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Charge-transfer excited state properties of chiral transition metal coordination compounds studied by chiroptical spectroscopy

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Contents

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Abstract

Chiroptical properties of chiral coordination compounds can be used to assign absolute configuration of ground and excited states. We discuss examples of transition metal complexes where MLCT, LMCT, MMCT and exciton LCT transitions have been observed. Such models are dimolybdenum complexes, cyclometallated Pt and Pd complexes, helicates, and complexes with Schiff-bases, conjugated diimines, catecholates and hydroxamates as ligands. The theoretical methods to assign configurations, i.e. comparison methods, exciton theory or quantum mechanical calculations, are reviewed and shown for selected examples.

Keywords: Circular dichroism, CD; Circular polarized luminesence, CPL; Exciton theory; Calculation of rotational strength; DFT; Helical path rule; Tris(diimine) complexes; Cyclometallated complexes; Hydroxamates; Catecholates; Helicates; MLCT, LMCT, MMCT

1. Introduction

Recent synthetic advances in the preparation of enantiomerically pure coordination compounds [1] have risen great interest in the study of spectroscopic properties of such compounds, which are promising new materials in fields such as enantioselective catalysis [2], luminescent materials for photoconversion [3–6], non-linear optics [7,8], helicates [9], knots [10–13], and supramolecular chemistry in general [14]. Almost all metal complexes have to be resolved or synthesized enantioselectively, since it is only seldom that nature provides optically active complexes (such as in chlorophyll or vitamin B_{12}), in contrast to the many enantiopure organic compounds (chiral pool) available in nature.

The elucidation of the absolute configuration and the assignment of transitions by means of chiroptical spectroscopy are two aspects of imminent importance which we would like to discuss here and which are useful in the discussion of general concepts of stereochemistry in coordination compounds [15].

The first resolution of a chiral metal complex into its enantiomers was achieved by Werner in 1911 [16]. The phenomenon of optical rotation and circular dichroism in solution of the transition metal complexes Cu^{II} and Cr^{III} with tartrate and malate as ligands, was, however, reported already by Cotton in the 1890s [17,18]. The chiroptical properties of Werner-type complexes were the subject of research in the 1930s, most notably by Jaeger [19], Mathieu [20], Lowry [21], and Kuhn [22,23]. Reports of chiroptical studies of coordination compounds have been covered by several extended series [24–28], general reviews [29–31], and specialized reviews on ligand field transitions [32,33]. All of these reviews are essentially treating ligand field and ligand centered transitions, however not explicitely mentioning charge-transfer states.

Our aim is to show how chiroptical methods, inlcuding new techniques such as circularly polarized luminescence (CPL) and time dependant circular dichroism (CD), can be used to study coordination compouds in view of the assignment of absolute configuration, assignment of transitions and generally speaking gathering information about the excited state of such compounds. We will concentrate on charge-transfer optical transitions, described conveniently in a localized orbital model as ligand-to-metal charge-transfer (LMCT), metal-to-ligand charge-transfer (MLCT), ligand-to-ligand charge-transfer (LLCT), metal-to-metal charge-transfer (MMCT) and ligand-centered charge-transfer (LCT). Metal-centered transitions (MC) have been a subject of several earlier reviews [31–33], and they are therefore not be considered here.

We have included LCT, although this transition is not usually referred as a charge-transfer transition. However, it is important to note, that the degeneracy of the excited states of highly symmetric complexes with at least two chromophoric ligands is lifted by coupling of LCT and that large changes in dipole moments, which is characteristic for CT transitions [34], can occurr in LCT. Moreover, LCT can give large CD-bands.

Metal-to-solvent, ligand-to-solvent transitions or intermolecular charge-transfer will not be considered although these may play an important role in some cases.

1.1. Chiroptical spectroscopy and the assignment of absolute configurations

A prerequisite for observing CD- or ORD-spectra is the presence of an enantiomeric excess of a chiral species. Enantiomers give signals with opposite sign. Very often, CD- or ORD-spectra are just used to give experimental proof of the presence of a chiral species in a non-racemic ratio of the two enantiomers even though chromatography offers nowadays much more quantitative tools. However, CD- and ORD-spectra contain in principle a lot of structural information and can be used to elucidate absolute configurations in coordination compounds. This can be done in various ways:

1. Using a correlation method, i.e. by comparison with a spectrum of similar compounds where the absolute configuration had been determined by Bijvoet's method [35], by which a number of coordination compounds have been studied [26,36,37]. This method is based on the assumption that small geometrical and electronic changes would not change significantly chiroptical properties. A case where the same configuration of a similar compound yielded nearly mirror

image CD is known for a spiro compound [38] and the application of correlation methods must be applied with some care.

2. Comparing the sign of Cotton effects of transition bands with so called sector rules; such rules are available for ligand field transitions (Co^{III} [39], metal complexes of pseudo tetragonal class [40], and metal complexes with amino acids [41–43]). The use of these rules, however, is problematic, and a number of exceptions are known [33].
3. Comparing ORD- or CD-spectra with spectra calculated from models such as exciton theory, semiempirical, or ab initio quantum mechanical methods. A more detailed overview of available methods is given in Section 3.

As no direct spectroscopical method such as X-ray diffraction is readily available for the determination of structures in solution or in the gas phase, chiroptical methods are often the only means for the determination of absolute configurations. Moreover, the change of CD-spectra with solvent points out that solution conformation is solvent dependant [44–47].

1.2. Charge-transfer transitions in chiral coordination compounds

There are only a limited number of ligand types giving rise to charge-transfer excited states in coordination compounds in accessible spectral regions. Only a small fraction of complexes with such ligands is chiral and only some of the chiral ones have been resolved into a non-racemic form.

LMCT transitions are often observed at low energies if the metal is in a relative high oxidation state, as e.g. Co^{III}, Fe^{III}, Ni^{IV}, and Cu^{II} with oxo or halide ligands or in Cr^{VI} or Mn^{VII} in complexes such as CrO_4^{2-} or MnO_4^-. Recent chiral examples include chiral cyclometallated Pt^{IV} complexes [48,49], Co^{II}, Ni^{II}, and Cu^{II} complexes with diamines [50] and Schiff-bases [51–53].

MLCT transitions are observed at low energies if the metal is reducing and the ligand offering a low lying empty orbital. Classical examples of chiral complexes are $[Ru(bpy)_3]^{2+}$, organometallics with metals in a low oxidation state and π-accepting ligands such as Pt–olefin complexes [54], or iron-η^4-diene complexes [55,56]. Other MLCT transitions are occurring in Cu^I, Ag^I, Rh^{II} and Pt^{II} [57] complexes with conjugated ligands such as bpy or phen. A special class of complexes with interesting optical properties are cyclometallated complexes with Ir^{III}, Rh^{III}, Pt^{II}, and Pd^{II} [58–61].

MMCT transitions occur only in the absorption of polynuclear complexes or metal clusters. However, only rare cases of enantiomerically pure complexes are known to display MMCT. An interesting example are dimolybdenum complexes [62–64]. In electrochemically reduced systems, intervalence charge-transfer can be observed. No chiroptical investigation of such charge-transfer has been reported.

LLCT are occurring if strongly oxidizing and strongly reducing ligands are present. Many examples of LLCT transitions in coordination compounds have been described recently by Vogler and Yersin [65,66]. Whereas MLCT, MMCT and LMCT are strongly metal dependant, LLCT transitions are independant of the coordinating metal, as shown for achiral complexes of Ni^{II}, Pd^{II} and Pt^{II} [67].

Chiral molecules where LLCT has been studied by chiroptical spectroscopy are not known, however, they could reveal interesting properties.

In view of the rather limited scope of this field, which seems to be just in a state where it gains increasing importance in its applications, our discussion will be limited to a few cases, that serve as models, where chiroptical spectroscopy has contributed substantially. The underlying theories are reviewed in the theoretical section and a short overview of available experimental techniques will be presented.

2. Experimental techniques

2.1. *Optical rotation, optical rotatory dispersion (ORD) and circular dichroism (CD)*

Conventional measurement of optical rotation using a polarimeter at just one wavelength (usually referred to as the Na–D line at 589 nm) is today a standard analytical tool for characterization of enantiopurity of chiral compounds. Measuring CD- or ORD-spectra over a range of wave lengths can be done with conventional techniques. ORD- and CD-spectra reflect ground state properties, i.e. result from the excitation of the ground state into excited states by the absorption of light. ORD- and CD-spectra can be interconverted [68] by the Kronig–Kramers [69,70] formalism.

A phase modulated CD-spectrometer where optical rotation could be measured in two different polarization directions allows to measure CD-bands of oriented samples (crystals) and distinguish between overlapping CD-bands corresponding to absorptions of different polarization directions as exemplified on the d–d transitions of Λ-(+)-Co(en)$^{3+}$ [71]. No case of a phase modulated CD-spectrum for a charge-transfer transition, however, has been reported and this interesting technique has not found further applications.

2.2. *Linear dichroism (LD)*

Linear dichroism (LD) is a related technique applied to oriented samples, not necessarily being chiral, into which a recent book [72] gives an excellent introduction. LD will not be discussed here further.

2.3. *Magnetically induced circular dichroism (MCD)*

A technique to assign the nature of transitions in achiral substances is magnetically induced circular dichroism (MCD), where a magnetic field is applied along the direction of propagation of the circularily polarized light. MCD has been used to study charge-transfer transitions in a number of achiral metal halides [73], in Co^{II} protein complexes [74], lanthanides [75], or in organic compounds [76]. MCD will not be discussed further in this paper.

2.4. Circular polarized luminescence (CPL) and fluorescence detected CD

There are two chiroptical techniques based upon the measurement of molecular luminescence. In circularly polarized luminescence spectroscopy (CPL) one analyzes the luminescence for the usually very small difference in intensities between left and right circular polarization of the emitted light. In fluorescence detected circular dichroism (FDCD), the difference in absorption between left and right circularly polarized light is monitored through detection of the difference in total emission intensities associated with the different absorption polarizations. CPL is therefore a probe of an excited state structure, whereas FDCD is, like CD, a probe of the molecular ground state. A comprehensive review about CPL and FDCD is available [77].

2.5. Time resolved CD and CPL

Time-resolved CPL is a very recent advancement [77,78]. The generation of optically enriched excited states from a racemic solution through enantioselective quenching by an added chiral species, which was proven by the lack of any measurable CD—thus no chiral discrimination in the ground state—is an interesting technique to probe chiral discrimination in excited states [77,79–81]. This technique has also been applied to solids [82] and to phosphorescence from proteins [83]. The decay rates for CPL may indicate the nature of the emitting state and may be different than the overall decay rate for emission.

3. Theoretical models

CD, both in absorption and emission, is produced when an electron is moving along a helical path in the chromophore. This is only possible if the molecule is lacking axes of improper rotation, i.e. if it is chiral. As a consequence such a transition has a net electric and magnetic dipole transition moment designated $\vec{\mu}$[1] and $\vec{m}$, respectively. The intensity of a transition in a collection of randomly oriented molecules is then given by the imaginary part of the scalar product of the magnetic dipole and the electric dipole moments, which is the Rosenfeld equation [84]. Symbols have their usual significance.

$$\begin{aligned} R_{0a} &= \vec{\mu} \cdot \vec{m} = \mathrm{Im}\{\langle 0|\hat{\mu}|a\rangle \cdot \langle a|\hat{m}|0\rangle\} \\ &= -\frac{e^2\hbar}{2mc}\langle 0|\sum_j \vec{r}_j\,|a\rangle \cdot \langle a|\sum_j (\vec{r}_j \times \vec{\nabla}_j)\,|0\rangle \end{aligned} \tag{1}$$

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[1] Note that the transition moment follows the direction of a transition, i.e. it points from positive to negative charge. The direction of an electric dipole moment is, by definition, from negative to positive charge.

The CD-spectra $\Delta\varepsilon(\tilde{\upsilon})$ can then be calculated from R_{0a} and from the transition energy $\tilde{\upsilon}_a$ (cm^{-1}) of all transitions to possible excited states using a Gaussian bandwidth function with a standard deviation σ_a [85].

$$\Delta\varepsilon(\tilde{\upsilon}) = 18.8 \cdot 10^{37} \sum_a \frac{R_{0a}\tilde{\upsilon}_a \mathrm{e}^{-\left(\frac{\tilde{\upsilon}-\tilde{\upsilon}_a}{2\sigma_a^2}\right)^2}}{\sigma_a} \tag{2}$$

All units are in the cgsu system that is still used by CD-spectroscopists although not recommended by IUPAC. R values in Debye–Bohr magnetons (DB) can be obtained from R (in DB) $= 1.0783 \cdot 10^{38}$ R (in cgs), where $1\mathrm{DB} = 3.094 \cdot 10^{-53}$ A C m^3. Throughout our discussion, we will report the maximum $\Delta\varepsilon$ values of a CD-band $\Delta\varepsilon_{\max}$ (M cm^{-1}).

R values can be obtained from experimental CD-bands according to

$$R_{0a} = 2.30 \cdot 10^{-39} \int \frac{\Delta\varepsilon(\tilde{\upsilon})}{\tilde{\upsilon}} \, \mathrm{d}\tilde{\upsilon} \tag{3}$$

A value characteristic for the nature of a transition is the dimensionless ratio of circular dichroic to isotropic aborbance ($\Delta\varepsilon/\varepsilon$, or g number), also called the anisotropy or dissymmetry factor [86,87].

Typically, one finds $g \geq 5 \cdot 10^{-3}$ for magnetic dipole allowed and electric dipole forbidden transitions (ligand field transitions, n–π^* transitions). For electric dipole allowed and magnetic dipole forbidden transitions (CT and most π–π^* transitions), $g \leq 5 \cdot 10^{-3}$. However, with molecules of high helicity [9], also CT and π–π^* transitions may give rise to a high magnetic dipole moment, and thus g numbers as large as $6.5 \cdot 10^{-3}$ [88]. A similar dissymmetry factor can also be defined for CPL [77,78,89].

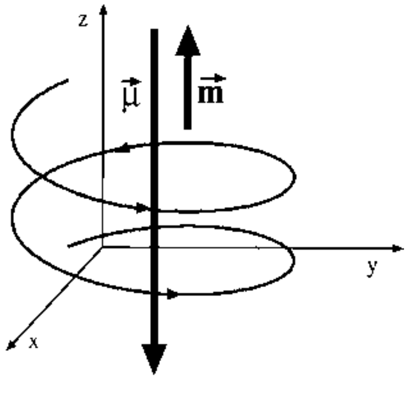

Fig. 1. Left-handed charge displacement along the negative z-axis with electric and magnetic transition dipole moments $\vec{\mu}$ and $\vec{m}$.

3.1. A simple helical path rule for isolated charge-transfer transitions

A helical charge displacement (Fig. 1) will have a magnetic dipole moment parallel either in the same or in the opposite direction than the overall electric dipole moment. Therefore, it is possible to deduce the sign of a Cotton band knowing the helicity of the electron flow during the charge-transfer excitation, i.e. from $\vec{\mu}$ and $\vec{m}$ according to Eq. (1) [90].

In the coordinate frame chosen, a left-handed charge displacement will lead to a negative sign of R, since the produced magnetic field is in the opposite direction as the electric dipole moment. Electron movement along a right handed helix will accordingly give a positive Cotton effect.

The electron flow can be illustrated pictorially by looking at the electronic transition probability density[2] $\Psi\Psi^*$, i.e. the probability of finding positive or negative electron density during the transition. Ψ and Ψ^* denote the ground and excited state wavefunction. The sign of the Cotton band of a charge-transfer transition is a function of the relative spatial arrangement of both Ψ and Ψ^*, and $\Psi\Psi^*$ equals $\phi_{\mathrm{homo}}\phi_{\mathrm{lumo}}$ if only one spin orbital is changed during the transition, according to Slater's rule. Given that the spatial arrangement of ϕ_{homo} and ϕ_{lumo} is known, the sign of a CD-bands can be determined by looking on the charge displacement of this transition probability density [91].

Usually, the most intense charge-transfer bands are those along the dipole moment, which in most cases corresponds to the direction of charge-transfer. Accordingly, these have also the largest $\Delta\varepsilon$ values. Therefore, the sign of the Cotton effect of an intensive CT-band will indicate the helicity of the charge-displacement in the direction of the charge-transfer.

Attention must be paid to the fact, that helical path of the electronic charge during a transition is not necessarily related to the helicity of the molecule. For example in helicenes, the transition charge distributions along two perpendicular axes (orthogonal to a C_2-axes) have opposite senses and thus opposite $\Delta\varepsilon$ values.

This simple model also neglects higher order multipoles which have been shown to contribute in case of chirally substituted diaminoanthraquinones [92] and is limited to cases of pure charge-transfer transitions without admixture of ligand field states.

As an example, we will look at the metal to metal charge-transfer in dimolybdenum complexes with chiral diamine and diphosphine ligands [62–64].

3.2. Coupled oscillators (exciton theory)

In coordination compounds with two or more identical or very similar strong ligand chromophores ($\varepsilon > 1000$) arranged in a chiral configuration, the helical charge movement within a chromophore is obtained by the influence of an external electric field induced in a neighbor chromophore.

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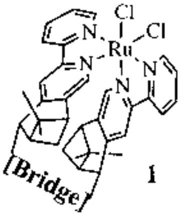
[2] A rigourous definition of such a probability density can be given in terms of a reduced density matrix connecting ground and excited state but is beyond this level of theory. Other quantities to characterize the electron flow are the transition current density or density differences of ground and excited states.



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Scheme 1.

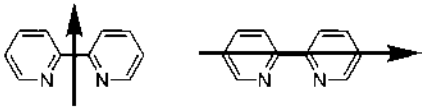
The CD-spectra of such compounds can be rationalized in terms of two or more electric dipole transition moments coupling with each other by a dipole–dipole interaction (exciton theory). This model was proposed originally by Kuhn et al. [93] and applied to the tris complexes $Co(en)_3^{3+}$ and $Co(ox)_3^{3-}$. Later Bosnich [94,95] and Mason [96] have applied it to $[Ru(bpy)_3]^{2+}$, $[Ru(bpy)_2(phen)]^{2+}$ and other related systems. An experimental proof by X-ray for the theory was given by Saito [26,36], and numerous crystal structures which are now available, confirm the predictions of absolute configuration from this theory. Exciton theory has found wide application and it is covered widely in the literature [97–99]. However, a clear and concise methodology for the application of this method is somehow missing and should therefore by exemplified here on a typical example of a complex with the chiragen ligand family [100–102] derived from **1** where alkanes or substituted xylyl have been used as bridges. The two chloride atoms can be exchanged readily by bpy, dmbpy or bpym (Scheme 1).

First, the electric dipole transition moment within a chromophore must be known. In bypridine-type ligands e.g. there are two strong π–π^* transitions, long axis and a short axis polarized, respectively (Scheme 2).

The direction and size of the transition dipole moment within a chromophore can be obtained with sufficient accuracy from quantum mechanical calculations or from experimental data.

In the octahedral complex shown in Fig. 2, coupling of long and short axis polarized transitions will give rise to an exciton doublet in the CD-spectra as shown in Fig. 3.

We use a right-handed coordinate system out of the two electric dipole excitation vectors in the chromophore and a connecting vector between them and look at the angle γ which is the dihedral angle between $\vec{\mu}_1$ and $\vec{\mu}_2$. For $0 < \gamma < 180°$ the three vectors form a right-handed parallelepiped and R will be positive and for $180 < \gamma < 360°$ it will be negative as is shown in the following in detail.



Scheme 2.

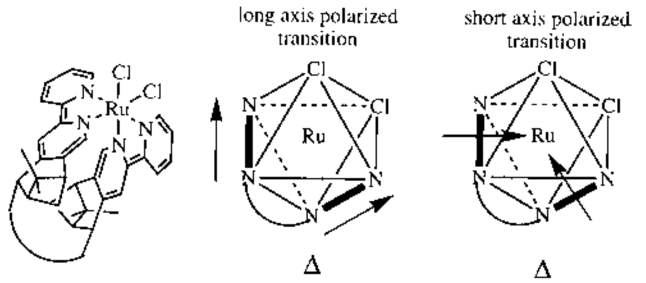


Fig. 2. Long and short axis polarized ligand centred transitions in **1**.

The coulomb coupling V_{12} of two degenerate transitions on two chromophores will split the degeneracy (to zeroth order) of the transitions $\vec{\mu}_1$ and $\vec{\mu}_2$ into a transition of lower energy $\vec{\mu}^-$ where the transition dipole moments are opposite to

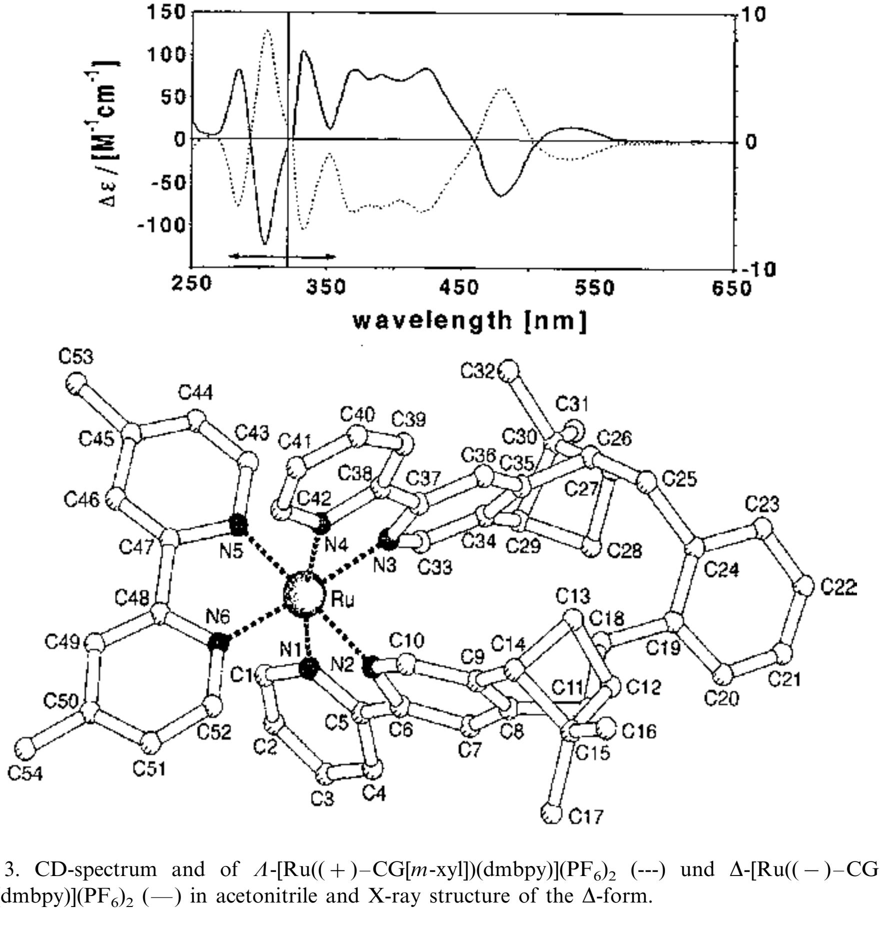


Fig. 3. CD-spectrum and of Λ-[Ru((+)–CG[*m*-xyl])(dmbpy)](PF$_6$)$_2$ (---) und Δ-[Ru((−)–CG[*m*-xyl])(dmbpy)](PF$_6$)$_2$ (—) in acetonitrile and X-ray structure of the Δ-form.

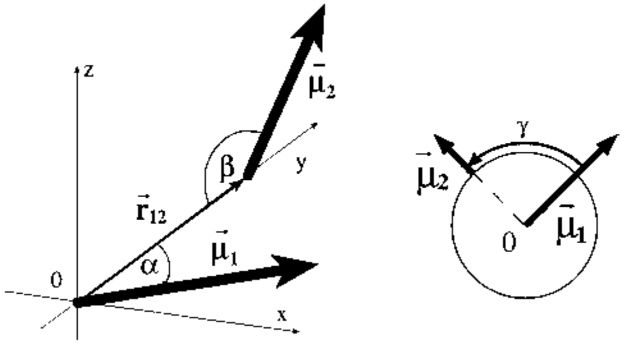


Fig. 4. Coupling of two degenerate transitions with electric dipole moments μ_1 and μ_2.

each other and a transition of higher energy $\vec{\mu}^+$ where the dipole moments are in alignment. $\vec{\mu}^+$ and $\vec{\mu}^-$ correspond to the *in phase* or *out of phase* combination of the two degenerate transitions in the chromophore.

$$\vec{\mu}^{\pm} = \frac{1}{\sqrt{2}}(\vec{\mu}_1 \pm \vec{\mu}_2) \tag{4}$$

The transition energy of $\vec{\mu}^+$ and $\vec{\mu}^-$ is given by

$$\varepsilon(\vec{\mu}^{\pm}) = \varepsilon(\vec{\mu}_1) \pm V_{12} \tag{5}$$

and the Coulomb coupling energy V_{12} is usually written in a first approximation as

$$V_{12} = \frac{1}{4\pi\varepsilon_0}\left(\frac{\vec{\mu}_1 \cdot \vec{\mu}_2}{r_{12}^3} - \frac{3(\vec{\mu}_1 \cdot \vec{r}_{12})(\vec{\mu}_2 \cdot \vec{r}_{12})}{r_{12}^5}\right) \tag{6}$$

or using the angle notation defined in Fig. 4

$$V_{12} = \frac{1}{4\pi\varepsilon_0}\frac{\mu^2}{r_{12}^3}(\sin\alpha\,\sin\beta\,\cos\gamma + 2\cos\alpha\,\cos\beta) \tag{7}$$

Considering that the magnetic transition moment for an electric dipole allowed ligand transition (e.g. π–π^*) is zero, one obtains an equation relating R to $\vec{\mu}_1$, $\vec{\mu}_2$ and the connecting vector $\vec{r}_{12}$ between them:

$$R^{\pm} = \pm 0.5\pi\tilde{v}\vec{r}_{12} \cdot (\vec{\mu}_2 \times \vec{\mu}_1) = \pm 0.5\pi\tilde{v}\mu^2 r_{12} \sin\alpha\,\sin\beta\,\sin\gamma \tag{8}$$

The CD-spectrum of **1** will therefore have two bands with opposite sign separated by an energy of the order of V_{12}. However, due to the overlap and cancellation of the two CD-bands, the separation of the band maxima is always larger than the splitting V_{12}, which is illustrated in Scheme 3.

Thus, V_{12} cannot directly be read from the separation of the two exciton band maxima as it is done frequently in literature [103]. Assuming a band shape as defined in Eq. (2), with a band half with σ_a, the separation of maxima and minima on the abscissa (in cm^{-1}) of an exciton couplet is simply $2\sigma_a$ for $V_{12} \ll \sigma_a$ (Fig. 5).

The two extreme cases where the dipole transition moments are parallel to each other will give of course no CD-signal. The intensity of the electric dipole transition is proportional to the square of the dipole moment and in such cases where the coupling of dipole moments will give zero overall transition dipole, no absorption band will be observable (dotted lines).

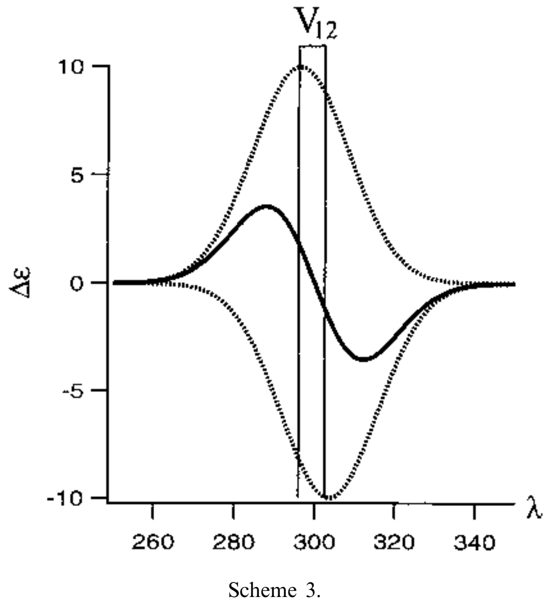
In a C_2-symmetrical system with the C_2-axis relating the two chromophores to each other (and therefore making them identical) which is the case for a number of coordination compounds, $\alpha=\beta$ and the equations simplify to:

$$R^{\pm} = \pm 0.5\pi\tilde{\nu}\mu^2 r_{12}\sin^2\alpha\,\sin\gamma$$

$$V_{12}=\frac{1}{4\pi\varepsilon_0}\frac{\mu^2}{r_{12}^3}(\sin^2\alpha\,(\cos\gamma-2)+2) \tag{9}$$

$R^+$and V_{12} as a function of angles α and γ are depicted in Fig. 6. Although R is maximal when α and γ are all 90°, there will be no CD-signal since V_{12} is zero and the two opposite CD-bands will cancel each other to zero. A measure for the size of the CD-effect is the product $R\cdot V$ which is shown as a graph 'Total CD-signal' in Fig. 6. The sign of the function corresponds to the sign of the cotton effect on the higher energy CD-couplet. This figure is useful for the discussion of the sign of Cotton effects resulting from two coupled oscillators.

One must note that the sign of the higher energy transition of the exciton couplet may change going from $\alpha=50$ to 60° for $\gamma=160°$, i.e. without changing formally configuration. The angular dependant part of R will change from 0.20 to 0.26 whereas the V_{12} will switch from 0.27 to -0.20 thus reversing the order of the exciton couplet in the CD-spectrum.



Scheme 3.

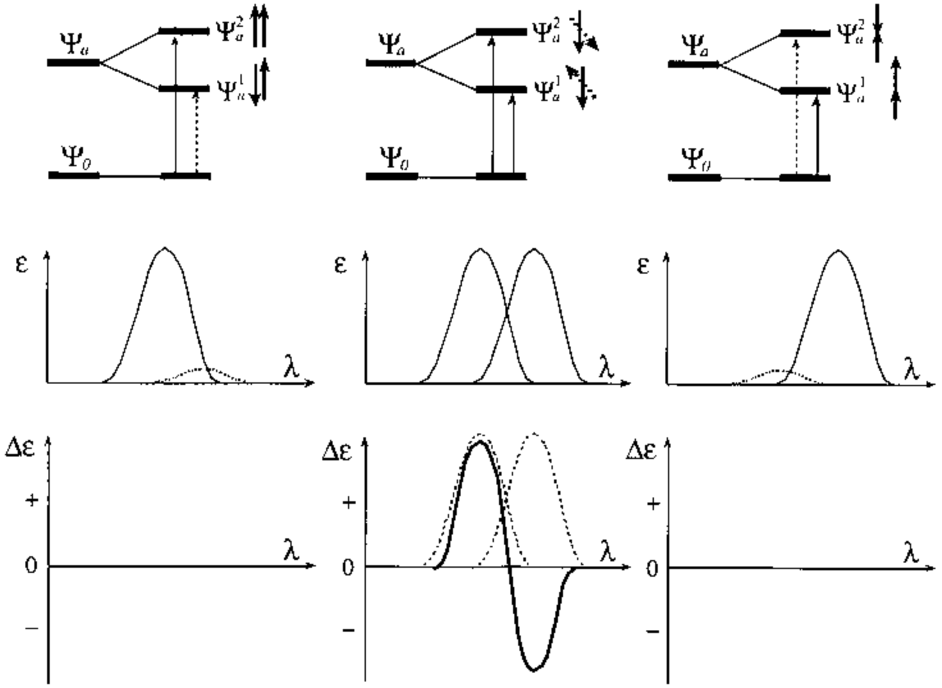


Fig. 5. Exciton coupling of two degenerate transitions.

If we want to apply this theory now to the complex **1**, we have already stated the direction of the two possible ligand centred transitions, which are short- and long-axis polarized, respectively. The first statement we can find, is that the coupling of short axis transitions will give zero rotational strength since the two transition dipole moments will be coplanar, and thus $\gamma = 0°$. The long axis polarized transition dipole moments can be readily written as

$$\mu_1 = \left(\frac{1}{2}, \frac{1}{2}, 0\right)d$$

$$\mu_2 = \left(\frac{1}{2}, \frac{1}{2}, 0\right)d$$

$$r_{12} = \left(1, \frac{1}{2}, -\frac{1}{2}\right)d \qquad (10)$$

using the coordinate system and designations as depicted in Scheme 4.

R and the energy ε for this in phase coupling can be derived

$$R = -\frac{1}{2}\pi\tilde{v}\mu^2 d^3$$

$$\varepsilon = \varepsilon_0 - \frac{1}{4\pi\varepsilon_0}\frac{1}{2\sqrt{6}}\frac{\mu^2}{d^3} \tag{11}$$

The coupling that corresponds to the out of phase coupling will just change sign and therefore corresponds to the higher energy transition having a positive CD-band. This is indeed exactly found in the experimental CD-spectrum.

A similar procedure can now be outlined for near-degenerate coupled oscillators where two transitions at energies $\tilde{\nu}_1$ and $\tilde{\nu}_2$ are present [104]:

$$R(\tilde{\nu}_1) = 2\pi V_{12}\frac{\tilde{\nu}_1\tilde{\nu}_2}{\tilde{\nu}_1^2 - \tilde{\nu}_2^2}\vec{r}_{12} \cdot (\vec{\mu}_1 \times \vec{\mu}_2) \tag{12}$$

where the dipole interaction energy V_{12} is given in Eq. (6).

Inspection of Eq. (12) shows that the sign of $R(\tilde{\nu}_1)$ is the same as the sign of the lower energy transition in the degenerate case. This leads to the important result that substitution of a ligand under retention of configuration in the case of

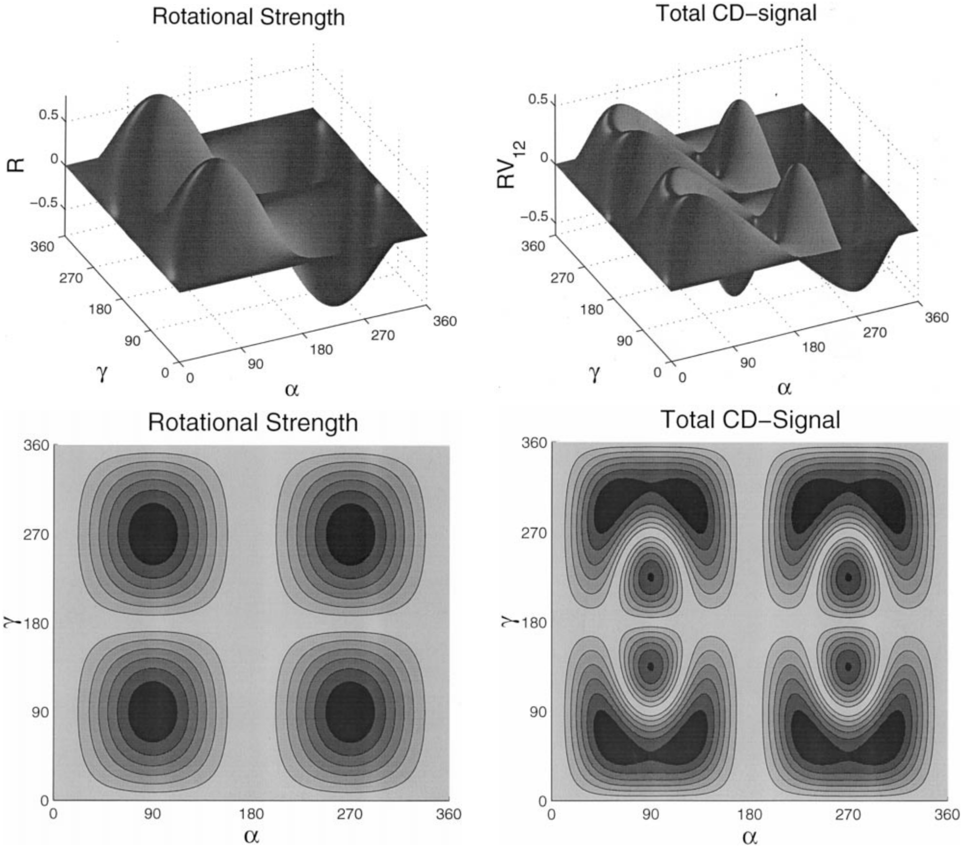
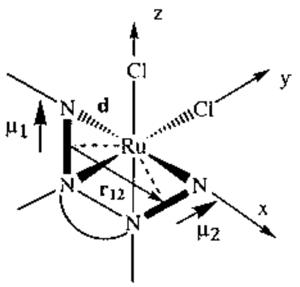


Fig. 6. R and total CD-signal which corresponds to the sign of the higher energy transition of the exciton couplet. Only the angular dependant part of Eq. (9) is shown.



Scheme 4.

degenerate coupling with a similar chromophore does not change the CD-spectrum qualitatively. CD-spectra of enantiomerically pure $[Ru(bpy)_2phen]^{2+}$, $[Ru(byp)_2py_2]^{2+}$ and $[Ru(bpy)_3]^{2+}$ and other complexes show this behavior.

The part $V_{12}\vec{r}_{12} \cdot (\vec{\mu}_1 \times \vec{\mu}_2)$ of Eq. (12) has already been depicted in Fig. 6 and is therefore also applicable to give a qualitative measure for non-degenerate coupled oscillators. Note that $R(\tilde{v}_1) = -R(\tilde{v}_2)$ if 1 and 2 are changed.

The exciton model is applicable for identical or similar chromophores with high electric dipole transition moments ($\varepsilon > 1000$). It must be applied with care in case of ligand chromophores with significant overlap, in case of large vibronic coupling, and in case of coupling with other transitions with a high magnetic moment, for example ligand field transitions.

Exciton theory is a very efficient method for the calculation of optical activity of large molecular systems, possibly a polymer, which can be devided into small molecular chromophores [104]. An extension of the exciton model in terms of induced dipole moments, oscillators and polarizabilities associated with the various groups into which the molecule is subdivided, is known as the DeVoe method [105,106] and was applied to calculate ligand centred transitions in Ni^{II} complexes with chiral Schiff-bases [107].

The CD of a guest chromophore induced inside the cavity of a helical host molecules has been calculated also [108] using the non-degenerate coupled oscillator theory (Eq. (12)).

Ligand centered transitions can couple with the charge-transfer or with ligand field transitions. Simple expressions and symmetry rules for the coupling of electric to magnetic transition dipole moments are available [109]. The estimation of the sign of CD-bands of transitions that couple significantly with other transitions is delicate, however, and simple model predictions inadequate.

3.3. Quantum mechanical calculations

If wave functions of ground and excited states are available, CD-spectra can be calculated from Eq. (2). This has been done using a variety of methods (EH [110,111], CNDO [112], AM1/MRD-CI [113], DFT [114], DFT-CI [115–117] and RPA [118,119]) with good results for ab initio methods for organic molecules. A review on the field of calculating CD-spectra covering the development until 1994 is available [120].

The first calculation to transition metal complexes dates back to 1956 when Moffit introduced a one-electron crystal-field model, usually referred to as the ionic model [121]. Transition metal complexes have been investigated extensively and computational efforts on metal centred transition have been reviewed until 1979 [32].

Recent contributions include the calculation of a d–d transition for $[Co(en)_3]^{3+}$ with a RHF/LFCI model [122], a cellular ligand field (CLF) model applied to trigonal–bipyramidal Co^{II} and Ni^{II} [123,124] and a general perturbation analysis for magnetic dipole allowed transitions [125] EHT calculations (with three parameters describing the mixing of metal and ligand wavefunctions) of tris(di-imine) complexes of Fe^{II} and Ru^{II} yielded reasonable results [111]. Newer developments include the calculation of R within the density functional framework which will allow to perform ab inito calculations for larger systems. DFT has proven to be especially useful in case of transition metal compounds to yield accurate energies and other molecular properties, e.g. for the MLCT states of $[Ru(bpy)_3]^{2+}$ [126]. A DFT study of $[Ru(bpy)_3]^{2+}$ yielded an accurate qualitative CD-spectrum [114], depicted in Fig. 7.

In most cited calculations, Slater-type or Gaussian orbitals were used as basis sets, although gauge invariant London atomic orbitals [127] should be advantageous over other basis sets.

For flexible molecules, Boltzmann averaging of all possible conformations is necessary. CD-spectra of all conformations have then to be calculated separately and averaged accordingly. Such calculations have been carried out for flexible organic molecules [128–133].

Recent theoretical studies also include CD with two photon absorption [134] and circular vibrational dichroism (VCD) [135–139].

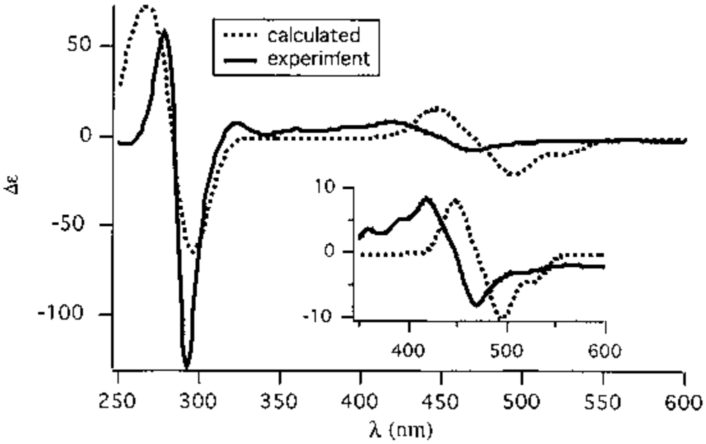


Fig. 7. Calculated and experimental CD-spectrum of Δ-$[Ru(bpy)_3]^{2+}$

4. Discussion of examples

In coordination compounds, four different sources of chirality in the chromophoric system can be distinguished:

1. Inherent planar or helical chirality of the complex,
2. Inherent chirality of the ligand,
3. Chirality at the coordinating metal center arising from configuration, i.e. from the spatial distribution of the ligand around the coordination center. Only a limited number of such distributions exist for various coordination geometries and coordination numbers [15].
4. Chirality arising from a chiral conformation of the ligand.

For example in $[Co(en)_3]^{3+}$ both (iii) and (iv) are valid, since a tris-bidentate complex can have two different octahedral configurations (Λ and Δ) and two possible conformations of each ethylendiamine ligand (lel or ob, δ and λ, respectively).

For the complex **1** both (ii) and (iii) are present since the ligand itself is chiral and two chiral configurations Λ and Δ are possible. In fact, in this case, the ligand chirality predetermines the configuration on the metal.

4.1. Bis and tris(diimine) complexes

Bipyridine and phenanthroline octahedral metal complexes are the classical examples to show chirality at the metal center (iii) if at least two of them are coordinated to the metal in a skew arrangement. Resolution of racemates has been accomplished either by using chromatography with chiral stationary phase, diastereoselective crystallization with chiral ions or enantioselective synthesis.

The absolute configuration of bis heteroleptic complexes, such as $Ru(bpy)_2Cl_2$, $[Ru(bpy)_2py_2]^{2+}$ and tris homoleptic compounds, such as $[Ru(bpy)_3]^{2+}$, $[Ru(phen)_3]^{2+}$ is easily deduced from the π–π^* transition on the ligands coupling with each other (exciton theory). This work has been pioneered by Mason [96] and Bosnich [95] and can be summarized in a simple rule:

> For long-axis polarized LCT transitions, the circular dichroism will appear strongly positive at lower energies and strongly negative at higher energies if the molecule has the absolute configuration related to Λ-(−)-$[Fe(phen)_3]^{2+}$, which has been solved by X-ray diffraction studies [37].

Details of exciton theory applied to bis and tris(diimine) complexes are given in Section 3.2. A resonance splitting energy V_{12} as defined in Eq. (6) is obtained of the order of 660–890 cm^{-1} [96]. If vibronic coupling is considered, this value reduces to 100 cm^{-1} [140]. Regardless of any discrepancies, the qualitative picture of a spliiting energy of several hundred wave numbers is found exactly in the CD-spectra.

MLCT transitions and their intensity have been investigated for tris(diimine) complexes of Fe^{II} and Ru^{II} already by Day and Sanders [141,142].

It is shown that these transitions can have signifiacant admixture of ligand field states, especially in the Fe^{II} case [111]. Therefore, simple predictions, such as the helical path rule, give unreliable results for the assignment of absolute configurations.

In a number of recent publications about the successful synthesis of enantio- and diastereomerically pure polynuclear ruthenium complexes, CD-spectroscopy has been the only structural proof for enantiopurity [143–148]. Interesting cases are Fe^{II} [149] and Ru^{II} [150,151] complexes with bipyridine derivatives of peptides where upon complexation the peptide forming a three-helix bundle of defined twist predetermines the metal chirality (Fig. 8).

Stereoselective triple helix formation of Fe^{II}, Zn^{II} and Cd^{II} complexes with chiral bis 2,2′-bipyridine ligands has been achieved recently and monitored with CD-spectroscopy [152].

4.1.1. Nature of the excited state of $[Ru(bpy)_3]^{2+}$

Even though a number of publications have appeared, the electronic structure of the excited states of such complexes remains a matter of debate. Whereas the ground-state transitions of the model compound $[Ru(bpy)_3]^{2+}$ are relatively well understood from CD [126,153], MCD [154] and single crystal polarization measurements [155], the excited-state spectrum is still lacking complete assignment. It is generally agreed that the absorption properties are related to transitions from the thermally equilibrated ground state to the nonequilibrium excited states which are largely of singlet character. Emission from excited states to nonequilibrium ground states occurs from states largely triplet in character. McCusker et al. [156] have reported the femtosecond dynamics of excited-state evolution in $[Ru(bpy)_3]^{2+}$ and found that the equilibrated ^{3}MLCT state is formed within 300 fs and that it does not pass through the different vibronic states after a Franck–Condon excitation in the course of excited-state relaxation. Ligand-to-ligand charge hopping is believed to occur within 1 ns [157]. Kinetic data indicate that the lowest excited state of $[Ru(bpy)_3]^{2+}$ has a lifetime of about 600 ns at 20°C in water [158] and that quantum yields for racemization and decomposition are low [159,160]. The transient circular dichroism absorption spectrum of the luminescent excited state of $[Ru(bpy)_3]^{2+}$ was determined by Creutz [161] and Grätzel [162] and later on a nanosecond time scale by Kliger et al. [163], who found significantly smaller CD in the excited state transient absorption spectra than in ground state transient CD. The transitions in the excited state transient absorption CD were attributed to single ligand localized $\pi^*–\pi^*$ transitions (370 nm) and to interligand $\pi–\pi^*$ transitions or LMCT (at 315 nm). It was concluded from CD-spectra that the lowest MLCT excited state of $[Ru(bpy)_3]^{2+}$ had the transferred electron localized on a single ligand. However, whether the lowest excited ^{3}MLCT state is best to be described in a localized or delocalized picture remains a matter of debate. Evidence for the localized nature of the lowest-excited ^{3}MLCT states have been claimed in a number of experimental work including luminescence, excitation line narrowing and spectral hole-burning experiments [164–166], by time-resolved resonance Raman [167] and absorption polarization [157] spectroscopy, in recent electroabsorption studies [168,169] and by solvatochromic studies earlier [34]. Yersin et al. have reported experimental data on the emission decay properties that are in favour of

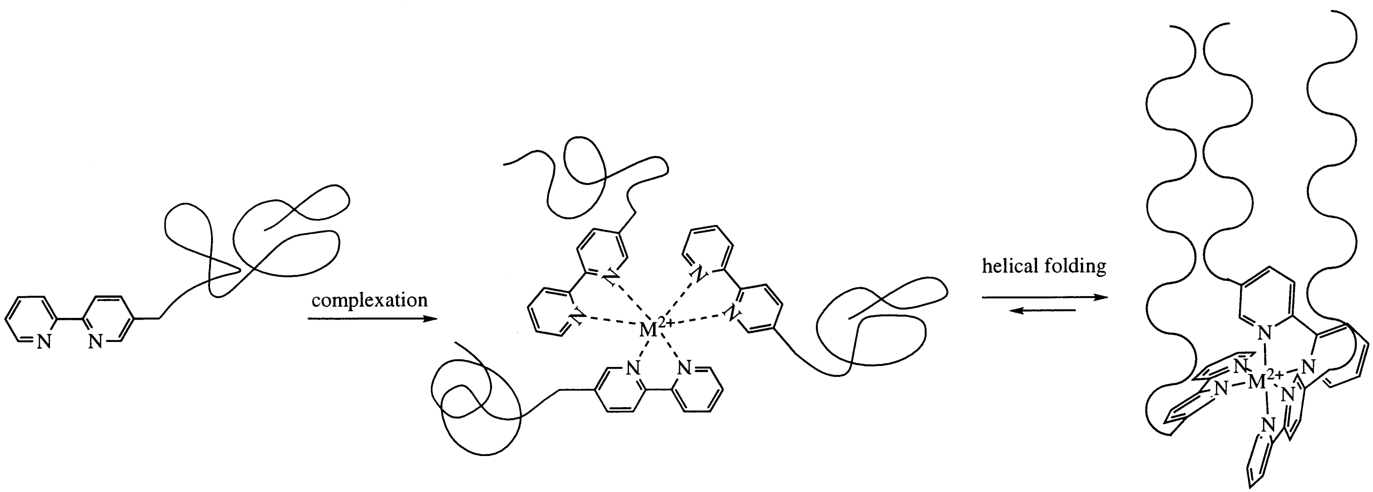


Fig. 8. A triple helix of peptide chains that induces chirality at the metal center upon complexation.

a delocalized ^{3}MLCT [170,171]. Turro suggested from Raman data that the $[Ru(phen)_3]^{2+}$ displays delocalized excited-state behaviour or that at least the electron hopping among ligands is faster than vibrations [167].

4.1.2. Circularly polarized luminescence (CPL)

CPL studies [89] of an Os^{II} analog to complex **1** and of $[Os(bpy)_3]^{2+}$ showed almost identical negative CPL around 13 000 and 15 000 cm^{-1}. These two transitions were tentatively assigned to the proposed emitting ^{3}MLCT manyfold [172–179]. The reported dissymmetry factor for absorption was 2.5 times larger in magnitude than the emission dissymmetry factor in the CD–CPL spectral overlap region (15 000–13 000 cm^{-1}) which implies that the degree of helicity in the equilibrium ground state is different from that in the emitting state.

4.1.3. Chiral discrimination in excited states

Chiral discrimination in excited states has been monitored by the quenching of luminescence and the differences in excited-state lifetimes in presence of chiral quenchers [77,79–81,180]. Quenching experiments of racemic lanthanide complexes $[Tb(dpa)_3]^{3+}$ nd $[Dy(dpa)_3]^{3+}$ in the presence of enantiopure $[Ru(phen)_3]^{2+}$ [181,182] showed that homochiral quenching in water was 1.2 times more efficient than heterochiral. However, in MeOH and MeOD heterochiral quenching was 1.5 times more efficient. Quenching by $[Ru(bpy)_3]^{2+}$ was much less diastereoselective with a difference in quenching rates for racemic Tb^{III} of only 1% difference for the two enantiomers [182]. The differences in luminescence due to chiral interaction in the excited state is a measure of the strength of this interaction. The enantiomeric excess of the lanthanide complexes in the excited state was monitored by CPL and the absolute configuration determined by comparison methods.

4.2. Dimolybdenum complexes

The simple helicity rule (chapter 3.1) is applicable for inter-metal charge-transfer transitions in dimolybdenum complexes with chiral diamine and diphosphine ligands [62–64].

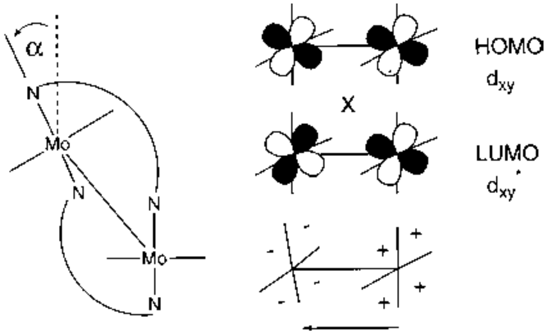
The two lowest energy transition d_{xy}–d^*_{xy} (480–740 nm) and d_{xy}–$d^*_{x^2-y^2}$ (360–470 nm) show opposite Cotton effects that are related to the twist angle α as depicted in Scheme 5.

For the d_{xy}–d^*_{xy} transition in a left handed helical arrangment of the bridging ligands, R will be negative if $0 < \alpha < 45°$ and positive if $45 < \alpha < 90°$ as can be seen from the charge rotation during the transition (Scheme 6).

Using the same arguments, it can be shown that for the d_{xy}–$d^*_{x^2-y^2}$ transition, R will have opposite sign than of the R-value of the d_{xy}–d^*_{xy} transition.

The validity of the model is evident from the $\Delta\varepsilon$-values reported in Table 1.

For $Mo_2Cl_4(S,S\text{-dppb})_2$, the depicted left-handed helical arrangement with a twist angle of 23° is found [183] with a corresponding negative R value.

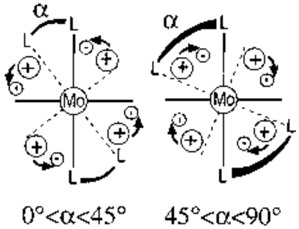


Scheme 5.

4.3. Bis-cyclometallated complexes with Pt^{II}, Pt^{IV} and Pd^{II}

Bis-cyclometallated square planar complexes with Pt^{II} or Pd^{II} are a novel class of liminescent complexes [185,186] that exhibit interesting photochemical properties [187,188]. The achiral $Pt(2\text{-thpy})_2$ (**2**) complex has been investigated in detail by high resolution spectroscopy, e.g. phosphorescence and triplet excitation spectra where radiative decay paths could be shown to proceed via direct spin–orbit coupling or via vibronic Herzberg–Teller coupling [60,170,189]. The lowest exited state is a ^{3}LCT (π–π^*) split by a zero-field splitting of 16 cm^{-1} into three sublevels. The relatively large zero-field splitting and the analysis of vibrational satellite structures shows a significant MLCT admixture. Such an admixture is less pronounced in the corresponding $Pd(2\text{-thpy})_2$ complex [60]. The absorption spectra can be assigned to MLCT transitions at around 450 nm [61,190–193] and LCT transitions in the UV region. The MLCT transitions show pronounced solvatochromic shifts, a proof for the large change of dipole moment during the MLCT transition.

Such complexes can become chiral if strong steric interactions disturb the square planar geometry in such a way that it becomes a two-bladed helix [194,195]. The helical chirality at the metal center can be predetermined [196]. Examples are the cis-bis-homoleptic complexes **3**–**15** derived from a chiral thienylpyridine ligand where the element of chirality is in the 4,5 or 5,6 position (Scheme 7; Fig. 9)



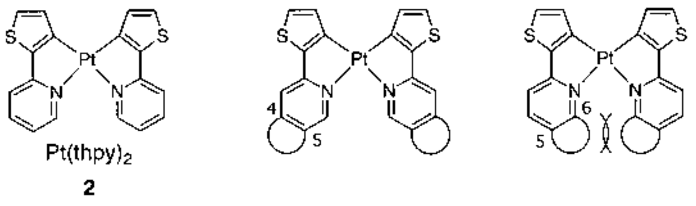
Scheme 6.

Table 1
Absorption and circular dichroism ($\Delta\varepsilon$, l mol^{-1} cm^{-1}) of MMCT transitions for various dimolybdenum complexes

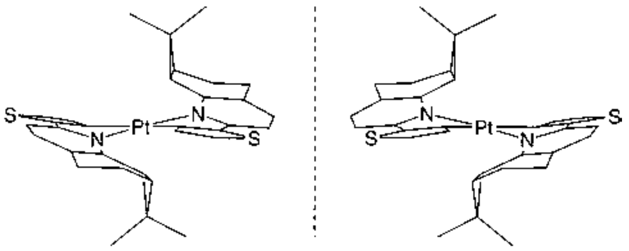
Product	d_{xy}–d^*_{xy} (10^{-3} cm^{-1})	$\Delta\varepsilon/\varepsilon$ (10^3)	d_{xy}–$d^*_{x^2-y^2}$ (10^{-3} cm^{-1})	$\Delta\varepsilon/\varepsilon$ (10^2)	α (°)	Ref.
Mo_2Cl_4(*S*,*S*-dppb)$_2$	13.7	−5.8	21.1	+7.3	23	[183]
Mo_2Cl_4(*R*-dppb)$_2$	13.3	+7.5	21.7	−6.7	0–45	[62]
Mo_2Cl_4(*R*-phenphos)$_2$	13.2	+6.0	21.5	−6.2	0–45	[62]
Mo_2Cl_4(*S*-chairphos)$_2$	14.3	−2.0	21.3	+1.1	0–45	[62]
Mo_2Cl_4(*S*,*S*-skewphos)$_2$	13.9	−10.8	20.8	+3.7	0–45	[62]
Mo_2Cl_4(*R*,*R*-dach)$_2$	18.0	>0	22.2	<0	0–45	[64]
Mo_2Br_4(*S*,*S*-dppb)$_2$	13.2	−3.2	20.7	+8.5	0–45	[62]
Mo_2Br_4(*R*-dppb)$_2$	12.8	+3.0	20.8	−4.5	0–45	[62]
$Mo_2(MeCO_2)_2$(*S*,*S*-dppb) (MeCN)$_2$	19.2	+0.35	25.6	−0.32	1–2	[184]
Mo_2(*R*-pn)$_4$	21.0	−9.1	27.8	+17.0	45–90	[62]

Examples of chiral bis-cyclometallated Pt^{II} complexes are shown in Scheme 8 and examples of chiral bis-cyclometallated Pt^{IV} complexes are shown in Scheme 9.

The spectroscopic properties of cyclometallated Pt^{II} complexes are well understood. A MO scheme of Fig. 12 has been obtained from EH calculation of complex **3** and **5**. More detailed DFT calculations [197] reveal that the transitions ^{1}MLCT (d_{z^2}–π) and ^{1}MLCT ($d_{x^2-y^2}$–π) lie at 20 353 and at 20 395 cm^{-1}, respectively. A shoulder, present in the absorption spectrum at around 500 nm, is attributed to a ^{3}MLCT (d_{z^2}–π) transition, which is also the emitting state. The complexes can be considered as distorted from C_{2v} geometry where transitions with a dipole moment along the dipole axis (z-axis, transforming as A_1) will carry most intensity in the absorption spectra. Such a transition is the MLCT $d_{xz} \rightarrow \pi^*$ or MLCT $d_{z^2} \rightarrow \pi^*$ (HOMO–LUMO) which transform as A_1 in C_{2v} symmetry. If one assumes that the



Scheme 7.



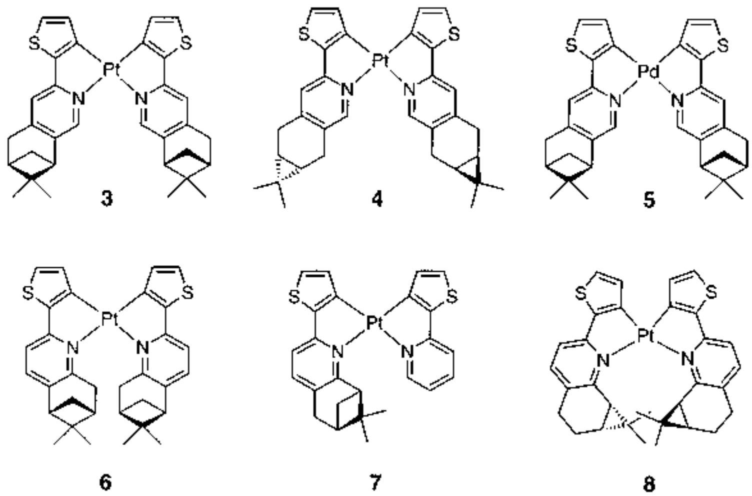
Δ-Pt(th5,6capy)$_2$

8

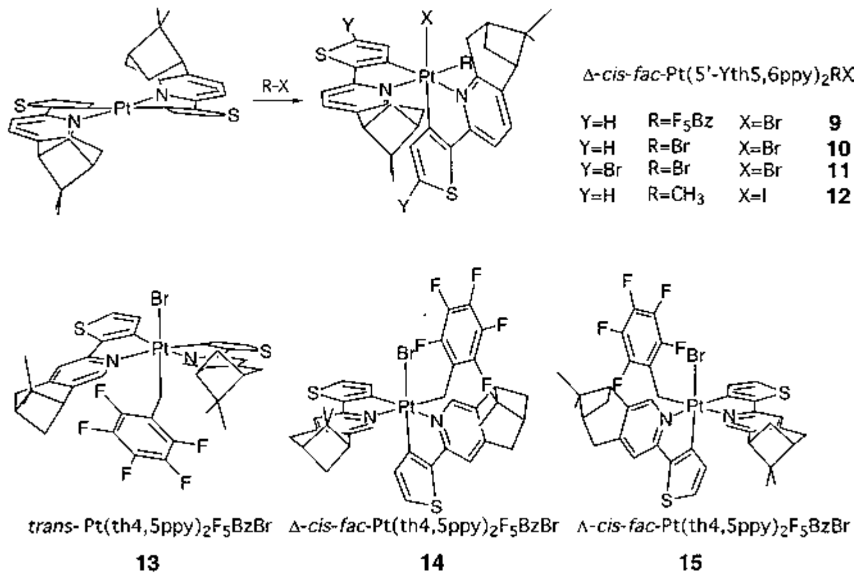
Λ-Pt(th5,6capy)$_2$

Fig. 9. Enantiomers of Pt(th5,6capy)$_2$ derived from (+)-2-carene and (−)-2-carene.

CD-activity will only result from a pure MLCT transition without admixture of ligand field states, then it will be sufficient to determine the transition along a helical path looking from the metal center towards the ligand. Due to the distortion the transition dipole moment of MLCT $\mathrm{d}_{xz}\rightarrow\pi^*$ or MLCT $\mathrm{d}_{z^2}\rightarrow\pi^*$ would decrease since the overlap of involved states formally decreases. Going from **3** to **6** indeed lowers the epsilon values and increases the transition energies of the MLCT transitions which is consistent with this hypothesis. The effect of the chiral distortion on the nature of electronic states seems to be important, since the MLCT transitions are shifted by about 40 nm going from the planar complex **2** to a strongly distorted complex **6**. The assumption that pure MLCT states are present is usually not valid for coordination compounds and it is known for $[\mathrm{Ru(bpy)_3}]^{2+}$ that MLCT transition can borrow a magnetic dipole from admixture with ligand field states. However, bis-cylcometallated Pt$^{\mathrm{II}}$ complexes are supposed to have



Scheme 8.



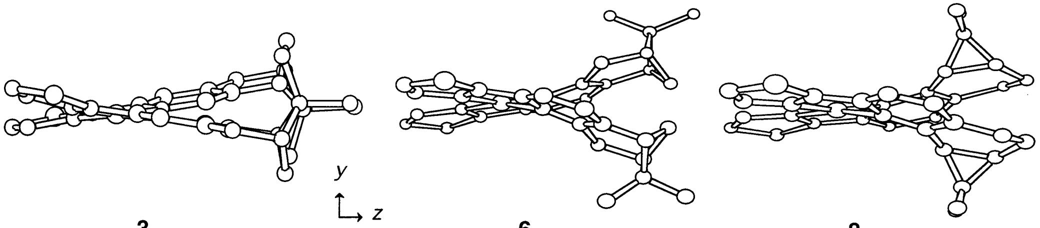
Scheme 9.

ligand field states below 300 nm, e.g. ^3E_g–$^1A_{1g}$ (288 nm), $^1A_{2g}$–$^1A_{1g}$ (256 nm), ^1E_g–$^1A_{1g}$ (226 nm) in [Pt(en)(*S*-pn)]$^{2+}$ [198] or similarly in [Pt$_2$(en)$_2$(*S*,*S*-nbn)$_2$]Cl$_4$ [199] assuming an idealized D_{4h} symmetry. $\Delta\varepsilon$ values recorded were below 2. Related Pd diene complexes, e.g. [PdCl(Et$_4$dien)]$^+$ have their lowest lying ligand field transition $^1A_{2g}$–$^1A_{1g}$ at 334 nm [200,201].

Assuming a pure MLCT transition, a Δ-configuration as shown in Fig. 10, will induce a charge-transfer along a left-handed helical path according to the 'helical path rule' and therefore to a negative Cotton effect. This general rule has been observed with a number chiral complexes of this type (Table 2).

Such bis cyclometallated d^8 complexes can undergo oxidative addition reactions [49] with complete retention of configuration [48] to form Pt^{IV} complexes. The products show LMCT transitions between 360 and 380 nm [49] for which, in principle, the same helical path rule applies. A transition from the ligand towards the metal will then have the same CD-sign as a MLCT transition along the opposite direction. The longest wavelength LMCT transition shows a CD-value of the same sign as the MLCT transition in the precursor complex. Photochemical oxidative addition is also possible and current studies show that this process is also stereoselective. After reduction, the initial enantiomerically pure compounds can be recovered (Fig. 11).

Other chiral Pt and Pd phosphine complexes with their CD-spectra have been recently described, e.g. as macrocyclic molecular squares [202,203] where ligand field transitions are observed. No assignment is made by the authors. Small CD-values ($\Delta\varepsilon$ from 0.01 to 1.1) are reported for singlet and triplet d–d transitions of Pt^{II} and Pt^{IV} complexes with L-methylcysteine and L-methylcysteine sulfoxide,



3
Δ-Pt(th4,5ppy)$_2$

6
Δ-Pt(th5,6ppy)$_2$

8
Δ-Pt(th5,6capy)$_2$

Fig. 10. Crystal structure of chiral bis(cyclometallated) compounds.

with L-methionine and L-methionine sulfoxide from where the absolute configuration of the sulfoxide was claimed on the basis of comparison [204,205]. A chiral Pt^{II} complex with very small $\Delta\varepsilon$ values (below 0.1 and 0.2) for unassigned transitions at 400 and 750 nm with an exciton couplet at 300 nm ($\Delta\varepsilon = +0.4$ at 275 nm/-0.6 at 300 nm) were recorded for a spontaneously resolving *cis*-bis-[2-(2-benzoaxzoylyl)-phenyl] dichloroplatinum(II) in a KBr pellet [206]. However, the very small $\Delta\varepsilon$ values of this couplet, also in comparison with other transitions at higher wavelength, are not favoring an assignment as exciton couplet.

4.4. Bioinorganic complexes

A recent book on CD in biomolecules [207] covers the main aspects of modern research in this area, but does not include transition metals explicitely. However, metals are important structural elements in many proteins and structural changes of complex protein structures upon metal complexation are studied often with CD-spectroscopy [208].

A few examples are discussed in the following.

4.4.1. Polypeptides, proteins and polynucleotides containing Pd^{II}, Cu^{II} and Co^{III}

Protein conformation studies using CD-data have appeared only very recently [209,210] and rely on exciton theory. Nevertheless, CT transitions can also be used to elucidate the configuration around the complexing metal center. In one case, NMR and CD-studies showed the conformational behaviour of Pd^{II} complexd with

Table 2
Absorption and circular dichroism (ε, $\Delta\varepsilon$, l mol^{-1} cm^{-1}) of MLCT transitions (CT, nm) data for various bis-cyclometallated Pt^{II} and Pt^{IV} complexes[a]

Product	Abs (λ, ε)	λ (CT, nm)	$\Delta\varepsilon$
th4,5ppy	308 (15 000)		
th5,6ppy	312 (14 600)		
Pt(thpy)$_2$ (**2**)	417 (10 700)		
Λ[b]-Pt(th4,5ppy)$_2$ (**3**)	415 (11 800)	415	12.6
Δ[b]-Pt(th4,5capy)$_2$ (**4**)	410 (12 000)	410	−6.3
Λ[b]-Pd(th4,5ppy)$_2$ (**5**)	382 (9400)	377	9.2
Δ-Pt(th5,6ppy)$_2$ (**6**)	444 (6800)	444	−24.7
Λ-Pt(thpy)(th5,6βppy) (**7**)	424 (5200)	423	9.5
Δ-Pt(th5,6capy)$_2$ (**8**)	442 (7100)	445	−30.0
Δ-Pt(th5,6ppy)$_2$F$_5$BzBr (**9**)	356 (11 500)	373	−18.2
Δ-Pt(th5,6ppy)$_2$Br$_2$ (**10**)	350 (12 200)	360	−13.9
Δ-Pt(5′–Brth5,6ppy)$_2$Br$_2$ (**11**)	362 (22800)	367	−20.1
Δ-Pt(th5,6ppy)$_2$CH$_3$I (**12**)	355 (14 400)	367	−30.8
Δ[b]-Pt(th4,5ppy)$_2$F$_5$BzBr (**14**)	350 (16 000)	364	−18.1
Λ[b]-Pt(th4,5ppy)$_2$F$_5$BzBr (**15**)	350 (16 000)	364	17.3

[a] All data are from deareated CH$_2$Cl$_2$ solutions.

[b] Tentative assignment from week CD-values. All other configurations are obtained from X-ray data and related geometrical considerations.

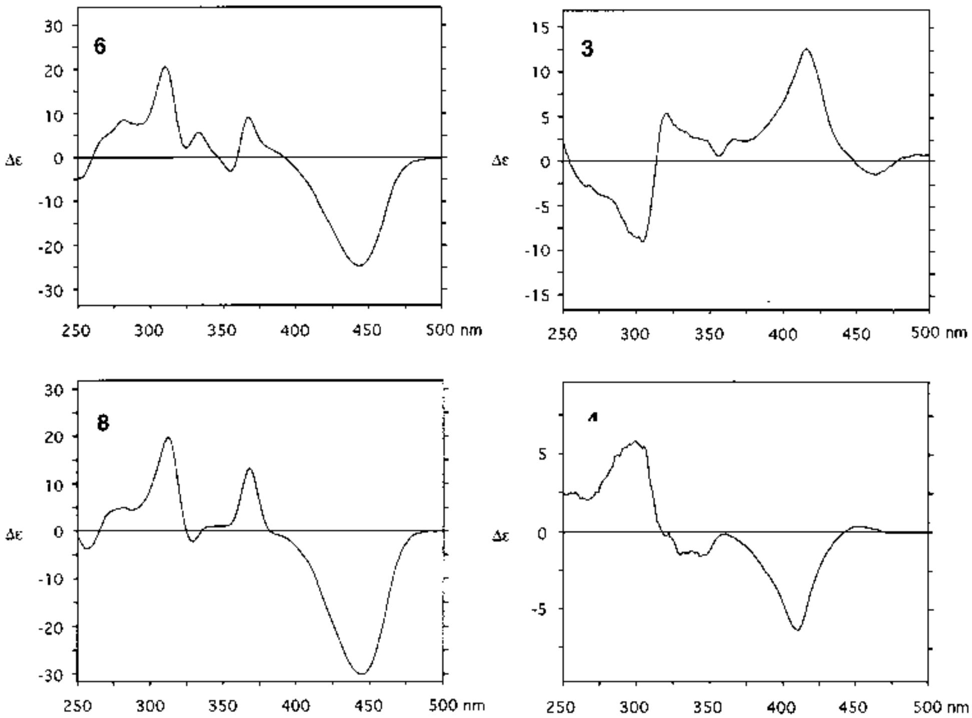


Fig. 11. CD-spectra of Λ-Pt(th4,5ppy)$_2$ (**3**), Δ-Pt(th4,5capy)$_2$ (**4**), Δ-Pt(th5,6ppy)$_2$ (**6**) and Δ-Pt(th5,6capy)$_2$ (**8**) [196].

S-methyl-L-cysteine-containing peptides [211]. In another example, N$_3^-$–Cu^{II} LMCT and MCT were studied in Rhus Laccase where CD-spectra allowed to determine the nonbridging nature of the azide ligand between two antiferromagnetically coupled Cu^{II} sites [212]. Solvent dependent CD-spectra of ternary amino acid Cu^{II} complexes showed that π–π stacking between aromatic rings is important in solution and leads to charge-transfer band between stacked aromatic rings at 320–400 nm [213].

Chiroptical properties in the UV region, due to exciton coupling, and in the ligand field region (400–500 nm) of Co^{III} mimochrome I, a hemoprotein model, corresponded to the three-dimensional structure determined by NMR in solution [214].

4.4.2. *Porphyrine and biliverdine complexes with Zn^{II}*

CD in zinc biliverdine induced by complexation of chiral amines and amino acid esters was used to determine the helicity of the parent zinc biliverdine structure [215]. The sign is deduced by comparison with known spectra and with quantum chemical calculations on model compounds [216–219]. The exciton coupling between two linked zinc porphyrines was used to propose a solution structure [220]. An assignment of the optical spectra of metal phthalocyaninine anions was proposed also on the basis of MCD measurements and ZINDO calculations [221].

4.4.3. Enterobactin, hydroxamate and catecholate complexes

An important class of compounds where circular dichroism spectroscopy has been useful for characterization are complexes of ketons, keto amides, hydroxamate or catecholates with high spin d^5 ferric ions. Kinetically inert complexes can be obtained by choosing a rigid ligand geometry that induces the configuration at the metal center and prevents from racemization. Remarkable kinetic stability was reported for the enterobactin complex Fe(**16**)$^{3+}$ [222], a natural chiral siderophore, that acts as a biological iron transporting agent [223,224] and binds metal ions preferentially in a Δ configuration in aqueous solution [225]. A number of enterobactin analogues [226–230] have been prepared to study such helical iron binders in more detail (Fig. 14).

The absolute configuration of complexes with ferric ions was deduced from the optical transitions to excitonic states [103] and from LMCT transitions by comparison with complexes of known configuration [225,231]. An X-ray structure of the related V^{IV} enterobactin complex [232] confirms the assignments of helicity.

The absolute configurations of siderophore model compounds with Cr^{III} [233–236] and Rh^{III} [237] complexes of this type have been determined by comparison of the CD in the MCT transitions with tris(catecholate) complexes of Cr^{III} and Rh^{III} of known configuration. From these analyses, it was deduced, that the Cr^{III} and Rh^{III} enterobactin complexes preferentially form right handed helices (Δ configuration).

Related tris(thiohydroxamate) and tris(hydroxypyridinethionate) complexes with Fe^{III}, Cr^{III} and Co^{III} have been reported also [238] where the same confor-

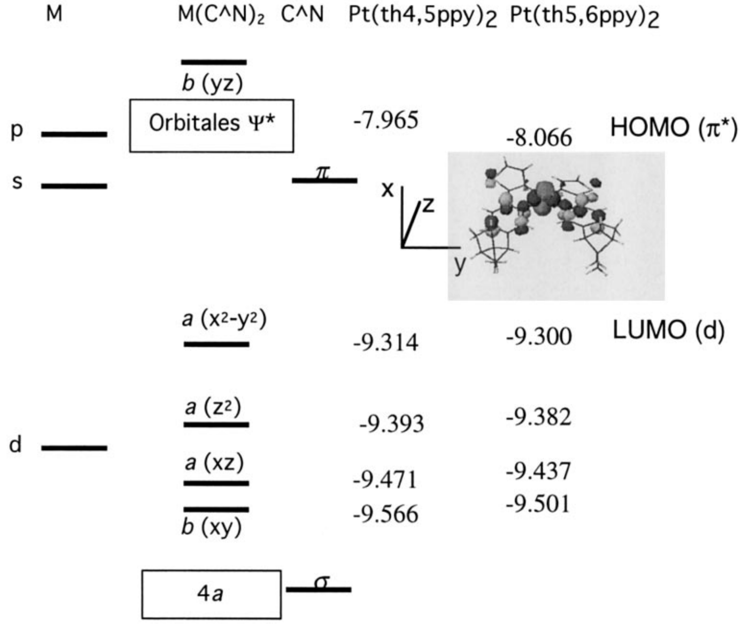


Fig. 12. Orbital scheme of bis(cyclometallated) complexes (EH-calculation) with energies (in eV) for given orbitals whose main components transform as the irreducible representation given.

Table 3
Circular dichroism data of Fe^{III} and V^{IV} tris(catecholate) enterobactin analogues

Product	λ ($\Delta\varepsilon$)	Ref.
17	227.5 (5.2); 218 (0); 205 (−5.2)	[241]
Δ-Fe(**26a**)$^{3+}$	248 (−132); 257 (0); 267 (145)	[103]
Δ-Al(**26a**)$^{3+}$	256 (−249); 266 (0); 278 (307)	[103]
Δ-Ga(**26a**)$^{3+}$	257 (−250); 267 (0); 280 (280)	[103]
Δ-In(**26a**)$^{3+}$	258 (−177); 269 (0); 282 (199)	[103]
Λ-*cis*-Fe(**26b**)$^{3+}$	345 (−3.64); 450 (+2.4)	[227]
Δ-*cis*-Fe(**16**)$^{3-}$	420 (4.0); 535 (−4.0)	[229]
Λ-*cis*-Fe(**18**)$^{3-}$	345 (−1.5[a]); 450 (0.1[a])	[228]
Δ-*cis*-Fe(**23**)$^{3-}$	432 (4.2); 550 (−2.3)	[229]
Δ-*cis*-Fe(**24**)$^{3-}$	435 (3.5); 560 (−1.0)	[229]
Δ-*cis*-Fe(**21**)$^{3-}$	428 (3.8); 540 (−2.9)	[229]
Δ-*cis*-Fe(**22**)$^{3-}$	430 (3.5); 548 (−1.6)	[229]
Δ-*cis*-V(**16**)$^{2-}$	262 (−20.5); 327 (13.6); 437 (−11.9); 544 (31.7); 691 (−13.9)	[231]
Δ-Fe$_2$(25)$_3$	372 (2.73); 464 (−1.41)	[226]
fac-Λ-[Y(l−moba)$_3$]	318 (−6.4); 349 (+7.2)	[239]
Λ-K[As(cat)$_3$]	202 (−151); 258 (150)	[242]
Λ-*cis*-Fe(bmat)$_3$	365 (−2.7[a]); 455 (1.2[a])	[243]

[a] Values estimated from reported spectra.

mational preferences were found as for the parent tris(hydroxamate) complexes. Detailed values for the CD-spectra are given in Table 3.

One can assume that pure excitonic states are responsible for the absorption and circular dichroism in the UV region, i.e. the region of the ligand absorption. Charge-transfer or ligand field states admixture to these transitions is generally not observed, thus exciton theory applicable. However, due to the lability of these complexes, the enantiopurity is not precisely known. In a number of chiral tris(1,3-diketone) complexes with Sc, Y, La, Al, Ga and In, the absolute configuration was assigned by looking at the exciton couplet and comparison to (−)-[Si(acac)$_3$]$^+$ [239].

MLCT transition in Fe^{III} tris(catecholates) have also been assigned using MCD and single crystal polarized absorption spectroscopy [240].

In high spin Fe^{III} complexes, all d–d transitions are symmetry forbidden and not observable in the absorption spectrum. However, mixing of MCT into the LMCT transitions between 300 and 500 nm is possible. Therefore, the helical path rule for these charge-transfer transition is not valid (Fig. 13).

4.5. Schiff-base complexes with Mn^{II}, Fe^{II}, Co^{II}, Co^{III}, Ni^{II} and Cu^{II}

Square planar complexes of Cu^{II}, Co^{II} and Ni^{II} with tetradentate Schiff-bases of optically active diamines (salen derivatives) and their absolute configuration are discussed in detail by Pasini et al. [244] using arguments from exciton theory. A recent study [53] about Co^{II} and Co^{III} complexes containing such optically active tetradentate Schiff-base ligands with δ gauche or λ gauche conformations of a flexible ligand correlates the absolute configuration using CD-spectra with results known from Pasini. The exciton type CD-bands in optically active Schiff-bases have been analyzed in detail for organic compounds [245].

Chiral complexes of Cu^{II} of the Schiff-base from *R*-1,2-propanediamine and acetylaceton have been investigated in detail by Larsen et al. [246,247] CD-spectra in solution [246] and phase modulated CD-spectra of crystals [247] allowed to show the same chiral distortion of the two acetylacetoneimine parts in solution and in crystal structure and the absolute configuration to be assigned as Λ. Preparation, reactivities and optical spectra of chiral Mn^{III} and Cu^{II} complexes of binaphthyl Schiff-bases have been reported recently by Ho et al., however without assignment of configurations [248].

Bernauer et al. [249–253] have studied a large variety of Cu^{II}, Co^{III} and Ni^{II} complexes with optically active Schiff-bases and triamines. Electron-transfer kinetics between $[Co(L)H_2O]^+$ (L = *N*,*N*′-((pyridine-2,6-diyl)bis(methylene))bis(proline) (promp or MeO–promp) and the optically active (Fe(*S*,*S*)–L′) (*L*′ = promp, MeO–promp or *N*,*N*′-((pyridine-2,6-diyl)bis(methylene)bis(alanine) (alamp)) have been measured by CD [253]. The observed stereoselectivity is always in favor of the heterochiral diasteroisomeric pair. Mean k_{DL}/k_{LL} ratios of about 2 were recorded for $[Co(promp)H_2O]^+$ and $[Co(MeO–promp)H_2O]^+$, respectively, with the three optically active Fe^{II} complexes. CD-bands observed are, however, ligand field transitions.

N,*N*′-(1*R*,2*R*)-(−)-1,2-Cyclohexylenebis(salicylideneiminato) and other chiral salen ligands complexed to Ni^{II} [51] and to Cu^{II} [52] were studied recently and CD-bands originating from LMCT are found consistent with the observed tetrahedral distortion originating from the chiral configuration of the ligand. The LMCT arise

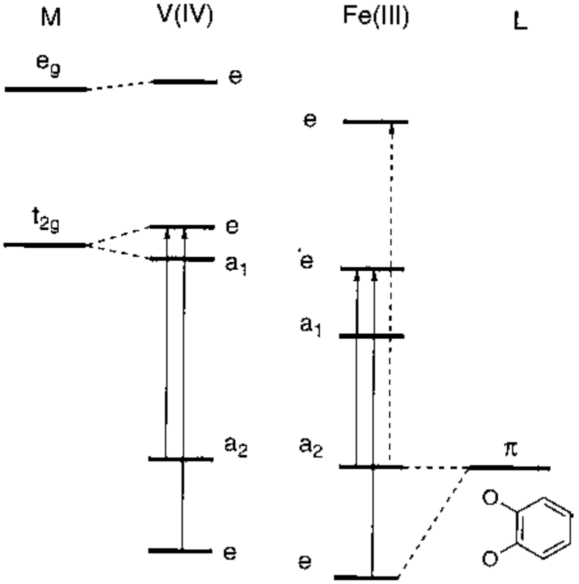


Fig. 13. Schematic MO picture of LMCT transition in Fe^{III} and V^{IV} tris(catecholates).

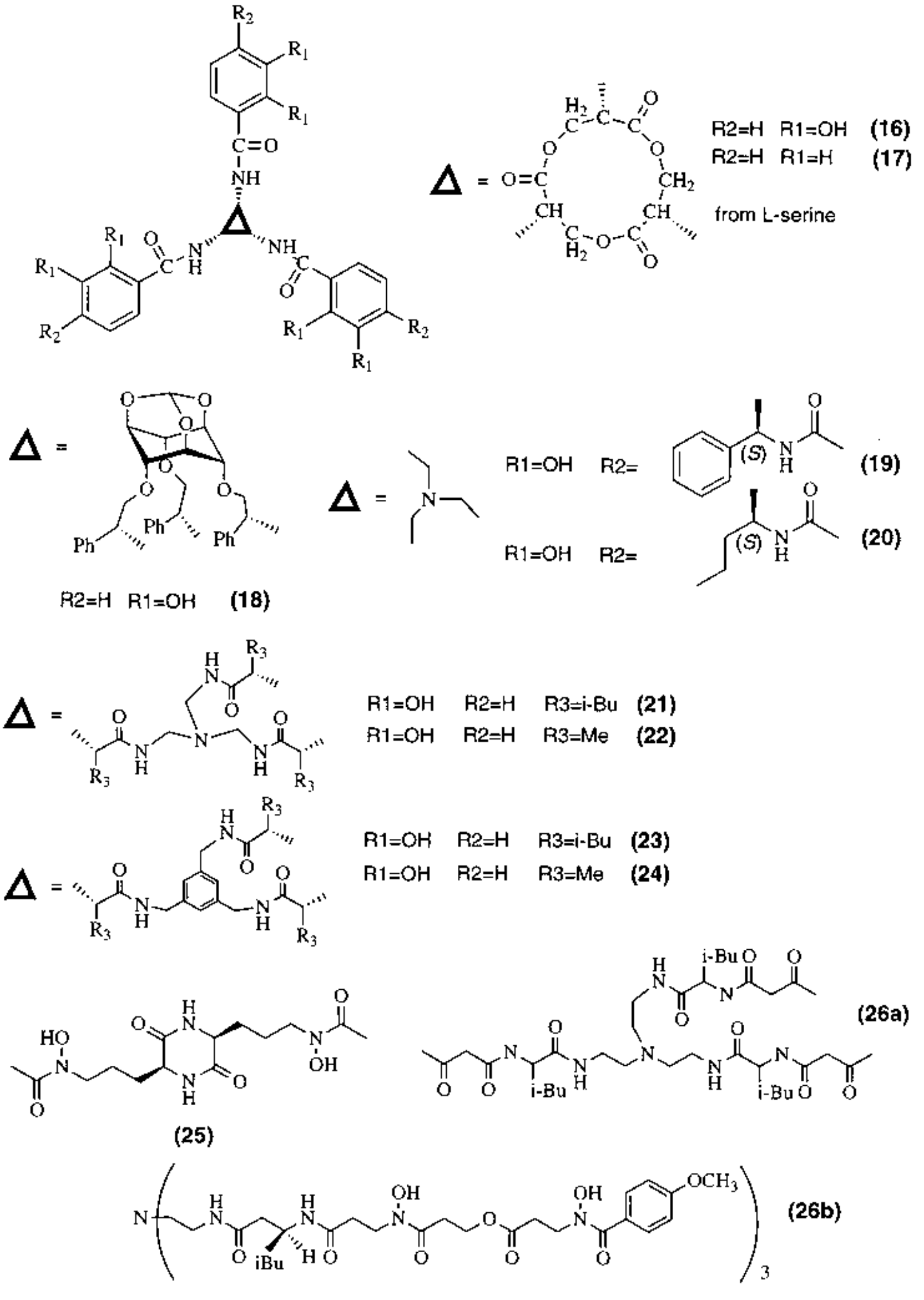


Fig. 14. Enterobactin and related analogues.

from ligand π-orbitals and non-bonding oxygen orbitals to the strongly antibonding $3d_{x^2-y^2}$ orbital. The sign of the most intensive CD-bands at around 340 and 400 nm is essentially negative. Such charge-transfer being only a function of helicity of the ligand coordinated to the metal, the helical path rule correspondingly gives the correct sign.

The inversion of the Cotton LMCT bands at 396 and 450 nm during the addition of PPh_3– to $[Ru(\eta\text{-}MeC_6H_4^iPr\text{-}p)(H_2O)((S)\text{-}(\alpha\text{-methylbenzyl})salicylaldimine)]^+$ was interpreted as a proof for inversion of the metal configuration [254]. However, the electronic nature of transitions could be changed considerable upon PPh_3 addition and no detailed electronic analysis is given. A number of chiral half-sandwich ruthenium complexes with phosphine ligands are reported [255] where it proved impossible to correlate the CD-spectra with the absolute configurations of the metal center.

$[M((S,S)\text{-cypim})]^{2+}$ M = Zn, Cu, Ni, Co, Mn complexes were studied [256] where the two azomethine moieties generate an exciton couplet, from where the absolute configuration was determined to be Δ for all metals except for Mn which is Λ. This is believed to be due to the larger radius of the Mn^{II} ions. Ligand field transitions in the Co^{II} complexes confirmed the Δ-configuration by comparison. The same arguments for the azomethine coupling has been used to determine absolute configuration of reaction products of $Ti(salen)Cl_2$ with (*R*) or (*S*)-α-hydroxy carboxylic acids [257].

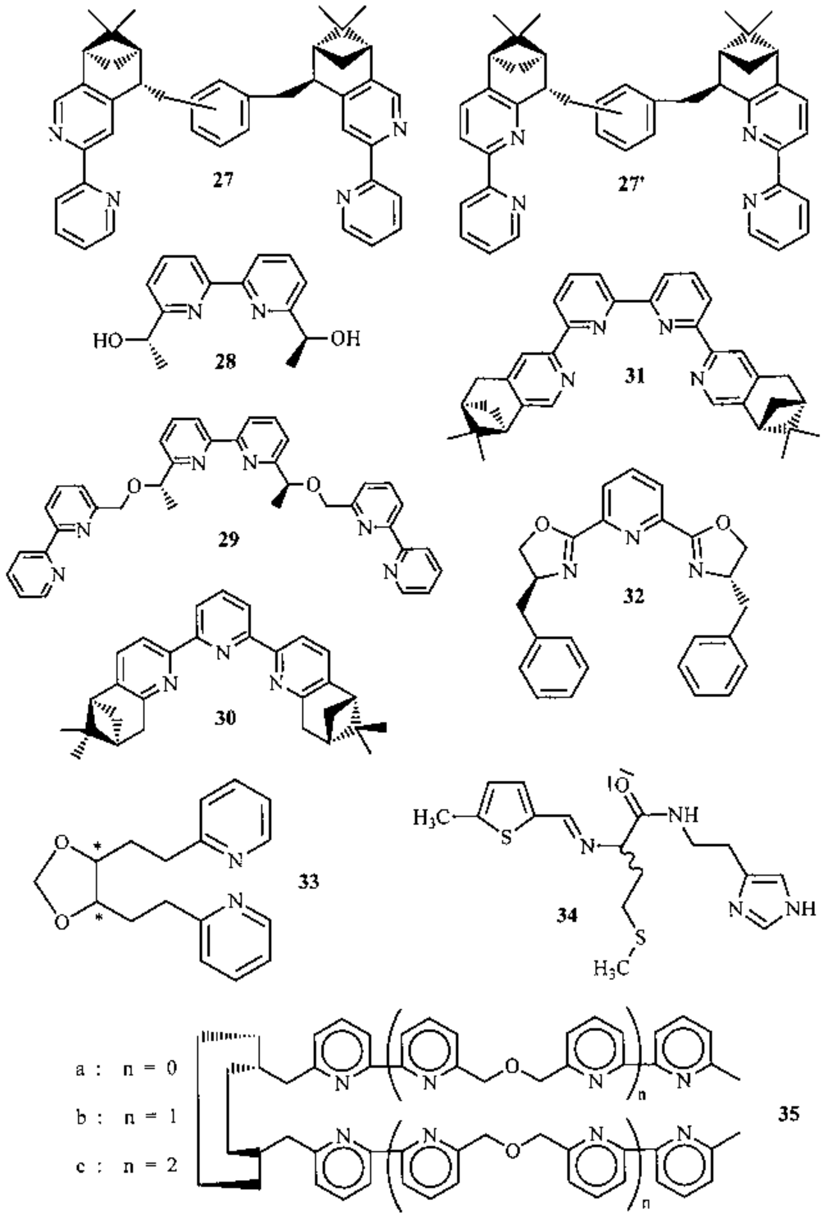
An interesting case of a right handed helical conjugated ladder polymer was reported for Ni^{II} complexes with helicene bridged salen where a large $\Delta\varepsilon$ value at 590 nm ($\Delta\varepsilon = +105$) is attributed to a LMCT transition [258]. However, no further structural information is available.

A number of Cu^{II} complexes of optically active bidentate ligands, *N,N′*-bis[2-pyridylmethyl and 2-(2-pyridyl)ethyl]-(*S*)-malamide and related amides, were characterized by their CD-spectra [259]. $\Delta\varepsilon$ values between $+1$ and -2 in the LMCT transitions show a tetrahedrally distorted coordination geometry, however, no structural assignment is possible from the recorded data.

The sign of Cotton effects of in the charge-transfer band region (35 000–45 000 cm^{-1}) of *N*-glycosylamine ligands from 1,3-diamonopropane and aldopentoses has very recently been related also to the absolute configuration by comparison with an X-ray structure and correlation on the MCT bands with other complexes. The sign of the Cotton LMCT band may in fact be interpreted using the helical path rule.

4.6. Helicates

Unlike for polypeptides, where the tertiary structure (α-helix, β-sheet, β-turn, random coil) leads to distinctive CD-spectra and where the content of each of these structural elements can be estimated from CD-spectra, there is no systematic attempt to study helicates [9] and their structures by means of CD-spectroscopy. A number of chiral ligands **27**–**32** have been shown to give predetermined helicity upon complexation (Scheme 10).



Scheme 10.

Triple helicates with octahedral coordination geometry of the metal centers can be described by the configuration at each metal center. If the coordinated metals are well separated from each other, i.e. no electronic overlap possible, then a helicate can be assumed to consist of individual chromophoric units consisting of one metal with its coordination sphere. CD-bands will then just be the sum of all transitions in the chromophores. This is, however, rarely the case, since bridging units have significant influence on both energies and intensities of transitions.

4.6.1. Octahedral triple helicates with Fe^{II}, Ni^{II}, Cu^{II}, Zn^{II} and Cd^{II}

In the dinuclear triple helicates [152] with Fe^{II}, Zn^{II} and Cd^{II} and ligand **27** the optical activity of the individual chromophores results from exciton coupling in the LCT transitions and from MLCT transitions with ligand field admixture. The $\Delta\varepsilon$ values reported for the dinuclear triple helicates (Table 4) are only slightly bigger than the corresponding mononuclear complex. This may be an intrinsic behaviour or due to partial fast racemisation in aqueous solution [260].

In an other case, spontanous resolution of a racemic Ni^{II}-triple helix into enantiomers was confirmed by X-ray analysis and by CD-spectra of dissolved single crystals [261].

A right-handed helical twist in the solution structure of pentacoordinated Zn^{II} and Cu^{II} with bis(2-quinolylmethyl)-(*S*)-2-pyridyl-1-ethylamine and one chloride ion as ligands were deduced from strong exciton coupling (225 nm, + 25; 245 nm, − 160) and from sterical arguments [88,262].

4.6.2. Helicates with Cu^{I}

Cu^{I} complexes with polypyridyl ligands show MLCT transitions between 400 and 550 nm [141,142,265,266] and a number of helicates with a helical solid state

Table 4
LCT and MLCT transitions of dinuclear Fe^{II} helicates

Product	λ ($\Delta\varepsilon$)	Ref.	Assignment
Δ, Δ-$[Fe_2(-)CG(m\text{-xyl})_3]^{4+}$	295 (242)	[152]	LC
	315 (−529)		
	395 (13.6)		MLCT
	477 (12)		MLCT
	526 (−7.5)		MLCT/d–d
Λ, Λ-$[Fe_2(+)CG(m\text{-xyl})_3]^{4+}$	295 (−236)	[152]	LC
	315 (566)		
	395 (−12)		MLCT
	477 (−11)		MLCT
	526 (7.9)		MLCT/d–d
Δ-$[Fe(bpy)_3]^{2+}$	284 (150)	[263]	LC
	300 (−500)		
	385 (3.2)		MLCT
	476 (−12)		MLCT
	545 (19)		MLCT/d–d
Λ-$[Fe(bpy)_3]^{2+}$	284 (−149)	[264]	LC
	299 (401)		
	392 (−5.7)		MLCT
	479 (17)		MLCT
	556 (−26)		MLCT/d–d

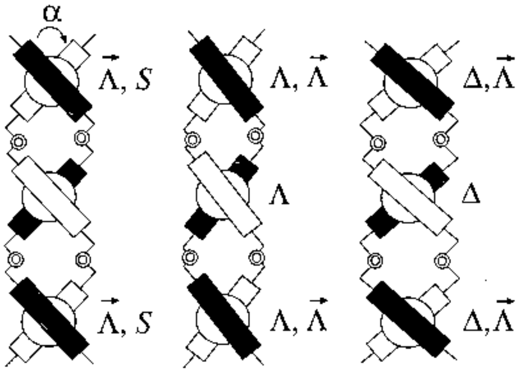


Fig. 15. Local configurations of a M helix with a ligand with three bidentate binding sites.

structure have been reported [9]. Such helicates with linear or tetrahedral coordination geometries that are inherently achiral at the metal center will show significant CD-bands if the ligands are distorted significantly from planarity or from a perpendicular position. The configuration at the metal center for a given M-helix may in fact be both Λ ($\alpha < 90°$) or Δ ($\alpha > 90°$) using the IUPAC designation for skew lines (Fig. 15), independently of the helical chirality descriptor. However, for this type of complex the oriented line reference system [15,267] can be applied which will attribute a $\vec{\Lambda}$ (or *S* according to CIP rules) configuration if the bridging part has higher priority than the non-bridging. Clearly all M helices of this type will have $\vec{\Lambda}$ configuration at the metal centres at the ends of the helix.

If the helix has ligand centred transitions that are exactly perpendicular to each other, no exciton CD-activity will result and no Cotton effect will arise in the MLCT transitions. Only the perturbation induced by the bridging part of the ligand will be responsible for CD-activity, which in this case, however, will be small. Cases of Cu^{I} complexes with almost perpendicular chiral ligands, which preferentially form one diastereomer, as can be monitored by NMR, show almost no CD-activity at all, especially not in the region of MLCT transitions [268].

A trinuclear helix (Fig. 15) was reported for the complex P-$[Cu_3(\mathbf{29})_2]^{3+}$ by Lehn et al. [269]. A positive Cotton effect was observed at 475 nm ($\Delta\varepsilon = 4.7$, estimated from the curve), whereas for the corresponding mononuclear complex $[Cu(\mathbf{28})_2]^+$, almost no CD-activity in the region of the MLCT transitions was recorded ($0.6 > \Delta\varepsilon > -0.5$). Unfortunately the CD-spectra in the UV region where exciton bands would be expected is not presented. Similarly, for the resolved dicopper(I) molecular trefoil knot [13], an exciton couplet is found around 310 nm with a large positive Cotton effect at higher wavelength ($\Delta\varepsilon = +620$ at 330 nm), that can be interpreted as intrinsic for Λ configuration of the ligands around the metal. Furthermore the MLCT band shows a broad positive Cotton effect ($\Delta\varepsilon = +20.7$) at the absorption maximum near 510 nm which, according to the helicity rule for pure MLCT transitions, corresponds to a right-handed screw sense at the Cu^{I} center. With ligands **35a**–**c**, Siegel et al. [270,271] have obtained a number of Cu^{I} helicates with an almost identical CD-spectrum: an exciton couplet around 300 nm ($\Delta\varepsilon = +233$ at 313 nm) and a broad

Table 5
Absorption and circular dichroism (ε, $\Delta\varepsilon$, 1 mol^{-1} cm^{-1}) of polynuclear helical Ag^{I} complexes (in acetonitrile)

Product	λ ($\Delta\varepsilon$)	Helix	Ref.	Assignment
$[Ag_2(\mathbf{32})_2]^{2+}$	301 (10.15) abs: ($\varepsilon = 1547$, sh)	P	[280]	MLCT
$[Ag_2(\mathbf{31})_2]^{2+}$	300 (-180)[a] 330 ($+360$)[a]	P	[277]	LC
$[Ag_2(\mathbf{31\text{-}})_2]^{2+}$	300 ($+180$)[a] 330 (-360)[a]	M	[277]	LC
$[Ag_2(\mathbf{30})_2]^{2+}$	292 (-20) 330 ($+57$)	P	[279]	LC
$[Ag_6(\mathbf{27})_6]^{6+}$	290 (-5) 314 ($+16$)	P	[278]	LC

[a] Estimated from published spectra

positive Cotton effect in the MLCT bands ($\Delta\varepsilon = +5.2$ at 480 nm). This configuration was assigned to a P helical descriptor based on comparison with CD-spectra of Lehn's structure and based on geometric reasons.

4.6.3. Helicates with Ag^{I}

A number of early cases for a helical solid state structure of dinuclear complexes of Ag^{I} and Cu^{I} with chiral pyridine–imine ligands was described by van Koten et al. [272–274], however, no CD-data were given. Only later, the Ag^{I} complex with ligand **34**, which forms a helical polymer in the solid, was studied in methanolic solutions [275]. However, the small $\Delta\varepsilon$ values for the ligand centered transitions ($\Delta\varepsilon = +2.6$ at 270 nm; -5.2 at 310 nm) and a strong concentration dependency indicate, that there is probably an equilibrium between different solution structures. Similarly, Ag^{I} forms polynuclear polymeric complexes with a predermined helical structure with ligand **33** in the solid state, however the solution structure remains unclear [276].

Ag^{I} complexes show almost identical coordination geometry as the related Cu^{I} complexes and usually similar helicate structures. Optical transitions are supposed to be ligand centred. A large positive CD-band at lower energy in a P-helix is reported by Constable [277]. If these transitions are attributed to π–π^* transitions and exciton coupling assumed, the local configuration at the metal center of the P-helix would be Λ (see Fig. 15). Similar exciton couplets are found for related Ag^{I} helicates with the ligands **27**′ [278] and **30** [279]. Williams et al. reported a Ag^{I} complex $[Ag_2(\mathbf{32})_2]^{2+}$ where a transition at 301 nm is described to have mainly MLCT character [280]. However, π–π^* transitions should occur also in this region. In fact, exciton splitting bands can be of small intensity, if the deviation from a planar, mutually perpendicular structure is small (Table 5).

Acknowledgements

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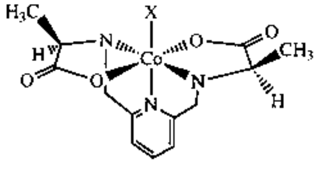
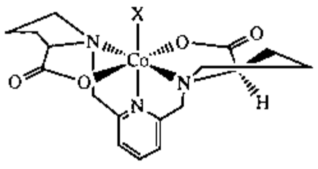
Appendix Ligand abreviations

acac	acetylacetonate
l-moba	4-(l-menthyloxy)-1-phenyl-1,3-butanediolate
dpa	2,6-pyridinedicarboxylate
phen	1,10-phenanthroline
bpy	2,2′-bipyridine
bpym	2,2′-bipyrimidine
py	pyridine
dmbpy	4,4′-dimethyl-2,2′-bipyridine
S,*S*-dppb	(2*S*,3*S*)-bis(diphenylphosphino)butane
R-phenphos	(*R*)-1-phenyl-1,2-bis(diphenylphosphino)ethane
S-chairphos	(*S*)-1,3-bis (diphenylphosphino)butane
S,*S*-skewphos	(*S*,*S*)-2,4-bis(diphenylphosphino)pentane
dach	diaminocyclohexane
R-pn	(*R*)-1,2-diaminopropane
en	ethylenediamine
dien	diethylenetriamine
Et_4dien	1,1,7,7-tetraethyldiethylenetriamine
S,*S*-nbn	(2*S*,3*S*)-2,3-diamino-bicyclo[2.2.1]heptane
cat	catecholate, 1,2-benzenediolate
bmat	benzohydroxamate
(+)-CG[*m*-xyl]	CHIRAGEN derived from (1*R*)-(+)-α-myrtenal with *m*-xylyl as a bridge (ligand **27**) (Scheme 11sch11“>Scheme 11


Δ-[Co((*R*,*R*)-alamp)X]+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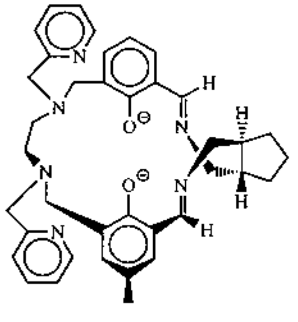
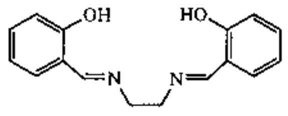

S,*S*-cypim


salen

Scheme 11.

References

[1] U. Knof, A. Von Zelewsky, in press.
[2] R. Noyori, Asymmetric Catalysis In Organic Synthesis, Wiley, New York, 1994, p. 378.
[3] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. Von Zelewsky, Coord. Chem. Rev. 84 (1988) 85.
[4] R. Büchner, J.S. Field, H. Raymond, Inorg. Chem. 36 (1997) 3952.
[5] V.H. Houlding, V.M. Miskowski, Coord. Chem. Rev. 111 (1991) 145.
[6] A. Von Zelewsky, P. Belser, P. Hayoz, R. Dux, X. Hua, A. Suckling, et al., Coord. Chem. Rev 132 (1994) 75.
[7] J. Zyss, C. Dhenaut, T. Chauvan, I. Ledoux, Chem. Phys. Lett. 206 (1993) 409.
[8] N.J. Long, Angew. Chem. 107 (1995) 37.
[9] C. Piguet, G. Bernardinelli, G. Hopfgartner, Chem. Rev. 97 (1997) 2005.
[10] C.O. Dietrich-Buchecker, J.P. Sauvage, Chem. Rev. 87 (1987) 795.
[11] C.O. Dietrich-Buchecker, J. Guilhem, C. Pascard, J.P. Sauvage, Angew. Chem, Int. Ed. Engl. 29 (1990) 1154.
[12] C.O. Dietrich-Buchecker, J.-P. Sauvage, Angew. Chem. Int. Ed. Engl. 28 (1989) 189.
[13] G. Rapenne, C. Dietrich-Buchecker, J.-P. Sauvage, J. Am. Chem. Soc. 118 (1996) 10932.
[14] V. Balzani, L. De Cola (Eds.), Supramolecular Chemistry, NATO ASI Series, Kluwer Academic Publishers, Dordrecht, 1992.
[15] A. Von Zelewsky, Stereochemistry of Coordination Compounds, Wiley, New York, 1996, p. 254.
[16] A. Werner, Ber. 44 (1911) 1887.
[17] A. Cotton, Compt. Rend. 120 (1885) 1044.
[18] A. Cotton, Ann. Chim. Phys. 8 (1896) 347.
[19] F.M. Jaeger, Spatial Arrangements of Atomic Systems and Optical Activity, vol. 7, Cornell University Press, Ithaca, 1930.
[20] J.P. Mathieu, Les Théories Moleculaires du Pouvoir Rotatoire Naturell, Gautier-Villars, Paris, 1946.
[21] T.M. Lowry, Optical Rotatory Power, Republication, Dover Publications, Dover, 1964.
[22] W. Kuhn, Z. Phys. Chem. Abt. B (1929) 14.
[23] W. Kuhn, Z. Phys. Chem. Abt. B (1933) 325.
[24] P. Day (Ed.), Electronic Structure and Magnetism of Inorganic Compounds, The Chemical Society, London, 1970–1976.
[25] P. Day (Ed.), Spectroscopic Properties of Inorganic and Organometallic Compounds, The Chemical Society, London, 1967–1969.
[26] Y. Saito, in: E.L. Eliel, N.L. Allinger (Eds.), Topics in Stereochemistry, vol. 10, Wiley, New York, 1978, p. 95.
[27] S.F. Mason, Molecular Optical Activity and the Chiral Discriminations, Cambridge University Press, Cambridge, 1982.
[28] B.E. Douglas, Y. Saito (Eds.), Stereochemistry of Optically Active Transition Metal Compounds, ACD Symposium Series, 1980.
[29] H.G. Brittain, in: S.G. Schulman (Ed.), Molecular Luminenscence Spectroscopy: Methods and Applications, Part 1, Wiley, New York, 1985, p. 583.
[30] H.G. Brittain, Photochem. Photobiol. 46 (1987) 1027.
[31] H.G. Brittain, Chirality 8 (1996) 357.
[32] F.S. Richardson, Chem. Rev. 79 (1979) 17.
[33] R. Kuroda, Y. Saito, in: K. Nakanishi, N. Berova, R.W. Woody (Eds.), Circular Dichroism. Principles and Applications, VCH, New York, 1994, p. 217.
[34] E.M. Kober, P. Sullivan, T.J. Meyer, Inorg. Chem. 23 (1984) 2098.
[35] J.M. Bijvoet, A.F. Peerdeman, A.J. Van Bommel, Nature 168 (1951) 271.
[36] Y. Saito, K. Nakatsu, M. Shiro, H. Kuroya, Acta Crystallogr. 8 (1955) 729.
[37] S.F. Mason, B.J. Norman, Inorg. Nucl. Chem. Lett. 3 (1967) 285.
[38] L. Ripa, A. Hallberg, J. Sandstroem, J. Am. Chem. Soc. 119 (1997) 5701.

[39] C.J. Hawkins, E. Larsen, Acta Chem. Scand. 19 (1965) 1969.
[40] F.S. Richardson, J. Chem. Phys. 54 (1971) 2453.
[41] A.J. McCafferey, S.F. Mason, B.J. Norman, J. Chem. Soc. (1965) 5094.
[42] J.M. Tsangaris, R.B. Martin, J. Am. Chem. Soc. 92 (1970) 4255.
[43] R.B. Martin, J.M. Tsangaris, J.W. Chang, J. Am. Chem. Soc. 90 (1968) 821.
[44] T. Arai, K. Takei, N. Nishino, T. Fujimoto, Chem. Commun. (1996) 2133.
[45] Y.M. Pu, A.F. McDonagh, D.A. Lightner, J. Am. Chem. Soc. 115 (1993) 377.
[46] A. Gossauer, F. Fehr, F. Nydegger, H. Stöckli-Evans, J. Am. Chem. Soc. 119 (1997) 1599.
[47] N.C. Fletcher, F.R. Keene, M. Ziegler, H. Stoeckli-Evans, H. Viebrock, A. Von Zelewsky, Helv. Chim. Acta 79 (1996) 1192.
[48] M. Gianini, A. Forster, P. Haag, A. Von Zelewsky, H. Stoeckli-Evans, Inorg. Chem. 35 (1996) 4889.
[49] A. Von Zelewsky, A.P. Suckling, H. Stoeckli-Evans, Inorg. Chem. 32 (1993) 4585.
[50] T. Tanase, Y. Yasuda, T. Onaka, S. Yano, J. Chem. Soc., Dalton Trans. (1998) 345.
[51] A. Wojtczak, E. Szlyk, M. Jaskolski, E. Larsen, Acta Chem. Scand. 51 (1997) 274.
[52] E. Larsen, K. Hoppe, E. Szlyk, Monogr. Ser. Int. Conf. Coord. Chem. 3 (1997) 43.
[53] M. Hirotsu, M. Kojima, N. Kiyohiko, K. Setsuo, Y. Yoshikawa, Bull. Chem. Soc. Jpn. 69 (1996) 2549.
[54] A.I. Scott, A.D. Wrixon, J. Chem. Soc. D (1969) 1184.
[55] G.R. Stephenson, P. Howard, S. Taylor, J. Chem. Soc., Chem. Commun. (1991) 127.
[56] R. Brünner, H. Gerlach, Tetrahedron: Asymmetry 7 (1996) 1515.
[57] H.-K. Yip, L.-K. Cheng, K.-K. Cheung, C.-M. Che, J. Chem. Soc., Dalton Trans. (1993) 2933.
[58] A. Zilian, U. Maeder, A. Von Zelewsky, H.U. Guedel, J. Am. Chem. Soc. 111 (1989) 3855.
[59] H. Yersin, S. Schuetzenmeier, H. Wiedenhofer, A. Von Zelewsky, J. Phys. Chem. 97 (1993) 13496.
[60] H. Wiedenhofer, S. Schuetzenmeier, A. Von Zelewsky, H. Yersin, J. Phys. Chem. 99 (1995) 13385.
[61] P. Jolliet, M. Gianini, A. Von Zelewsky, G. Bernardinelli, H. Stoeckli-Evans, Inorg. Chem. 35 (1996) 4883.
[62] I.F. Fraser, A. McVitie, R.D. Peacock, Polyhedron 5 (1986) 39.
[63] P. Agaskar, F.A. Cotton, I.F. Fraser, R.D. Peacock, J. Am. Chem. Soc. 106 (1984) 1851.
[64] M. Gerards, Inorg. Chim. Acta 229 (1995) 101.
[65] A. Vogler, H. Kunkely, Comments Inorg. Chem. 9 (1990) 201.
[66] D. Donges, J. Nagle, H. Yersin, Inorg. Chem. 36 (1997) 3040.
[67] A. Vogler, H. Kunkely, J. Hlavatsch, A. Merz, Inorg. Chem. 23 (1984) 506.
[68] C.A. Emeis, L.J. Oosterhoff, G. de Vries, Proc. R. Soc. A 297 (1967) 54.
[69] R.L. Kronig, J. Opt. Soc. Am. 12 (1926) 547.
[70] H.A. Kramers, Atti Congr. Int. Fis. 2 (1927) 545.
[71] H.P. Jensen, F. Galsbøl, Inorg. Chem. 16 (1977) 1294.
[72] A. Rodger, B. Nordén, Circular Dichroism and Linear Dichroism, Oxford University Press, New York, 1997, p. 150.
[73] G.N. Henning, P.A. Dobosh, A.J. McCaffery, P.N. Schatz, J. Am. Chem. Soc. 92 (1970) 5377.
[74] J.A. Larrabee, C.M. Alessi, E.T. Asiedu, J.O. Cook, K.R. Hoerning, L.J. Klingler, et al., J. Am. Chem. Soc. 119 (1997) 4182.
[75] L. Fluyt, I. Couwenberg, H. Lambaerts, K. Binnemans, C. Gorller-Walrand, J. Chem. Phys. 105 (1996) 6117.
[76] C. Djerassi, E. Bunnenberg, D.L. Elder, Pure Appl. Chem. 25 (1971) 57.
[77] J.P. Riehl, Tech. Instrum. Anal. Chem. 14 (1994) 207.
[78] S. Wenzel, V. Buss, Rev. Sci. Instrum. 68 (1997) 1886.
[79] H.P.J.M. Dekkers, in: K. Nakanishi, N. Berova, R.W. Woody (Eds.), Circular Dichroism, Principles and Applications, VCH, New York, 1994, p. 121.
[80] J.P. Riehl, Acta Phys. Pol. A 90 (1996) 55.
[81] F.S. Richardson, D.H. Metcalf, in: K. Nakanishi, N. Berova, R.W. Woody (Eds.), Circular Dichroism. Principles and Applications, VCH, New York, 1994, p. 153.
[82] M.F. Reid, J. Lumin. 45 (1990) 384.
[83] J.A. Schauerte, D.G. Steel, A. Gafni, Proc. Natl. Acad. Sci. USA 89 (1992) 10154.

[84] L. Rosenfeld, Z. Phys. 52 (1928) 161.
[85] S.F. Mason, R.H. Seal, D.R. Roberts, Tetrahedron 30 (1974) 1671.
[86] W. Kuhn, Trans. Faraday Soc. 26 (1930) 293.
[87] E.L. Eliel, S.H. Wilen, Stereochemistry of Organic Compounds, Wiley, New York, 1994.
[88] J.W. Canary, C.S. Allen, J.M. Castagnetto, Y. Wang, J. Am. Chem. Soc. 117 (1995) 8484.
[89] K.E. Gunde, A. Credi, E. Jandrasics, A. Von Zelewsky, F.S. Richardson, Inorg. Chem. 36 (1997) 426.
[90] G. Snatzke, in: K. Nakanishi, N. Berova, W.R. Woody (Eds.), Circular Dichroism. Principles and Applications, VCH, New York, 1994, p. 1.
[91] G. Snatzke, Angew. Chem. Int. Ed. Engl. 18 (1979) 363.
[92] H.G. Kuball, G. Sieber, S. Neubrech, B. Schultheis, A. Schoenhofer, Chem. Phys. 169 (1993) 335.
[93] W. Kuhn, K. Bein, Z. Phys. Chem. Abt. B (1934) 335.
[94] B. Bosnich, Acc. Chem. Res. (1966) 266.
[95] B. Bosnich, Inorg. Chem. 7 (1968) 2379.
[96] S.F. Mason, Inorg. Chim. Acta 14 (1968) 89.
[97] O. Gimple, P. Schreier, H.-U. Humpf, Tetrahedron: Asymmetry 8 (1997) 11.
[98] S. Shinoda, Kagaku 52 (2) (1997) 66.
[99] D.A. Lightner, Tech. Instrum. Anal. Chem. 14 (1994) 131.
[100] P. Hayoz, A. Von Zelewsky, H. Stoeckli-Evans, J. Am. Chem. Soc. 115 (1993) 5111.
[101] H. Muerner, A. Von Zelewsky, H. Stoeckli-Evans, Inorg. Chem. 35 (1996) 3931.
[102] H. Muerner, P. Belser, A. Von Zelewsky, J. Am. Chem. Soc. 118 (1996) 7989.
[103] Y. Tor, A. Shanzer, A. Scherz, Inorg. Chem. 29 (1990) 4096.
[104] I. Tinoco, Adv. Chem. Phys. 4 (1962) 113.
[105] H. De Voe, J. Chem. Phys. 43 (1965) 3199.
[106] J. Applequist, K.R. Sundberg, M.L. Olson, L.C. Weiss, J. Chem. Phys. 70 (1979) 1240.
[107] M. Zandomeneghi, C. Rosini, P. Salvadori, Chem. Phys. Lett. 44 (1976) 533.
[108] M. Kodaka, J. Chem. Soc. Faraday Trans. 93 (1997) 2057.
[109] J.A. Schellmann, Acc. Chem. Res. 1 (1968) 144.
[110] R.R. Gould, R. Hoffmann, J. Am. Chem. Soc. 92 (1970) 1813.
[111] C. Daul, C.W. Schlaepfer, J. Chem. Soc., Dalton Trans. (1988) 393.
[112] A. Volosov, Int. J. Quant. Chem. 36 (1989) 473.
[113] S. Grimme, S.D. Peyerimhoff, S. Bartram, F. Vögtle, A. Breest, J. Hormes, Chem. Phys. Lett. 213 (1993) 32.
[114] M. Ziegler, M. Buchs, C. Daul, E.J. Baerends, in preparation.
[115] I. Pischel, S. Grimme, S. Kotila, M. Niegler, F. Vögtle, Tetrahedron: Asymmetry 7 (1996) 109.
[116] S. Grimme, I. Pischel, F. Vögtle, M. Nieger, J. Am. Chem. Soc. 117 (1995) 157.
[117] S. Grimme, Chem. Phys. Lett. 259 (1996) 128.
[118] T.D. Bouman, A.E. Hansen, B. Voigt, S. Rettrup, Int. J. Quant. Chem. 23 (1983) 595.
[119] H.J.A. Jensen, H. Koch, P. Jorgensen, P.J. Olsen, J. Chem. Phys. 119 (1988) 297.
[120] A. Volosov, R.W. Woody, in: K. Nakanishi, N. Berova, R.W. Woody (Eds.), Circular Dichroism. Principles and Applications, VCH, New York, 1994, p. 335.
[121] W. Moffitt, J. Chem. Phys. 25 (1956) 1956.
[122] M.C. Ernst, D.J. Royer, Inorg. Chem. 32 (1993) 1226.
[123] N.D. Fenton, M. Gerlach, Inorg. Chem. 29 (1990) 3726.
[124] N.D. Fenton, M. Gerlach, Inorg. Chem 29 (1990) 3718.
[125] P.E. Schipper, J. Chem. Phys. 93 (1990) 7020.
[126] C. Daul, E.J. Baerends, P. Vernooijs, Inorg. Chem. 33 (1994) 3538.
[127] K.L. Bak, A.E. Hansen, K. Ruud, T. Helgaker, J. Olsen, P. Jorgensen, Theor. Chim. Acta 90 (1995) 441.
[128] T.M. Hooker, J.A. Schellmann, Biopolymers 9 (1970) 1319.
[129] J. Fleischhauer, A. Koslowski, B. Kramer, E. Zobel, G. Bringmann, K.P. Gulden, et al., Z. Naturforsch. B: Chem. Sci. 48 (1993) 140.
[130] G. Bringmann, U. Dauer, O. Schupp, M. Lankers, J. Popp, U. Posset, et al., Inorg. Chim. Acta 222 (1994) 247.

[131] G. Bringmann, Bull. Soc. Chim. Belg. 105 (1996) 601.
[132] G. Bringmann, S. Busemann, K. Krohn, K. Beckmann, Tetrahedron 53 (1997) 1655.
[133] J. Fleischhauer, J. Groetzinger, B. Kramer, P. Krueger, A. Wollmer, R.W. Woody, et al., Biophys. Chem. 49 (1994) 141.
[134] K.E. Gunde, G.W. Burdicka, F.S. Richardson, Chem. Phys. 208 (1996) 195.
[135] M.W. Evans, S. Woszniak, G. Wagnière, Physica B 179 (1992) 133.
[136] F.J. Devlin, J.W. Finley, P.J. Stephens, M.J. Frisch, J. Phys. Chem. 99 (1995) 16883.
[137] F.J. Devlin, P.J. Stephens, J.R. Cheeseman, M.J. Frisch, J. Phys. Chem. A 101 (1997) 6322.
[138] P.J. Stephens, C.S. Ashvar, F.J. Devlin, J.R. Cheeseman, M.J. Frisch, Mol. Phys. 89 (1996) 579.
[139] D. Tsankov, V. Dimitrov, H. Wieser, Mikrochim. Acta Suppl. 14 (1997) 535.
[140] R.G. Bray, J. Ferguson, C.J. Hawkins, Aust. J. Chem. 22 (1969) 2091.
[141] P. Day, N.J. Sanders, J. Chem. Soc. A (1967) 1536.
[142] P. Day, N.J. Sanders, J. Chem. Soc. A (1967) 1530.
[143] K. Waernmark, J.A. Thomas, O. Heyke, J.-M. Lehn, Chem. Commun. (1996) 701.
[144] K. Waernmark, O. Heyke, J.A. Thomas, J.-M. Lehn, Chem. Commun. (1996) 2603.
[145] D. Tzalis, Y. Tor, J. Am. Chem. Soc. 119 (1997) 852.
[146] F.M. MacDonnell, S. Bodige, Inorg. Chem. 35 (1996) 5758.
[147] N.C. Fletcher, F.R. Keene, H. Viebrock, A. Von Zelewsky, Inorg. Chem. 36 (1997) 1113.
[148] Y. Inose, S. Moniwa, A. Aramata, A. Yamagishi, N. Kyaw, Chem. Commun. (1997) 111.
[149] M. Lieberman, S. Tomikazu, J. Am. Chem. Soc. 113 (1991) 1470.
[150] M.R. Ghadiri, C. Soares, C. Choi, J. Am. Chem. Soc. 114 (1992) 825.
[151] M.R. Ghadiri, M.A. Case, Angew. Chem. Int. Ed. Engl. 32 (1993) 1594.
[152] H. Mürner, G. Hopfgartner, A. Von Zelewsky, Inorg. Chem. Acta 271 (1998) 36.
[153] P. Belser, C. Daul, A. Von Zelewsky, Chem. Phys. Lett. 79 (1981) 596.
[154] F. Felix, J. Ferguson, H.U. Güdel, A. Ludi, J. Am. Chem. Soc. 102 (1980) 4096.
[155] J. Ferguson, E. Krausz, J. Vrbancich, J. Chem. Phys. Lett. (1986) 463.
[156] N.H. Damrauer, G. Cerullo, A. Yeh, T.R. Boussie, C.V. Shank, J.K. McCusker, Science 275 (1997) 54.
[157] R.A. Malone, D.F. Kelley, J. Chem. Phys. 95 (1991) 8970.
[158] J. Van Houten, R. Watts, J. Am. Chem. Soc. 98 (1976) 4853.
[159] G.B. Porter, R.H. Sparks, J. Photochem. 13 (1980) 123.
[160] J. Van Houten, R.J. Watts, Inorg. Chem. 17 (1978) 3381.
[161] C. Creutz, M. Chou, T.L. Netzel, M. Okumura, N. Sutin, J. Am. Chem. Soc. 102 (1980) 1309.
[162] U. Lachish, P.P. Infelta, M. Grätzel, Chem. Phys. Lett. 62 (1979) 317.
[163] J.S. Gold, S.J. Milder, J.W. Lewis, D.S. Kliger, J. Am. Chem. Soc. 107 (1985) 8285.
[164] H. Riesen, E.J. Krausz, J. Phys. Chem. 99 (1993) 7614.
[165] H. Riesen, L. Wallace, E.J. Krausz, J. Phys. Chem. 99 (1995) 16807.
[166] H. Riesen, L. Wallace, E.J. Krausz, Mol. Phys. 87 (1996) 1299.
[167] C. Turro, Y.C. Chung, N. Leventis, M.E. Kuchenmeister, P.J. Wagner, G.E. Leroi, Inorg. Chem. 35 (1996) 5104.
[168] D.H. Oh, S.G. Boxer, J. Am. Chem. Soc. 111 (1989) 1130.
[169] L. Karki, J. Hupp, 36 (1997) 3318.
[170] J. Schmidt, J. Strasser, H. Yersin, Inorg. Chem. 36 (1997) 3957.
[171] H. Yersin, W. Humbs, J. Strasser, J. Coord. Chem. Rev. (1997) 159.
[172] B.J. Pankuch, D.E. Lacky, G.A. Crosby, J. Phys. Chem. 84 (1980) 2061.
[173] J. Ferguson, F. Herren, Chem. Phys. 76 (1983) 45.
[174] E.M. Kober, T.J. Meyer, J. Inorg. Chem. 23 (1984) 3877.
[175] J.V. Caspar, T.D. Westmoreland, G.H. Allen, P.G. Bradley, T.J. Meyer, W.H. Woodruff, J. Am. Chem. Soc. 106 (1984) 3492.
[176] J. Ferguson, G. Herren, E.R. Krausz, M. Maeder, J. Vrbancich, Coord. Chem. Rev. 64 (1985) 21.
[177] T. Meyer, Pure Appl. Chem. 58 (1986) 1193.
[178] G. Giuffrida, G. Calogero, G. Guglielmo, V. Ricevuto, M. Ciano, S. Campagna, Inorg. Chem. 32 (1993) 1179.
[179] H. Riesen, L. Wallace, E.J. Krausz, J. Chem. Phys. 102 (1995) 4823.

[180] J.P. Bolender, D.H. Metcalf, F.S. Richardson, Chem. Phys. Lett. 213 (1993) 131.
[181] R.B. Rexwinkel, S.C.J. Meskers, H.P.J.M. Dekkers, J.P. Riehl, J. Phys. Chem. 97 (1993) 13519.
[182] D.H. Metcalf, S.W. Snyder, J.N. Demas, F.S. Richardson, J. Am. Chem. Soc. 112 (1990) 5681.
[183] F.L. Campbell III, F.A. Cotton, G.L. Powell, Inorg. Chem. 24 (1985) 117.
[184] L.J. Farrugia, A. McVitie, R.D. Peacock, Inorg. Chem. 27 (1988) 1257.
[185] L. Chassot, A. Von Zelewsky, Helv. Chim. Acta 66 (1983) 2443.
[186] L. Chassot, E. Mueller, A. Von Zelewsky, Inorg. Chem. 23 (1984) 4249.
[187] M. Maestri, C. Deuschel-Cornioley, A. Von Zelewsky, J. Photochem. Photobiol. A 67 (1992) 173.
[188] M. Maestri, V. Balzani, C. Deuschel-Cornioley, A. Von Zelewsky, Adv. Photochem. 17 (1992) 1.
[189] J. Schmidt, H. Wiedenhofer, A. Von Zelewsky, H. Yersin, J. Phys. Chem. 99 (1995) 226.
[190] D. Sandrini, M. Maestri, V. Balzani, L. Chassot, A. Von Zelewsky, J. Am. Chem. Soc. 109 (1987) 7720.
[191] D. Sandrini, M. Maestri, M. Ciano, V. Balzani, R. Lueoend, C. Deuschel-Cornioley, et al., Gazz. Chim. Ital. 118 (1988) 661.
[192] D. Sandrini, M. Maestri, V. Balzani, U. Maeder, A. Von Zelewsky, Inorg. Chem. 27 (1988) 2640.
[193] D. Sandrini, M. Maestri, M. Ciano, U. Maeder, A. Von Zelewsky, Helv. Chim. Acta 73 (1990) 1306.
[194] C. Deuschel-Cornioley, R. Lueoend, A. Von Zelewsky, Helv. Chim. Acta 72 (1989) 377.
[195] C. Deuschel-Cornioley, H. Stoeckli-Evans, A. Von Zelewsky, J. Chem. Soc., Chem. Commun. (1990) 121.
[196] M. Gianini, A. Von Zelewsky, H. Stoeckli-Evans, Inorg. Chem. 36 (1997) 6094.
[197] C.A. Stueckl, personal communication.
[198] H. Ito, J. Fujita, K. Saito, Bull. Chem. Soc. Jpn. 40 (1967) 2584.
[199] K. Hatano, R. Saito, Bull. Chem. Soc. Jpn. 66 (1993) 3818.
[200] G. Mahal, R. Van Eldik, Inorg. Chem. 26 (1987) 1837.
[201] E.A. Sullivan, Can. J. Chem. 57 (1979) 67.
[202] B. Olenyuk, J.A. Whiteford, P.J. Stang, J. Am. Chem. Soc. 118 (1996) 8221.
[203] P.J. Stang, B. Olenyuk, Angew. Chem. Int. Ed. Engl. 35 (1996) 732.
[204] O.P. Slydkin, I.A. Baidina, L.N. Dolbina, Khord. Khim. 23 (1997) 440.
[205] O.P. Slydkin, I.A. Baidina, L.N. Dolbina, Khord. Khim. 23 (1997) 434.
[206] A. Furuhashi, K. Endo, Y. Kondo, A. Ouchi, Croat. Chem. Acta C62 (1989) 141.
[207] G.D. Fasman (Ed.), Circular Dichroism and the Conformational Analysis of Biomolecules, Plenum Press, New York, 1996, p. 738.
[208] G.K. Walkup, B. Imperiali, J. Am. Chem. Soc. 119 (1997) 3443.
[209] K.A. Bode, J. Applequist, Macromolecules 30 (1997) 2144.
[210] G. Kurapkat, P. Krueger, A. Wollmer, J. Fleischhauer, B. Kramer, E. Zobel, et al., Biopolymers 41 (1997) 267.
[211] B. Decock-Le Reverend, C. Loucheux, T. Kowalik, H. Kozlowski, Inorg. Chim. Acta 66 (1982) 205.
[212] D.J. Spira-Solomon, E.I. Solomon, J. Am. Chem. Soc. 109 (1986) 6421.
[213] T. Sugimori, H. Masuda, N. Ohata, K. Koiwai, A. Odani, O. Yamauchi, Inorg. Chem. 36 (1997) 576.
[214] G. D'Auria, O. Maglio, F. Nastri, A. Lombardi, M. Mazzeo, G. Morelli, et al., Chem. Eur. J. 3 (1997) 350.
[215] T. Mizutani, S. Yagi, A. Honmaru, H. Ogoshi, J. Am. Chem. Soc. 118 (1996) 5318.
[216] M.J. Bulke, D.C. Pratt, A. Moscowitz, Biochemistry 11 (1972) 4025.
[217] G. Blauer, G. Wagnière, J. Am. Chem. Soc. 97 (1975) 1949.
[218] G. Wagnière, G. Blauer, J. Am. Chem. Soc. 98 (1976) 7806.
[219] H. Scheer, H. Formanek, S. Schneider, J. Photochem. Photobiol. 36 (1982) 259.
[220] T. Hayashi, M. Nonoguchi, T. Arya, H. Ogoshi, Tetrahedron Lett. 38 (1997) 1603.
[221] J. Mack, M.J. Stillman, Inorg. Chem. 36 (1997) 413.
[222] L.D. Loomis, K.N. Raymond, Inorg. Chem. 30 (1991) 906.
[223] M. Matzanke, F. Berthold, G.I. Muller, K.N. Raymond, Biochem. Biophys. Res. Commun. 121 (1984) 922.

[224] G. Müller, B.F. Matzanke, K.N. Raymond, Biochem. Biophys. Res. Commun. 121 (1984) 922.
[225] T.B. Karpishin, T.D.P. Stack, K.N. Raymond, J. Am. Chem. Soc. 115 (1993) 6115.
[226] C.J. Carrano, K.N. Raymond, J. Am. Chem. Soc. 100 (1978) 5371.
[227] J. Libman, Y. Tor, A. Shanzer, J. Am. Chem. Soc. 109 (1987) 5880.
[228] B. Tse, Y. Kishi, J. Am. Chem. Soc. 115 (1993) 7892.
[229] Y. Tor, J. Libman, A. Shanzer, C.E. Felder, S. Lifson, J. Am. Chem. Soc. 114 (1992) 6661.
[230] Y. Hisaeda, T. Ihara, T. Ohno, Y. Murakami, Chem. Lett. (1991) 2139.
[231] T.B. Karpishin, T.D.P. Stack, K.N. Raymond, J. Am. Chem. Soc. 115 (1993) 1842.
[232] T.B. Karpishin, K.N. Raymond, Angew. Chem. Int. Ed. Engl. 31 (1992) 466.
[233] S.S. Isied, G. Kuo, K.N. Raymond, J. Am. Chem. Soc. 98 (1976) 1763.
[234] J. Leong, K.N. Raymond, J. Am. Chem. Soc. 97 (1975) 293.
[235] J. Leong, K.N. Raymond, J. Am. Chem. Soc. 96 (1974) 1757.
[236] J. Leong, K.N. Raymond, J. Am. Chem. Soc. 96 (1974) 6628.
[237] J.V. McArdle, S.R. Sofen, S.R. Cooper, K.N. Raymond, Inorg. Chem. 17 (1978) 3075.
[238] K. Abu-Dari, K.N. Raymond, J. Coord. Chem. 26 (1992) 1.
[239] H. Okawa, H. Tokunaga, T. Katsuki, M. Koikawa, S. Kida, Inorg. Chem. 27 (1988) 4373.
[240] T.B. Karpishin, M.S. Gebhard, E.I. Solomon, K.N. Raymond, J. Am. Chem. Soc. 113 (1991) 2977.
[241] A. Shanzer, J. Libman, S. Lifson, C.E. Felder, J. Am. Chem. Soc. 108 (1986) 7609.
[242] T. Ito, A. Kobayashi, F. Marumo, Y. Saito, Inorg. Nucl. Chem. Lett. 7 (1971) 1097.
[243] K. Abu-Dari, K.N. Raymond, J. Am. Chem. Soc. 99 (1977) 2003.
[244] A. Pasini, M. Gullotti, R. Ugo, J. Chem. Soc., Dalton Trans. (1977) 346.
[245] D. Gargiulo, N. Ikemoto, J. Odingo, N. Bozhkova, T. Iwashita, N. Berova, K. Nakanishi, J. Am. Chem. Soc. 116 (1994) 3760.
[246] E. Larsen, S. Larsen, S. Røen, K.J. Watson, Acta Chem. Scand. A 30 (1976) 125.
[247] H.P. Jensen, Acta Chem. Scand. A 30 (1976) 137.
[248] C.-W. Ho, W.-C. Cheng, M.-C. Cheng, S.-M. Peng, K.-F. Cheng, C.-M. Che, J. Chem. Soc., Dalton Trans. (1996) 405.
[249] K. Bernauer, P. Pousaz, Helv. Chim. Acta 67 (1984) 796.
[250] K. Bernauer, H. Stoeckli-Evans, D. Hugi-Cleary, H.J. Hilgers, H. Abd-el-Khalek, J. Porret, et al., Helv. Chim. Acta 75 (1992) 2327.
[251] K. Bernauer, F. Gretillat, H. Stoeckli-Evans, R. Warmuth, Helv. Chim. Acta 76 (1993) 545.
[252] K. Bernauer, T. Chuard, H. Stoeckli-Evans, Helv. Chim. Acta 76 (1993) 2263.
[253] K. Bernauer, E. Fuchs, D. Hugi-Cleary, Inorg. Chim. Acta 218 (1994) 73.
[254] S.K. Mandal, A.R. Chakravarty, Inorg. Chem. 32 (1993) 3851.
[255] G. Consiglio, F. Morandini, Chem. Rev. 87 (1987) 761.
[256] C. Fraser, R. Ostrander, A.L. Rheingold, C. White, B. Bosnich, Inorg. Chem. 33 (1994) 324.
[257] K.M. Carroll, J. Schwartz, D.M. Ho, Inorg. Chem. 33 (1994) 2707.
[258] Y. Dai, T.J. Katz, D.A. Nichols, Angew. Chem. Int. Ed. Engl. 35 (1996) 2109.
[259] K. Nonoyama, W. Mori, K. Nakajima, M. Nonoyama, Polyhedron 16 (1997) 3815.
[260] P.N. Hawker, M.V. Twigg, Comprehensive Coordination Chemistry, Vol. 4, Pergamon Press, Oxford, p. 1214.
[261] R. Krämer, J.M. Lehn, A. De Cian, J. Fischer, Angew. Chem. Int. Ed. Engl. 32 (1993) 703.
[262] J.M. Castagnetto, J.W. Canary, C.S. Allen, Y. Wang, Dynamic control of topological asymmetry, in: Royal Society of Chemistry, Cambridge, Electron. Conf. Heterocycl. Chem. (Proc.), 1997.
[263] J. Hidaka, B.E. Douglas, Inorg. Chem. 3 (1964) 1180.
[264] S.F. Mason, B.J. Peart, J.Chem. Soc., Dalton Trans. (1973) 949.
[265] A. Pfeil, J.-M. Lehn, J. Chem. Soc., Chem. Commun. (1992) 838.
[266] K.T. Potts, M. Keshavarz-K, F.S. Tham, K.A.G. Raiford, C. Arana, H.D. Abruna, Inorg. Chem. 32 (1993) 5477.
[267] T. Damhus, C.E. Schäffer, Inorg. Chem. 22 (1983) 2406.
[268] A. Von Zelewsky, unpublished work.
[269] W. Zarges, J. Hall, J.M. Lehn, C. Bolm, Helv. Chim. Acta 74 (1991) 1843.
[270] C.R. Woods, M. Benaglia, P. Blom, A. Fuchicello, F. Cozzi, J.S. Siegel, Polym. Prep. 37 (2) (1996) 480.

[271] C.R. Woods, M. Benaglia, F. Cozzi, J.S. Siegel, Angew. Chem. Int. Ed. Engl. 35 (1996) 1830.
[272] G.C. Van Stein, G. Van Koten, C. Brevard, J. Organomet. Chem. 226 (1982) 27.
[273] G.C. Van Stein, G. Van Koten, B. De Bok, L.C. Taylor, K. Vrieze, C. Brevard, Inorg. Chim. Acta 89 (1984) 29.
[274] G.C. Van Stein, G. Van Koten, K. Vrieze, C. Brévard, A.L. Spek, J. Am. Chem. Soc. 106 (1984) 4486.
[275] J.F. Modder, K. Vrieze, A.L. Spek, G. Challa, G. van Koten, Inorg. Chem. 31 (1992) 1238.
[276] T. Suzuki, H. Kotsuki, K. Isobe, N. Moriya, Y. Nakagawa, M. Ochi, Inorg. Chem. 34 (1995) 530.
[277] G. Baum, E.C. Constable, D. Fenske, T. Kulke, Chem. Commun. (1997) 2043.
[278] O. Mamula, A. Von Zelewsky, Angew. Chem. Int. Ed. Engl. 37 (1998) 289.
[279] M. Ziegler, V. Monney, H. Stoeckli-Evans, A. Von Zelewsky, I. Sasaki, G. Dupic, et al., submitted for publication.
[280] C. Provent, S. Hewage, G. Brand, G. Bernardinelli, L.J. Charbonniere, A.F. Williams, Angew. Chem. Int. Ed. Engl. 36 (1997) 1287.