti_2\mathbf{87a}_3]^{4-}$ binds sodium much better than lithium but that potassium is the most appropriate guest (Figure 40).[201]

Due to the small size of the lithium cation, an unusual coordination geometry is observed for this metal in $[(H_2O)_2Li\subset\{Ti_2\mathbf{87a}_3\}]^{3-}$. The geometry at the lithium can be described to be distorted square planar. The lithium is coordinated by two internal oxygen atoms of one of the ligand strands **87a** of $[Ti_2\mathbf{87a}_3]^{4-}$ and two water molecules which undergo additional hydrogen bonding with the internal oxygen atoms of the two other ligand strands **87a**. The distance of the two internal O atoms of **87a** (4 Å) forces the lithium cation to undergo a close to linear coordination to those donors (O−Li−O = 164.2°). This forces the water molecules to move outward, resulting in an angle $O_{water}-Li-O_{water} = 148.7°$. The unusual geometry at the lithium is stabilized due to the special requirements of the cavity, the high negative charge, and the additional hydrogen-bond fixation of the water molecules and possesses some relevance toward the function of enzymes which are able to stabilize unusual geometries of reaction intermediates by a combination of stereoelectronic effects and hydrogen bonding. Due to the small size and the resulting weak binding of the lithium ion, no splitting of the ^{6}Li NMR signal of $^6Li_4[Ti_2\mathbf{87a}_3]$ at $\delta_{Li} = 0.92$ can be observed in methanol-d_4, even at low temperatures (193 K), indicating a fast exchange of bound and "free" lithium cations.[199]

Ligands **87b**-H_4 and **87c**-H_4 form dinuclear triple-stranded titanium(IV) helicates $[Ti_2\mathbf{87b}_3]^{4-}$ and $[Ti_2\mathbf{87c}_3]^{4-}$. The X-ray structure of the potassium salt of $[Ti_2\mathbf{87c}_3]^{4-}$ shows that the helicate binds in its large hydrophobic interior not only one but two potassium counterions together with two water and four DMF molecules. In solution a fast exchange of bound and unbound cations seems to occur.[201]

Ligands **88**-H_4 with one, three, or five methylene units in the spacer form triple-stranded meso-helicates $[Ti_2\mathbf{88}_3]^{4-}$ with titanium(IV) ions.[26]

The structure of the methylene-bridged meso-helicate $[Ti_2\mathbf{88a}_3]^{4-}$ reveals the meso-relation of the two metal complex units. In solution the same meso-structure can be observed. Two doublets are observed by ^{1}H NMR spectroscopy for the diasterotopic protons of the spacer. The protons would be homotopic in the corresponding helicate and should lead to one singlet.[203]

If the preparation of $[Ti_2\mathbf{88a}_3]^{4-}$ is attempted in the presence of potassium cations, no defined product is formed. Although elemental analysis reveals a composition "$K_4[Ti_2\mathbf{88a}_3]$" of the isolated material, no defined NMR spectra can be observed. ESI MS shows that a mixture of oligomers is present. On the other hand, in the case of $Na_4[Ti_2\mathbf{88a}_3]$ and $Li_4[Ti_2\mathbf{88a}_3]$, well-defined dinuclear complexes are obtained. This is attributed to the templating ability of the small lithium or sodium cations. Potassium seems to be too big for the stabilization of dinuclear $[Ti_2\mathbf{88a}_3]^{4-}$.[203] This perception is supported by an experiment in which sodium or lithium ions are added to "$K_4[Ti_2\mathbf{88a}_3]$". Within a few hours dinuclear triple-stranded complexes are formed.[204] However, the X-ray structure as well as NMR studies of $Li_4[Ti_2\mathbf{88a}_3]$ indicate that templating does not proceed by binding of the cation in the interior of the helicate $[Ti_2\mathbf{88a}_3]^{4-}$ but by binding from the outside. The X-ray structure of $[\{(DMF)Li\}_3\{Ti_2\mathbf{88a}_3\}]^{-}$ shows that three lithium cations are coordinating to the tetraoxygen squares of the internal catecholato oxygen atoms. Additionally, one DMF binds to each of the alkali metal cations (Figure 41).[203]

In solution the structural situation seems to be different. At room temperature a ^{1}H NMR spectrum of a highly symmetric species is observed for $Li_4[Ti_2\mathbf{88a}_3]$. However, upon cooling, the signals split

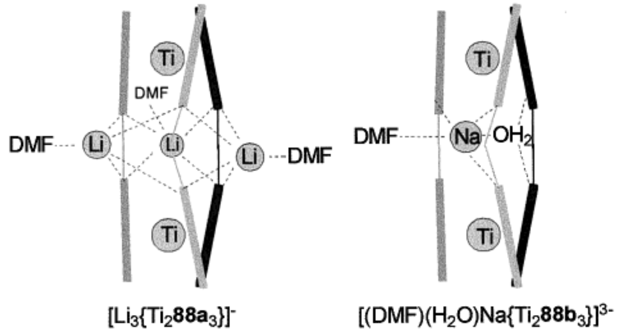


Figure 41.

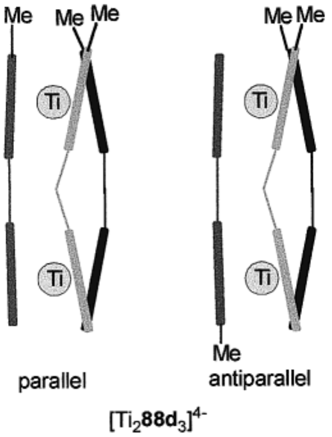


Figure 42.

and distinct sets of resonances are observed for each of the three ligand strands. ^{6}Li NMR spectroscopy of $Li_4[Ti_2\mathbf{88a}_3]$ in methanol-d_4 shows only one signal at room temperature. Cooling results in a splitting of the signals, and two sharp (δ_{Li} = 1.66, 0.99) and one broad (δ_{Li} = 0.90) resonance (1:1:2) are observed at 193 K. This can be explained due to the presence of a species $[Li_2Ti_2\mathbf{88a}_3]^{2-}$ which possesses only two lithium cations coordinating to the tetraanionic meso-helicate $[Ti_2\mathbf{88a}_3]^{4-}$. The two alkali metal ions are diastereotopic and lead to two sharp signals in the ^{6}Li NMR and to a desymmetrization in the ^{1}H NMR spectrum at low temperatures.[204]

The related methylene-bridged ligand **88d**-H_4 bears a methyl group attached to one of the catechol units, and thus, directionality is introduced into the ligand strand. Two different dinuclear triple-stranded complexes $[Ti_2\mathbf{88d}_3]^{4-}$ can be formed: one symmetric coordination compound with all ligands orientated parallel and one unsymmetric with an antiparallel orientation. The parallel and antiparallel isomers of $[Ti_2\mathbf{88d}_3]^{4-}$ are formed in a ratio of 1:4, which is close to the statistical ratio (1:3) (Figure 42).[204]

Ligand **88e**-H_4 bears one methyl group attached to the methylene spacer. In the dinuclear complex $[Ti_2\mathbf{88e}_3]^{4-}$ this substituent can be orientated toward the inside or outside of the meso-helicate. Thus, four different isomers (in−in−in, out−out−out, in−in−out, in−out−out) of $[Ti_2\mathbf{88e}_3]^{4-}$ may be formed. Only one symmetric species is observed by NMR spectroscopy, which for steric reasons should be the out−out−out isomer.[204]

The dinuclear $(CH_2)_3$-bridged complex $[Ti_2\mathbf{88b}_3]^{4-}$ adopts the meso-helicate structure in the solid state and in solution. The X-ray structure of $Na_4[Ti_2\mathbf{88b}_3]$ shows that one sodium ion together with one water and one DMF are bound in the interior of the dinuclear complex in the solid state.[205] ^{23}Na NMR reveals that the encapsulation of sodium which was observed in the solid state also occurs in solution.[201]

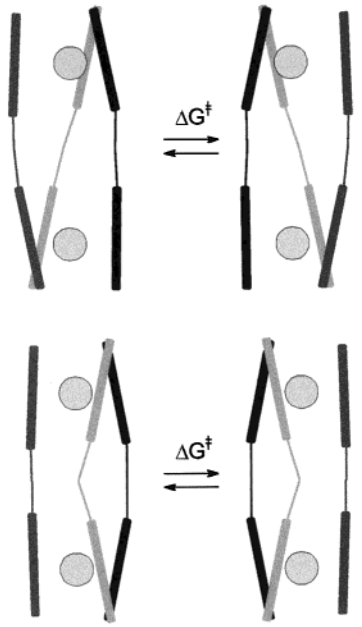
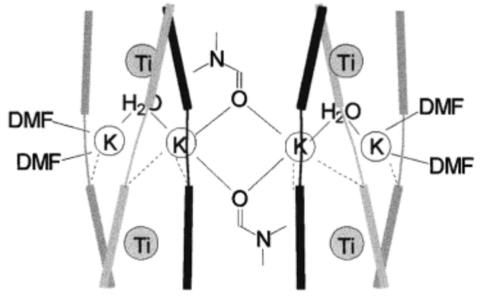


Figure 43. (Top) Inversion of the left-handed triple-stranded helicate into the right-handed one and vice versa. (Bottom) Degenerated inversion of a meso-helicate (ΛΔ ⇔ ΔΛ).

Ligands **87** with an even number of methylene units in the spacer lead to the helicates $[Ti_2\mathbf{87}_3]^{4-}$, while ligands **88** with an odd number of methylene units form meso-helicates $[Ti_2\mathbf{88}_3]^{4-}$. The high diastereoselectivity of this self-assembly process again is due to the preferred zigzag conformation of the alkyl spacer as already discussed and outlined in Figure 9.[26]

In solution the left-handed and the right-handed helices $[Ti_2\mathbf{87}_3]^{4-}$ are in a dynamic equilibrium (Figure 43). The meso-helicates $[Ti_2\mathbf{88}_3]^{4-}$ undergo a similar degenerated rearrangement reaction (ΔΛ ↔ ΛΔ). This symmetrization/racemization can be observed by NMR at variable temperature using the diastereotopic protons of the spacer as a stereochemical probe. The activation barrier for this equilibration process can be calculated from the coalescence temperature of the relevant resonances. Investigations in the presence of uncoordinated ligands show that the inversion process proceeds via a nondissociative mechanism.[199,205,206]

It was found that the symmetrization of the helicates or meso-helicates is influenced by different factors. (1) meso-Helicates typically show higher inversion barriers than the helicates. This might be due to the enhanced structural reorganization for the meso-helicate compared to the helicate. (2) The observed free energies of activation are lower for systems with longer chain length within the series of helicates or meso-helicates, respectively. (3) Different countercations have different influences on the symmetrization of the complexes. This should be due



$[\{M\text{-}Ti_2\mathbf{90b}_3\}(DMF)_2(H_2O)K_2(\mu\text{-}DMF)_2K_2(H_2O)(DMF)_2\{P\text{-}Ti_2\mathbf{90b}_3\}]^{4-}$

Figure 44.

to a different binding behavior of the cations in the interior of the cryptand-type dinuclear complexes.[206] No inversion could be observed for the very rigid dinuclear complex $[Ti_2\mathbf{88a}_3]^{4-}$.[203]

In addition to the control of the diastereoselectivity of helicate versus meso-helicate formation, enantiomerically pure complexes are obtained by introducing chiral groups at the ligand. The ethylene-bridged ligand **89**-H_4 bears chiral (*S*)-configured 1-phenylethylamide substituents and forms the enantiomerically pure helicate $[Ti_2\mathbf{89}_3]^{4-}$ with $[\alpha]_D = +970°$ ($c = 1$, methanol). Upon complex formation the amide groups of **89** form hydrogen bonds to the terminal catecholato oxygen atom and thus bring the chiral substituents close to the metal complex units. Only one of the three possible diastereomers is observed by NMR, and the spectrum shows the C_2 symmetry of the helicate.[207]

The rigid linear ligand systems **90**-H_4 can only lead to helicates $[Ti_2\mathbf{90}_3]^{4-}$. Distortion of the linear ligands to form a bent structure would be the unfavored possibility to obtain the meso-complex.[26] In derivative **90a**-H_4 two catechol units are connected by a direct bond.[198] Thus, **90a**-H_4 represents the central part of *Mastigophorene A* and *Mastigophorene B*, which show interesting biological activity.[208] The formation of the helicate $[Ti_2\mathbf{90a}_3]^{4-}$ shows that ligands such as **90a** are able to form triple-stranded dinuclear complexes.[26]

The triple-stranded helicate $[Ti_2\mathbf{90b}_3]^{4-}$ was crystallized and characterized by X-ray diffraction. In the solid state two potassium ions are bound in the interior of the helicate. One of the potassium ions additionally is bound to two DMF molecules, and one water is bridging the potassium ions. The second potassium is coordinated to two DMF molecules which act as bridging ligands between two oppositely configured helicates (Figure 44).[209]

The helicates $[Ti_2\mathbf{90c}_3]^{4-}$ with biphenylene spacers were characterized by NMR spectroscopy and positive FAB mass spectrometry.[210]

Williamson ether synthesis with gallic acid derivatives opens a way to the ether-linked ligand **91**-H_4 which forms a triple-stranded dinuclear complex $[Ti_2\mathbf{91}_3]^{4-}$. Although this complex gives a very simple well-defined NMR spectrum, it is not possible to distinguish if the complex adopts the structure of a helicate or a meso-helicate.[211]

The arylamide-bridged ligands **92**-H_4 form triple-stranded dinuclear helicates $[Ga_2\mathbf{92}_3]^{6-}$ and $[Fe_2\mathbf{92}_3]^{6-}$ with gallium(III) or iron(III) ions.[212] $[Ga_2\mathbf{92a}_3]^{6-}$ and $[Ga_2\mathbf{92b}_3]^{6-}$ could be characterized in the solid state showing the helical arrangement of the three ligand strands. For the iron(III) complex $[Fe_2\mathbf{92d}_3]^{6-}$ of the chiral ligand **92d**-H_4, it was shown by CD spectroscopy that the *S*-configured substituent induces an (*M*)-configuration of the triple-stranded helix, and the NMR spectrum of the analogous gallium complex $[Ga_2\mathbf{92d}_3]^{6-}$ reveals that only one enantiomerically pure diastereomer is formed. Ligand **92e**-H_4 possesses some directionality due to the different substituents at the termini of the ligand strand. The parallel and antiparallel isomers of $[Ga_2\mathbf{92e}_3]^{6-}$ are formed in a statistical ratio of 1:3.[212]

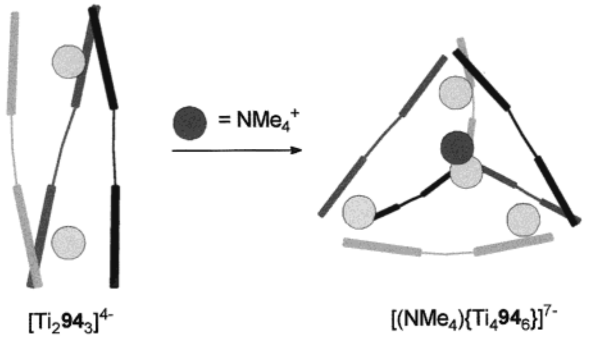


Figure 45.

The racemization behavior of complexes $[Ga_2\mathbf{92}_3]^{6-}$ can be studied due to the presence of the isopropyl groups of ligand **92c**-H_4 which upon complexation to the metals and formation of $[Ga_2\mathbf{92c}_3]^{6-}$ lead to signals of diastereotopic methyl groups. Thorough investigations show that the inversion process at low pH is proton dependent, indicating a dissociative mechanism for the symmetrization, while under basic conditions the nondissociative Bailar-twist rearrangement becomes the only possible mechanism.[212]

Comparison of the racemization barriers of $[Ga_2\mathbf{92c}_3]^{6-}$ and a related mononuclear tris(catecholisopropylamide) gallium(III) complex shows that the racemization of the dinuclear complex $[Ga_2\mathbf{92c}_3]^{6-}$ proceeds approximately with the same energy barrier as that observed for the mononuclear complex. This means that the inversion does not occur via a simultaneous inversion of both metal centers. Here, an energy barrier would result for $[Ga_2\mathbf{92c}_3]^{6-}$ that should be twice as high as the one for the mononuclear gallium complex. The inversion proceeds through a stepwise mechanism with subsequent inversion of the two metal complex units. A meso-helicate is a high-energy intermediate in this rearrangement reaction.[212]

Using the same analytical approach it could be shown that the trinuclear titanium(IV) helicate $[Ti_3\mathbf{93}_3]^{6-}$ inverts with nearly the same barrier as that observed for the dinuclear complex $[Ti_2\mathbf{87a}_3]^{4-}$, if the same counterions (sodium or potassium) are present. $[Ti_3\mathbf{93}_3]^{6-}$ probably initially epimerizes at one of the terminal complex units, and the inversion of the helical twist propagates through the helicate.[213]

With the anthracenyl-bridged ligand **94**-H_4, the triple-stranded helicates $[Ti_2\mathbf{94}_3]^{4-}$ and $[Ga_2\mathbf{94}_3]^{6-}$ are obtained (Figure 45). Addition of tetramethylammo-

XLV

Figure 46.

nium salts to the titanium complex $[Ti_2\mathbf{94}_3]^{4-}$ induces a rearrangement reaction and the tetrahedral complex $[(Me_4N)\subset\{Ti_4\mathbf{94}_6\}]^{7-}$ is formed. Here, the template Me_4N^+ induces this reorganization and forms the stable host–guest complex $[(Me_4N)\subset\{Ti_4\mathbf{94}_6\}]^{7-}$.[214]

With iron(III) ligand **95a**-H_4 leads to a triple-stranded helicate $[Fe_2\mathbf{95a}_3]^{6-}$ if the complex formation is performed in the presence of an excess of ligand. With 2 equiv of ligand the dinuclear double-stranded meso-complex $[Fe_2\mathbf{95a}_2(\mu\text{-}OH)_2]^{4-}$ with two bridging hydroxy groups (**XLV**) is obtained (Figure 46).[215] The analogous chiral dimethyl derivative **95b**-H_4 does not yield a helicate, but a tetranuclear tetrahedral complex $[Fe_4\mathbf{95b}_6]^{12-}$ is formed.[216]

Triple-stranded helicates $[Ga_2(\mathbf{95c-e})_3]^{6-}$ are obtained with ligands **95c**–**e**-H_4 and are characterized by NMR spectroscopy. It was shown by X-ray structure analysis that the chiral ligand **95e** induces an (*M*)-configuration of the triple-stranded helix.[217]

With the amino acid-bridged derivatives **96**-H_4,[218] triple-stranded helicates $[Ti_2\mathbf{96}_3]^{4-}$ are only formed in minor traces. As a major product complexes such as **XLV** are obtained. Solid-state X-ray investigations of $[Ti_2\mathbf{96b}_2(\mu\text{-}OH)_2]^{2-}$, $[Ti_2\mathbf{96c}_2(\mu\text{-}OMe)_2]^{2-}$, $[Ti_2\mathbf{96d}_2(\mu\text{-}OH)_2]^{2-}$, and $[Ti_2(R\text{-}\mathbf{96e})(S\text{-}\mathbf{96e})(\mu\text{-}OMe)_2]^{2-}$ were performed, showing the structure with two biscatechol ligands **96** and two co-ligands bridging the two titanium(IV) centers which possess a meso-relation ($\Lambda\Delta$).[219]

Ligand **97**-H_2 is a simple catecholphosphane. With titanium(IV) or tin(IV) ions it yields mononuclear complexes $[Ti\mathbf{97}_3]^{2-}$ and $[Sn\mathbf{97}_3]^{2-}$. Reaction of $[Ti\mathbf{97}_3]^{2-}$ with *trans*-$PdBr_2$ leads to a triple-stranded meso-helicate $[Ti_2(\mathbf{97}_2PdBr_2)_3]^{4-}$ in which *trans*-$PdBr_2$ units act as spacers connecting the two $[Ti\mathbf{97}_3]^{2-}$-complex moieties.[220] This dinuclear titanium complex $[Ti_2(\mathbf{97}_2PdBr_2)_3]^{4-}$ possesses a structure which is very similar to the one of $[Ru_2Cu_3\mathbf{51}_6]^+$ (see Figure 24).[130]

The bishydroxypyridinone ligand **98**-H_2 is geometrically related to the biscatechol ligands. With gallium(III) or aluminum(III) ions it forms triple-stranded dinuclear complexes $[Ga_2\mathbf{98}_3]$ and $[Al_2\mathbf{98}_3]$. In solid-state and solution studies it was found that complexes $[Ga_2\mathbf{98}_3]$ and $[Al_2\mathbf{98}_3]$ adopt a compressed meso-helicate structure if no water is present. In the presence of water, one molecule of H_2O is bound in the interior of the complex and the more stretched chiral helicate $[(H_2O)\subset\{M_2\mathbf{98}_3\}]$ (M = Al, Ga) is obtained. Here the relative stereochemistry of the two complex units is influenced by the presence of a guest species.[28] The stereochemical information which is encoded in the spacer with an odd number of carbon atoms (preferring the meso-structure) is overridden by the guest which needs enough space for an optimized binding in the interior. Thus, the helicate with a larger cavity is formed.[26]

IV. Mixed Oxygen/Nitrogen Donors as Ligands for Double- and Triple-Stranded Helicates

Piguets ligands **69**, **70**, and **73** which possess a nitrogen as well as a carbonyl oxygen binding site for metal ions were described earlier in this paper[163,164,170,172] and will not be discussed in this section.

A typical oxygen/nitrogen donor ligand is the bipyridine/catechol derivative **99**-H_2. However, up to now no helicates have been isolated with this ligand. However, it is possible to obtain mononuclear complexes $[Fe(\mathbf{99}\text{-}H_2)_3]^{2+}$ and $[Ti\mathbf{99}_3]^{2-}$ with the iron(II) coordinating selectively to the bipyridine and the titanium(IV) to the catecholate binding site of ligand **99**. Upon addition of titanium(IV) as well as iron(II) to ligand **99**, a precipitate—probably oligomeric or polymeric material—is formed.[221]

1. 8-Hydroxyquinoline Derivatives

8-Hydroxyquinoline possesses a self-complementary hydrogen-bond donor/acceptor site and upon deprotonation is able to coordinate to metal ions.[222] Therefore, it is an ideal building block for supramolecular as well as metallosupramolecular chemistry. However, very few examples have been described in the literature, where 8-hydroxyquinoline is used for this purpose (Figure 47).[223]

Alkyl-bridged bis(8-hydroxyquinoline) derivatives **100**–**104**-H_2 were introduced to form dinuclear triple-stranded helicates.[224] The bis(8-hydroxyquinoline) derivative **101a**-H_2 with an ethylene spacer in the 7- and 7′-positions with gallium(III) ions forms neutral insoluble coordination compounds of composition **101a**:Ga = 3:2 (elemental analysis). The obtained material might be insoluble because it is neutral or because oligomeric or polymeric complexes are formed.[225] With the alkyl-bridged ligands **101b**–**d**-H_2, similar gallium complexes are formed which are soluble in nonpolar solvents if decyl substituents are attached to the ligand (**101c,d**). MALDI TOF and FAB MS spectrometric investigations of the gallium complexes of **101c** and **101d** show the presence of triple-stranded dinuclear $[Ga_2(\mathbf{101c,d})_3]$ and of hexa-stranded tetranuclear complexes $[Ga_4(\mathbf{101c,d})_6]$. This reveals that at least a mixture of two, probably more, oligomeric components $[Ga_2(\mathbf{101c,d})_3]_n$ is present.[226,227]

The insoluble material formed from ligand **101a** can be solubilized by the addition of appropriate metal salts to the preformed mixture of complexes (or during the complex formation). After heating overnight one defined species $[M\subset\{Ga_2\mathbf{101a}_3\}]^+$ (M = Na, K) is formed quantitatively which is positively charged and is soluble in DMSO.[225–227]

The gallium complexes of ligands **101** represent a further example for the principle of dynamic combinatorial chemistry. In the first step—the complex formation—a mixture (= library) of supramolecular coordination compounds is formed. All the components of this dynamic library are in equilibrium with each other. In a second step—the selection step—this library can be transformed into one defined compound by addition of an appropriate template. By binding of this template all the components of the

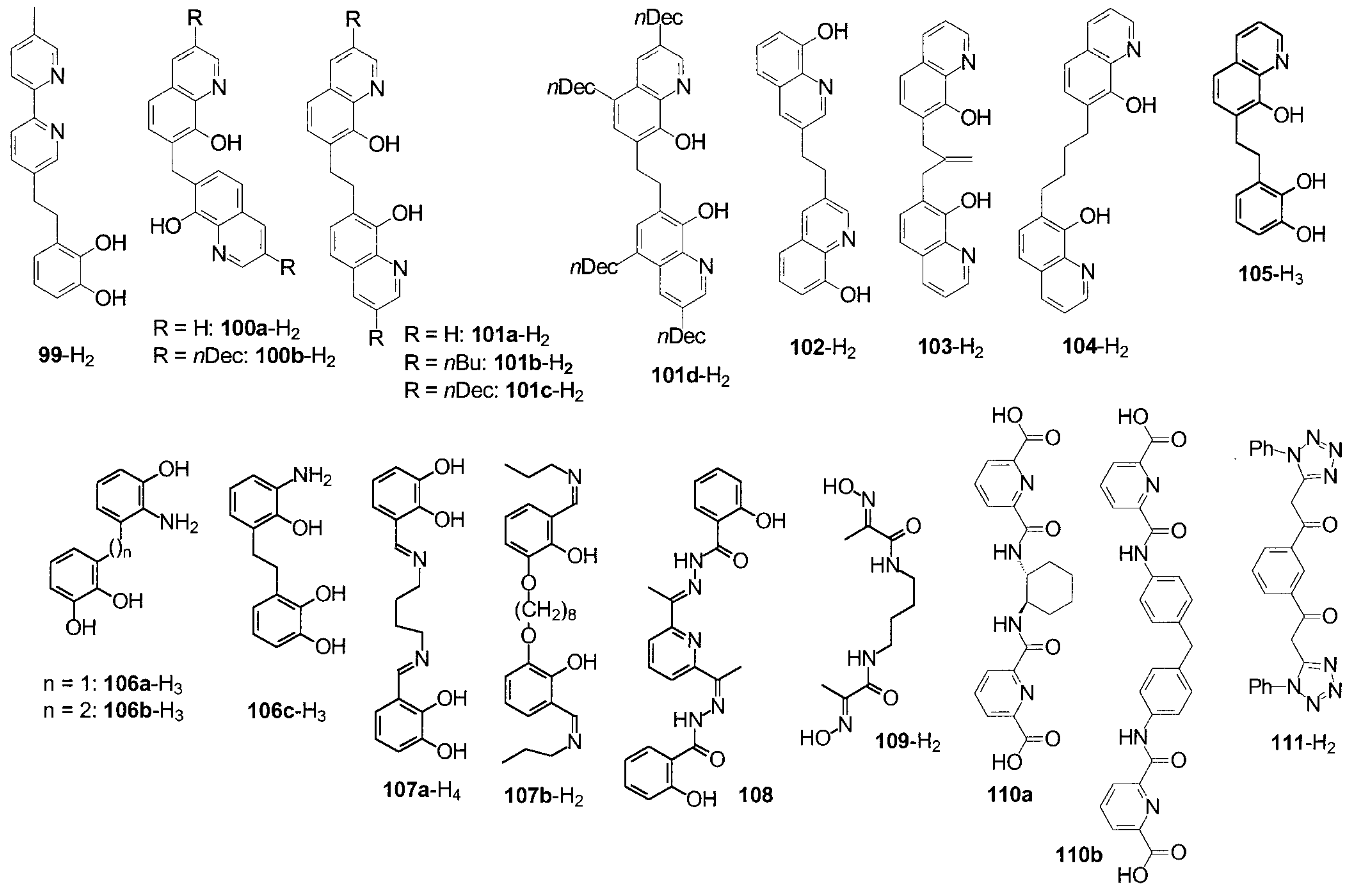


Figure 47.

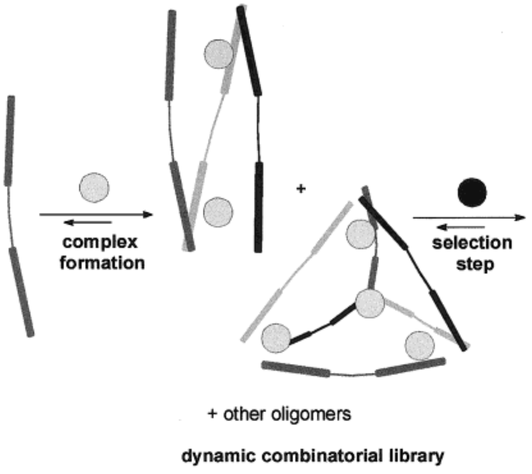


Figure 48.

mixture are transformed into the one species which is the most favored host for the template (Figure 48).[15]

Adding cations (M = Na, K, Rb, NH$_4$) to the library of complexes [Ga$_2$**101a**$_3$]$_n$ leads to the triple-stranded helicates [M$\subset${Ga$_2$**101a**$_3$}]$^+$. The cryptate-type structure was shown by X-ray analysis for M = Na, K.[226] However, due to the different size of the guests, the metallacryptand [Ga$_2$**101a**$_3$] has to adopt a more stretched or more condensed structure depending on the template. This can be observed by NMR spectroscopy using the proton in the 2-position of the ligand as a probe, which experiences different anisotropic shifts depending on the expansion of the dinuclear gallium complex.[226] The helicates [M$\subset${Ga$_2$**101d**$_3$}]$^+$ (M = Na, K, NH$_4$) possess long alkyl chains, making the complexes soluble in nonpolar solvents such as hexane or benzene.[227]

The related ethylene-bridged ligand **102**-H$_2$ with an inverted pattern of the oxygen and nitrogen donors forms a mixture of different gallium complexes [Ga$_2$**102**$_3$]$_n$. However, no solubilization is observed upon addition of alkali metal ions due to the lack of internal oxygen atoms which are essential for the binding of the cations.[225]

Compound **100a**-H$_2$ with only one methylene unit bridging the two hydroxyquinoline moieties cannot be used for complex formation due to its low solubility in appropriate solvents. However, the decyl-substituted derivative **100b**-H$_2$ forms dinuclear triple-stranded complexes [Ga$_2$**102b**$_3$] in chloroform solution, although an excess of lithium or sodium cations has to be present. NMR investigations show that the meso-helicate is obtained (two doublets are observed for the diastereotopic protons of the spacer), and it is supposed that two or three alkali metal cations are bound to the dinuclear complex [Ga$_2$**102b**$_3$].[228]

The C$_3$-bridged ligand **103**-H$_2$ was introduced by Hiratani[229] and can be used for the formation of dinuclear triple-stranded gallium complexes [M$\subset${Ga$_2$**103**$_3$}]$^+$ (M = K, NH$_4$, Rb, Cs). X-ray structural investigations of, e.g., [Cs$\subset${Ga$_2$**103**$_3$}]$^+$ show that the complex adopts a meso-helicate structure.[230] The

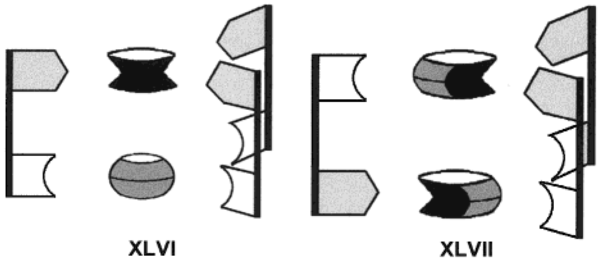


Figure 49.

templating metals which are bound in the interior of the dinuclear complex show an unusual coordination geometry. They are only binding to the internal oxygen atoms of ligands **103** with remaining binding sites blocked by the $C{=}CH_2$ units. By NMR spectroscopic and structural studies it can be ruled out that a binding interaction of the alkali–metal with the vinylidene units of **103** does occur.[228]

Ligand **104**-H_2 forms dinuclear gallium complexes $[Cs\subset\{Ga_2\mathbf{104}_3\}]^+$ in the presence of the large cesium cation.[228]

From all those studies it can be seen that the formation of dinuclear triple-stranded coordination compounds highly depends on the presence of templates with an appropriate size. Dinuclear gallium complexes of the smallest ligand **100** are formed in the presence of Li or Na cation, of the ethylene-linked derivatives **101** in the presence of Na, K, NH_4, or Rb cation, of Hiratanis ligand **103** in the presence of K, NH_4, Rb, or Cs cation, and of the large bis(hydroxyquinoline) **104** only with Cs cation.

The gallium(III) complexes of ligands **101** and **103** have already been discussed; however, helicate-type coordination compounds are also obtained with other metals: $[M\subset\{Al_2\mathbf{101a,c}_3\}]^+$ (M = Na, K), $[M\subset\{Fe_2\mathbf{101a,c}_3\}]^+$ (M = Na, K), $[M\subset\{Cr_2\mathbf{101a,c}_3\}]^+$ (M = Na, K), $[M\subset\{Al_2\mathbf{103}_3\}]^+$ (M = Na, K, NH_4, Rb, Cs), and $[M\subset\{Fe_2\mathbf{103}_3\}]^+$ (M = Na, K, NH_4, Rb, Cs).[228] The zinc(II) complexes $[M\subset\{Zn_2\mathbf{101a}_3\}]^-$ (M = Li, Na, K) and $[K\subset\{Zn_2\mathbf{103}_3\}]^-$ are negatively charged, and thus, one of the countercations is encapsulated in the interior of the triple-stranded helicate-type complexes.[226]

Ligands **105**-H_3 and **106**-H_3 represent sequential ligands with one catechol and one 8-hydroxyquinoline (**105**)[231] or the related 2-aminophenole (**106**)[232] as binding site for metal ions. Therefore, the ligands possess a sequence of two electronically different but geometrically very similar ligand units. Upon formation of triple-stranded dinuclear helicate-type complexes, the ligands are able to adopt a parallel (**XLVI**) or an antiparallel (**XLVII**) orientation (Figure 49). This relative orientation is controlled by the choice of appropriate metal ions or a combination thereof.[232]

The regiochemistry of the ligand orientation can be controlled since the two electronically different binding sites prefer coordination to electronically different metal centers. Thus, sequential ligands such as **105** or **106** upon reaction with a 1:1 mixture of two different metal ions should lead to heterodinuclear complexes with a parallel orientation of the ligand strands (**XLVI**). One of the chelating units binds to one kind of metal ion and the other one to the other. Complexes with an antiparallel ligand orientation are formed if only one kind of metal ion is used for the self-assembly of the dinuclear complexes. In the resulting coordination compounds both metals are similar and in a thermodynamically controlled system prefer to have a coordination environment as similar as possible. “Nature tries to minimize charge separation”. This is only possible if complexes such as **XLVII** are formed.[232]

Reaction of the hydroxyquinoline/catechol ligand **105**-H_3 with gallium(III) nitrate and potassium carbonate leads to the dinuclear triple-stranded helicate $[Ga_2\mathbf{105}_3]^{3-}$. FAB mass spectrometry shows the presence of the dinuclear complex, while 2D NMR spectroscopy reveals that the unsymmetric complex with an antiparallel orientation of ligand strands **XLVII** is obtained. No signals of the symmetric complex **XLVI** can be detected. Reaction of the same ligand **105**-H_3 with a mixture of titanium(IV) and gallium(III) ions does not lead to a complex like **XLVI**. An insoluble material is obtained which cannot be characterized.[231]

The catechol/aminophenole derivatives **106**-H_3 on the other hand lead to complexes **XLVI** as well as **XLVII**. With gallium(III) or titanium(IV) ions the meso-helicate-type coordination compounds $[M_2\mathbf{106a}_3]^{n-}$ (M = Ga, $n = 3$; M = Ti, $n = 1$) with an antiparallel orientation of the ligands are obtained. ^{13}C NMR spectra of complexes $[M_2\mathbf{106a}_3]^{n-}$ show all 39 signals which are expected for an unsymmetric **XLVII** complex, no more and no less. A 1:1 mixture of gallium(III) and titanium(IV) ions on the other hand leads to the symmetric complex (with a C_3 axis) $[GaTi\mathbf{106a}_3]^{2-}$ of type **XLVI**. NMR spectroscopy reveals only one set of 13 signals for ligand **106a**. The potassium salt of $[GaTi\mathbf{106a}_3]^{2-}$ was characterized by X-ray structure analysis, showing that titanium(IV) binds to the catechol and gallium(III) to the aminophenole binding site. Intramolecular hydrogen bonding occurs between the amino group and the internal oxygen donor atom of ligand **106a** leading to further stabilization of the dinuclear complex $[GaTi\mathbf{106a}_3]^{2-}$. Here the self-assembly is not controlled by the templating abilities of countercations. Instead, the hydrogen bridges act as a kind of internal template.[232]

The ethylene-bridged ligands **106b,c**-H_3[233] lead to the corresponding triple-stranded dinuclear helicates $[Ga_2\mathbf{106b,c}_3]^{3-}$ (**XLVII**) or $[GaTi\mathbf{106b,c}_3]^{2-}$ (**XLVI**). In complexes of ligand **106b** with internal amino groups, stabilization of the dinuclear helicates occurs by hydrogen bonding. However, due to the larger distance of the complex units (compared to **106a**), this stabilization is not very effective and the dinuclear complexes slowly decompose in solution. With ligand **106c**, the complex formation depends on the templating ability of the countercations and stable helicates $[Ga_2\mathbf{106c}_3]^{3-}$ or $[GaTi\mathbf{106c}_3]^{2-}$ are formed in the presence of sodium or potassium cations.[234]

Binding of the cations indirectly could be shown by dynamic NMR spectroscopy at variable temperature in methanol-d_4. Complexes $[GaTi\mathbf{106b}_3]^{2-}$ with internal hydrogen bonds show similar inversion barriers for the sodium ($\Delta G^{\ddagger} = 16.0$ kcal/mol) as well as for the potassium salt ($\Delta G^{\ddagger} = 16.2$ kcal/mol). However, for the “templated” [GaTi**106c**$_3$]$^{2-}$, a dramatic influence of the cations can be observed (sodium, $\Delta G^{\ddagger} = 11.5$ kcal/mol; potassium, $\Delta G^{\ddagger} = 15.8$ kcal/mol), indicating the binding of the cations to this helicate.[234]

2. Imine- and Carbonyl-Based Ligands

Helicates can be prepared by electrochemical methods using the corresponding transition metal as cathodic material in the presence of appropriate ligands such as catechol/imine donors **107a**-H_4 or **108**. However, **107a**-H_4 with copper does not lead to a helicate but to a bishelical trinuclear complex [Cu_3**107a**(**107a**-H_2)] with two external hydroxy groups of one ligand strand being uncoordinated.[235] However, the related ligand **107b**-H_2 forms a dinuclear double-stranded helicate [Ni_2**107b**$_2$] which possesses two square-planar nickel(II) complex units and shows a helical twist which is introduced by the alkyl spacer.[236]

With nickel and ligand **108**, double-stranded helicates [Ni_2**108**$_2$] and [Ni_2**108**$_2$(pyridine)$_2$] are obtained electrochemically. [Ni_2**108**$_2$] is formed in the absence of pyridine. X-ray structural analysis shows that both nickel centers are pseudooctahedrally coordinated, each binding to the amide oxygens and the imines with the two pyridine units bridging the two metal centers. The phenolic OH groups do not interfere with binding. In [Ni_2**108**$_2$(pyridine)$_2$] both metal centers are also hexacoordinated. One of them binds to two amide oxygens, two imines, and the two pyridine units of the two ligand strands **108**, while the second is coordinated to two amides, two imines of the strands, and two additional pyridines.[237]

Ligand **109**-H_2 possesses two oxygen/nitrogen chelating units and forms a dinuclear complex [Cu_2(**109**-H)$_2$(H_2O)$_2$]$^{2+}$ with copper(II) ions. However, this double-stranded complex is not helical but planar with water molecules coordinating to the copper centers. Intramolecular hydrogen bonding between $-$OH and $-O^-$ stabilizes this complex.[238]

Two tridentate dioxygen/nitrogen donor units of ligands **110a/b** are able to bind to europium(III) ions in water and to form triple-stranded dinuclear complexes [Eu_2**110**$_3$]$^{6+}$ which are highly luminescent in water. Model considerations seem to indicate that complexes [Eu_2**110**$_3$]$^{6+}$ possess the structure of a triple-stranded helicate.[239]

Ligand **111**-H_2 should also be mentioned here. **111** does not form a helicate but a tetranuclear complex [Zn_4**111**$_4$] which possesses two double-helical subunits [Zn_2**111**$_2$] which are connected by coordination of two amide oxygen atoms of each double helix to the zinc centers of the other.[240]

V. Ligands Possessing Sulfur, Carbon, or Phosphorus Donors

Ligand **8d**, which possesses sulfur as well as nitrogen donor sites, has already been discussed.[51−53] Other ligands with sulfur atoms in the strand are the thioethers **112a** and **112b** (Figure 50).[241]

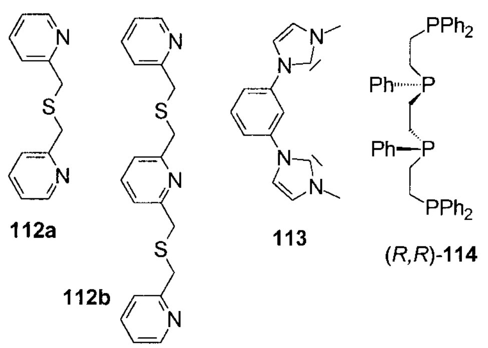


Figure 50.

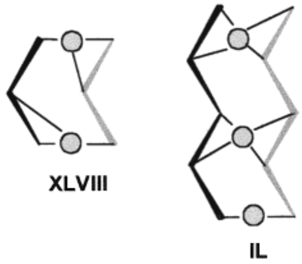


Figure 51.

Derivatives **112a/b** form double-stranded complexes [Ag_2**112a**$_2$]$^{2+}$ and [Ag_3**112b**$_2$]$^{3+}$ with silver(I) ions. In the dinuclear complex [Ag_2**112a**$_2$]$^{2+}$, both silver centers are trigonal planar coordinated binding to one pyridine unit of one ligand and to a nitrogen and a sulfur atom of the other. Ligands **112a** adopt a parallel bent structure **XLVIII** (Figure 51).[241]

In the trinuclear complex [Ag_3**112b**$_2$]$^{3+}$, again the two ligand strands are arranged parallel (**IL**). Here, one terminal ion and the central silver ion have a tetracoordinated N_2S_2-coordination environment while the silver at the second terminus is dicoordinated binding to two pyridine moieties.[241]

The stable biscarbene **113** forms a dinuclear complex [Hg_2**113**$_2$]$^{4+}$ with mercury(II) ions in which the two ligand strands wrap around the mercury ions. They are bound by the carbenes and possess a linear dicoordinated geometry. The pyridine units of **113** do not interact with the metal centers.[242]

The tetraphosphane derivatives (R,R)-**114** or (S,S)-**114** form double-stranded dinuclear complexes [M_2**114**$_2$]$^{2+}$ with silver(I) or gold(I) ions. Crystal structure analysis shows the presence of the helicate (M)-[Ag_2{(R,R)-**114**}$_2$]$^{2+}$ and meso-type complex Λ,Δ-[Ag_2{(R,R)-**114**}$_2$]$^{2+}$ in a 1:1 ratio in the crystal. For the gold complex only helicate (M)-[Au_2{(R,R)-**114**}$_2$]$^{2+}$ is observed in the solid state.[243]

VI. Ligand Self-Recognition in Helicate Chemistry

The use of mixtures of different ligands for the formation of helicate-type complexes can lead to mixtures of heteroleptic and homoleptic oligonuclear coordination compounds (Figure 52). If such a mixture is formed, there is no self- or heterorecognition of the ligand strands. Here, the self-assembly process is highly unspecific.[9]

If only the homoleptic complexes, with one kind of ligand per coordination compound, are formed, a sorting of the ligands proceeds by self-recognition during the self-assembly of the metallosupramolecu-

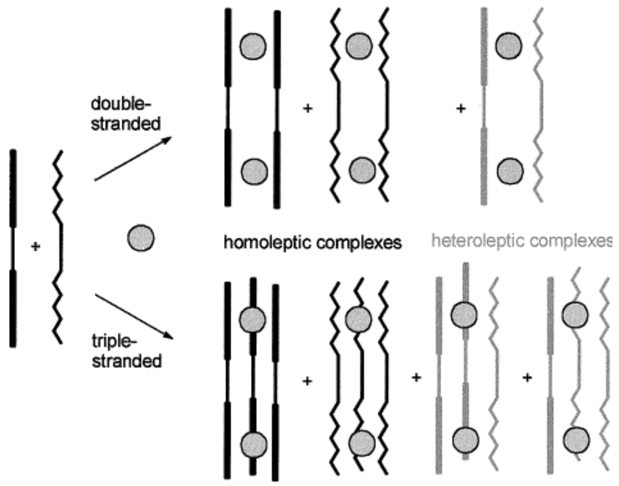


Figure 52.

lar aggregates. On the other hand, exclusively heteroleptic complexes can be formed by heterorecognition.

There are different ways to control self- or heterorecognition of ligands during the self-assembly of helicate-type complexes.[15]

1. Control of Self-Recognition by the Number of Binding Sites

The first self-recognition experiments were described in 1993 using bipyridine derivatives as ligands. The reaction of ether-linked oligobipyridine derivatives **7m,n,o,i** with copper(I) ions does not lead to a complex mixture of copper compounds. Only the four homoleptic double-stranded helicates $[Cu_2\mathbf{7m}_2]^{2+}$, $[Cu_3\mathbf{7n}_2]^{3+}$, $[Cu_4\mathbf{7o}_2]^{4+}$, and $[Cu_5\mathbf{7i}_2]^{5+}$ are formed by self-sorting or self-recognition of the ligands during the self-assembly process (Figure 53).[244]

The imine-bridged bipyridine derivatives **9a** and **9b** show similar self-recognition in the helicate formation with silver(I) or copper(I) ions.[55]

2. Self-Recognition by Coordination Geometry

Derivatives **7b** and **15b** are different with respect to the position in which the spacer is attached to the bipyridine units (Figure 54). Thus, ligand **7b** prefers a tetrahedral coordination geometry at the metal, leading to double-stranded helicates, while ligand **15b** can form octahedral metal complexes (→ triple-stranded helicate).[244]

A mixture of ligands **7b** and **15b** in the presence of copper(I) and nickel(II) ions leads to a sorting of not only the ligands but also the metals. The double-stranded copper helicate $[Cu_3\mathbf{7b}_2]^{3+}$ and the triple-stranded nickel helicate $[Ni_3\mathbf{15b}_3]^{6+}$ are exclusively observed. In this example "homo"-self-recognition proceeds.[244]

On the other hand, choosing the right system allows the observation of heterorecognition. Mixing ligands **7b** (three bipyridine binding sites) and the tris(terpyridine) ligand **25c** and performing coordination studies with copper(II) ions leads exclusively to the formation of the hetero-double-stranded helicate $[Cu_3(\mathbf{7b})(\mathbf{25c})]^{6+}$ (Figure 55). This is due to the preferred high coordination number (5 or 6) at the copper(II) ions. $[Cu_3(\mathbf{7b})(\mathbf{25c})]^{6+}$ could be characterized by X-ray analysis and shows three pentacoordinated copper(II) centers with the two different ligands **7b** and **25c** wrapping around them.[56,245]

Substituting bipyridine in one position of the trischelate **7b** by phenanthroline (e.g., **8a**) does not lead to self-recognition, if a mixture of, e.g., **7b** and **8a** is reacted with copper(I) or silver(I) ions. The bipyridine and phenanthroline binding sites are too similar to distinguish between them.[53,54,66]

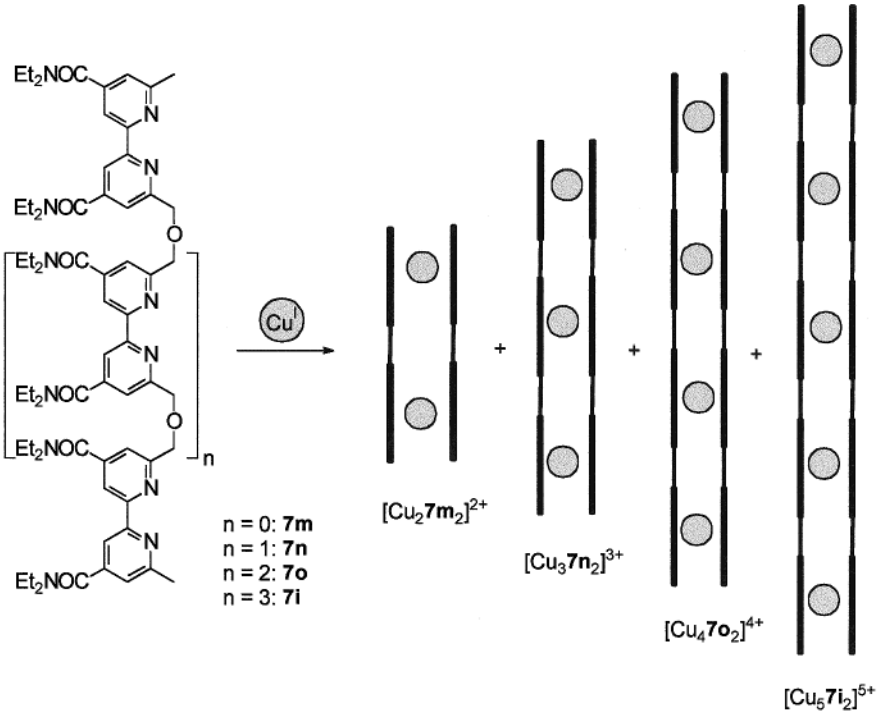


Figure 53.

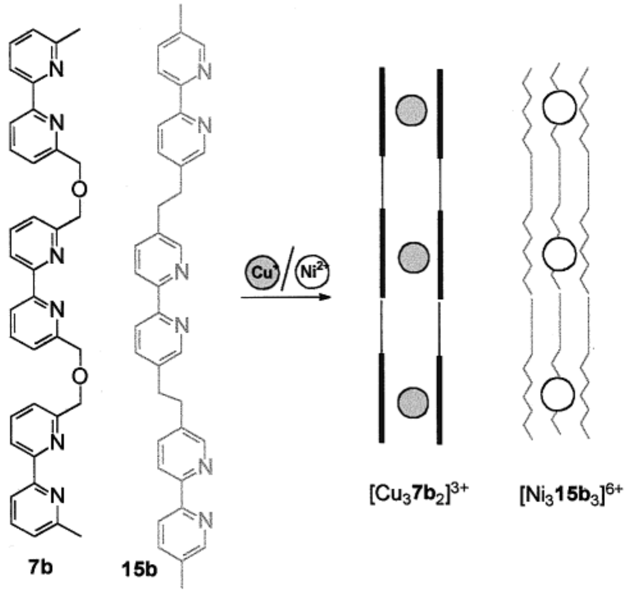


Figure 54.

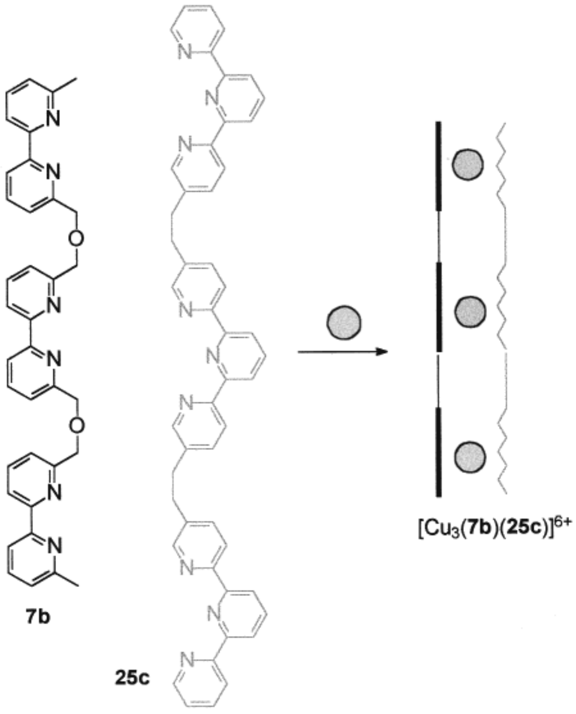


Figure 55.

3. Size Control of Self-Recognition

A further possibility of controlling self-recognition in the formation of helicates is to use rigid ligands with significant differences in the distances of the metal binding sites.[246]

Derivatives **92f**-H_4, **92a**-H_4, and **92g**-H_4 represent three ligands which are rigid and possess different separations of the catechol units (Figure 56). Mixing the three ligands and performing a coordination study with gallium(III) ions with size-controlled self-recognition or self-sorting of the ligands leads to the three homoleptic triple-stranded helicates $[Ga_2\mathbf{92f}_3]^{6-}$, $[Ga_2\mathbf{92a}_3]^{6-}$, and $[Ga_2\mathbf{92g}_3]^{6-}$.[246]

4. Template Control of Self-Recognition

It was discussed earlier in this paper that the self-assembly of triple-stranded helicates and meso-helicates from alkyl-bridged di(catechol) ligands **87**–**89**-H_4 depends on the templating ability of the countercations.[203] Therefore, the templates also should be able to control the self- (or hetero-)recognition of ligands in the self-assembly of helicate-type complexes.

The alkyl-bridged dicatechol ligands **87a**-H_4 and **88a**-H_4 possess very similar distances of the two catechol units. Thus, in principle, a mixture of **87a**-H_4 and **88a**-H_4 could lead to four different triple-stranded dinuclear titanium(IV) complexes—two homoleptic and two heteroleptic—and oligomeric or polymeric material (Figure 57). However, experiments show that the result of a coordination study depends on the alkali-metal cation which is present. NMR spectroscopic and MS spectrometric studies show that complex formation of a mixture of **87a**-H_4 and **88a**-H_4 with titanium(IV) ions leads to the homoleptic dinuclear complex $[Ti_2\mathbf{87a}_3]^{4-}$ and oligomeric material “$[Ti_2\mathbf{88a}_3]_n{}^{4-}$”. It was described earlier that ligand **88a** does not form a specific dinuclear titanium(IV) complex in the presence of potassium ions. Therefore, with self-recognition of the ligands the homoleptic dinuclear complex of ligand **87a** and oligomeric material of **88a** are obtained. However, in the presence of sodium cations, dinuclear complexes $[Ti_2\mathbf{88a}_3]^{4-}$ can be formed. Self-recognition leads to a mixture of the two homoleptic dinuclear complexes $[Ti_2\mathbf{87a}_3]^{4-}$ and $[Ti_2\mathbf{88a}_3]$.$^{4-}$ No heteroleptic coordination compounds can be observed by spectroscopic methods.[247]

The situation gets somewhat more complicated if lithium cations are used. Here, the two homoleptic complexes $[Ti_2\mathbf{87a}_3]^{4-}$ and $[Ti_2\mathbf{88a}_3]^{4-}$ as well as the heteroleptic complex $[Ti_2\mathbf{88a}_2\mathbf{87a}]^{4-}$ are observed by NMR as well as MS. The second possible heteroleptic complex $[Ti_2\mathbf{87a}_2\mathbf{88a}]^{4-}$ is not found at all. Those findings show that the self-recognition of ligands in helicate self-recognition not only depends on the shape of the ligands but also can be controlled by appropriate templates.[247]

Self-assembly of helicate-type complexes from a mixture of the bis(8-hydroxyquinoline) ligands **101a**-H_2 and **103**-H_2 with gallium(III) ions in the presence of a 1:1 mixture of NaCl and CsCl yields only the homoleptic complexes $[Na\subset\{Ga_2\mathbf{101a}_3\}]^+$ and $[Cs\subset\{Ga_2\mathbf{103a}_3\}]^+$. Here a double recognition mechanism takes place. Self-recognition of the ligands proceeds with a simultaneous recognition of the appropriate alkali-metal cation.[230]

5. Self-Recognition of Chiral Ligands

Another possibility for the control of ligand self-recognition is the use of chirality at the ligand strands. Thus, a racemic mixture of ligands **41** with copper(I) ions yields only the homoleptic helicates $\Lambda\Lambda$-$[Cu_2(RR\text{-}\mathbf{41})_2]^{2+}$ and $\Delta\Delta$-$[Cu_2(SS\text{-}\mathbf{41})_2]^{2+}$.[115]

In the case of the chiral ligand **31**, the discrimination is not so pronounced, leading to mixtures of

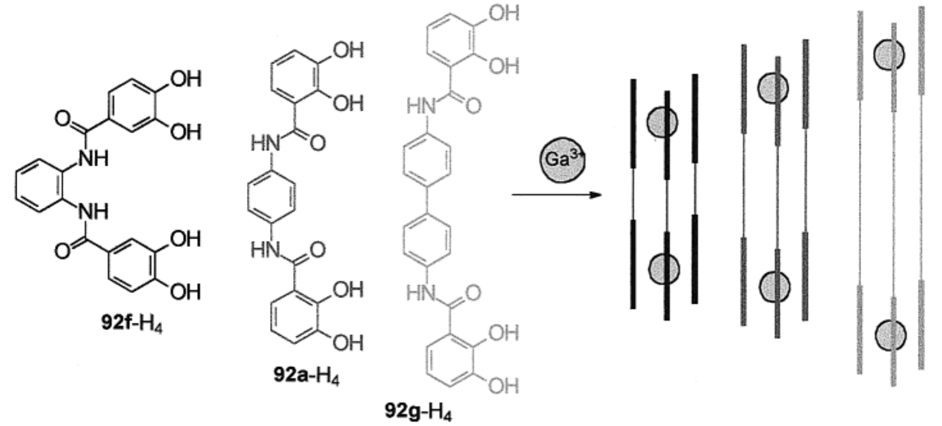


Figure 56.

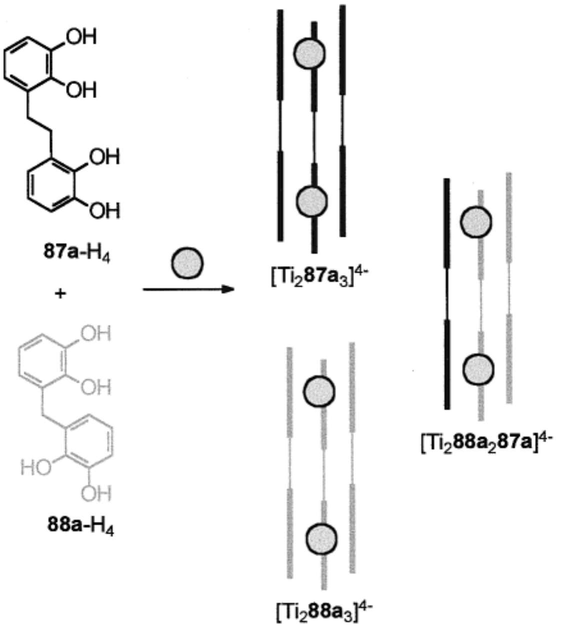


Figure 57.

different diastereoisomers upon complex formation with copper(I) ions.[248]

VII. Quadruple- and Hexa-Stranded Helicates

There are only few examples known where helicate-type complexes are formed from more than three ligand strands.

The bipyridine ligand **115** yields a quadruple-stranded complex $[Cu_2\mathbf{115}_4(H_2O)_4]^{4+}$ with copper(II) ions in which four ligands bridge two copper centers (Figure 58). However, the ligands are arranged linearly so that no helical structure is observed.[249] A similar but twisted complex is formed from ligand **116** and palladium(II). Here a quadruple-helicate $[Pd_2\mathbf{116}_4]^{4+}$ is obtained in which the helicity is introduced by a twist of the ligands.[250]

A series of quadruple-stranded helical complexes is isolated by reaction of ligands **117** with copper, nickel, cobalt, chromium, ruthenium, or rhodium as the metal. The metals are binding to the nitrogen atoms of the pyridines and the deprotonated bridging amines. Metal−metal interaction occurs, and the helix is terminated by coligands X (X = Cl, BF_4).[251]

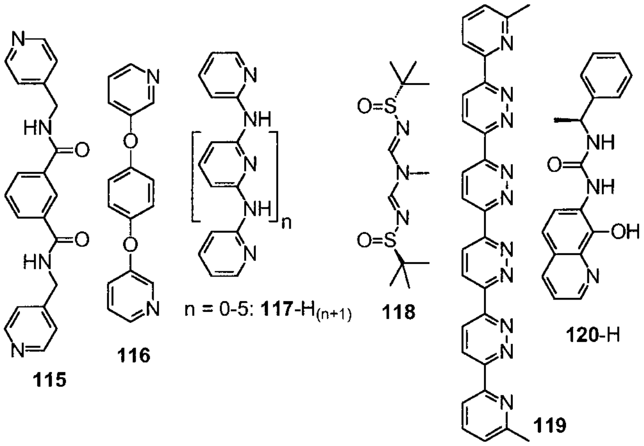


Figure 58.

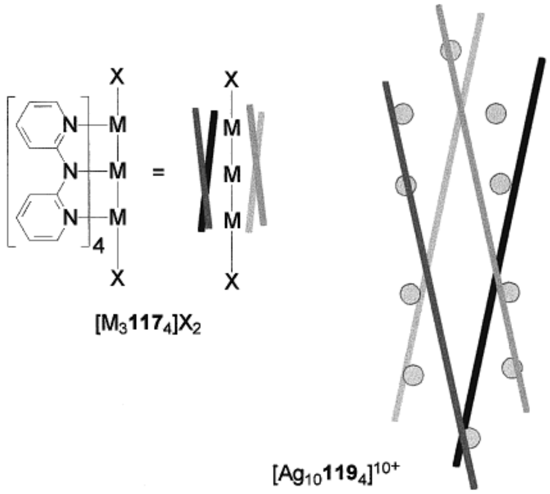
Ligand **118** is a chiral bis(sulfinyl)imidoamidine derivative which forms a quadruple-stranded chiral copper complex $[Cu_2\mathbf{118}_4]^{4+}$ with one chloride counterion bound in the interior of the dinuclear complex. Complexes such as $[Cu_2\mathbf{118}_4]^{4+}$ are used as Lewis acids for asymmetric catalysis.[29]

The pentatopic ligand **119** forms two different supramolecular architectures with silver(I) ions, which both could be characterized by X-ray structural analysis. One of them adopts the structure of a [4+5] grid $[Ag_{20}\mathbf{119}_9]^{20+}$. The other is a quadruple-stranded helicate $[Ag_{10}\mathbf{119}_4]^{10+}$ with 4 ligand strands binding to a total of 10 silver(I) ions and are wrapping around the metals (Figure 59).[252]

Helical structures with more than four ligand strands are also known. Ligands such as **85c**−**e** or **111b** form bis(triple-helical) metal complexes with six ligand strands wrapping around metaloxo clusters $[M_8O_2]^{12+}$ (M = Zn(II), Cd(II), Mn(II)).[253]

The simple urea-substituted 8-hydroxyquinoline **120**-H forms a hexa-stranded helicate $[Zn_3\mathbf{120}_6]$ in which the three metal centers are linearly arranged and the six ligands are orientated alternating “up” and “down” (Figure 60).[254]

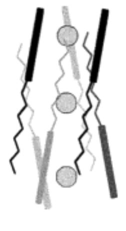
Due to the chiral substituent at the urea, complex $[Zn_3\mathbf{120}_6]$ is formed in a highly stereoselective fashion with an *S*-configuration at ligand **120** inducing a (*P*)-configuration of the helix. The trinuclear complex $[Zn_3\mathbf{120}_6]$ shows an optical rotation of $[\alpha]_D = -1750$ (dioxane, $c = 0.1$).[254]



$[M_3\mathbf{117}_4]X_2$

$[Ag_{10}\mathbf{119}_4]^{10+}$

Figure 59.



$[M_3\mathbf{120}_6]$

Figure 60.

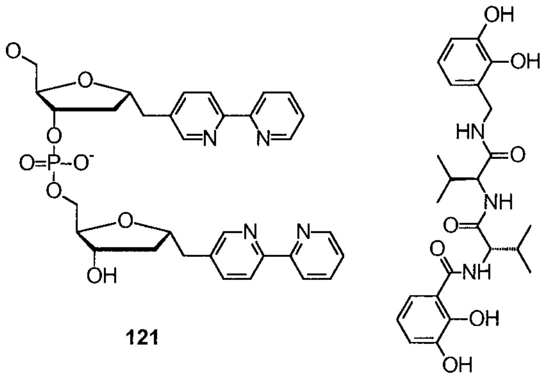
VIII. Conclusions

Double- and triple-stranded helicates and related oligonuclear metallosupramolecular coordination compounds possess fascinating structures and are excellent model systems for the study of mechanisms in supramolecular chemistry.

The formation of helicates in some cases proceeds in cooperative self-assembly processes, although examples are known where the special features of the ligand strands lead to a noncooperative "stepwise" formation of the oligonuclear complexes. If the formation of the helicates is directed by templates, dynamic combinatorial chemistry is the principle which controls the specific formation of defined coordination compounds and not of mixtures of oligomers or polymers.

The use of sequential or directional ligands for helicate formation leads to questions regarding the regioselectivity of self-assembly processes. The regiochemistry can be controlled either by steric interactions between ligand strands, special geometric features of the ligands and/or metals, or by the molecular recognition of electronically different binding sites by different metal ions.

Supramolecular stereochemistry is important for the specific formation of chiral helicates versus achiral meso-helicates. Most helicate-type complexes are obtained with high diastereoselectivity. Here, different mechanisms can influence the relative configuration of complex units. The diastereoselectivity can be controlled by rigid ligands, by the ligand spacer (even versus odd length of alkyl spacers), or by templates. Introducing chiral substituents at the spacer allows the formation of diasteromerically and enantiomerically pure helicates.



121

122-H_4

Figure 61.

Mixtures of ligands can be used in self-recognition studies to obtain a self-sorting of the ligands in selective reactions. In highly specific reactions either homoleptic complexes are formed by self-recognition or heteroleptic complexes are formed by self-discrimination. Here, the number of binding sites at the ligand, the separation of the binding sites, geometric constraints, or templating effects play an important role in the formation of specific oligonuclear complexes.

Just recently substructures of nucleic acids or of peptides were introduced into helicate chemistry. Ligands such as **121** or **122** form double-stranded $[Ag_2\mathbf{121}_2]^{2+}$ [255] or triple-stranded $[Ti_2\mathbf{122}_3]^{4-}$ helicate-type complexes (Figure 61).[256] Future investigations will show if compounds of this type can interact with biological systems.

All of the described mechanistic and structural studies are important to gain deeper insight into the chemistry of helicates, which is necessary to be able to use them for future applications. The first studies on helicates regarding electron-transfer properties, liquid crystalline behavior, or the potential for their use in organic synthesis (e.g., synthesis of molecular knots) give an indication as to which direction this chemistry might develop in the future. However, the mechanistic findings in helicate chemistry help to rationally construct even larger metallosupramolecular architectures which grow into nanometer dimensions and are able to act as catalysts or stabilize unusual or highly reactive molecular species.[13,14,257]

IX. Addendum

A series of papers regarding helicate chemistry has appeared since the submission of this manuscript.

The pyridine/imine ligand **123** was shown to form an arc-shaped double-stranded helicate $[Cu_2\mathbf{123}_2]^{2+}$ which by $\pi-\pi$-interaction forms a cyclic tetramer $\{[Cu_2\mathbf{123}_2]_4\}^{8+}$ in the solid state (Figure 62).[258]

Ligands **124** and **125** (and some related ligands) form double-stranded dinuclear complexes with copper(I) ions. Here, the structure of a double-stranded helicate is observed for $[Cu_2\mathbf{124}_2]^{2+}$ in the solid state. For the complex of **125**, a heterochiral meso-helicate $[Cu_2(R\text{-}\mathbf{125})(S\text{-}\mathbf{125})]^{2+}$ is found in the crystal while

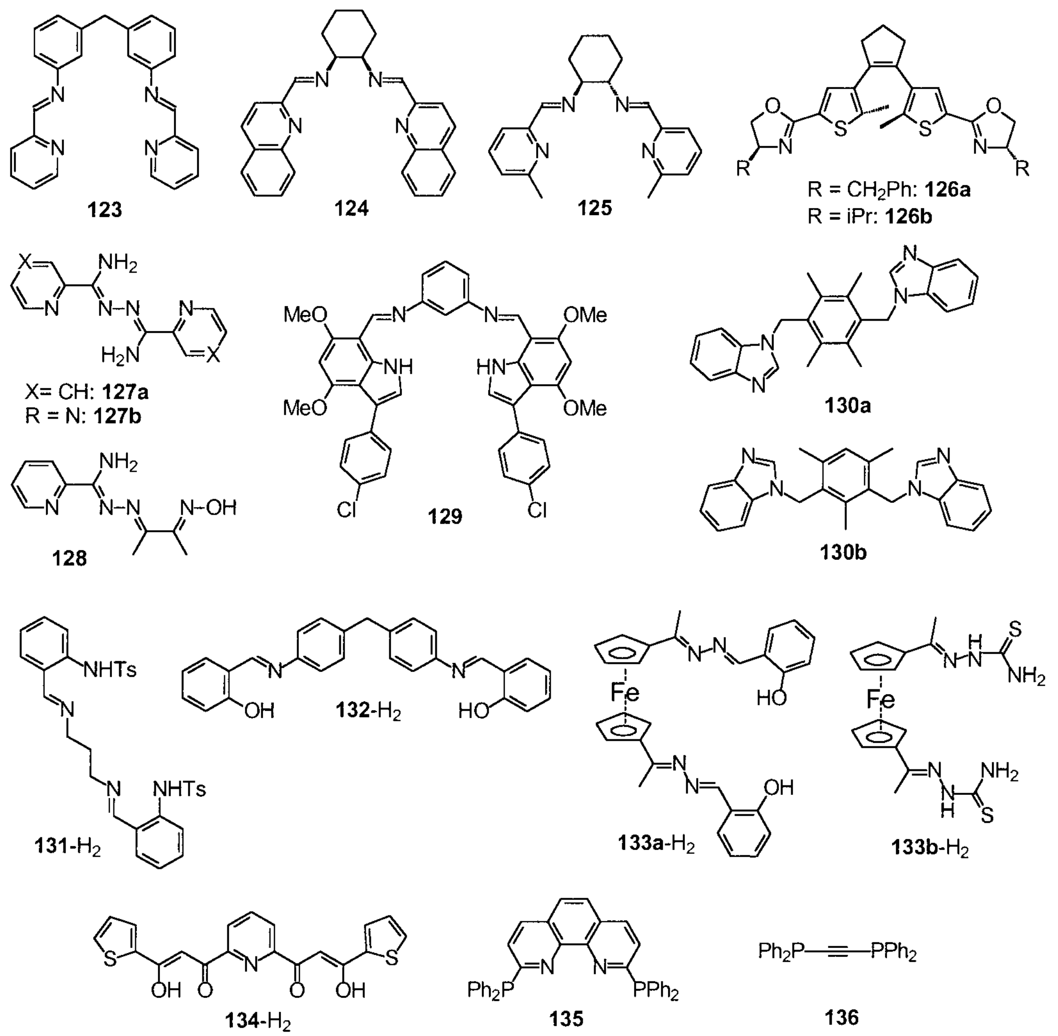


Figure 62.

NMR spectroscopy indicates that only helical homochiral complexes $[Cu_2(R\text{-}\mathbf{125})_2]^{2+}$ and $[Cu_2(S\text{-}\mathbf{125})_2]^{2+}$ are present in solution. This shows that a fast rearrangement occurs during dissolving or crystallizing the complex.[259]

The copper(I) complexes of **124** and **125** can be switched electrochemically showing molecular hysteresis, e.g., two-electron oxidation of $[Cu_2\mathbf{124}_2]^{2+}$ leads to $[Cu_2\mathbf{124}_2]^{4+}$ which rearranges to form the corresponding mononuclear compound $[Cu\mathbf{124}]^{2+}$ which can be reduced to form $[Cu\mathbf{124}]^{+}$. This species undergoes a rearrangement reaction to obtain the dinuclear $[Cu_2\mathbf{124}_2]^{2+}$ again.[259]

The double-stranded helicates $[Cu_2(\mathbf{126a,b})_2]^{2+}$ possess two linearly dicoordinated copper(I) centers which bind to the oxazoline nitrogen atoms. During irradiation (313 nm), the 1,2-dithienylethene moiety undergoes an electrocyclic ring closure and the stereochemistry of this reaction is controlled by the metal complex units.[260]

Depending on reaction conditions, different helicates are made from ligands **127a,b** and **128**. Either double-stranded coordination compounds with coligands $[(Cd(H_2O)(NO_3))_2\mathbf{127a}_2]^{2+}$ and $[(MnCl_2)_2\mathbf{128}_2]$ or triple-stranded complexes $[Zn_2\mathbf{127a}_3]^{4+}$ and $[Ni_2\mathbf{128}_3]^{4+}$ are obtained.[261] In the case of the complexes of sequential ligand **128**, antiparallel orientation of the ligand strands is observed in the solid-state structures[261] as expected.[232]

A series of imine/indole-based ligands was prepared to obtain double-stranded helicate-type coordination compounds. Here, the X-ray structure of the meso-helicate $[Ni_2\mathbf{129}_2]$ could be investigated.[262]

130a forms a linear triple-stranded complex $[Ag_2\mathbf{130a}_3]^{2+}$ with trigonal planar silver centers, and **130b** yields a quadruple-stranded linear complex $[Cu_2\mathbf{130b}_4]^{4+}$. Both compounds possess the structure of a molecular box and are able to encapsulate anionic guests.[263]

The double-stranded dinuclear helicate $[Ni_2\mathbf{131}_2]$ is obtained by electrochemical methods.[264]

The phenolate/imine ligand **132**-H$_2$ leads to neutral double-stranded helicates $[M_2\mathbf{132}_2]$ (M = Cu(II), Co(II)) which were characterized by X-ray structure analysis.[265] Ligand **133a**-H$_2$ also possesses an imine/phenolate binding site and forms the corresponding copper(II) helicate $[Cu_2\mathbf{133a}_2]$ with ferrocene units in the spacer.[266] The related complex $[Zn_2\mathbf{133b}_2]$ was also described.[267]

A triple-stranded metallacryptate $\{K\subset[Fe_2\mathbf{134}_3]\}^{+}$ was obtained from the thiophene-substituted ligand **134**-H$_2$.[268]

Chiral, enantiomerically pure (or enriched) helicates were obtained by induction of chirality at

$[\mathrm{Ga}_2\mathbf{92a}_3]^{6-}$ with the chiral (*S*)-*N*-methylnicotinium cation[269] or by separation of the enantiomers by chromatography on paper.[270]

The phosphane ligands **135** and **136** form triple-stranded gold(I) $[\mathrm{Au}_2\mathbf{135}_3]^{2+}$ or silver(I) $[\mathrm{Ag}_2\mathbf{136}_3]^{2+}$ complexes. The metal centers are trigonal-planar with three phosphane units coordinating. Here, $[\mathrm{Au}_2\mathbf{135}_3]^{2+}$ is able to trap linearly coordinated mercury(0) in its interior[271] while $[\mathrm{Ag}_2\mathbf{136}_3]^{2+}$ undergoes ring-opening polymerization to form a coordination polymer.[272]

X. Acknowledgments

Since the introduction of “helicates” by Lehn, many groups entered this very interesting field of self-assembly which is directed by metals. The wonderful work by those who are engaged with helicate chemistry is cited in the reference list.

I especially thank my co-workers Dr. Cyrill Riether, Dr. Oliver Blau, Dr. Matthias Schneider, Matthias Napp, Oliver Spie*β*, Karen Witt, Jeanette Zauner, and Michael Wagner. Their commitment to this chemistry enabled me to have my own small input in this field. Many collaborations with groups in Germany (Dr. Roland Fröhlich/Münster; Dr. Herbert Röttele, Prof. Manfred Kappes, Dr. Patrick Weis/Karlsruhe) and outside (Prof. Kari Rissanen, Dr. Sirpa Kotila, Dr. Elina Wegelis, Dr. Maija Nissinen/Jyväskylä, Finland; Dr. Peter Burger, Zürich, Switzerland) contributed to the success of this work.

Finally, I have to thank the institutions—Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie—which provided the money for our research.

XI. References

(1) Jung, J. H.; Ono, Y.; Shinkai, S. *Chem. Eur. J.* **2000**, *6*, 4552−4557.
(2) Meurer, K. P.; Vögtle, F. *Top. Curr. Chem.* **1985**, *127*, 1.
(3) Wu, H.-C. H.; Sarko, A. *Carbohydr. Res.* **1978**, *61*, 27−40.
(4) Watson, J. D.; Crick, F. C. H. *Nature* **1953**, *171*, 737−738.
(5) Fersht, A. *Structure and Mechanism in Protein Science*; W. H. Freeman: New York, 1998.
(6) Berl, V.; Huc, I.; Khoury, R. G.; Krische, M. J.; Lehn, J.-M. *Nature* **2000**, *407*, 720−723.
(7) (a) Hanessian, S.; Gomtsyan, A.; Simard, M.; Roelens, S. *J. Am. Chem. Soc.* **1994**, *116*, 4495−4496. (b) Hanessian, S.; Simard, M.; Roelens, S. *J. Am. Chem. Soc.* **1995**, *117*, 7630−7645.
(8) (a) Rowan, I. E.; Nolte, R. J. M. *Angew. Chem.* **1998**, *110*, 65−71; *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 62−68. (b) Feiters, M. C.; Nolte, R. J. M. *Adv. Supramol. Chem.* **2000**, *6*, 41−156.
(9) Lehn, J.-M. *Chem. Eur. J.* **2000**, *6*, 2097−2102.
(10) (a) Constable, E. C. *Tetrahedron* **1992**, *48*, 10013−10059. (b) Piguet, C. *J. Inclusion Phenom. Macrocyclic Chem.* **1999**, *34*, 361−391. (c) Williams, A. F. *Chimia* **2000**, *54*, 585−588. (d) Constable, E. In *Templating, Self-assembly and Self-organization*; Sauvage, J.-P., Hosseini, M. W., Eds.; Pergamon Press: Oxford, 1996; Vol. 9.
(11) Piguet, C.; Bernardinelli, G.; Hopfgartner, G. *Chem. Rev.* **1997**, *97*, 2005−2062.
(12) Albrecht, M. *Chem. Soc. Rev.* **1998**, *27*, 281−288.
(13) Caulder, D.; Raymond, K. N. *J. Chem. Soc., Dalton Trans.* **1999**, 1185−1200.
(14) Saalfrank, R. W.; Demleitner, B. In *Transition Metals in Supramolecular Chemistry*; Sauvage, J.-P., Ed.; John Wiley & Sons: New York, 1999; Vol. 5.
(15) Albrecht, M. *J. Inclusion Phenom. Macrocyclic Chem.* **2000**, *36*, 127−151.
(16) Mamula, O.; Monlien, F. J.; Porquet, A.; Hopfgartner, G.; Merbach, A. E.; Von Zelewsky, A. *Chem. Eur. J.* **2001**, *7*, 533−539.
(17) Lehn, J.-M.; Rigault, A.; Siegel, J.; Harrowfield, J.; Chevrier, B.; Moras, D. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 2565−2569.
(18) Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem.* **2000**, *112*, 3484−3530; *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 3348−3391.
(19) Lehn, J.-M. *Supramolecular Chemistry*; VCH: Weinheim, 1995.
(20) Hasenknopf, B.; Lehn, J.-M.; Kneisel, B. O.; Baum, G.; Fenske, D. *Angew. Chem.* **1996**, *108*, 1987−1990; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1838−1840.
(21) Chambron, J.-C.; Dietrich-Buchecker, C. O.; Sauvage, J.-P. In *Templating, Self-assembly and Self-organization*; Sauvage, J.-P., Hosseini, M. W., Eds.; Pergamon Press: Oxford, 1996; Vol. 9.
(22) (a) Libman, J.; Tor, Y.; Shanzer, A. *J. Am. Chem. Soc.* **1987**, *109*, 5880−5881. (b) Zelikovich, L.; Libman, J.; Shanzer, A. *Nature* **1995**, *374*, 790−792. (c) Woods, C. R.; Benaglia, M.; Cozzi, F.; Siegel, J. *Angew. Chem.* **1996**, *108*, 1977−1980; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1830−1833. (d) Blanc, S.; Yakirevich, P.; Leize, E.; Meyer, M.; Libman, J.; Van Dorsselaer, A.; Albrecht-Gary, A.-M.; Shanzer, A. *J. Am. Chem. Soc.* **1997**, *119*, 4934−4944. (e) Annunziata, R.; Benaglia, M.; Cinquini, M.; Cozzi, F.; Woods, C. R.; Siegel, J. *Eur. J. Org. Chem.* **2001**, 173−180.
(23) Werner, A. *Z. Anorg. Chem.* **1893**, *3*, 267.
(24) Von Zelewsky, A. *Stereochemistry of Coordination Compounds*; John Wiley & Sons: New York, 1996.
(25) Constable, E. C. *Metal and Ligand Reactivity*; VCH: Weinheim, 1995.
(26) Albrecht, M. *Chem. Eur. J.* **2000**, *6*, 3485−3489.
(27) Zarges, W.; Hall, J.; Lehn, J.-M.; Bolm, C. *Helv. Chim. Acta* **1991**, *74*, 1843−1852.
(28) Xu, J.; Parac, T. N.; Raymond, K. N. *Angew. Chem.* **1999**, *111*, 3055−3058; *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2878−2882.
(29) Owens, T. D.; Hollander, F. J.; Oliver, A. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2001**, *123*, 1539−1540.
(30) Struckmeier, G.; Thewalt, U.; Fuhrhop, J.-H. *J. Am. Chem. Soc.* **1976**, *98*, 278−279.
(31) Sheldrick, W. S.; Engel, J. *J. Chem. Soc., Chem. Commun.* **1980**, 5−6.
(32) Van Stein, G. C.; Van der Poel, H.; Van Koten, G.; Spek, A. L.; Duisenberg, A. J. M.; Pregosin, P. S. *J. Chem. Soc., Chem. Commun.* **1980**, 1016−1018.
(33) Lehn, J.-M.; Sauvage, J.-P.; Simon, J.; Ziessel, R. *Nouv. J. Chim.* **1983**, *7*, 413−420.
(34) Atkin, C. L.; Neilands, J. B. *Biochemistry* **1968**, *7*, 3734.
(35) Matzanke, B. F.; Müller-Matzanke, G.; Raymond, K. N. In *Iron Carriers and Iron Proteins*; Loehr, T. M., Ed.; VCH: New York, 1989.
(36) Carrano, C. J.; Raymond, K. N. *J. Am. Chem. Soc.* **1978**, *100*, 5371−5374.
(37) Scarrow, R. C.; White, D. L.; Raymond, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 6540−6546.
(38) Vögtle, F. *Supramolekulare Chemie*; Teubner Verlag: Stuttgart, 1992.
(39) Krämer, R.; Lehn, J.-M.; DeCian, A.; Fischer, J. *Angew. Chem.* **1993**, *105*, 764−767; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 703−706.
(40) Lehn, J.-M.; Rigault, A. *Angew. Chem.* **1988**, *100*, 1121−1122; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1095−1097.
(41) Garrett, T. M.; Koert, U.; Lehn, J.-M.; Rigault, A.; Meyer, D.; Fischer, J. *J. Chem. Soc., Chem. Commun.* **1990**, 557−558.
(42) (a) Pfeil, A.; Lehn, J.-M. *J. Chem. Soc., Chem. Commun.* **1992**, 838−840. (b) Fatin-Rouge, N.; Blanc, S.; Pfeil, A.; Rigault, A.; Albrecht-Gary, A.-M.; Lehn, J. M. *Helv. Chim. Acta* **2001**, *84*, 1694−1711.
(43) Lindsey, J. S. *New J. Chem.* **1991**, *15*, 153−180.
(44) Perlmutter-Hayman, B. *Acc. Chem. Res.* **1986**, *19*, 90−96.
(45) Marquis-Rigault, A.; Dupont-Gervais, A.; Van Dorsselaer, A.; Lehn, J.-M. *Chem. Eur. J.* **1996**, *2*, 1395−1398.
(46) Harding, M. M.; Koert, U.; Lehn, J.-M.; Marquis-Rigault, A.; Piguet, C.; Siegel, J. *Helv. Chim. Acta* **1991**, *74*, 594−610.
(47) Koert, U.; Harding, M. M.; Lehn, J.-M. *Nature* **1990**, *346*, 339−42.
(48) Schoentjes, B.; Lehn, J.-M. *Helv. Chim. Acta* **1995**, *78*, 1−12.
(49) Eisenbach, C. D.; Schubert, U. S.; Baker, G. R.; Newkome, G. R. *J. Chem. Soc., Chem. Commun.* **1995**, 69.
(50) Sanchez-Quesade, J.; Seel, C.; Prados, P.; de Mendoza, J.; Dalcol, I.; Giralt, E. *J. Am. Chem. Soc.* **1996**, *118*, 277−278.
(51) Greenwald, M.; Eassa, M.; Katz, E.; Willner, I.; Cohen, Y. *J. Electroanal. Chem.* **1997**, *434*, 77−82.
(52) Greenwald, M.; Wessely, D.; Goldberg, I.; Cohen, Y. *New J. Chem.* **1999**, *23*, 337−344.
(53) Greenwald, M.; Wessely, D.; Katz, E.; Willner, I.; Cohen, Y. *J. Org. Chem.* **2000**, *65*, 1050−1058.
(54) Shaul, M.; Cohen, Y. *J. Org. Chem.* **1999**, *64*, 9358−9364.
(55) Stiller, R.; Lehn, J.-M. *Eur. J. Inorg. Chem.* **1998**, 977−982.
(56) Smith, V. C. M.; Lehn, J.-M. *Chem. Commun.* **1996**, 2733−2734.
(57) Bilyk, A.; Harding, M. M.; Turner, P.; Hambley, T. W. *J. Chem. Soc., Dalton Trans.* **1994**, 2783−2790.
(58) Bilyk, A.; Harding, M. M.; Turner, P.; Hambley, T. W. *J. Chem. Soc., Dalton Trans.* **1995**, 2549−2553.

(59) (a) Bilyk, A.; Harding, M. M. *J. Chem. Soc., Chem. Commun.* **1995**, 1697−1698. (b) Houghton, M. A.; Bilyk, A.; Harding, M. M.; Turner, P.; Hambley, T. W. *J. Chem. Soc., Dalton Trans.* **1997**, 2725−2733.
(60) (a) Ganesan, A. *Angew. Chem.* **1998**, *110*, 1989−2992; *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2828−2831. (b) Sanders, J. K. M. *Chem. Eur. J.* **1998**, *4*, 1378. (c) Eliseev, A. V.; Lehn, J. M. *Curr. Top. Microbiol. Immunol.* **1999**, *243*, 159−172.
(61) Lehn, J.-M. *Chem. Eur. J.* **1999**, *5*, 2455−2463.
(62) Try, A. C.; Harding, M. M.; Hamilton, D. G.; Sanders, J. K. M. *Chem. Commun.* **1998**, 723−724.
(63) Baxter, P. N. W.; Lehn, J.-M.; Rissanen, K. *Chem. Commun.* **1997**, 1323−1324.
(64) Yongbing, H.; Lehn, J.-M. *Chem. J. Chinese Univ. (Engl. Ed.)* **1990**, *6*, 183−187.
(65) Youinou, M. T.; Ziessel, R.; Lehn, J.-M. *Inorg. Chem.* **1991**, *30*, 2144−2148.
(66) Funeriu, D.-P.; He, Y.-B.; Bister, H.-J.; Lehn, J.-M. *Bull. Soc. Chim. Fr.* **1996**, *133*, 673−678.
(67) Hasenknopf, B.; Lehn, J.-M.; Boumediene, N.; Leize, E.; Van Dorsselaer, A. *Angew. Chem.* **1998**, *110*, 3458−3460; *Angew. Chem., Int. Ed.* **1998**, *37*, 3265−3268.
(68) (a) Serr, B. R.; Andersen, K. A.; Elliott, C. M.; Anderson, O. P. *Inorg. Chem.* **1988**, *27*, 4499−4504. (b) Elliott, C. M.; Derr, D. L.; Ferrere, S.; Newton, M. D.; Liu, Y.-P. *J. Am. Chem. Soc.* **1996**, *118*, 5221−5228.
(69) Larson, S. L.; Hendrickson, S. M.; Ferrere, S.; Derr, D. L.; Elliott, C. M. *J. Am. Chem. Soc.* **1995**, *117*, 5881−5882.
(70) Jodry, J. J.; Lacour, J. *Chem. Eur. J.* **2000**, *6*, 4297−4304.
(71) Albrecht, M.; Riether, C. *Chem. Ber.* **1996**, *129*, 829−832.
(72) (a) Constable, E. C.; Hannon, M. J.; Tocher, D. A. *J. Chem. Soc., Dalton Trans.* **1993**, 1883−1890. (b) Constable, E. C.; Hannon, M. J.; Edwards, A. J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1994**, 2669−2677.
(73) Zurita, D.; Baret, P.; Pierre, J.-L. *New J. Chem.* **1994**, *18*, 1143−1146.
(74) (a) Hayoz, P.; Von Zelewsky, A. *Tetrahedron Lett.* **1992**, *33*, 5165−5168. (b) Baret, P.; Einhorn, J.; Gellon, G.; Pierre, J.-L. *Synthesis* **1998**, 431−435.
(75) Mürner, H.; Von Zelewsky, A.; Hopfgartner, G. *Inorg. Chim. Acta* **1998**, *271*, 36−39.
(76) Baret, P.; Gaude, D.; Gellon, G.; Pierre, J.-L. *New J. Chem.* **1997**, *21*, 1255−1257.
(77) Baum, G.; Constable, E. C.; Fenske, D.; Housecroft, C. E.; Kulke, T. *Chem. Commun.* **1999**, 195−196.
(78) Potts, K. T.; Raiford, K. A. G.; Keshavarz-K, M. *J. Am. Chem. Soc.* **1993**, *115*, 2793−2807.
(79) Hannon, M. J.; Painting, C. L.; Errington, W. *Chem. Commun.* **1997**, 307−308.
(80) Potts, K. T.; Keshavarz-K, M.; Tham, F. S.; Abruna, H. D.; Arana, C. R. *Inorg. Chem.* **1993**, *32*, 4450−4456.
(81) Constable, E. C.; Edwards, A. J.; Hannon, M. J.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1994**, 1991−1992.
(82) Baum, G.; Constable, E. C.; Fenske, D.; Housecroft, C. E.; Kulke, T. *Chem. Commun.* **1998**, 2659−2660.
(83) Baum, G.; Constable, E. C.; Fenske, D.; Housecroft, C. E.; Kulke, T.; Neuburger, M.; Zehnder, M. *J. Chem. Soc., Dalton Trans.* **2000**, 945−959.
(84) Constable, E. C.; Kulke, T.; Neuburger, M.; Zehnder, M. *Chem. Commun.* **1997**, 489−490.
(85) Crane, J. D.; Sauvage, J.-P. *New J. Chem.* **1992**, *16*, 649−650.
(86) Rapenne, G.; Patterson, B. T.; Sauvage, J.-P.; Keene, F. R. *Chem. Commun.* **1999**, 1853−1854.
(87) Hasenknopf, B.; Lehn, J.-M. *Helv. Chim. Acta* **1996**, *79*, 1643−1650.
(88) Ho, P. K.-K.; Peng, S.-M.; Wong, K.-Y.; Che, C.-M. *J. Chem. Soc., Dalton Trans.* **1996**, 1829−1834.
(89) Potts, K. T.; Horwitz, C. P.; Fessak, A.; Keshavarz-K, M.; Nash, K. E.; Toscano, P. J. *J. Am. Chem. Soc.* **1993**, *115*, 10444−10445.
(90) (a) Constable, E. C.; Hannon, M. J.; Martin, A.; Raithby, P. R.; Tocher, D. A. *Polyhedron* **1992**, *11*, 2967−2971. (b) Constable, E. C.; Elder, S. M.; Hannon, M. J.; Martin, A.; Raithby, P. R.; Tocher, D. A. *J. Chem. Soc., Dalton Trans.* **1996**, 2423−2433.
(91) Potts, K. T.; Keshavarz-K, M.; Tham, F. S.; Abruna, H. D.; Arana, C. R. *Inorg. Chem.* **1993**, *32*, 4422−4435.
(92) (a) Constable, E. C.; Heirtzler, F. R.; Neuburger, M.; Zehnder, M. *Supramol. Chem.* **1995**, *5*, 197−200. (b) Constable, E. C.; Heirtzler, F. R.; Neuburger, M.; Zehnder, M. *Chem. Commun.* **1996**, 933−934. (c) Constable, E. C.; Heirtzler, F. R.; Neuburger, M.; Zehnder, M. *J. Am. Chem. Soc.* **1997**, *119*, 5606−5617.
(93) Hung, C.-Y.; Wang, T.-L.; Shi, Z.; Thummel, R. P. *Tetrahedron* **1994**, *50*, 10685−10692.
(94) Baum, G.; Constable, E. C.; Fenske, D.; Kulke, T. *Chem. Commun.* **1997**, 2043−2044.
(95) Constable, E. C.; Elder, S. M.; Walker, J. V.; Wood, P. D.; Tocher, D. A. *J. Chem. Soc., Chem. Commun.* **1992**, 229−231.
(96) Constable, E. C.; Elder, S. M.; Healy, J.; Ward, M. D.; Tocher, D. A. *J. Am. Chem. Soc.* **1990**, *112*, 4590−4592.
(97) Fu, Y.; Sun, J.; Chen, Y.; Dai, W.; Wang, D.; Mak, T. C. W.; Tang, W.; Hu, H. *J. Chem. Soc., Dalton Trans.* **1996**, 2309−2313.
(98) Potts, K. T.; Keshavarz-K, M.; Tham, F. S.; Abruna, H. D.; Arana, C. R. *Inorg. Chem.* **1993**, *32*, 4436−4449.
(99) Ho, P. K.-K.; Cheung, K.-K.; Che, C.-M. *Chem. Commun.* **1996**, 1197−1198.
(100) Constable, E. C.; Neuburger, M.; Whall, L.; Zehnder, M. *New J. Chem.* **1998**, *22*, 219−220.
(101) Constable, E. C.; Edwards, A. J.; Raithby, P. R.; Walker, J. V. *Angew. Chem.* **1993**, *105*, 1486-1487; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1465−1466.
(102) Constable, E. C.; Walker, J. V. *J. Chem. Soc., Chem. Commun.* **1992**, 884−886.
(103) Constable, E. C.; Edwards, A. J.; Raithby, P. R.; Smith, D. R.; Walker, J. V.; Whall, L. *Chem. Commun.* **1996**, 2551−2552.
(104) Bell, T. W.; Jousselin, H. *Nature* **1994**, *367*, 441−444.
(105) Constable, E. C. *Nature* **1994**, *367*, 415−416.
(106) Constable, E. C.; Chotalia, R. *J. Chem. Soc., Chem. Commun.* **1992**, 64−66.
(107) Constable, E. C.; Ward, M. D.; Tocher, D. A. *J. Chem. Soc., Dalton Trans.* **1991**, 1675−1683.
(108) Constable, E. C.; Edwards, A. J.; Martinez-Manez, R.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1995**, 3253−3261.
(109) Chotalia, R.; Constable, E. C.; Neuburger, M.; Smith, D. R.; Zehnder, M. *J. Chem. Soc., Dalton Trans.* **1996**, 4207−4216.
(110) Potts, K. T.; Keshavarz-K, M.; Tham, F. S.; Raiford, K. A. G.; Arana, C. R.; Abruna, H. D. *Inorg. Chem.* **1993**, *32*, 5477−5484.
(111) Constable, E. C.; Neuburger, M.; Smith, D. R.; Zehnder, M. *Chem. Commun.* **1996**, 1917−1918.
(112) Potts, K. T.; Wentland, M. P.; Ganguly, D.; Storrier, G. D.; Cha, S. K.; Cha, J.; Abruna, H. D. *Inorg. Chim. Acta* **1999**, *288*, 189−199.
(113) Hannon, M. J.; Painting, C. L.; Jackson, A.; Hamblin, J.; Errington, W. *Chem. Commun.* **1997**, 1807−1808.
(114) Bowyer, P. K.; Porter, K. A.; Rae, A. D.; Willis, A. C.; Wild, S. B. *Chem. Commun.* **1998**, 1153−1154.
(115) Masood, M. A.; Enemark, E. J.; Stack, T. D. P. *Angew. Chem.* **1998**, *110*, 973−977; *Angew. Chem., Int. Ed.* **1998**, *37*, 928−932.
(116) (a) Ziessel, R.; Harriman, A.; Suffert, J.; Youinou, M. T.; De Cian, A.; Fischer, J. *Angew. Chem.* **1997**, *109*, 2612−2623; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2509−2511. (b) Ziessel, R.; Suffert, J. *J. Chem. Soc., Chem. Commun.* **1990**, 1105−1107.
(117) Ameerunisha, S.; Schneider, J.; Meyer, T.; Zacharias, P. S.; Bill, E.; Henkel, G. *Chem. Commun.* **2000**, 2155−2156.
(118) (a) El-ghayouy, A.; Douce, L.; Skoulios, A.; Ziessel, R. *Angew. Chem.* **1998**, *110*, 2327−2331; *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2205−2208. (b) Ziessel, R. *Coord. Chem. Rev.* **2001**, *216/217*, 195−223.
(119) Ziessel, R.; Harriman, A.; El-ghayouy, A.; Douce, L.; Leize, E.; Nierengarten, H.; Van Dorsselaer, A. *New J. Chem.* **2000**, *24*, 729−732.
(120) El-ghayouy, A.; Harriman, A.; De Cian, A.; Fischer, J.; Ziessel, R. *J. Am. Chem. Soc.* **1998**, *120*, 9973−9974.
(121) Cheng, H.; Chun-Ying, D.; Chen-Jie, F.; Quin-Jin, M. *J. Chem. Soc., Dalton Trans.* **2000**, 2419−2424.
(122) Hannon, M. J.; Painting, C. L.; Alcock, N. W. *Chem. Commun.* **1999**, 2023−2024.
(123) Hannon, M. J.; Bunce, S.; Clarke, A. I.; Alcock, N. W. *Angew. Chem.* **1999**, *111*, 1353−1355; *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1277−1278.
(124) (a) Shu, M.-H.; Sun, W.-Y.; Duan, C.-Y.; Fu, Y.-J.; Zhang, W.-J.; Tang, W.-X. *J. Chem. Soc., Dalton Trans.* **1999**, 729−734. (b) Shu, M.-H.; Sun, W.-Y.; Duan, C.-Y.; Tang, W.-X.; Zhang, W.-J. *Transition Met. Chem.* **1999**, *24*, 628−632.
(125) Bark, T.; Weyhermüller, T.; Heirtzler, F. R. *Chem. Commun.* **1998**, 1475−1476.
(126) Khoury, R. G.; Jaquinod, L.; Smith, K. M. *Tetrahedron* **1998**, *54*, 2339−2346.
(127) Zhang, Y.; Thompson, A.; Rettig, S. J.; Dolphin, D. *J. Am. Chem. Soc.* **1998**, *120*, 13537−13538.
(128) Thompson, A.; Dolphin, D. *J. Org. Chem.* **2000**, *65*, 7870−7877.
(129) Thompson, A.; Dolphin, D. *Org. Lett.* **2000**, *2*, 1315−1318.
(130) Lam, M. H. W.; Cheung, S. T. C.; Fung, K.-M.; Wong, W.-T. *Inorg. Chem.* **1997**, *36*, 4618−4619.
(131) Solanki, N. K.; Wheatley, A. N. H.; Radojevic, S.; McPartlin, M.; Halcrow, M. A. *J. Chem. Soc., Dalton Trans.* **1999**, 521−524.
(132) Carina, R. F.; Bernardinelli, G.; Williams, A. F. *Angew. Chem.* **1993**, *105*, 1483−1485; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1463−1465.
(133) Rüttimann, S.; Piguet, C.; Bernardinelli, G.; Bocquet, B.; Williams, A. F. *J. Am. Chem. Soc.* **1992**, *114*, 4230−4237.
(134) Carina, R. F.; Williams, A. F.; Piguet, C. *Helv. Chim. Acta* **1998**, *81*, 548−557.
(135) (a) Provent, C.; Hewage, S.; Brand, G.; Bernardinelli, G.; Charbonniere, L. J.; Williams, A. F. *Angew. Chem.* **1997**, *109*, 1346−1348; *Angew. Chem., Int. Ed.* **1997**, *36*, 1287−1289. (b) Provent, C.; Rivara-Minten, E.; Hewage, S.; Brunner, G.; Williams, A. F. *Chem. Eur. J.* **1999**, *5*, 3487−3494.

(136) Oshio, H.; Yamamoto, M.; Ito, T. *J. Chem. Soc., Dalton Trans.* **1999**, 2641−2644.
(137) Oshio, H.; Yaginuma, T.; Ito, T. *Inorg. Chem.* **1999**, *38*, 2050−2052.
(138) Rice, C. R.; Wörl, S.; Jeffery, J. C.; Paul, R. L.; Ward, M. D. *Chem. Commun.* **2000**, 1529−1530.
(139) Rice, C. R.; Wörl, S.; Jeffery, J. C.; Paul, R. L.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **2001**, 550−559.
(140) Haga, M.-A.; Hiratsuka, K.; Kato, M.; Kurosaki, H.; Goto, M.; Arakawa, R.; Yano, S. *Chem. Lett.* **1995**, 1143−1144.
(141) Williams, A. F.; Piguet, C.; Bernardinelli, G. *Angew. Chem* **1991**, *103*, 1530; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1490−1492.
(142) (a) Charbonniere, L. J.; Bernardinelli, G.; Piguet, C.; Sargeson, A. M.; Williams, A. F. *J. Chem. Soc., Chem. Commun.* **1994**, 1419−1420. (b) Charbonniere, L. J.; Gilet, M.-F.; Bernauer, K.; Williams, A. F. *Chem. Commun.* **1996**, 39−40.
(143) Charbonniere, L. J.; Williams, A. F.; Frey, U.; Merbach, A. E.; Kamalaprija, P.; Schaad, O. *J. Am. Chem. Soc.* **1997**, *119*, 2488−2496.
(144) Charbonniere, L. J.; Williams, A. F.; Piguet, C.; Bernardinelli, G.; Rivara-Minten, E. *Chem. Eur. J.* **1998**, *4*, 485−493.
(145) Yang, S.-P.; Chen, X.-M.; Ji, L.-N. *J. Chem. Soc., Dalton Trans.* **2000**, 2337−2344.
(146) Franceschi, F.; Guillemtot, G.; Solari, E.; Floriani, C.; Re, N.; Birkedal, H.; Pattison, P. *Chem. Eur. J.* **2001**, *7*, 1468−1478.
(147) Fleming, J. S.; Mann, K. L. V.; Couchman, S. M.; Jeffery, J. C.; McCleverty, J. A.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1998**, 2047−2052.
(148) Paul, R. L.; Couchman, S. M.; Jeffery, J. C.; McCleverty, J. A.; Reeves, Z. A.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **2000**, 845−851.
(149) Fleming, J. S.; Psillakis, E.; Jeffery, J. C.; Mann, K. L. V.; McCleverty, J. A.; Ward, M. D. *Polyhedron* **1998**, *17*, 1705−1714.
(150) Baker, A. T.; Craig, D. C.; Dong, G. *Inorg. Chem.* **1996**, *35*, 1091−1092.
(151) (a) Psillakis, E.; Jeffery, J. C.; McCleverty, J. A.; Ward, M. D. *Chem. Commun.* **1997**, 479−480. (b) Fleming, J. S.; Psillakis, E.; Couchman, S. M.; Jeffery, J. C.; McCleverty, J. A.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1998**, 537−543.
(152) O'Keefe, B. J.; Steel, P. J. *Inorg. Chem. Commun.* **2000**, *3*, 473−475.
(153) Piguet, C.; Bünzli, J.-C. G. *Chimia* **1998**, *52*, 579−584.
(154) Piguet, C.; Edder, C.; Rigault, S.; Bernardinelli, G.; Bünzli, J.-C. G.; Hopfgartner, G. *J. Chem. Soc., Dalton Trans.* **2000**, 3999−4006.
(155) Bernardinelli, G.; Piguet, C.; Williams, A. F. *Angew. Chem.* **1992**, *104*, 1662; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1622−1624.
(156) Piguet, C.; Bünzli, J.-C. G.; Bernardinelli, G.; Hopfgartner, G. *J. Am. Chem. Soc.* **1993**, *115*, 8197−8206.
(157) Martin, N.; Bünzli, J.-C. G.; McKee, V.; Piguet, C.; Hopfgartner, G. *Inorg. Chem.* **1998**, *37*, 577−589.
(158) (a) Elhabiri, M.; Scopelliti, R.; Bünzli, J.-C. G.; Piguet, C. *Chem. Commun.* **1998**, 2347−2348. (b) Elhabiri, M.; Scopelliti, R.; Bünzli, J.-C. G.; Piguet, C. *J. Am. Chem. Soc.* **1999**, *121*, 10747−10762.
(159) Iglesias, C. P.; Elhabiri, M.; Hollenstein, M.; Bünzli, J.-C. G.; Piguet, C. *J. Chem. Soc., Dalton Trans.* **2000**, 2031−2043.
(160) Piguet, C.; Bocquet, B.; Hopfgartner, G. *Helv. Chim. Acta* **1994**, *77*, 931−942.
(161) Piguet, C.; Hopfgartner, G.; Williams, A. F.; Bünzli, J.-C. G. *J. Chem. Soc., Chem. Commun.* **1995**, 491−492.
(162) Piguet, C.; Bernardinelli, G.; Bünzli, J.-C. G.; Petoud, S.; Hopfgartner, G. *J. Chem. Soc., Chem. Commun.* **1995**, 2575−2577.
(163) (a) Piguet, C.; Bünzli, J.-C. G.; Bernardinelli, G.; Hopfgartner, G.; Petoud, S.; Schaad, O. *J. Am. Chem. Soc.* **1996**, *118*, 6681−6697. (b) Edder, C.; Piguet, C.; Bünzli, J.-C. G.; Hopfgartner, G. *Chem. Eur. J.* **2001**, *7*, 3014−3024.
(164) Piguet, C.; Rivara-Minten, E.; Bernardinelli, G.; Bünzli, J.-C. G.; Hopfgartner, G. *J. Chem. Soc., Dalton Trans.* **1997**, 421−433.
(165) Rigault, S.; Piguet, C.; Bünzli, J.-C. G. *J. Chem. Soc., Dalton Trans.* **2000**, 2045−2053.
(166) Piguet, C.; Hopfgartner, G.; Bocquet, B.; Schaad, O.; Williams, A. F. *J. Am. Chem. Soc.* **1994**, *116*, 9092−9102.
(167) Piguet, C.; Bernardinelli, G.; Williams, A. F.; Bocquet, B. *Angew. Chem.* **1995**, *107*, 618−621; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 582−585.
(168) Edder, C.; Piguet, C.; Bernardinelli, G.; Mareda, J.; Bochet, C. G.; Bünzli, J.-C. G.; Hopfgartner, G. *Inorg. Chem.* **2000**, *39*, 5059−5073.
(169) Piguet, C.; Rivara-Minten, E.; Hopfgartner, G.; Bünzli, J.-C. G. *Helv. Chim. Acta* **1995**, *78*, 1541−1566.
(170) Edder, C.; Piguet, C.; Bünzli, J.-C. G.; Hopfgartner, G. *J. Chem. Soc., Dalton Trans.* **1997**, 4657−4663.
(171) Rigault, S.; Piguet, C.; Bernardinelli, G.; Hopfgartner, G. *Angew. Chem.* **1998**, *110*, 178−181; *Angew. Chem., Int. Ed.* **1998**, *37*, 169−172.
(172) Rigault, S.; Piguet, C. *J. Am. Chem. Soc.* **2000**, *122*, 9304−9305.
(173) Funeriu, D.-P.; Lehn, J.-M.; Baum, G.; Fenske, D. *Chem. Eur. J.* **1997**, *3*, 99−104.
(174) Bonnefous, C.; Bellec, N.; Thummel, R. P. *Chem. Commun.* **1999**, 1243−1244.
(175) Hasenknopf, B.; Lehn, J.-M.; Boumediene, N.; Dupont-Gervais, A.; Van Dorsselaer, A.; Kneisel, B. O.; Fenske, D. *J. Am. Chem. Soc.* **1997**, *119*, 10956−10962.
(176) Mamula, O.; Von Zelewsky, A.; Bernardinelli, G. *Angew. Chem.* **1998**, *110*, 302−305; *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 290−293.
(177) Jones, P. L.; Byrom, K. J.; Jeffery, J. C.; McCleverty, J. A.; Ward, M. D. *Chem. Commun.* **1997**, 1361−1362.
(178) Wenz, G. *Angew. Chem.* **1994**, *106*, 851; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 803.
(179) Chambron, J.-C.; Dietrich-Buchecker, C. O.; Heitz, V.; Nierengarten, J.-F.; Sauvage, J.-P. In *Transition Metals in Supramolecular Chemistry*; Fabbrizzi, L., Poggi, A., Eds.; Kluwer Academic Publishers: Doordrecht, 1994.
(180) Dietrich-Buchecker, C. O.; Sauvage, J.-P.; Kintzinger, J.-P.; Maltèse, P.; Pascard, C.; Guilhem, J. *New J. Chem.* **1992**, *16*, 931−942.
(181) (a) Dietrich-Buchecker, C. O.; Sauvage, J.-P.; De Cian, A.; Fischer, J. *J. Chem. Soc., Chem. Commun.* **1994**, 2231−2232. (b) Meyer, M.; Albrecht-Gary, A.-M.; Dietrich-Buchecker, C. O.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1997**, *119*, 4599−4607.
(182) Rapenne, G.; Dietrich-Buchecker, C. O.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1996**, *118*, 10932−10933.
(183) Dietrich-Buchecker, C. O.; Rapenne, G.; Sauvage, J.-P. *Chem. Commun.* **1997**, 2053−2054.
(184) Rapenne, G.; Dietrich-Buchecker, C. O.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1999**, *121*, 994−1001.
(185) Nierengarten, J.-F.; Dietrich-Buchecker, C. O.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1994**, *116*, 375−376.
(186) Dietrich-Buchecker, C. O.; Sauvage, J.-P. *Chem. Commun.* **1999**, 615−616.
(187) Carina, R. F.; Dietrich-Buchecker, C. O.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1996**, *118*, 9110−9116.
(188) Hou, Z.; Sunderland, C. J.; Nishio, T.; Raymond, K. N. *J. Am. Chem. Soc.* **1996**, *118*, 5148−5149.
(189) Goodgame, D. M. L.; Hill, S. P. W.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1993**, 1019−1021.
(190) Corey, E. J.; Cywin, C. L.; Noe, M. C. *Tetrahedron Lett.* **1994**, *35*, 69−72.
(191) Lukehart, C. M.; Torrence, G. P. *Inorg. Chim. Acta* **1977**, *22*, 131−134.
(192) Bonitatebus, P. J.; Mandal, S. K.; Armstrong, W. H. *Chem. Commun.* **1998**, 939−940.
(193) Grillo, V. A.; Seddon, E. J.; Grant, C. M.; Aromi, G.; Bollinger, J. C.; Folting, K.; Christou, G. *Chem. Commun.* **1997**, 1561−1562.
(194) Saalfrank, R. W.; Dresel, A.; Seitz, V.; Trummer, S.; Hampel, F.; Teichert, M.; Stalke, D.; Stadler, C.; Daub, J.; Schunemann, V.; Trautwein, A. X. *Chem. Eur. J.* **1997**, *3*, 2058−2062.
(195) Saalfrank, R. W.; Seitz, V.; Caulder, D.; Raymond, K. N.; Teichert, M.; Stalke, D. *Eur. J. Inorg. Chem.* **1998**, 1313−1317.
(196) (a) Duhme, A.-K.; Dauter, Z.; Hider, R. C.; Pohl, S. *Inorg. Chem.* **1996**, *35*, 3059−3061. (b) Duhme, A.-K. *J. Chem. Soc., Dalton Trans.* **1997**, 773−778.
(197) (a) Albrecht, M. *Synthesis* **1996**, 230−237. (b) Albrecht, M. *Tetrahedron* **1996**, *52*, 2385−2394.
(198) Albrecht, M.; Schneider, M. *Synthesis* **2000**, 1557−1560.
(199) Albrecht, M.; Kotila, S. *Angew. Chem.* **1996**, *108*, 1299−1300; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1208−1210.
(200) Albrecht, M.; Schneider, M.; Fröhlich, R.; Nissinen, M. Unpublished results.
(201) Albrecht, M.; Röttele, H.; Burger, P. *Chem. Eur. J.* **1996**, *2*, 1264−1268.
(202) Kintzinger, J. P.; Lehn, J.-M. *J. Am. Chem. Soc.* **1974**, *96*, 3313.
(203) Albrecht, M.; Kotila, S. *Chem. Commun.* **1996**, 2309−2310.
(204) Albrecht, M. *Chem. Eur. J.* **1997**, *3*, 1466−1471.
(205) Albrecht, M.; Kotila, S. *Angew. Chem.* **1995**, *107*, 2285−2287; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2134−2137.
(206) Albrecht, M.; Schneider, M.; Röttele, H. *Chem. Ber./Rec.* **1997**, *130*, 615−619.
(207) Albrecht, M. *Synlett* **1996**, 565−567.
(208) Bringmann, G.; Pabst, T.; Henschel, P.; Kraus, J.; Peters, K.; Peters, E.-M.; Rycroft, D. S.; Connolly, J. D. *J. Am. Chem. Soc.* **2000**, *122*, 9127−9133.
(209) Albrecht, M.; Schneider, M.; Fröhlich, R. *New J. Chem.* **1998**, 753−754.
(210) Albrecht, M.; Schneider, M. Unpublished results.
(211) Albrecht, M.; Schneider, M. *J. Prakt. Chem.* **1999**, *341*, 657−661.
(212) (a) Kersting, B.; Meyer, M.; Powers, R. E.; Raymond, K. N. *J. Am. Chem. Soc.* **1996**, *118*, 7221−7222. (b) Meyer, M.; Kersting, B.; Powers, R. E.; Raymond, K. N. *Inorg. Chem.* **1997**, *36*, 5179−5191.
(213) Albrecht, M.; Schneider, M. *Chem. Commun.* **1998**, 137−138.

(214) Scherer, M.; Caulder, D.; Johnson, D. W.; Raymond, K. N. *Angew. Chem.* **1999**, *111*, 1690−1694; *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1588−1592.

(215) Enemark, E. J.; Stack, T. D. P. *Inorg. Chem.* **1996**, *35*, 2719−2720.

(216) Enemark, E. J.; Stack, T. D. P. *Angew. Chem.* **1998**, *110*, 977−981; *Angew. Chem., Int. Ed.* **1998**, *37*, 932−935.

(217) Enemark, E. J.; Stack, T. D. P. *Angew. Chem.* **1995**, *107*, 1082−1084; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 996−998.

(218) Albrecht, M.; Napp, M.; Schneider, M. *Synthesis* **2001**, 468−472.

(219) Albrecht, M.; Napp, M.; Schneider, M.; Weis, P.; Fröhlich, R. *Chem. Commun.* **2001**, 409−410.

(220) (a) Sun, X.; Darren, W. J.; Caulder, D.; Powers, R. E.; Raymond, K. N.; Wong, E. H. *Angew. Chem.* **1999**, *111*, 1386-1390; *Angew. Chem., Int. Ed.* **1999**, *38*, 1303−1306. (b) Sun, X.; Johnson, D. W.; Caulder, D.; Raymond, K. N.; Wong, E. H. *J. Am. Chem. Soc.* **2001**, *123*, 2752−2763. (c) Sun, X.; Johnson, D. W.; Raymond, K. N.; Wong, E. H. *Inorg. Chem.* **2001**, *40*, 4504−4506.

(221) (a) Albrecht, M.; Riether, C. *Synlett* **1995**, 309−312. (b) Albrecht, M.; Riether, C. *Synthesis* **1997**, 957−962. (c) Albrecht, M.; Riether, C.; Fröhlich, R. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1343−1348.

(222) Larsson, R.; Eskilsson, O. *Acta Chem. Scand.* **1968**, *22*, 1067−1075.

(223) (a) Baret, P.; Beguin, C. G.; Boukhalfe, H.; Caris, C.; Laulhere, J.-P.; Pierre, J.-L.; Serratrice, G. *J. Am. Chem. Soc.* **1995**, *117*, 9760. (b) Vögtle, F.; Weber, E. *Angew. Chem.* **1979**, *91*, 813; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 753. (c) Zhang, X. X.; Bordunov, A. V.; Bradshaw, J. S.; Dalley, N. K.; Kou, X.; Izatt, R. M. *J. Am. Chem. Soc.* **1995**, *117*, 11507.

(224) Albrecht, M.; Blau, O. *Synthesis* **1997**, 213-216.

(225) Albrecht, M.; Blau, O. *Chem. Commun.* **1997**, 345−346.

(226) Albrecht, M.; Blau, O.; Fröhlich, R. *Chem. Eur. J.* **1999**, *5*, 48−56.

(227) Albrecht, M.; Blau, O.; Zauner, J. *Eur. J. Org. Chem.* **1999**, 3165−3169.

(228) Albrecht, M.; Blau, O.; Fröhlich, R. Unpublished results.

(229) Hiratani, K.; Takahashi, T.; Kasuga, K.; Sugihara, H.; Fujiwara, K.; Ohashi, K. *Tetrahedron Lett.* **1995**, *36*, 5567.

(230) Albrecht, M.; Blau, O.; Wegelius, E.; Rissanen, K. *New J. Chem.* **1999**, *5*, 667−668.

(231) Albrecht, M.; Blau, O.; Röttele, H. *New J. Chem.* **2000**, *24*, 619−622.

(232) Albrecht, M.; Fröhlich, R. *J. Am. Chem. Soc.* **1997**, *119*, 1656−1661.

(233) Albrecht, M.; Witt, K.; Blau, O. *J. Prakt. Chem./Chem.- Ztg.* **1998**, *340*, 562−566.

(234) Albrecht, M.; Blau, O. Unpublished results.

(235) Sanmartin, J.; Bermejo, M. R.; Garcia-Deibe, A. M.; Piro, O.; Castellano, E. E. *Chem. Commun.* **1999**, 1953−1954.

(236) Carbonaro, L.; Isola, M.; Liuzzo, V.; Marchetti, F.; Balzano, F.; Pomelli, C. S.; Raffaelli, A. *Eur. J. Inorg. Chem.* **2001**, 353−357.

(237) Bermejo, M. R.; Fondo, M.; Gonzales, A. M.; Hoyos, O. L.; Sousa, A.; McAuliffe, C. A.; Hussain, W.; Pritchard, R.; Novotorsev, V. M. *J. Chem. Soc., Dalton Trans.* **1999**, 2211−2218.

(238) Fritsky, I. O.; Kotzlowsky, H.; Prisyazhnaya, E. V.; Karaczyn, A.; Kalibabchuk, V. A.; Glowiak, T. *J. Chem. Soc., Dalton Trans.* **1998**, 1535−1536.

(239) Lessmann, J. J.; Horrocks, W. D. *Inorg. Chem.* **2000**, *39*, 3114−3124.

(240) Saalfrank, R. W.; Harbig, R.; Nachtrab, J.; Bauer, W.; Zeller, K.-P.; Stalke, D.; Teichert, M. *Chem. Eur. J.* **1996**, *2*, 1363−1367.

(241) Caradoc-Davies, P. L.; Hanton, L. R.; Lee, K. *Chem. Commun.* **2000**, 783−784.

(242) Chen, J. C. C. *J. Chem. Soc., Dalton Trans.* **2000**, 839−840.

(243) (a) Airey, A. L.; Swiegers, G. F.; Willis, A. C.; Wild, S. B. *J. Chem. Soc., Chem. Commun.* **1995**, 695−696. (b) Airey, A. L.; Swiegers, G. F.; Willis, A. C.; Wild, S. B. *Inorg. Chem.* **1997**, *36*, 1588−1597.

(244) Krämer, R.; Lehn, J.-M.; Marquis-Rigault, A. *Proc. Natl. Acad. Sci. U.S.A.* **1993**, *90*, 5394−5398.

(245) Hasenknopf, B.; Lehn, J.-M.; Baum, G.; Fenske, D. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 1397−1400.

(246) Caulder, D.; Raymond, K. N. *Angew. Chem.* **1997**, *109*, 1508−1510; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1440−1442.

(247) Albrecht, M.; Schneider, M.; Röttele, H. *Angew. Chem.* **1999**, *111*, 512−515; *Angew. Chem., Int. Ed.* **1999**, *38*, 557−559.

(248) Baum, G.; Constable, E. C.; Fenske, D.; Housecroft, C. E.; Kulke, T. *Chem. Eur. J.* **1999**, *5*, 1862−1873.

(249) Barbour, L. J.; Orr, G. W.; Atwood, J. L. *Nature* **1998**, *393*, 671−673.

(250) McMorran, D. A.; Steel, P. J. *Angew. Chem.* **1998**, *110*, 3495−3497; *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3295−3297.

(251) (a) Cotton, A. F.; Daniels, L. M.; Jordan, G. T.; Murillo, C. A. *J. Am. Chem. Soc.* **1997**, *119*, 10377−10381. (b) Chen, Y.-H.; Lee, C.-C.; Wang, C.-C.; Lee, G.-H.; Lai, S.-Y.; Li, F.-Y.; Mou, C.-Y.; Peng, S.-M. *Chem. Commun.* **1999**, 1667−1668.

(252) Baxter, P. N. W.; Lehn, J.-M.; Baum, G.; Fenske, D. *Chem. Eur. J.* **2000**, *6*, 4510−4517.

(253) Saalfrank, R. W.; Löw, N.; Trummer, S.; Sheldrick, G. M.; Teichert, M.; Stalke, D. *Eur. J. Inorg. Chem.* **1998**, 559−563.

(254) Albrecht, M.; Witt, K.; Röttele, H.; Fröhlich, R. *Chem. Commun.* **2001**, 1330−1331.

(255) Weizman, H.; Tor, Y. *Chem. Commun.* **2001**, 453−454.

(256) Albrecht, M.; Schneider, M.; Spie*β*, O.; Weis, P. Unpublished results.

(257) (a) Fujita, M. *Chem. Soc. Rev.* **1998**, *27*, 417−425. (b) Albrecht, M. *Angew. Chem.* **1999**, *111*, 3671−3674; *Angew. Chem., Int. Ed.* **1999**, *38*, 3463−3465. (c) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853−907. (d) Swiegers, G. F.; Malefetse, T. J. *Chem. Rev.* **2000**, *100*, 3483−3537. (e) Fujita, M. In *Templating, Self-assembly and Self-organization*; Sauvage, J.-P., Hosseini, M. W., Eds.; Pergamon Press: Oxford, 1996; Vol. 9. (f) Holliday, B. J.; Mirkin, C. A. *Angew. Chem.* **2001**, *113*, 2076−2097; *Angew. Chem., Int. Ed.* **2001**, *40*, 2022−2042. (g) Machado, V. G.; Baxter, P. N. W.; Lehn, J. M. *J. Braz. Chem. Soc.* **2001**, *12*, 431−462.

(258) Childs, L. J.; Alcock, N. W.; Hannon, M. J. *Angew. Chem.* **2001**, *113*, 1113−1115; *Angew. Chem., Int. Ed.* **2001**, *40*, 1079−1081.

(259) Amendola, V.; Fabbrizzi, L.; Gianelli, L.; Maggi, C.; Mangano, C.; Pallavicini, P.; Zema, M. *Inorg. Chem.* **2001**, *40*, 3579−3587.

(260) Murguly, E.; Norsten, T. B.; Branda, N. R. *Angew. Chem.* **2001**, *113*, 1802−1805; *Angew. Chem., Int. Ed.* **2001**, *40*, 1752−1755.

(261) Xu, Z.; Thompson, L. K.; Black, D. A.; Ralph, C.; Miller, D. O.; Leech, M. A.; Howard, J. A. K. *J. Chem. Soc., Dalton Trans.* **2001**, 2042−2048.

(262) Bowyer, P. K.; Black, D. S.; Craig, D. C.; Rae, A. D.; Willis, A. C. *J. Chem. Soc., Dalton Trans.* **2001**, 1948−1958.

(263) Su, C.-Y.; Cai, Y.-P.; Chen, C.-L.; Zhang, H.-X.; Kang, B.-S. *J. Chem. Soc., Dalton Trans.* **2001**, 359−361.

(264) Vazquez, M.; Bermejo, M. R.; Fondo, M.; Gonzales, A. M.; Mahia, J.; Sorace, L.; Gatteschi, D. *Eur. J. Inorg. Chem.* **2001**, 1863−1868.

(265) Kruger, P. E.; Martin, N.; Nieuwenhuyzen, M. *J. Chem. Soc., Dalton Trans.* **2001**, 1966−1970.

(266) Chen-Jie, F.; Chun-Ying, D.; Hong, M.; Cheng, H.; Quing-Jin, M.; Yong-Jiang, L.; Yu-Hua, M.; Zhe-Ming, W. *Organometallics* **2001**, *20*, 2525−2532.

(267) Chen-Jie, F.; Chun-Ying, D.; Cheng, H.; Quing-Jin, M. *Chem. Commun.* **2001**, 1187−1188.

(268) Saalfrank, R. W.; Seitz, V.; Heinemann, F. W.; Göbel, C.; Herbst-Irmer, R. *J. Chem. Soc., Dalton Trans.* **2001**, 599−603.

(269) Yeh, R. M.; Ziegler, M.; Johnson, D. W.; Terpin, A. J.; Raymond, K. N. *Inorg. Chem.* **2001**, *40*, 2216−2217.

(270) Hannon, M. J.; Meistermann, I.; Isaac, C. J.; Blomme, C.; Aldrich-Wright, J. R.; Rodger, A. *Chem. Commun.* **2001**, 1078−1079.

(271) Catalano, V. J.; Malwitz, M. A.; Noll, B. C. *Chem. Commun.* **2001**, 581−582.

(272) Lozano, E.; Nieuwenhuyzen, M.; James, S. L. *Chem. Eur. J.* **2001**, *7*, 2644−2651.

CR0103672