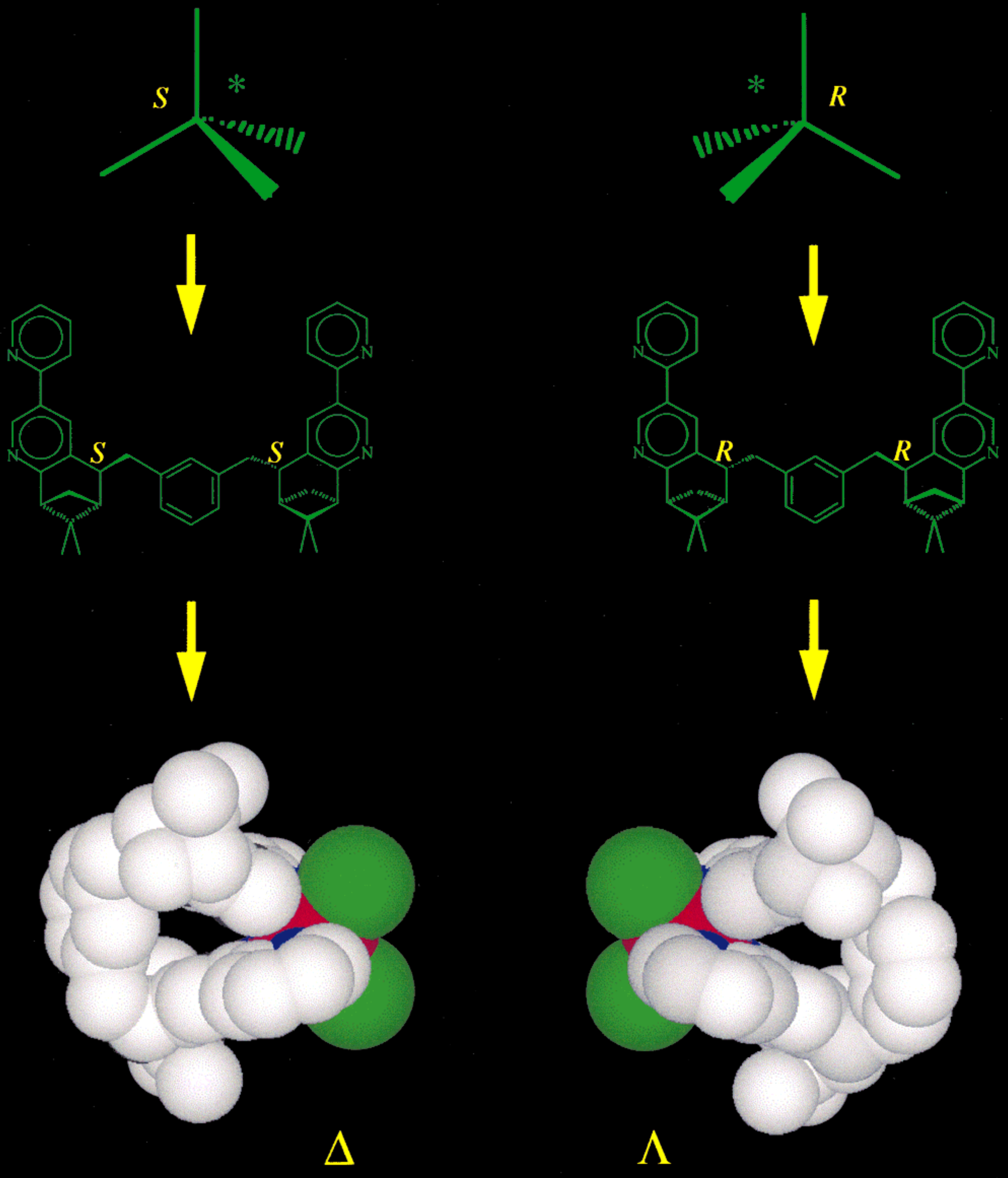
Transfer of Chirality to Metal Centers



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Predetermined Chirality at Metal Centers

Ulrich Knof and Alex von Zelewsky*

Enantiopure compounds are of central importance in many domains of chemistry. A classical method for the preparation of an enantiopure substance is the resolution of a racemate. Much more effective is, however, the selective synthesis of the desired stereoisomer. Stereoselective methods of synthesis have belonged for a long time to the standard repertoire of organic chemistry. The method of "asymmetric synthesis" has been known since the 19th century[1] and asymmetric catalysis has seen an enormous development in recent decades. A similar development has just about started in inorganic chemistry. One hundred years after the formulation of the theory of coordination compounds by Alfred Werner, stereochemical considerations are again of central interest in the development of the chemistry of coordination compounds. We describe here the state of the art of stereoselective synthesis in coordination chemistry. The enormous variability of the stereochemistry of metal complexes as a consequence of the many possible central atoms and a variable coordination geometry, makes a reasonably comprehensive coverage of the field an endeavor of considerable dimensions. The use of organic ligands, where the configuration can be controlled by known methods, is the main feature by which chiral information can be transferred to the metal center. In this way, a predetermination of the absolute configuration at the metal center can be reached. The multidisciplinary and fascinating field of stereoselective synthesis and of stereoselective self-association of coordination compounds is in this way closely linked to classic organic stereochemistry.

Keywords: chirality · coordination chemistry · helical structures · supramolecular chemistry · transition metals

1. Introduction

1.1. Scope and Limits

A comprehensive description of the predetermination of chirality at carbon centers would require a multivolume publication. Predetermination of chirality at tetrahedral carbon centers has for a long time been the central interest in synthetic organic chemistry. The first big challenge was the stereoselective generation of carbon centers in the classical synthesis of natural compounds. Organic chemists have developed efficient methods for the creation of stereogenic centers with predetermined chirality. Today such methods form the highly sophisticated science and art of organic synthesis. Originally chemists were not able to synthesize synthetic analogues of natural compounds in an enantioselective way. This even gave rise to a criminal story in which the murderer was identified because the toxin (muscarin) was used in the racemic form to poison the victim.[2] Contrary to the highly developed asymmetric synthesis in organic chemistry, predetermination of chirality at metal centers has become only recently a subject of systematic investigation. This is of course a consequence of the fact that the chirality of coordination compounds is a much more complex phenomenon than that of organic compounds, because of the higher coordination numbers and the multitude of possible central atoms.[3, 4]

Chiral coordination compounds that are synthesized from racemic or achiral species are, of course, formed as racemates. There are exceptions, as for instance in the spontaneous enrichment of one enantiomer upon crystallization. We do not treat these rare cases here. Such processes are only observable when a chiral induction occurs upon nucleation, and a rapid racemization takes place in solution at the same time. Such very special conditions are only realized in rare cases and a general applicability or a predetermination of chirality is therefore not possible in this way. We describe here how stereoselective synthesis of coordination compounds can be achieved through enantiopure chiral ligands. This predetermination of the chirality of the metal center yields, just as in organic chemistry, preferentially products of *one* absolute configuration.

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[*] Prof. Dr. A. von Zelewsky, Dr. U. Knof
Institut für Anorganische Chemie
Universität Fribourg, CH-1700 Fribourg (Switzerland)
Fax: (+41) 26-300-97-38
E-mail: alexander.vonzelewsky@unifr.ch

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1.2. Chirality in Coordination Chemistry

Predetermination of chirality in coordination compounds has up to now received relatively little attention. This is mirrored in the relatively small number of papers published in this field over the years. In recent times, however, interest in inorganic stereochemistry seems to have risen rapidly. In particular, stereochemically well-defined building blocks are needed for the assembly of supramolecular structures, a field that has found great interest in coordination chemistry. It is evident that upon formation of supramolecular structures from a large number of racemic components a large number of stereoisomers can be formed. The functionality of these aggregates is therefore not exactly defined. The preparation of species with predetermined chirality is therefore a strong challenge for the contemporary coordination chemist.

The coordination geometry of central importance in inorganic stereochemistry is the octahedron. We designate, from IUPAC nomenclature,[5] this geometry as *OC*-6. A total of 144 "edge configurations" can be formed in *OC*-6 through the use of chelates, cage ligands, or macrocycles, or a combination thereof.[3, 6] Half of these edge configurations, that means 72, are inherently chiral. Δ and Λ are today the generally accepted descriptors for the chirality of these helical structures.[5] Figure 1 shows as an example the complex $[Ru(bpy)_3]^{2+}$ where the three bipyridine (bpy) ligands form either a right or a left helix. Typical octahedral complexes are $[M(aa)_3]$ and $[M(aa)_2X_2]$. In the first case, a homoleptic tris complex with a didentate ligand, D_3 symmetry results (Figure 1). In the second case with only two didentate ligands, the symmetry is C_2. The complex $[Co(en)_2(Cl)(NH_3)]^{2+}$ with two didentate and two monodentate ligands belongs to this second group. In 1911 A. Werner[7] achieved for the first time the resolution of an octahedral complex into the enantiomers with this complex.

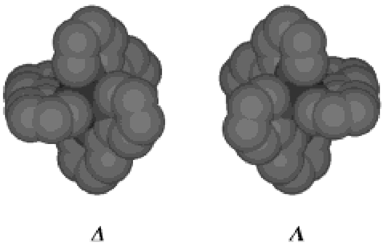
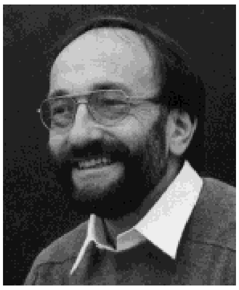


Figure 1. The pair of enantiomers Δ/Λ-$[Ru(bpy)_3]^{2+}$. For a stereo representation see also ref. [3] and table of contents text.

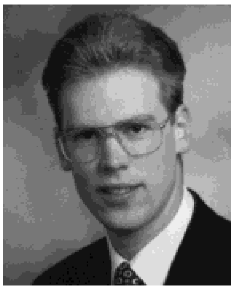
As an example we consider a typical case where chiral didentate ligands with carbon centers of the absolute configuration *R* are coordinated to an octahedral metal center. Two possible species can be formed: Δ-(aa[*R*])$_3$ and Λ-(aa[*R*])$_3$. The complexes with Δ and Λ configuration are no longer enantiomers but are instead diastereomers because of the chiral ligands. We speak of predetermination of chirality at a metal center if one of the two species is preferentially formed in a diastereoselective synthesis of a metal complex. In some cases it is possible that chirality can be predetermined through other mechanisms, for example, through the diastereoselective formation of ion pairs with consecutive electron transfer.

Tetrahedral configuration of four different ligands (*T*-4 from IUPAC) is the source of chirality in innumerable cases of organic compounds. The fact that stereoisomers, which are only distinguished in the configuration at such a center, can often be prepared without racemization is in the first-line a consequence of the generally high substitution stability of carbon centers. In contrast *T*-4 metal centers are very often highly labile. It is even difficult to prepare species with four different monodentate ligands in most cases, and the aimed synthesis of one enantiomer is therefore in most cases excluded. The first *T*-4 complexes where racemates could be resolved were species where one ligand was an aromatic π acceptor of the cyclopentadienyl anion type.[8–10] Even though enantiopure substances have been obtained in some cases, a comparable manifoldness of methods and compounds such as in organic chemistry is excluded.

Alexander von Zelewsky, was born on July 17 1936 in Zürich. He studied chemistry at the ETH Zürich where he received his doctoral degree with a thesis on single crystal EPR spectroscopy. From 1965–1967 he worked at the University of California at Berkeley as a Miller Fellow in the field of NMR spectroscopy. In 1968 he returned to the ETH and was appointed as full professor at the University of Fribourg (Switzerland) in 1969 where he initially investigated spectroscopic problems in coordination chemistry. His main research topic is now stereoselective synthesis in coordination chemistry and especially predetermination of chirality at metal centers. In the present review this subject is discussed starting with early developments up to the newest results from the laboratory of Fribourg.



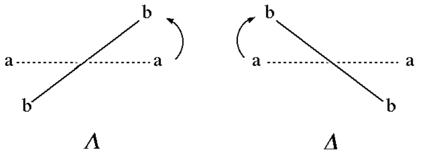
A. von Zelewsky



U. Knof

Ulrich Knof was born in 1968 in Essen and studied chemistry from 1987 to 1992 at the Ruhr-Universität Bochum (Germany). He obtained his PhD degree with Karl Wieghardt in 1995, whom he followed afterwards to the Max-Planck-Institut für Strahlenchemie in Mülheim. Since 1996 he has worked as a Postdoc in the group of A. von Zelewsky in the field of stereoselective synthesis of coordination compounds.

The other well known coordination geometry with coordination number four is square planar (*SP*-4). This geometry, however, is inherently achiral. An *SP*-4 center with four different ligands (Mabcd) does not yield one pair of enantiomers such as in *T*-4, but it results in three achiral stereoisomers. However, *SP*-4 complexes that deviate significantly from planarity can be chiral, and it was recently shown that this chirality can be predetermined.[11, 12] The helicity in these non-octahedral compounds is indicated by the general "skew-line system", which projects the ligand onto lines.[3] If the line in the back has to be turned clockwise (through an acute angle) to be congruent with the front line the arrangement is designated as Δ, while the opposite case is termed Λ (Scheme 1).



Scheme 1. Definition of the configurations Δ and Λ in non-octahedral complexes.

What has been said for *T*-4 complexes in respect to lability is even more true for coordination number five. The well known stereochemical lability of complexes with coordination number five leads in most cases to an extremely rapid racemization.

The strongest motivation for a systematic investigation of the predetermination of chirality in the sense discussed above was, and still is, the assembly of complex structures, notably of polynuclear metal complexes with well defined configuration. This field is presently expanding rapidly and it will require methods for the stereoselective assembly of supramolecular structures in the future.

2. Predetermined Chirality in Octahedral Complexes

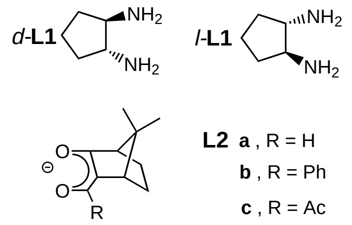
2.1. Complexes with Didentate Ligands

2.1.1. Complexes with Three Chiral Didentate Ligands

Octahedral complexes have represented since the beginning of coordination chemistry one of the most investigated types of complexes. Octahedral metal complexes with nonracemic chiral ligands were already reported in the beginning of the century.[13–15] The understanding for this form of isomerism was, however, still quite limited in the first publications. A report published by Smirnoff, shortly after Werner's death, can be considered to be a breakthrough in the field.[16] Smirnoff investigated platinum(IV) complexes with nonracemic *l* and *d* forms of propylendiamine (pn) (following the modern nomenclature (*S*)- and (*R*)-1,2-diaminopropane). The absolutely correct analysis of the stereochemical conditions was based exclusively on polarimetric measurements. Smirnoff prepared a series of complexes where one, two, or three optically active propylenediamine ligands were coordinated to one platinum center. The other coordination sites were occupied with nonchiral ligands. Smirnoff expected that the molar rotations of the investigated compounds would be proportional to the number of the optically active substituents, that is in a ratio of 1:2:3. The measurements showed, however, a significantly higher value for the tris-substituted $[Pt(pn)_3]^{4+}$ complex. In the 1920 publication Smirnoff analyzed this observation as follows: "The excess of rotation must be due to the asymmetry of the complex itself".[16] His conclusions were: "‥, that optically active diamine molecules of a given configuration will be bound to the Pt atom in only one of two possible forms of mirror isomers". This is a very clear description of the concept of predetermination of chirality at a metal center.

The pioneering work of Smirnoff and Werner was continued during several decades by the groups of Gillard and Bailar.[17–23] These authors reproduced the synthesis of the platinum complexes and made similar investigations with coordination compounds of cobalt, chromium, and rhodium as the central atoms. In all these cases, the Λ configuration was preferred for *l*-pn and the Δ configuration for *d*-pn. Dwyer et al. determined in 1959 the equilibrium constant between the Δ and the Λ form of $[Co(l\text{-pn})_3]^{3+}$ to be 5.75.[24]

A classical series of investigations of the stereochemistry of octahedral coordination compounds was described in a paper of Jaeger and Blumendal in 1928.[25] Cobalt(III) complexes with the chiral ligand 1,2-diaminocyclopentane (**L1**) were investigated. It was observed through oxidation of solutions that contained the racemic ligand and cobalt(II) ions that in a first step either *trans*-$[Co(d\text{-}\mathbf{L1})_2Cl_2]^+$ or *trans*-$[Co(l\text{-}\mathbf{L1})_2Cl_2]^+$ were formed. Complexes where both ligand forms were mixed were not observed. Both *trans* complexes form the inherently chiral *cis* form upon heating. The *d*-**L1** ligand forms thereby exclusively the Λ-configured complex Λ-*cis*-$[Co(d\text{-}\mathbf{L1})_2Cl_2]^+$. With another *d*-**L1** molecule a species Λ-$[Co(d\text{-}\mathbf{L1})_3]^{3+}$ was obtained. If the *cis* complex was treated with *l*-**L1**, no mixed complex was formed but the two species $\Lambda[Co(d\text{-}\mathbf{L1})_3]^{3+}$ and Δ-$[Co(l\text{-}\mathbf{L1})_3]^{3+}$ were formed in a ratio of 2:1. The stereoselectivity seems to be high in this case. Microscopic investigations of the crystals formed did not show the formation of other isomers. In these investigations mainly racemic ligands were used. Therefore one cannot really speak of predetermined chirality at the metal center.



Other ligands, which were important for the development of asymmetric synthesis in coordination chemistry, are the β-ketoenolates of camphene. Camphene is a natural product and is easily available in enantiopure form, and the simple transformation of the hydroxymethylene form (**L2a**) was already described in 1894.[26] The spectra and the mutarotation of a series of complexes of the benzoyl derivative (**L2b**) were investigated by Lowry et al. in the 1920s.[27–32] A systematic investigation of this group of sterically demanding ligands was started by Lifschitz.[33, 34] This author observed only one isomer of cobalt(III) and chromium(III) complexes of the ligand (+)-**L2a**. A definitive assignment of the absolute configuration was not possible at this time. Mason et al. proved 40 years later with more developed analytical methods that the complexes described formed diastereoselectively were Λ-configured species.[35–37]

Gillard et al. investigated also chromium, cobalt, and rhodium as central atoms with these ligands. [Rh((+)-**L2a**)$_3$]$^{3+}$ was the first complex of the ligand (+)-**L2a** that seemed to be formed preferentially in the Δ configuration,[38] despite the higher thermodynamic stability of the Λ configuration. The Δ isomer is formed in a kinetically controlled way.

Everett et al. investigated the cobalt(III) and vanadium(III) complex with (+)- and (−)-**L2a** and the acyl derivative (+)-**L2c**.[39] The results observed with (+)-**L2a** are in agreement with those of Gillard et al.[38] In 1968 it was proved that the enantiomers (+)- and (−)-**L2a** form complexes of opposite helicity (Λ/Δ). The vanadium(III) complexes of (+)-**L2a** are highly labile.[39] It was shown that all four possible isomeric forms (Δ-*mer*, Λ-*mer*, Δ-*fac*, Λ-*fac*) are in thermodynamic equilibrium. *mer* signifies an arrangement of three groups on a meridian, whereas *fac* designates a facial arrangement where the ligands mount a face of an octahedron (Figure 2).

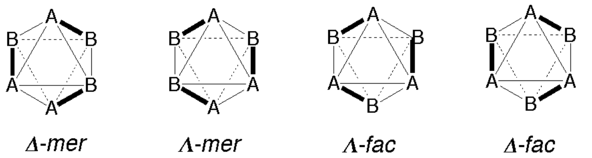
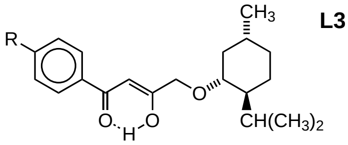
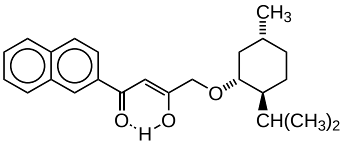


Figure 2. Schematic representation of isomers [M(AB)$_3$] where AB is a didentate ligand.

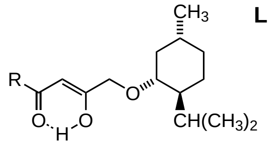
A series of detailed investigations of trisdidentate complexes with chiral ligands were carried out by Okawa et al. with the *l*-menthyl-substituted acetylacetonate ligands **L3**–**5**.[40–42] In all these ligands a *l*-menthyl group was bound to an acetylacetonate unit and was substituted additionally by a phenyl (**L3**), a naphthyl (**L4**), or an alkyl group (**L5**). The metal centers Sc^{III}, Y^{III}, La^{III}, Al^{III}, Ga^{III}, and In^{III} form preferentially facially Λ-configured complexes with the phenyl substituted ligands **L3a** and **L3b** in solution.[40] The stereoselectivity increases with increasing size of the metal ion; the lanthanum complexes (r(La^{3+}) = 1.02 Å) were formed with a very high stereoselectivity, whereas for Al^{III}, which has a radius of about 50% of that for lanthanum (0.51 Å), a lower selectivity was observed. It seems that the stereochemically active groups are oriented in such a way that the mutual interaction is stronger in the case of the larger central atoms, which leads therefore to higher selectivity. The authors discussed three noncovalent CH–π interactions between the methyl groups of the menthyl units and the aromatic π systems of the aryl rings as a cause for this behavior. As shown with the example of [Al(**L3b**)]$^{3+}$, it is possible that in the solid state another configuration is preferred compared to the solution state. In the solid state this complex is present preferentially in the Δ configuration (Figure 3), whereas in solution an excess of Λ configuration is formed.[40]



L3 **a**, R = H
b, R = Me
c, R = Br



L4



L5 **a**, R = Et
b, R = *n*Pr
c, R = *i*Pr
d, R = *n*Bu
e, R = *i*Bu
f, R = *n*Am
g, R = *i*Am
h, R = Me

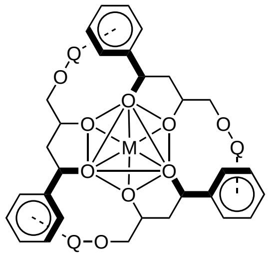


Figure 3. Schematic representation of the hydrophobic CHQ–π interaction in *cis*-Δ-[M(**L3**)$_3$] with Q = *l*-menthyl, M = Al.

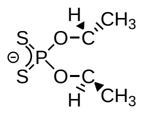
The Δ form is preferred apparently also in solution for the complexes with Co^{III}, Cr^{III}, Mn^{III}, Pr^{III}, Nd^{III}, Eu^{III}, Gd^{III}, Dy^{III}, Ho^{III}, Er^{III}, and Tm^{III}.[41, 43, 44] The observation that larger ions showed high stereoselectivities is only valid for Λ-configured complexes. Cobalt forms almost exclusively complexes of the Δ form with these ligands, despite the smaller ionic radius. It seems that there is no unambiguous correlation between the radius of the metal ion and the preferred configuration. Complexes with Ga^{III} (0.62 Å) formed preferentially the Λ configuration, whereas Co^{III} with almost the same radius (0.63 Å) preferred the Δ configuration.

The aromatic ring in ligand **L3a** can be substituted with one methyl group (**L3b**) and one bromo (**L3c**) in the *para* position.[45, 46] The stereoselectivity in the Co^{III} complexes with these substituted ligands increases in the series (**L3c** < **L3a** < **L3b**). It seems that the selectivity is in the first-line a consequence of electronic factors and not steric influences. The CH–π interaction and therewith also the selectivity is increased parallel to the increase of π electron density in the ring. The preference of the Δ configuration is not influenced by this substitution.

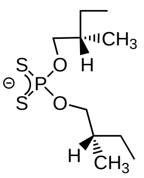
Another possible way to increase the CH–π interaction is to enlarge the aromatic π system. Ligand **L4** is obtained if the phenyl group is replaced by a naphthyl group.[47] The selectivity increases as predicted for the complexes of Co^{III}, Cr^{III}, and Mn^{III} with this ligand relative to ligand **L3a**. The preference for the Δ configuration is preserved also in this case.

Finally, it is possible to replace the aromatic groups of the ligand **L3** and **L4** by various alkyl groups (**L5a–f**).[42] The CH–π interactions are no longer possible. They are replaced by menthyl–methyl interactions, which are, however, much less pronounced. Consequently, the equilibrium shows only weak preference for a given configuration. Already small variations suffice for inversion of the preferred helicity at the metal center. Whereas the facial Δ configuration is preferred in the Co^{II} and Co^{III} complexes with the ethyl (**L5a**) and the iso-butyl (**L5e**) substituted ligands, the iso-propyl (**L5c**) and iso-amyl (**L5f**) substituted forms give preferentially the *fac*-Λ configuration. However, *n*-propyl (**L5c**), *n*-butyl (**L5d**) and *n*-amyl (**L5f**) groups yield no preference at all. There are obviously two possibilities for the relative orientation of the menthyl and alkyl groups: One of them prefers the formation of the *fac*-Δ-isomer (**L5a,e**) whereas the other leads to *fac*-Λ-isomer (**L5c,g**). For **L5b,d,f** the difference in energy is too small to lead to any stereoselectivity. This behavior shows the relative strength of the CH–π relative to the menthyl–methyl interactions. The Cr^{III} and Co^{III} complexes in a methyl substituted form of the ligand (**L5h**) show interesting aspects.[48] This ligand forms complexes, as with those ligands with odd numbers of substituted alkyl groups (**L5c**, **L5f**), preferentially in the Λ configuration. Ligands with the even numbered alkyl chains (**L5a** and **L5e**) form, on the other hand, preferentially complexes of the Δ form.

The equilibria between the isomers and the analysis of the factors that influence this equilibria were studied in a series of publications by Biscarini and Kuroda.[49–53] When the (*R*,*R*) form of ligand **L6**[49] is treated with Cr^{III} in a synthesis under kinetically controlled conditions the Δ isomer is formed in a first step. After equilibration an excess of the Λ form ($K = 0.86$) is present.[52] In a publication of 1988 the influence of the solvent on the preferred configuration was investigated.[49] The Λ-*R*,*R* form of $[Cr((-)\text{-}\mathbf{L6})_3]$ is preferred in the solid state and in THF, acetonitrile, and acetone, whereas the Δ-*R*,*R* form is present in higher concentrations in all solvents that form hydrogen bridges such as chloroform, dichloromethane, and ethanol. Cr^{III} forms complexes preferentially of the Λ configuration with ligand **L7** in the *S*,*S* form, independent of the solvent.[53] In the solid state $[Cr((S,S)\text{-}\mathbf{L7})_3]$ crystallizes in a molecular packing that contains the Δ and Λ complexes in a 1:1 ratio. No selectivity would have been found if only the crystalline product had been analyzed. This example shows



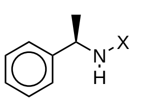
L6



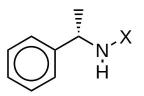
L7

clearly that the analysis of molecular structures in single crystals does not always give clues to the compositions in solution.

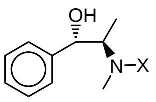
The unsymmetrical ligand groups of the hydroxypyridinethione **L8a–d**[54] coordinates with oxygen and sulfur donor atoms and forms C_3-symmetric complexes with Fe^{III}, Cr^{III}, and Co^{III}. The two enantiomeric forms of the ligands (**L8a** and **L8b**) form, as expected, complexes of opposite helicity.



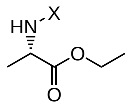
L8 a



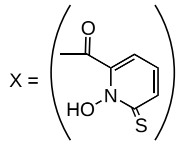
L8 b



L8 c

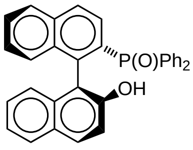


L8 d

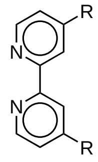


Whereas **L8a** yields Λ-configured Fe^{III} and Co^{III} complexes, ligand **L8b** forms Δ complexes of these metals. It is quite unexpected, however, that Cr^{III} shows an opposite preference. In this case the *R* form yields Δ and the *S* form Λ complexes. The same behavior is observed in complexes of ligands **L8c** and **L8d**. **L8c** forms Λ-configured complexes with Fe^{III} and Co^{III} whereas Cr^{III} prefers the Δ form. Correspondingly, **L8d** yields Δ-configured iron complexes but Λ-configured chromium complexes.

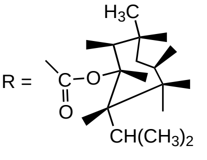
Complexes of chiral binaphthol ligands have been used frequently for asymmetric catalysis. In general, the stereochemistry of the catalytically active complexes has not been investigated in detail. Exceptions are the thoroughly investigated complexes of iron(III) and vanadium(III) complexes of ligand **L9**.[55] The *S* form of the ligand yields the Λ-configured complex, while the *R* form yields a Δ-configured complex. The synthesis seems to be completely stereoselective; the other isomer cannot be found.



L9



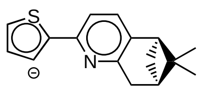
L10



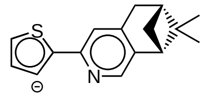
Ruthenium complexes of chiral enantiopure ligands have been used as catalysts for photocatalytic synthesis. Whereas Δ- and Λ-$[Ru(bpy)_3]^{2+}$ complexes racemize, chiral bipyridine ligands such as **L10** are preferred because their configurations are relatively stable and they can be used therefore during a much longer time.[56–59]

2.1.2. Complexes with Two Chiral Didentate Ligands

One of the rare modern examples for a chiral predetermination by two didentate ligands has been described for platinum(IV) compounds.[11] Thienylpyridine ligands that are substituted with terpene groups in the *R*,*R* form (**L11**) give distorted square-planar platinum complexes with predetermined chirality (see Section 3.1). Oxidative addition of alkyl halides yields, in a completely stereoselective reaction, exclusively the Δ product of edge configuration. The chiral predetermination has therefore been completely preserved upon the transition from four to six coordination. If the steric constraint through the chelate ligand is diminished through a different orientation of the pinene group, as in **L12**, a mixture of isomers is found upon oxidative addition.



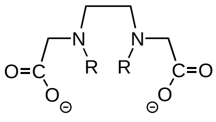
L11



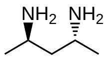
L12

2.1.3. Complexes with One Chiral Didentate Ligand

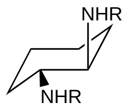
Investigations on this type of complexes have been carried out by Yashiro and Yeno with the achiral tetradentate ligand **L13a** and the enantiopure diamine ligand (*R*,*R*)-**L14** and (*R*,*R*)-**L15a**.[60, 61] The stereoselectivity $\Lambda/\Delta = 3{:}97$ is surprisingly high in the [Co^{III}(**L13a**)] complex with the chiral ligand (*R*,*R*)-**L14**—[Co^{III}(**L13a**)((*R*,*R*)-**L14**)]$^+$—as compared with a Λ/Δ ratio of only 60:40 for the corresponding (*R*,*R*)-**L15a** complex. X-ray analyses show that the chelate rings of the didentate ligands have a chair form in the Λ-configured complex whereas the Δ configuration makes a "skew-boat" form necessary, which explains the high stereoselectivity in the former case. This type of steric interaction is much more pronounced in chelates that form six-membered rings (**L14**) with the metal, relative to five-membered rings (**L15a**). Therefore a stronger stereochemical preference is to be expected for the six-membered rings.



L13 **a**, R = H
b, R = Et



L14

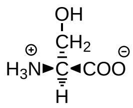


L15 **a**, R = H
b, R = Et

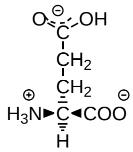
To increase the diastereoselectivity also in the case of the five-membered chelates, ligands **L13a** and **L15a** were N-ethylated. As a consequence, ligands **L13b** and **L15b** show much more pronounced stereoselectivities. With **L13b** and *R*,*R*-**L15a** a stereoselectivity $\Lambda{:}\Delta$ of 96:4 is reached. The steric interaction between the *N*-alkyl substituent in **L13b** and the NH groups in (*R*,*R*)-**L15a** are responsible for the strongly preferred formation of the Λ diastereomer. Two effects result from the use of the bisethylated **L15b** and the nonsubstituted (**L13a**) ligands: The ratio $\Lambda{:}\Delta$ of 2:98 shows an increased stereoselectivity and, more surprisingly, the preferred configuration changes from Δ to Λ. The reason for this behavior is the interaction between the *N*-alkyl substituent of the didentate ligand and the acetate-chelate ring that forms the tetradentate ligand.

Ligand **L3a**, which has already been discussed, was also used to predetermine the configuration in complexes with tetradentate Schiff-base ligands of the salen type.[62] The ligand forms cobalt(III) complexes with Schiff bases of the type *N*,*N'*-disalicylidenethylendiamine in the Λ configuration of the edge configuration ***11*** (see Figure 6). The selectivity can be traced back to the CH–π interaction that has already been discussed in detail between the *l*-menthyl group and the aromatic ring of the Schiff-bases.

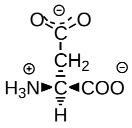
A limiting case of stereoselectivity is the coordination of one amino acid and two achiral didentate ligands on one metal center. Only sterically demanding ligands lead to measurable effects in the chiral induction upon complex formation. The structures of Λ and Δ-[M(polypyridine)$_2$-(amino acid)] can be studied by equilibria, because small influences in the side chains of the amino acid can have a strong influence on the position of the equilibrium. The coordination of an (*S*)-amino acid with an apolar side chain leads in general to a preference of the Λ form of the complex. The chiral induction can be traced back in this case to the repulsive intramolecular ligand–ligand interaction in the less preferred Δ isomer.[63–67] The interpretation of the results for the (*S*)-amino acids with polar side chains are less straightforward. In this case the metal ion and the diimine ligand determine the helicity of the final product. As an example, (*S*)-serin (**L16**) as the chiral ligand, gives a stronger preference of the Δ isomer in the case of Ru^{II} complexes relative to Co^{III} as the central metal.[68, 69] In addition it was observed that in Ru^{II} complexes with (*S*)-glutamate (**L17**), (*S*)-aspartate (**L18**), and (*S*)-serine (**L16**) a stronger discrimination is obtained with 2,2'-bipyridine (**L16**) relative to 1,10-phenanthroline (**L17**).[68, 70, 71] This effect is explained by a higher flexibility of the bipyridine ligand,[70] which leads to a decrease of the intramolecular ligand–ligand interaction and therewith to an amplification of other noncovalent interactions. Therefore hydrogen bridges, hydrophobic interactions, or solvation effects[72, 73] can play a more important role. The sensitivity of the equilibrium situation in this series is documented by the fact that the chiral induction that leads to the preferred formation of the Δ form is observed only for (*S*)-glutamate (**L17**) and (*S*)-threonin (**L19**), whereas (*S*)-aspartate (**L18**) and (*S*)-serin (**L16**) show no selection at all.[68, 70, 71, 74]



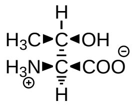
L16



L17



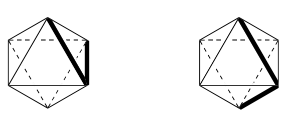
L18



L19

2.2. Complexes with Terdentate Ligands

Predetermination of chirality in octahedral complexes has been studied only in a few cases with terdentate ligands. Such ligands can have edge configuration ***3*** or ***4***, where ***4*** is

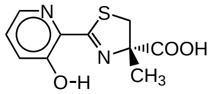


3 **4**

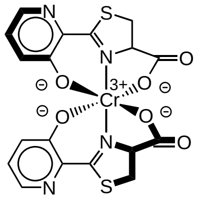
Figure 4. Edge configurations in octahedral complexes with tridentate ligands.

inherently achiral for ligands of the symmetry ABA (Figure 4).

Raymond et al.[75] used the demetallated form of ferrithiocine (**L20**) as a ligand. This siderophore is neither a catecholate nor a hydroxamate and it is therefore basically different from the siderophores described in Section 2.5. The ligand coordinates through a central nitrogen atom, a phenolate, and a carboxylate oxygen atom. The natural enzyme (**L20**) forms a 2:1 complex with iron. In order to study the stereochemistry the kinetically more stable Cr^{III} and Co^{III} complexes were investigated. The meridional edge configuration ***4*** was obtained. The mirror plane of this configuration is, however, no longer present in this ligand of the ABC type (Scheme 2). The enantiopure ligand, for instance in the *S* configuration, forms exclusively meridional Δ and Λ diastereomers (see Figure 2). The Cr^{III} complex is formed in a Λ:Δ diastereomeric ratio of 62.5:37.5, that is the selectivity is relatively weak.

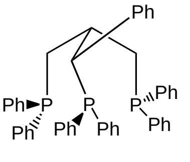


L20

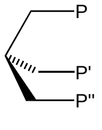


Scheme 2. Arrangement of **L20** in the Cr^{III} complex.

The tripod ligand **L21**[76a] has three phosphorus donor atoms. The Λ configuration is obtained through coordination of the *R* form of the ligand in a rhodium(I) center. This result was evident from an X-ray analysis of the solid (Figure 5), but NMR spectra showed that the same form is also strongly favored in solution. The free coordination sites are occupied with a norbornadiene group.



L21



L22	P	P'	P''
a	PPh_2	$P(2\text{-}Tol)_2$	$P(4\text{-}Tol)_2$
b	PPh_2	DBP	$P(3,5\text{-}Mes)_2$
c	PPh_2	DBP	$P(4\text{-}Tol)_2$
d	PPh_2	DBP	PEt_2

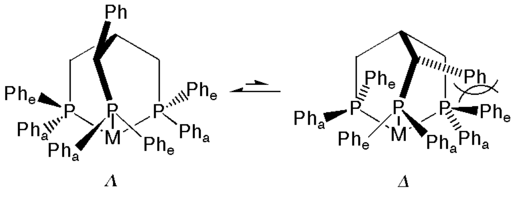
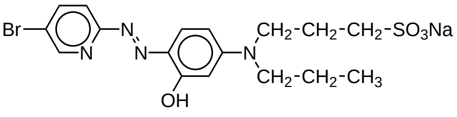


Figure 5. Schematic representations of Δ and Λ diastereomers of a Rh complex with (*R*)-**L21**.

A group of tripod ligands (**L22**) described by Huttner shows another type of chirality (DBP = dibenzophospholyl).[76b] It is not the edge configuration that is chiral, but the tripod ligand coordinates with three different phosphane groups and generates therewith a chiral environment. The other coordination sites of the Ir^{III} complex are occupied with acetonitrile molecules.

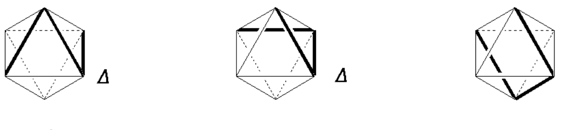
Another limiting case of chiral predetermination of metal centers is their synthesis at chiral ammonium interfaces as templates. Publications from Kunitake[77] show that a glutamine-functionalized surface can induce chirality in complexes with tridentate N_2O ligands (**L23**).



L23

2.3. Complexes with Tetradentate Ligands

Octahedral complexes with tetradentate ligands have two "free" coordination sites where substitution reactions can occur. Such complexes can be used as enantiopure building blocks, for example for the synthesis of polynuclear metal complexes if they can be prepared stereoselectively. Tetradentate ligands, which are not branched, can wrap around an octahedron according to the edge configurations ***8***, ***11***, or ***14*** (Figure 6), where ***14*** is inherently achiral through the mirror plane. Besides the classification of the complexes according to edge configurations, the designations *cis-α* for ***8*** and *cis-β* for ***11*** has been frequently used. The achiral form ***14*** can be called a *trans* configuration.



8 *cis*-α ***11*** *cis*-β ***14*** achiral

Figure 6. Edge configurations for linear tetradentate ligands.

The possibility of predetermination of chirality in octahedral complexes with tetradentate ligands was already reported in 1990 by Bosnich.[78] Ligand (*S*,*S*)-**L24** coordinates through four nitrogen donor atoms and yields Δ-configured complexes of edge configuration ***11***. In this case chirality is not only induced at the metal center but also at the coordinating nitrogen atoms (Figure 7)

The group of Vagg and Williams synthesized a series of cobalt(III) complexes with linear tetradentate N_4 ligands with

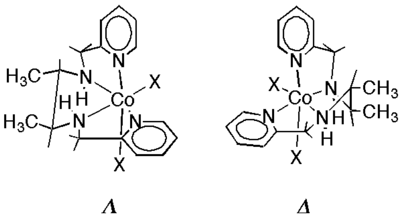
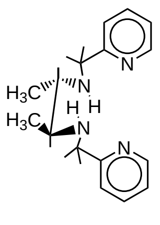
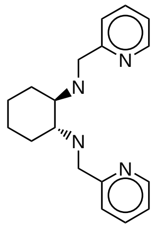


Figure 7. Λ and Δ diastereomers of [Co(**L24**)X_2].

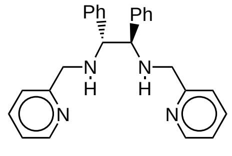
terminal pyridyl groups. Of special interest are the influences of C and N substitution on the stereoselectivity. In this respect one can generally distinguish two sorts of stereoselectivity: the arrangement of the ligand in a given edge configuration and the helicity of the metal center. A series of ligands (**L24**–**30**) was obtained through substitution of a given molecular skeleton. Contrary to (*S*,*S*)-**L24**, *Λ*-configured complexes of edge configuration ***11*** were obtained with the ligands (*R*,*R*)-**L25**[74] and (*R*,*R*)-**L26**.[79] It was also proved for **L26** that rhodium(III) shows the same stereochemical preference. The substitution of the pyridine groups in ligand **L25** by diphenylphosphane groups (**L27**) showed no influence on the stereochemistry of the complex formation. Again, the *Λ*-configured edge configuration ***11*** was obtained for the cobalt complex.[80]



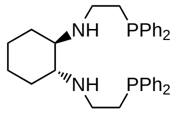
L24



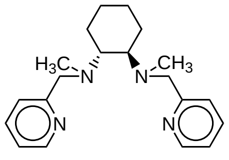
L25



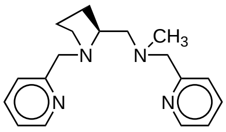
L26



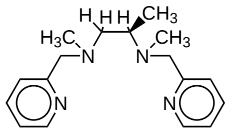
L27



L28

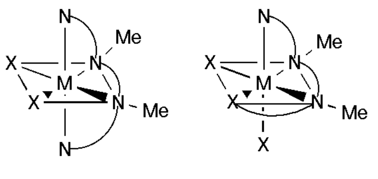


L29a



L29b

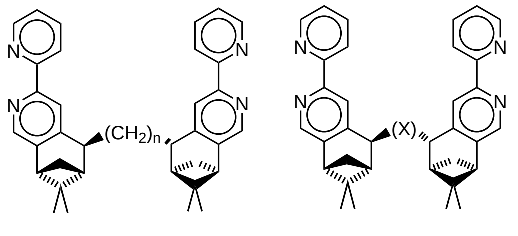
The stereochemistry of coordination compounds often changes drastically even if only small changes occur in a ligand. The methylation of the secondary amine of ligand (*R*,*R*)-**L25** gives ligand (*R*,*R*)-**L28**.[81] This variation is sufficient to change from a ***11*-*Λ*** to a ***8*-*Δ*** preference. This effect is also observed with complexes of the unsymmetrical ligand (*S*)-**L29a** (Figure 8). Analogous results are obtained for the easily accessible dimethyl derivative (*R*)-**L29b**. The latter forms stereoselective *Δ*-configured cobalt complexes of edge configuration ***8***.[82]. The two coordination sites that are occupied with chloride ligands can be substituted in stereospecific substitution reactions.



8*-*Δ ***11*-*Λ***

Figure 8. Comparison of a *Δ*-configured complex of edge configuration ***8*** as shown for **L28** and a *Λ*-configurated complex with edge configuration ***11***.

Besides the cobalt complexes with aliphatic N_4-donor ligands, ruthenium(II) complexes with chiral bipyridine derivatives have found a wide interest. The so called CHIRAGENs (from CHIRAlity GENerator) **L30** and **L31**[83, 84] can coordinate only in edge configuration ***8***. Therewith one source of isomerism is already eliminated. The other, the chirality at the metal center, is controlled through the use of enantiopure chiral ligands. The formation of several isomers is excluded in the case of these ligands. The method of synthesis of the chiral bipyridine derivatives is extremely variable and allows for the preparation of a large number of tetradentate ligands. The structure of these molecules can be engineered in various ways: The bridging group that links the two bipyridine rings can be any of a large number of aliphatic, aromatic, or even functionalized synthons, and the pinene group can be attached to one of the pyridine rings in either the 4,5-, or the 5,6-position (see Section 4.1).



L30 **a**, n = 0; **b**, n = 3; **c**, n = 4
d, n = 5; **e**, n = 6;
f, Brücke =$CH_2(H_3C_5N)_2CH_2$

(+)-L31 **a**, X = *o*-Xylylen
b, *m*-Xylylen
c, *p*-Xylylen

The first molecules of the series of the CHIRAGEN ligands were described 1993.[83] The bipyridine units are connected through aliphatic C_4, C_5, or C_6 bridges (**L30c**–**e**) and they yield exclusively the *Δ*-configured Ru complexes. An X-ray analysis of a complex of the C_6-bridged derivative (**L30e**) proves this assignment. Substitution of the monodentate ligands is possible in all these complexes under retention of the configuration of the metal center. Osmium(II) also forms mononuclear complexes of *Δ* configuration with **L30e**.[85]

Xylene bridged ligands were prepared to amplify the tendency for preorganisation by making the molecule more rigid. All three isomers, the *ortho*, *meta*, and *para* forms, have been used (**L31a**–**c**).[86] Ru complexes were also obtained stereoselectively in the *Δ* form with these ligands. *Λ*-configured complexes could not be detected. The assignment of the configuration can be again based on an X-ray structure analysis of the complex *Δ*-[Ru(**L31a**)(dmbpy)]$(PF_6)_2$ where dmbpy = 4,4′-dimethyl-2,2′-bipyridine. The application of CHIRAGEN ligands is not restricted to mononuclear complexes. If two "free" coordination sites are replaced by a potentially bridging ligand, dinuclear complexes can be prepared stereoselectively (see Section 4).

As already described in the introduction to this section, octahedral complexes of tetradentate ligands are promising for use in stereoselective catalysis because two coordination sites are available for substitution reactions. The catalytic decarboxylation and epimerization of amino acids at cobalt(III) complexes with enantiopure, chiral aliphatic N_4 ligands was investigated. The dichlorocobalt(III) complexes used had the inherently achiral edge configuration ***14*** (see Figure 6). The coordination of the amino acid changes the edge configuration to ***11***, which is formed in the Λ form. Chirality is in this case clearly not induced through the incoming ligand, because both forms of the amino acids (*R* and *S*) lead to complexes with the same helicity at the metal center. It is the tetradentate ligand that predetermines the chirality. The didentate ligand transforms the complexes into the inherently chiral edge configuration where the chiral predetermination becomes observable (Figure 9).

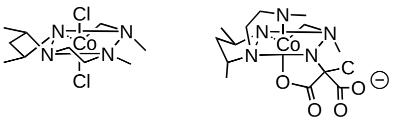
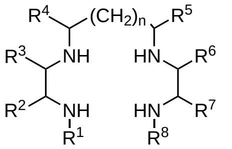


Figure 9. Stereoselective transformation of an achiral edge configuration (***14***, left) into a chiral (***11***, right) configuration through substitution of two monodentate ligands for a didentate ligand.

The ligands **L32**,[87–94] which were used for these investigations, are in all cases based on the same molecular skeleton in which the length of the bridge (n = 0, 1) and the substituents (R^1–R^8) can be varied. Only complexes with Λ stereochemistry were obtained, either with the tetradentate ligands (*S*)-**L32** or with (*R*)-**L32**. It is noteworthy that the ligands that are isolated in the *S* form are substituted at the outer bridges (R^2–R^3 and R^6–R^7), respectively, and the *R*-configured ligands are substituted at the middle bridge (R^4–R^5). It can be concluded that an *R* configuration of the middle bridge leads to a Λ complex in the same way as an *S* configuration of the outer bridge does.



L32

2.4. Complexes with Pentadentate Ligands

Octahedral complexes with pentadentate ligands have often been used for investigations of inner sphere electron transfer reactions, because only one site of the octahedron is available for substitution. Linear, pentadentate ligands can, in principle, coordinate as edge configurations ***22***, ***23***, ***28***, ***30***, of which number ***23*** is inherently achiral through a mirror plane (Figure 10).

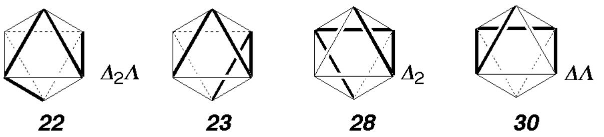
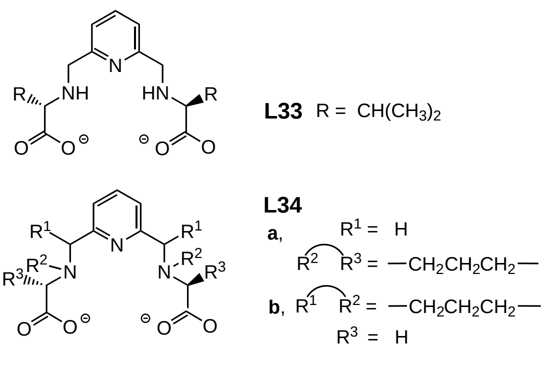


Figure 10. Edge configurations for linear pentadentate ligands. The descriptors with indices designate the relative number of edges that have Δ and Λ orientations.

Bernauer synthesized the ligand **L33** in 1984.[95] This ligand can coordinate for steric reasons only in the chiral configuration of highest symmetry ***28***. It was shown for the



cobalt(III) complex that the *S,S* form of the ligand yields exclusively the Λ configuration of the complex (Figure 11). Through variation of the number and of the nature of the substituents it was possible to investigate for **L34** the influence of steric factors on the helicity of the metal center as well as the influence of the chirality.[96] The X-ray analysis of Λ-[Co((*S,S*)-**L34a**)H_2O](ClO_4) is the basis for the spectroscopic investigation and characterization of further complexes. It was concluded that the Λ form of the cobalt(III) complex is also obtained from the Δ form of the ligand **L34b**, whereas (*S*)-**L34b** yields a Δ-configured complex. This example demonstrates, as has already been discussed, that purely geometrical aspects, as well as the chirality of the ligand, have to be considered in order to predict the preferred configuration correctly.

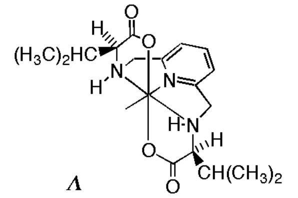
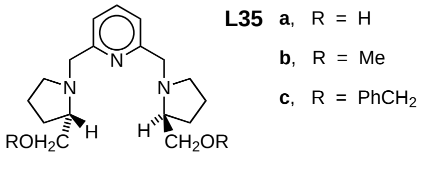


Figure 11. One diastereomer of the edge configuration ***28*** for chiral pentadentate ligands.

Not only can inert metal ions such as cobalt(III) be investigated with these pentadentate ligands, but the methodology of stereochemical predetermination is also applicable for labile metal ions. Copper(II) complexes have been synthesized and discussed in detail. For this purpose **L34** was modified. The terminal carboxylic acid groups were replaced by alcohol (**L35a**) or ether groups (**L35b,c**). The *S,S*-configured ligands **L35a–c** yield, in the same way as the structurally similar **L34** ligands, the Λ form of the complexes, in analogy to the cobalt(III) complexes described above. The chirality of the nitrogen atom of the pyrrolidine rings is fixed through complexation in the *R* configuration.



2.5. Complexes with Hexadentate Ligands

Out of the numerous possibilities of geometrical configurations of hexadentate chelate ligands in octahedral complexes, the following edge configurations have been observed: ***41***, ***52***, ***53***, ***54***, ***57***, ***83***, ***87*** (Figure 12). A classic paper, in which the predetermination of chirality at the metal center is the subject of investigation, describes the cobalt(III) complexes with nonracemic 1,2-propylenediaminetetracetate (**L36**) as the ligand. Only the inherently chiral edge configuration ***41*** is possible for this ligand. Dwyer and Garvan[97] showed that only one diastereomeric form can be isolated, that is, the configuration at the metal center is determined through the configuration at the chiral carbon center in the ligand. The isomeric purity of the complex was demonstrated by fractional crystallization, whereas its absolute configuration could not be determined, and therefore no reliable predictions were possible.

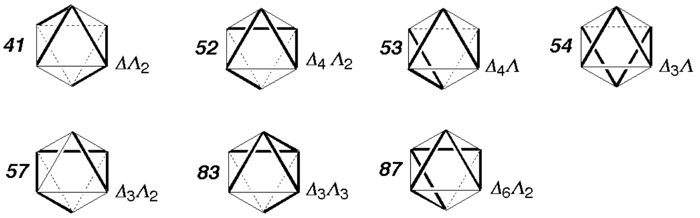
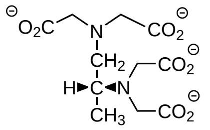
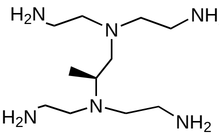


Figure 12. Edge configurations for hexadentate ligands.



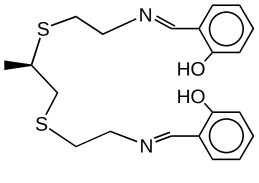
L36

Gollogly and Hawkins[98] calculated in 1967, by methods of conformational analysis, differences in energy for the diastereomeric forms of analogous complexes with **L37** as the ligands. These authors predicted a relatively large difference in energy based on van der Waals interactions for both configurations at the metal center for a given chirality of the ligand. This prediction was confirmed in 1974 through the X-ray analysis of the complex.[99] The predetermined absolute configuration is $[\Delta\text{-Co}((R)\text{-}\mathbf{L37})]^{3+}$.



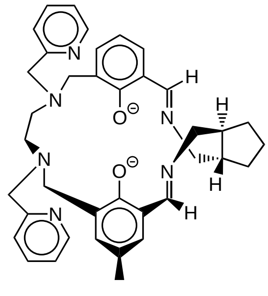
L37

Another relatively early publication comes again from the group of Dwyer.[23] This investigation concerns the nonbranched hexadentate ligand **L38**. Stereoselectivity is again demonstrated, but the results are less clear because the possibility of the formation of four different edge configurations ***52***, ***53***, ***54***, and ***57*** is not discussed in more detail. All these edge configurations are inherently chiral and it is not known which edge configuration is formed by this ligand.



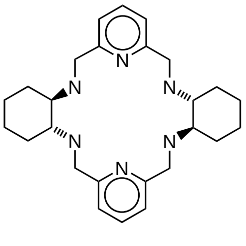
L38

A series of mono- and dinuclear species were synthesized in 1994 by the group of Bosnich.[100] The ligand (*S*,*S*)-**L39** is octadentate, and it can coordinate up to two metal centers. One coordination site is an octahedron, whereas the second represents a square where two oxygen donor atoms function as μ_2 bridges. The octahedral binding site can be considered as an open, twice branched ligand. This corresponds therefore to the edge configuration ***41***, that was already discussed for 1,2-propylene diaminetetraacetate (**L36**). The zinc and cobalt complexes, which were prepared with **L39** were obtained as single diastereoisomers. X-ray analysis shows Δ-configured Zn^{II} and Co^{III} centers for the octahedral coordination sites, whereas the Mn^{II} complex has an Λ configuration. The authors explain this "inversion" of the configuration by the larger ionic radius of Mn^{II}.

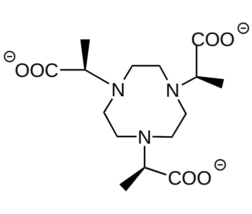


L39

Macrocyclic ligands have also been used for the stereoselective synthesis of metal complexes.[101] Replacement of the ethylene bridges in the hexadentate ligand pyan through enantiomerically pure 1,2-diaminocyclohexane yields the chiral ligand *trans*-**L40**. Metal complexes of the edge configuration ***87*** are obtained in defined stereochemistry with this ligand. Another edge configuration is ***83***. An example is the chiral ligand **L41**[102] where triazacyclononane has been functionalized with three propionate groups. The (*R*,*R*,*R*)-ligand forms Λ-configured cobalt and indium complexes.[103]

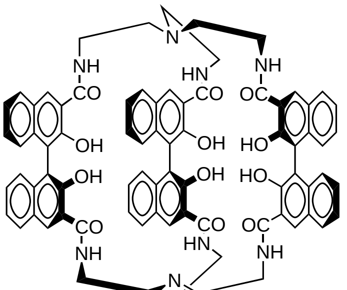


L40

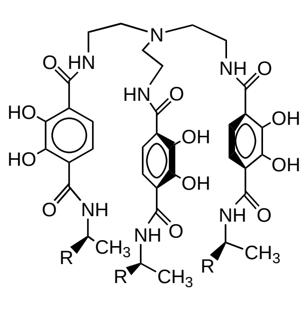


L41

Triscatecholates that have been built into completely closed sepulchrates or into open systems have also been applied in many cases in coordination chemistry. The sepulchrate of the bicapped tris(binaphthol) ligand **L42** comprises nine edges. The derived edge configuration can be described as an inverse

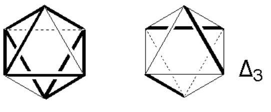


L42



L43, R = Et, Ph

“three-edge-case”. In an octahedron, a maximum of twelve edges can be occupied. If the occupied edges are replaced by nonoccupied ones, an x-edge configuration is transformed into the symmetry equivalent $(12-x)$ case. **L42** occupies therefore the edge configuration that is inverted to ***15***. It will be designated as $\underline{\mathbf{15}}$ (Figure 13). (R)-**L42** forms Λ-configured complexes with $\mathrm{Ga^{III}}$, $\mathrm{Cr^{III}}$, and $\mathrm{Fe^{III}}$.[104] As opposed to the sepulchrate, the tripodal triscatecholate ligand (S)-**L43**[105] corresponds to an open chain and assumes edge configuration ***83***, just like the tripodal ligand **L41**. The $\mathrm{Fe^{III}}$ and $\mathrm{Ga^{III}}$ complexes also show a stereoselectivity, which can be attributed to nonbonding interactions between weakly polar groups.

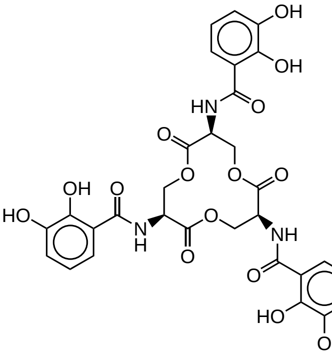


$\underline{\mathbf{15}}$ ***15***

Figure 13. Complementary edge configurations $\underline{\mathit{15}}$ and *15*.

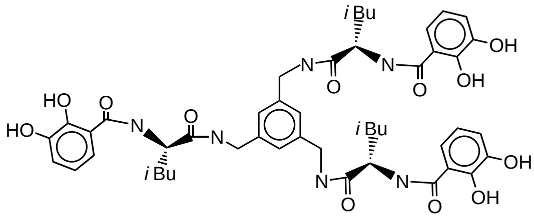
2.5.1. Biological Systems

Chiral predetermination has also been observed in biological systems. In such cases, chiral information can be transferred from the apoproteine to the coordinating metal center. Particularly investigated examples for such cases are the siderophores. The siderophores are biomolecules that bind $\mathrm{Fe^{III}}$ sufficiently strongly to make it available to the cell under physiological conditions. A well investigated and documented case is enterobactin $[\mathrm{Fe}(\mathbf{L44})]^{3-}$, which is responsible for the transport of iron in bacteria. It is one of the strongest natural $\mathrm{Fe^{III}}$ binders known. Natural enterobactin is optically active and its Δ configuration can be deduced from the CD spectrum.[106] An X-ray analysis of the analogous vanadium(IV) complex confirms this assumption.[107] The stereochemistry of the metal center is in this case of importance, because bacteria can make use only of the Δ form of the complex.

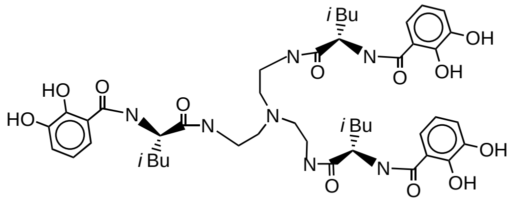


L44

Shanzer et al.[108] presented a concept for the synthesis of model compounds in 1986. The predetermination of the chirality of the metal center is attributed to the favorable steric interactions and the formation of hydrogen bridges. This principle seems to be generally applicable in this family of compounds. In order to understand the structures and the mechanisms of the action of the siderophores several low molecular iron complexes with triscatecholate ligands have been synthesized as model compounds in the past 15 years. The first chiral model complex that is formed selectively in the natural Δ configuration was prepared in 1987 by Shanzer et al.[109] The tripodal triscatecholate ligand **L45** is based on 1,3,5-tris(aminomethyl)benzene, and it occupies the edge configuration ***83***. Later, the tris(2-aminoethyl)amine building block was also used for the synthesis of a triscatecholate ligand **L46**.[110] The stability constant for the $\mathrm{Fe^{III}}$ complex of this ligand reaches almost the value of the natural enterobactin ligand. One reason for the increased stability is the preorganization through formation of hydrogen bridges in ligand **L46**. In contrast to that, ligand **L45** is accidentally orientated in protic solvents.

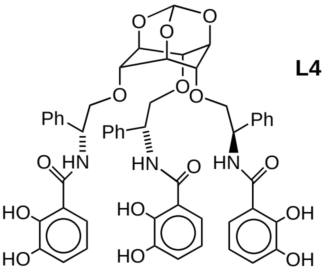


L45



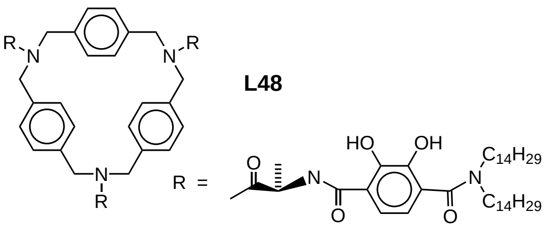
L46

Ferrichrom is also a growth factor for bacteria. The catecholate groups in enterobactin (**L44**) are replaced by hydroxamate groups and it shows no C_3 molecular symmetry. Model investigations for this biomolecule have been carried out with a trishydroxamate ligand (**L47**) with a sterically less-demanding quartenary carbon atom as the basic structure. The chirality is controlled through Λ-amino acids, and it corresponds again to edge configuration ***83*** (see Figure 12).[111] The hydrogen bridging system of this molecule leads, through a propeller-like structure, to a Λ-*cis* configuration.[112] The effectiveness of this model compound was shown in cultures of bacteria.



L47

The group of Murakami[113] combined a hexapus cyclophane as a C_3-symmetric ground structure through an alanine group with the coordinating catecholate segments (**L48**). The Λ form of the amino acid leads to $\mathrm{Fe^{III}}$ complexes with Λ configuration. This example shows that the amino acid determines the stereochemical preference in a given ground structure. The group of Kishi et al. synthesized models for



L48

enterobactin from the C_3-symmetric ligand **L47**.[114] The *S* form yields preferentially the Δ-configured complex. The stereochemical preferences were determined with isostructural diamagnetic Ga^{III} complexes.

Raymond et al.[107, 115] looked at the stereochemistry of enterobactin analogues through a new perspective, by variation of the metal and not the biomolecule. In 1978[106] a rhodium(III) complex of the enterobactin ligand (**L44**) was prepared. A comparison of the CD spectra with that of enantiopure rhodium(III)-triscatecholate complexes with known configuration led to the determination of the chirality of the metal center in the siderophore. Thereby it was assumed that a ligand of a given configuration yields complexes of the same metal helicity with different metals. There are, however, cases where this assumption is not valid.[54, 100] Only some time later was the first X-ray structural characterization of a metal enterobactin complex successful, and yielded the absolute configuration of the vanadium complex of apoferritine.[107, 115] This was the first definitive proof of the configuration of the metal center in the biomolecule almost 20 years after it had been derived from other information. The siderophores show clearly that in biological systems nonracemic ligands are used for the predetermination of chirality at metal centers.

3. Predetermined Chirality in Mononuclear, Nonoctahedral Complexes

3.1. "Square-Planar" Complexes

Square-planar coordination geometry is particularly prominent in coordination compounds of d^8 metals. This coordination geometry is inherently achiral. It can be, however, distorted into a chiral structure by sterically demanding ligands. Achiral ligands of this kind yield in such cases racemates.[116] Nonracemic chiral ligands can also predetermine the chirality in square-planar complexes. Pt^{II} for example forms Δ-*cis*-configured complexes of the form $[PtL_2]$ stereoselectively with the didentate ligands (*R*,*R*)-**L11**, (*R*,*R*)-**L12**, and (6*R*,7*S*)-**L49** (Figure 14).[11, 12]

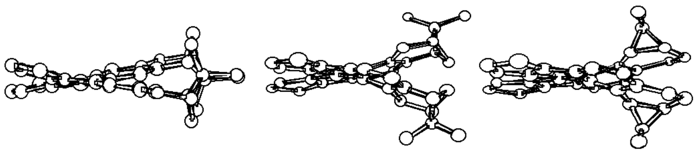
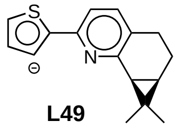
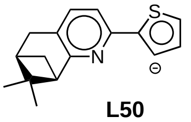

Δ-[Pt(**L12**)$_2$] Δ-[Pt(**L11**)$_2$] Δ-[Pt(**L49**)$_2$]

Figure 14. Helical distortion in "quadratic-planar" coordination geometry in $[PtL_2]$ complexes.

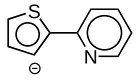
The steric requirements of these ligands are decisive for the predetermination of chirality in square-planar complexes. The orientation of the pinene group in ligand **L50**, which is derived from (−)-β-pinene, determines the chirality of the complex [Pt(**L50**)(**L51**)] at the metal center. The configuration is predetermined, even though **L51** is an achiral ligand. In the complex [Pt(**L52**)$_2$], on the other hand, no unambiguous predetermination of the configuration is observed. The chiral groups point outwards in this case and do not interact sufficiently strongly.



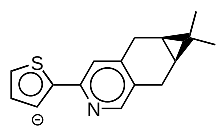
L49



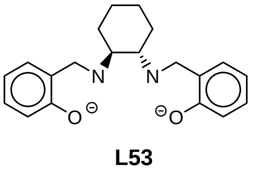
L50



L51



L52

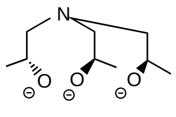


L53

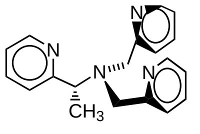
Ligand **L53**, which is obtained through condensation of (*R*,*R*)-cyclohexanediamine with salicylaldehyde, predetermines the chirality in its *SP*-4 complex with Pt^{II}.[117] The X-ray structure analysis confirms a small but significant chiral distortion, and the CD spectrum shows the preference for one configuration in solution. An analysis of the published data shows that this complex has a Λ configuration.

3.2. Trigonal-Bipyramidal Complexes

Trigonal-bipyramidal coordination geometry occurs preferentially with tripodal ligands. There are several factors that can cause chirality at the metal center in this case. One possibility is the tripod ligand has three different ligand arms.[118] Another case is represented by a C_3-symmetric ligand where each of the arms carries a chiral center. An example is ligand **L54**, where the chirality of the complex is predetermined through the chirality of the ligands.[119]



L54



L55

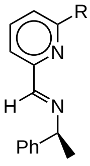
Canary et al. report the propeller-like orientation of a tripod ligand coordinated to a metal center.[120] The ligand (**L55**) was prepared in enantiopure form and it already shows a helical orientation in its free form. The *R* form of the ligand forms a chiral Λ-configured metal center upon coordination with Zn^{II} and Cu^{II}.

3.3. Tetrahedral Complexes

The most common source of chirality in organic chemistry, a tetrahedrally coordinated M*abcd* center with four monodentate ligands, is rare in coordination chemistry.[8–10, 121, 122] Moreover, chiral predetermination of tetrahedral centers in coordination chemistry is very unlikely because the "coordination properties" of metal and carbon centers are very different.

T-4 complexes with two symmetric didentate ligands AA show the symmetry D_{2d} and are therefore inherently achiral. Two unsymmetrical ligands AB lead in *T*-4 to C_2-symmetric complexes, which are in principle chiral. This chirality can be predetermined through the use of nonracemic chiral AB ligands.

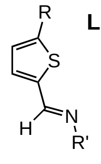
Pioneering work in this field was carried out by van Koten et al.[123, 124] Chiral pyridinecarbaldehydeimine derivatives **L56** in the *S* form strongly prefer the Λ configuration in silver(I) and copper(I) complexes. The ligand with an unsubstituted pyridine ring (**L56a**) yields a higher diastereoselectivity relative to the one with a methyl group (**L56b**). The silver complexes show a diastereomeric ratio of Λ-(*S*)-**L56a**:Δ-(*S*)-**L56a** = 99:1 and Λ-(*S*)-**L56b**:Δ-(*S*)-**L56b** = 95:5. The copper complexes show generally smaller selectivities of Λ-(*S*)-**L56a**:Δ-(*S*)-**L56a** = 85:15 and Λ-(*S*)-**L56b**:Δ-(*S*)-**L56b** = 75:25. A similar behavior was observed in the case of copper(I) and silver(I) complexes with thiophene-2-carbaldehydeimine ligands (**L57**).[125] The stereoselectivity is higher for the silver complexes relative to the copper species.



L56

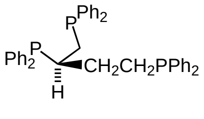
a, R = H

b, R = Me

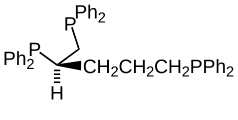


L57	R	R'
a	H	(*S*)-CHMePh
b	Me	(*S*)-CHMePh
c	TBS	(*S*)-CHMePh

Diastereoselectivity can also be observed in a *T*-4 complex with two monodentate ligands and an asymmetric didentate ligand of the form [Co(CO)(NO)(triphos)], as shown by Brunner et al.[126] **L58** forms 83% of the *S*-configured cobalt complex. The longer alkyl chain (by one CH_2 group) in **L59** decreases the diastereoselectivity significantly to 63% (Figure 15).



L58



L59

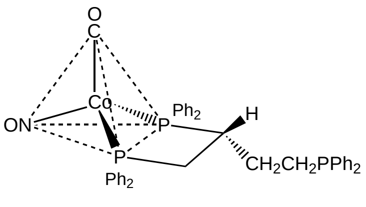
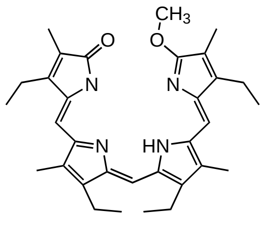
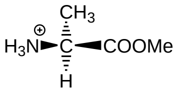


Figure 15. Example of a tetrahedral cobalt complex with **L58**.

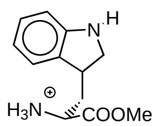
A limiting case for the predetermination of metal centers is presented in the work of Mizutani, Ogoshi et al.[127] These authors do not investigate primarily predetermination of chirality at the metal center, but the transfer of chirality. The chirality of esters of amino acids is in this case used to induce one preferred helicity in racemic zinc–biliverdine (**L60**) complexes. The interaction between the chelate ligand and the esters of the amino acid is in this case a consequence of the zinc atom, which forms a fivefold coordinated complex. The observed enantiomeric excesses are dependent on the host molecule and they lie between 42% for the *S*-alanine methylester (**L61**) and 73% for the *S*-tryptophane methylester (**L62**).



L60



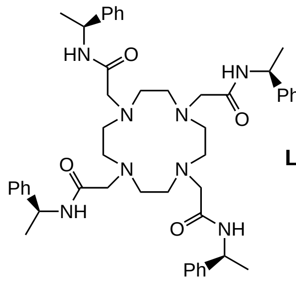
L61



L62

3.4. Square-Antiprismatic Complexes

Coordination number eight often leads to a square-antiprismatic coordination geometry. This coordination number is rarely encountered in transition metal coordination chemistry, but it is frequent in complexes of the lanthanides. Parker et al. investigated the Pr, Eu, Tb, Dy, and Yb complexes of the chiral C_4-symmetric ligand **L63**.[128] Both forms of the ligand (*R*,*R*,*R*,*R* and *S*,*S*,*S*,*S*) were prepared and it was shown that the chirality of the stereocenters of the amide groups determines the chirality of the N-substituents and therewith the configuration of the macrocyclic 12-membered ring. The chirality of the terbium complex was investigated in view of its photophysical properties.



L63

4. Predetermined Chirality in Polynuclear Complexes

The methods for the control of chirality in mononuclear coordination compounds, discussed in the preceding chapters can be, in principle, transferred to polynuclear complexes. Predetermination of chirality in polynuclear complexes is especially important from a practical point of view, since the number of possible isomers increases exponentially with the number of metal centers. Separation of the isomers becomes more and more difficult. Polynuclear coordination species can be used potentially in molecular devices. The functions that can be carried out by molecular devices can, however, be only well defined if the compounds are stereochemically pure. Polynuclear ruthenium(II) complexes have often been investigated in this connection. The CHIRAGENs **L30** and **L31**[83, 84, 86] (described in Section 2.3) have been used successfully for the synthesis of oligonuclear ruthenium complexes in stereochemically well-defined form. An example is the synthesis of Δ,Δ-$[Ru_2((-)$-**L31b**$)_2(bpym)](PF_6)_4$ from **L31**.[84] Two Δ-$[Ru((-)$-**L31b**$)]^{2+}$-fragments are connected in this complex through a 2,2′-bipyrimidine (bpym) bridge. Both complexes, the homochiral and the heterochiral meso form Δ,Λ-$[Ru((-)$-**L31b**$)(bpym)Ru((+)$-**L31b**$)](PF_6)_4$ can be prepared from the enantiomerically pure building blocks (Figure 16).

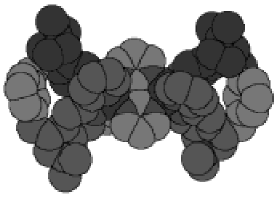
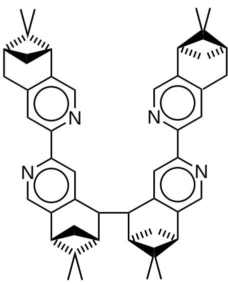


Figure 16. Structure of a dinuclear meso complex Λ,Δ-$[Ru_2((+)$-**L31b**$)(bpym)((-)$-**L31b**$)](PF_6)_4$ with chiral metal centers.

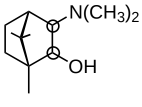
Similar ligands where the two pinenobipyridine groups are not connected through an aryl group but through a propyl chain (**L30b**) or even if they are directly connected (**L30a**) cannot coordinate in a tetradentate manner at one metal center for steric reasons. Instead, these ligands can coordinate as bridging units in a bisdidentate way. The Δ,Δ- and the Λ,Λ-configured complexes can be formed stereoselectively from nonracemic $[Ru(bpy)_2]^{2+}$ fragments with **L30b** and **L30a**. A CHIRAGEN ligand with 5,5′-dimethylene-2,2′-bipyridine as a bridge[129] represents a trisdidentate ligand (**L30f**). This ligand can bind three $[Ru(bpy)_2]^{2+}$ fragments, to yield Δ,Δ,Δ- and Λ,Λ,Λ-configured complexes if enantiomerically pure building blocks are used. These nonracemic building blocks can be obtained either through classical resolution of a racemate with tartrates[130, 131] or through stereoselective synthesis. An example for the latter case are the mononuclear ruthenium complexes with the *m*-xylene-bridged ligand **L31b**, which were already discussed in Section 2.3. The predetermined fragment Δ-[Ru(**L31b**)] has also been treated with the ligands **L30a,b,** and **f**.



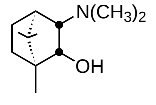
L64

Another interesting ligand of the CHIRAGEN series is the Super CHIRAGEN **L64**. Both pyridine rings of this ligand are condensed in the 4,5-position to pinene groups. The resulting ligands are C_2 symmetric and sterically demanding. The chiral information is amplified through this multiplication of pinene groups. The coordination chemistry of these ligands is similarly varied as that of the directly bridged ligands (**L30a**).

Polynuclear metal complexes can be built not only from ruthenium centers, but also tetrahedral zinc atoms can be formed in dimeric complexes in a chirally predetermined manner.[132] Noyori et al. have prepared the dimeric zinc complex $[Zn_2($**L65**$)_2(CH_3)_2]$ from a trigonal methylzinc complex of the ligand (2*S*)- or (2*R*)-**L65**. The enantiomerically



(*S*)-**L65**



(*R*)-**L65**

pure *S* form of the ligand forms *S*-configured metal centers. The heterochiral dimer, which is formed from the racemic ligand is more stable in solution as well as in the solid (Figure 17).

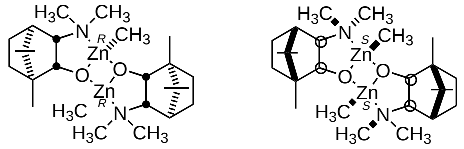


Figure 17. Dimers with *R*,*R*- and *S*,*S*-configured zinc coordination centers.

4.1. Helicates

In helical, polynuclear metal complexes two forms of chirality must be distinguished. The first is the chirality at the metal center, which has already been discussed in detail, and the second is the orientation of the bridging ligands in the complex, which determines the sense of rotation of the resulting helix. The latter is designated with the descriptors *P* for right-handed and *M* for left-handed orientations (Figure 18). Achiral ligands yield racemates of *P*- and *M*-configured helicates. The chirality of the metal center and therewith the helicity of the whole molecule can be, however, again predetermined through the use of chiral ligands.[133]

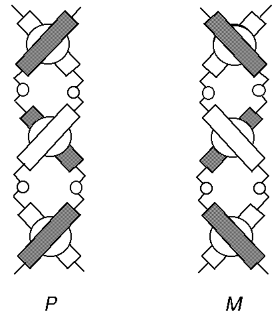
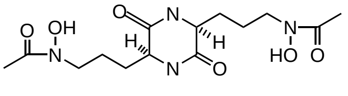


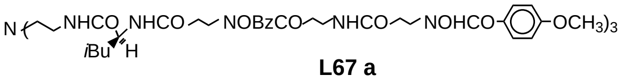
Figure 18. *P*- and *M*-configured helices.

The first example of a helix with predetermined chirality was published by Raymond et al.[134] Dinuclear iron complexes with rhodothorulicacid (**L66**), a dihydroxamate siderophore, were synthesized to investigate mechanisms of microbial transport of iron (see Section 2.5.1). The dinuclear complex $[Fe_2($**L66**$)_3]$ with clearly Δ-*cis*-configured iron centers is formed as a triple helix between pH 4 and 11. Even though the chirality of the helix is not explicitly discussed in this publication, it is evident from the given data that it has a *P* configuration.

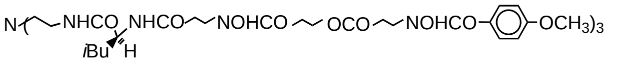
Shanzer et al.[135] described in 1987 the predetermination of the chirality of a dinuclear triple helix that is stabilized through hydrogen bridges between the single strands. The ligand **L67a** is constructed on the basis of tris(2-aminoethyl)amine. The chirality is introduced through the L-leucine



L66



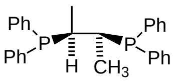
L67 a



L67 b

groups and the three arms of the ligands are built up as an alternating sequence of hydroxamate and amide groups. This ligand forms stable, dinuclear complexes of P-helicity with iron(III). The configuration is stabilized through hydrogen bridges between the peripheric amide proton of one strand and the central amide carbonyl group of the neighboring strand. In order to test the hydrogen bridge hypothesis a ligand was synthesized where the peripheral amides are replaced by ester groups (**L67b**). Hydrogen bridges cannot be formed anymore in the same way. The result is an inversion of the helix and, indeed, the M form is preferred.

A series of investigations where helical chirality is predetermined were carried out around 1985.[136–138] It is interesting to note that the concept of a "helix" is not used. The complexes were discussed in terms of configuration chirality. Stereoselective synthesis of helical systems of this sort have been developed for molybdenum dimers. Cotton, Peacock et al. described in 1984 the synthesis of a bis(S,S)-2,3-(diphenylphosphanyl)butane (**L68**) bridged dinuclear molybdenum complex where the "free" coordination sites are occupied with four chloride or bromide ions (Figure 19).[139, 140] These complexes can be designated as M-configured double helices from the current nomenclature. It should be noted that in these cases the metal itself cannot be considered to be a center of chirality. The helicity is defined only through the orientation of the ligands relative to each other. If the bridging diphosphane ligands are substituted by (R,R)-*trans*-1,2-diaminocyclohexane (dach), a complex $[\mathrm{Mo_2Cl_4}((R,R)\text{-dach})_2]$, is obtained in a P configuration.[141]



L68

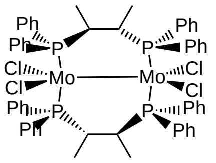
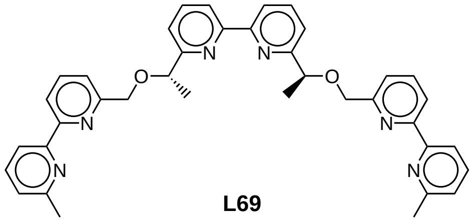


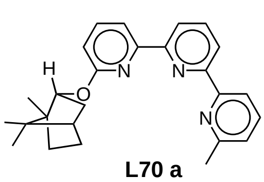
Figure 19. The orientation of chiral bridging ligands that determine the configuration in $[\mathrm{Mo_2}(\mathbf{L68})\mathrm{Cl_4}]$.

Helical silver(I) and copper(I) systems have been the subject of many investigations. The group of Lehn[142] have described the coordination chemistry of these metals with a ligand where three bipyridine units are connected through chiral bridges. This hexadentate ligand **L69** forms only one diastereomeric form of the trinuclear complex with copper(I) and silver(I) ions. Other diastereomers were not observed in the NMR spectra, which indicates an abundance of less than 5%. The Δ configuration can be derived from the sign of the CD spectra in the case of the copper(I) complex. A strong indication for the formation of oligonuclear helical metal complexes is the amplification of the Cotton effect relative to the monomers.[4]

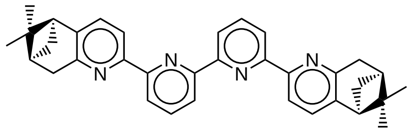


L69

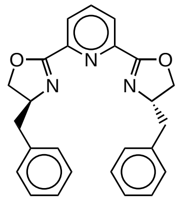
Constable et al. have described an example where the helicity could be predetermined through the use of an unsymmetrical chiral terpyridine ligand.[143] Beside the helicity of the metal center, the described complexes can, in principle, also form other isomers, namely head–head (HH) and head–tail (HT) coordination. Both kinds of isomerism are predetermined in the case of the dinuclear copper(I) complex of the nonracemic ligand (**L70a**). The M-configured complex of the HT form is obtained in a diastereomeric ratio of 6.5:1. An increased stereoselectivity is obtained through the synthesis of a C_2-symmetric ligand (**L70b**) from four pyridine and two pinene units.[144] In this case there are no head–tail isomers and the introduction of a second chiral group increases the diastereoselectivity to 95.3%. The S-configured ligand forms a P helix and the R-configured ligand as expected an M helix. Williams et al. obtained a high selectivity in the formation of a dinuclear double helix with the C_2-symmetric ligand **L71**.[145]



L70 a

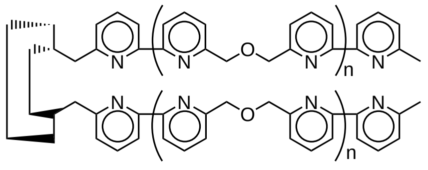


L70 b

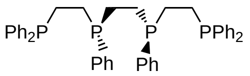


L71

Siegel et al. showed that the chirality of a helix can also be defined by a terminal chiral element.[146, 147] An example is the formation of a trinuclear helix with copper(I) as the coordination center. The ligands **L72a–c** consist of up to three achiral bipyridine units, which are connected through ether bridges. Two such strands are anchored at a chiral backbone, which transforms the stereochemical information onto the



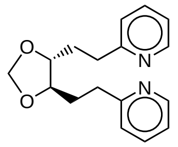
L72 **a**, n = 0; **b**, n = 1; **c**, n = 2



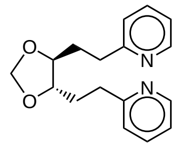
L73

helix. This transfer of chiral information can take place at a distance of up to 2 nm. The *P* form of the helix is obtained from the *R* enantiomer of the ligand. The formation of dinuclear silver helices is not restricted to nitrogen donor ligands. Tetradentate phosphor ligands such as **L73** form a D_2-symmetric *M*-double helix through spontaneous self association if the *S*,*S* form is used.[148]

Another example for the predetermination of the chirality of helices formed by silver ions with coordination number two has been described by Kotsuki et al.[149] These authors use an enantiomerically pure bispyridyl ligand based on an oxolane scaffold (**L74**). The *R*,*R* form of ligand **L74a** forms polymeric chains with *M* helicity, while the *S*,*S* form of **L74b** gives the enantiomeric complex with *P* helicity. It is interesting to note that the racemic ligand does not form mixtures of both polymers but discrete dinuclear species, which are formed through one *R*- and one *S*-configured ligand. This is a special type of molecular recognition of enantiomeric ligands, whereby two identical ligands in the homochiral complex are strongly disfavored. All three species are labile in solution and show identical NMR spectra. The stabilization of the heterochiral form is evident through its spontaneous formation from a mixture of both polymeric enantiomers.

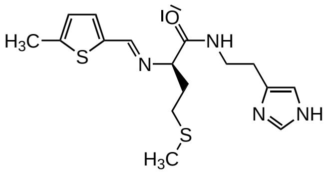


L74 a



L74 b

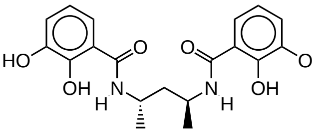
Van Koten et al. have synthesized polymeric silver(I) and copper(I) helices that are also stable in solution.[150, 151] A 1:1 mixture of the polydentate ligand **L75** with Cu^I and Ag^I salts yields stable complexes, which form polymeric chains in the solid state. Each ligand forms a bridge between three metal centers. The structural analysis of the silver complex shows a trigonal coordination of each silver center by one imidazole N, one imine N, and one methionine S atom. Weaker interactions can be attributed to an amide O and a thiophene S atom. If the ligand (*R*)-**L75** is used, the helix is Δ configured.



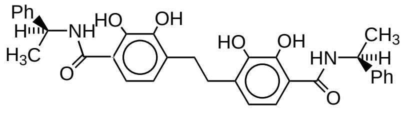
L75

Helically predisposed polymers that show helicity by themselves, can lead to helical complexes too. Stable helical metal complexes have, for example, been obtained by complex formation of nickel(II) ions with such a ligand.[152]

Catecholates are also suitable for the synthesis of helices with predetermined chirality. Gallium(III) complexes were obtained with ligand **L76** in the *S*,*S* as well as in the *R*,*R* form. The structure of the ligand prevents a tetradentate coordination to one central metal, instead two metal centers are bridged by the bisdidentate ligand. It is shown by X-ray analysis that the *R*,*R* form yields a Λ,Λ-configured complex. The reaction of the racemic ligand with gallium(III) ions shows that in this case helices formed from ligands with the same chirality are also less stable than the heterochiral analogues.[153] The heterochiral form is preferred over the homochiral one in a ratio of 6:1 under equilibrium conditions. The *S*,*S* form of the chiral biscatecholate ligand **L77** forms diastereoselectively only a homochiral isomer with Ti^{IV} ions.[154] The metal and the helical chirality cannot be assigned with certainty from the published data.



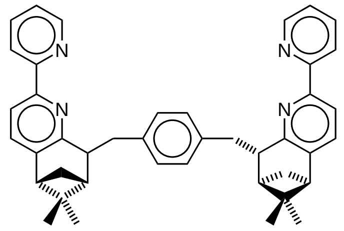
(*S*,*S*)- **L76**



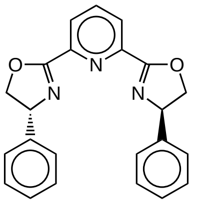
L77

4.1.1. *Cyclic Helices*

Cyclic helices have been obtained and characterized only in a few cases until now. A stereochemically completely predetermined cyclic molecular helicate is obtained from silver(I) ions with the tetradentate nonracemic ligand **L78** from the CHIRAGEN family.[155] Self assembly leads in this



L78



L79

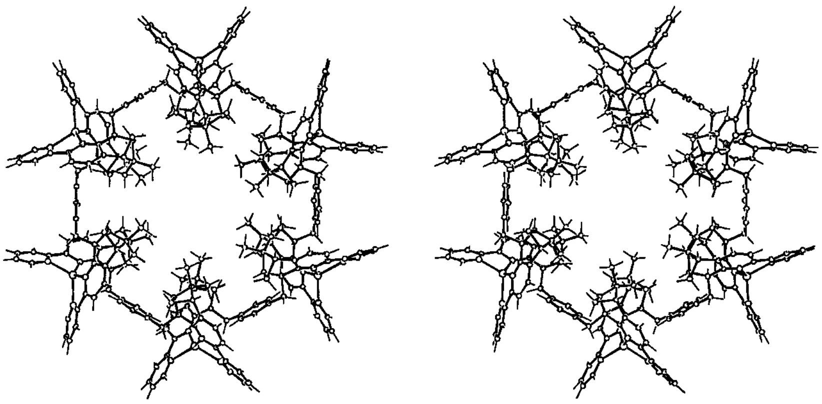
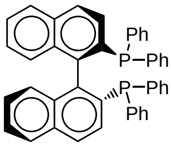


Figure 20. Chiral, predetermined hexanuclear cyclic helix with ligand **L78**.

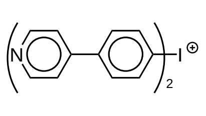
case to diastereoselective formation of a hexanuclear complex in almost quantitative yield. The nonracemic ligand (8*R*,10*R*)-**L78** is formed out of two (8*R*,10*R*)-5,6-pineno-2,2′-bipyridine units and it predetermines the *P* form of the single stranded helix. Isomers have not been observed (Figure 20). Another single stranded cyclic helix[*] with three silver centers is described by Williams et al.[145] The ligand (*R*,*R*)-oxazoline-pyridine (**L79**) is tridentate and it forms a trinuclear cyclic helix with *M* helicity.

4.1.2. Molecular Squares

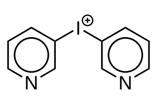
An aesthetically fascinating group of molecules are the molecular squares.[156–165] Only a few of them have been prepared in predetermined nonracemic form. Some examples have been described by the group of Stang.[166, 167] Two groups of squares can be distinguished: In the first group the molecular species are formed by four transition metal ions, whereas the second group consists of two transition metals and two iodonium ions. The *R*- or *S*-didentate ligands **L80**, which determine the chirality, are used as terminal ligands (Figure 21).



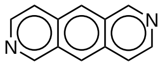
L80



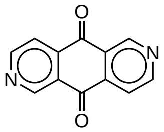
L81



L82



L83



L84

The hybrid molecules consisting of iodonium and transition metal ions are obtained from palladium(II)- or platinum(II)-**L80** triflates. The chirality of the metal center is determined in these fragments through the choice of the **L80** enantiomer. Both metal centers are chiral. The ligands **L81**, however, do not lead to helical chirality because of their high symmetry. Six diastereomeric structures are in principle possible with a ligand of lower symmetry such as bis(3-pyridyl)iodonium (**L82**). One of these diasteromers is clearly preferred in the case of palladium complexes, whereas the preference is less pronounced in the case of the platinum complex. A definitive assignment of the most abundant diastereomer is not possible from the published data.

In the squares with four metal centers, chiral Pt- and Pd-**L80** fragments are connected through the C_2-symmetric ligand 2,6-diazaanthracene (**L83**) and 2,6-diazaanthracene-9,10-dione (**L84**). **L83** yields only one diastereomer for Pt and Pd, whereas in the case of **L84** the diastereomeric excess is 81 % (Pd) and 72 % (Pt).

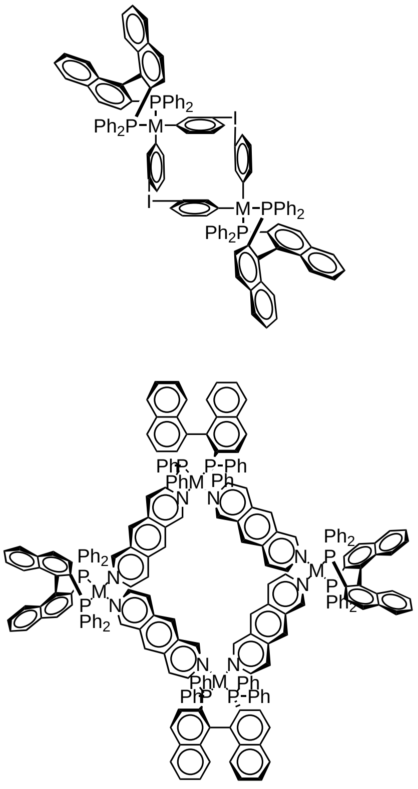


Figure 21. Two examples of chirally predetermined molecular squares. M = Pd, Pt.

5. Summary and Outlook

Predetermination of chirality in molecules can be reached, in general, only through diastereoselective processes. Chirality is therewith not generated in an absolute sense but it is induced. This induction takes place in coordination chemistry in general from a given chirality in the ligand sphere to a

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[*] The authors designate the structure as a triple stranded helix.

preferred chirality at the metal center. Chiral predetermination has been observed most often in octahedral coordination geometry. It is, however, also possible in tetrahedral, distorted planar, and fivefold coordinated species. It is useful to classify the complexes of octahedral coordination geometry by the denticity of the chiral ligands that predetermine the configuration at the metal center. Chiral induction is, as a general rule, not very efficient for didentate ligands, whereas for ligands of higher denticity, especially those with four, five, and six donor atoms, a complete chiral induction can often be observed.

The possibility of an asymmetric synthesis of coordination compounds had already been formulated in a clear way by Smirnoff in 1920[16]: "The examples of asymmetric synthesis described in this work prove that this concept is not restricted to the C-atom with its tetrahedral bonding scheme, but that it can be observed in a much stronger way also at atoms of heavy metals with completely different spatial conditions". In the decades following Smirnoff's publication, only sporadic contributions have been published for the asymmetric synthesis of coordination compounds. A systematic investigation has started only recently.

It is highly probable that this development will continue in an accelerated rhythm. Predetermined chirality at metal centers is of central interest from different points of view. In the first place it opens new possibilities and new viewpoints with respect to enantioselective catalysis, since catalytic processes at metal centers are enantioselective if the metal center itself determines the chirality of the product. A second very important field of application is supramolecular chemistry, where chiral structures with metal centers are formed in self-assembling systems. Geometrically and functionally defined aggregates can only be obtained when the chirality at the individual centers can be predetermined through a judicious choice of chiral building blocks. Finally, a third field where metal complexes with predetermined chirality are of special interest is bioinorganic chemistry. Moreover, the possibility to predetermine the chirality at metal centers is a relatively new field of basic research were new and unexpected results can be obtained.

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