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OPTICAL ACTIVITY OF COORDINATION COMPOUNDS

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CONTENTS

ABBREVIATIONS

Ligands

acacdnH	3-(2,4-dinitro-1-naphthyl)-2,4-pentanedione
acacH	acetylacetone (2,4-pentanedione)
aetH	2-aminoethanethiol
aetaH	3-(2-aminoethylthio)acetic acid
aetpH	3-(2-aminoethylthio)propionic acid
alaH	alanine
bgH	biguanide
bipy	2,2′-bipyridine
bispicen	1,6-bis(2′-pyridyl)-2,5-diazahexane
$catH_2$	*o*-dihydroxybenzene (catechol)
chxn	1,2-cyclohexanediamine
daes	di(2-aminoethyl)sulfide

dap	2,3-diaminopropionic acid
dien	diethylenetriamine
dmbpy	3,3′-dimethyl-2,2′-bipyridine
dppn	1,3-diphenyl-1,3-propanediamine
edda	ethylenediamine-N,N′-diacetic acid
edtaH$_4$	ethylenediaminetetraacetic acid
eea	2-(ethylthio)ethylamine
en	1,2-ethanediamine
glyH	glycine
idaH$_2$	iminodiacetic acid
mal H$_2$	malonic acid
mea	2-(methylthio)ethylamine
me-en	N-methylethylenediamine
me$_2$-en	N,N′-dimethylethylenediamine
mtaH	(methylthio)acetic acid
mtpH	3-(methylthio)propionic acid
ph	phenyl
phen	1,10-phenanthroline
pic	2-picolylamine
pr^i-en	N-isopropylethylenediamine
ptn	2,4-pentanediamine
salenH	N-(2-aminoethyl)salicylaldimine
sal-glyH	N-salicylideneglycine
sarH	sarcosine
sep	1,3,6,8,10,13,16,19-octaazabicyclo-[6.6.6.]-eicosane
tmd	tetramethylenediamine
tn	1,3-propanediamine
tren	2,2′,2″-triaminotriethylamine
trien	triethylenetetramine

Resolving agents

As-*d*-tart	arsenyl-*d*-tartrate
bcs	bromo-*d*-camphor sulfonate
benz-*d*-tart	(*R*,*R*)-O,O′-dibenzoyltartrate
bru	brucine
cysu	cysteinsulfinate
nc	(+)$_D$-nitrocamphor
Sb-*d*-tart	antimonyl-*d*-tartrate
stry	strychnine
tart	*d*-tartrate ((+)$_D$-tartrate, (*R*,*R*)-tartrate)

A. INTRODUCTION

Although chiral discriminations such as enantiomeric interactions, diastereoisomeric interactions and photo-discriminations together with phenomenological behaviour and modes of investigations, have been aptly reviewed recently [1,2], the state of the art of studying chiral and optically active coordination compounds is being developed so fast that a review at this time may not be redundant.* The focus of interest is still the ability of one chiral system to discriminate the enantiomers of another chiral system, be it in the form of interactions between matter and radiation or between matter and matter. Characteristically the relevant terminology is subject to discussion, e.g. the shorthand chirodiastaltic interaction has recently been suggested for the phenomenon discriminatory interaction between chiral molecules [3,4] as an alternative to the term diastereotopic interaction [5].

Whereas the symmetry conditions and much phenomenology of chiral discriminations are well-known, their "microscopic" interpretation is less well established, and the many recent efforts in this field together with experimental achievements form the main scope of our review.

B. SOME DEFINITIONS

Traditionally the phenomenon of optical activity has been discussed in terms of asymmetry and dissymmetry, which have now been replaced by the term chirality. Ruch and Ugi [6], in the following passage, give an exact definition of contemporary terminology:

"Stereoisomers are chemical compounds of identical chemical constitution differing in the spatial arrangement of their atoms. Molecules which cannot be brought into coincidence with their mirror images by rigid motions are termed chiral.

Chiral molecules exist as two species of equal chemical constitution, differing only by having the opposite configuration as an object and its mirror image. Species of this kind are called optical antipodes or enantiomers.

Stereoisomers which are not enantiomers are called diastereoisomers."

The use of the words catoptromer and catoptric has been suggested (see ref. 11 in ref. 61 of this paper) instead of the established words enantiomer and enantiomeric, the new words being derived from the Greek word for mirror.

For reasons of consistency we suggest the use of the following terms only: chiral, enantiomers (catoptromers) and diastereoisomers.

By definition, enantiomers and diastereoisomers constitute the whole class of stereoisomers. Consequently, the original meaning of the term diastereoisomer, i.e. a structure with two or more chiral centers, is lost. Accordingly, we deem the term chirodiastaltic more descriptive of phenomena related to chiral discrimination than the term diastereotopic.

Chemical reactions by which stereoisomers are formed or used up at different rates are called stereoselective reactions.

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* The present review is intended to cover essentially references from 1976 through mid 1978 (see Note added in Proof).

Chemical reactions by which specific stereochemical compounds are converted to specific stereochemical products are called stereospecific reactions.

An equal mixture of two enantiomers forms an optically inactive racemic mixture which may be resolved into its components.

Molecules which are not chiral are denoted achiral. Achiral molecules which are able to develop chirality by a single addition or substitution reaction are sometimes called prochiral.

C. PHENOMENOLOGY

(i) Production of chiral complexes

Resolutions and separations

Application of chirodiastaltic interactions in producing chiral metal complexes in one of their enantiomeric forms has significantly increased the number of such systems available. Thus resolutions of robust octahedral complexes with transition metal ions as centers of chirality have been accomplished by various resolving agents as may be seen from Table 1.

A common problem encountered with traditional resolution procedures such as those cited in Table 1 is whether a given resolution is complete. This question may in many cases be settled by chromatography.

Attempts at chromatographic resolutions carried out within the last decade have frequently resulted in clearly separated zones on the column after appropriate elution, thus proving the completeness of the resolution. Recent examples are given in Table 2.

As seen from Table 2, Sephadex ion exchangers especially have proven excellent column materials for the separation of enantiomers through elution with optically active eluents. Furthermore Sephadex ion exchangers are widely used in the separation of various mixtures of diastereoisomers into their components. An illustrative example of the combined separation of diastereoisomers and their subsequent resolution is that of the tris-[(±)-*trans*-1,2-cyclohexanediamine]cobalt(III) system [36] which exhibits four racemic pairs (Δ—λ_3, Λ—δ_3), (Δ—$\lambda_2\delta$, Λ—$\delta_2\lambda$), (Δ—$\delta_2\lambda$, Λ—$\lambda_2\delta$) and (Δ—δ_3, Λ—λ_3). These four pairs were separated on a column of Sephadex cation exchanger by elution with trisodium phosphate, and afterwards each pair was resolved on the same column by elution with diammonium $(+)_D$-tartrate.

Several similar chromatographic separations have been performed on Sephadex [32,37,38,42,45—50] as well as on other types of column material, e.g. silica gel [51], Dowex [52,53] and Al_2O_3 [16], and obviously chromatography is a powerful tool for component isolation and purification [54] as well as for the verification of the chiral purity of otherwise prepared samples.

Converting a chromatographic separation into a preparative technique, however, presents practical problems, e.g. quantity. Several authors, therefore, still employ traditional separation procedures using chiral agents (Table 1, [14,56—58]) as well as achiral agents [14,55—57].

TABLE 1

Recent resolutions of racemic octahedral transition metal complexes through the procedure of less soluble diastereoisomer

Compound	Resolving agent	Ref.
$[Co(en)_2(X)(NH_3)]^{2+}$	bcs	7
$[Co(en)_2(X)_2]^+$	Sb-*d*-tart, $(+)_D$-$[Co(edta)]^-$	7, 13
$[Co(en)_2(X)(X')]^+$ ($X = X' = N_3^-$, NCS^-, NO_2^-)	bcs	7
$[Co(en)_2(Cl)(CH_3NH_2)]^{2+}$	Sb-*d*-tart	8
$[Co(en)_2(acac)]^{2+}$	As-*d*-tart	9
$[Co(en)_2(dmbpy)]^{3+}$	$[Co(L\text{-}cysu)_3]^{3-}$	31
$[Co(en)_2(me\text{-}en)]^{3+}$	nc	10
$[Co(en)_2(me_2\text{-}en)]^{3+}$	nc	10
$[Co(en)_2(pr^i\text{-}en)]^{3+}$	$(-)_D$-$[Co(C_2O_4)]^{3-}$	10
$[Co(en)_2(C_2O_4)]^+$	tart	11
	Sb-*d*-tart	11
	bcs	11
	$(+)_D$-$[Co(edta)]^-$	11, 13
$[Co(en)_2(N\text{—}S)]^{2+,3+}$ (N—S = aet, mea, eea)	Sb-*d*-tart	12
$[Co(en)_2(O\text{—}S)]^{2+}$ (O—S = mta, mtp)	tart, Sb-*d*-tart	12
$[Co(am)(bgH)_2]^{3+}$ (am = gly, sar)	Sb-*d*-tart	14
$[Co(daes)_2]^{3+}$	As-*d*-tart	15
$[Co(sal\text{-}gly)_2]^-$	bru, stry	16
$[Co(N\text{-}3\text{-}met\text{-}sal)_2]^-$	stry	16
$[Co(salen)_2]^+$	benz-*d*-tart	17
$[Co(acac)(trien)]^{2+}$	As-*d*-tart	9
$[Co(dmbpy)(trien)]^{3+}$	$[Co(L\text{-}cysu)_3]^{3-}$	31
$[Co(X)_2(NH_3)_2(O\text{—}O)]^-$ ($X = CN^-$, NO_2^- and O—O = CO_3^{2-}, $C_2O_4^{2-}$, mal^{2-})	$(-)_D$-$[Co(NO_2)_2(en)_2]^+$ $(-)_D$-$[Co(C_2O_4)(en)_2]^+$	18
$[Co(NSO)(tame)]^{2+}$ (NSO = aeta, aetp)	$[Co(L\text{-}cysu)_3]^{3+}$	12
$[Co(aeta)_2]^+$		
trans-O	$(+)_D$-$[Co(edta)]^-$	19
all-*cis*	benz-*d*-tart	19
trans-N	Sb-*d*-tart	19
trans-S	spontaneous	19
$[Co(CO_3)_2(NH_3)_2]^-$	$(-)_D$-$[Co(C_2O_4)(en)_2]^+$	20
$[Co(acac)_2(phen)]^+$	benz-*d*-tart	30
$[Cr(en)_2(CN)_2]^+$	bcs	21
$[Cr(salen)_2]^+$	benz-*d*-tart	17
$[Cr(bipy)_2OH]_2^{4+}$	Sb-*d*-tart	22
$[Cr(phen)_2OH]_2^{4+}$	Sb-*d*-tart	22
$[Cr(pic)_2OH]_2^{4+}$	Sb-*d*-tart	23
$[Cr(bispicen)_2OH]_2^{4+}$	Sb-*d*-tart	24
$[Cr(cat)_3]^{3-}$	Δ-$[Co(en)_3]^{3+}$	25
$[Fe(phC(S){=}N(O))_3]^{3-}$	Δ-$[Co(en)_3]^{3+}$	26
$[Fe(phC(O){=}N(O))_3]^{3-}$	Δ-$[Co(en)_3]^{3+}$	26
$[Rh(en)_2(C_2O_4)]^+$	$(+)_D$-$[Co(edta)]^-$	13
	spontaneous	13
$[Rh(en)_2(NO_2)_2]^+$	$(+)_D$-$[Co(edta)]^-$	13
$[M(C_2O_4)_3]^{3-}$ (M = V, Cr, Mn, Fe, Co)	Λ- or Δ-$[M'(en)_3]^{3+}$ (M' = Co or Rh)	27
$[M(acac)_3]$ (M = Co, Cr, Rh, Ru)	diethyl-*d*-tartrate/α-pinene	28
$[M(phC(S){=}N(O))_3]^{3-}$ (M = Cr, Co, Fe)	Δ- and Λ-$[Co(en)_3]^{3+}$	29

TABLE 2

Recent resolutions of racemic octahedral transition metal complexes through chromatography

Compound	Column material	Eluent	Ref.
$[Co(acac)(bipy)_2]^{2+}$	Sephadex	tart	30
$[Co(acac)(phen)_2]^{2+}$			30
$[Co(acac)_2(bipy)]^{+}$			30
$[Co(tren)(dmbpy)]^{3+}$		Sb-*d*-tart	31
$[Co(trien)(dmbpy)]^{3+}$			31
$[Co(en)_2(dmbpy)]^{3+}$			31
$[Co(en)_2(dppn)]^{3+}$			32
$[Co(NH_3)_4(dppn)]^{3+}$			32
$[Co\ en_x\ tn_y\ tmd_z]^{3+}$ ($x, y, z = 0, 1, 2, 3$ and $x + y + z = 3$)			33
$[Co(en)_2(sar)]^{2+}$			34
$[Co(en)_2(amb)]^{2+}$ (amb = gly, β-ala)			35
$[Co((\pm)\text{-chxn})_3]^{3+}$			36
$[Co(\textit{meso}\text{-chxn})_3]^{3+}$		tart	37
$[Co(\textit{meso}\text{-ptn})_3]^{3+}$		Sb-*d*-tart	38
$[Co(ida)(dien)]^{+}$			39
$[Co(tren)(acacdn)]^{2+}$			40
$[Co(\beta\text{-ala})_3]$		tart	41
$[Cr((\pm)\text{-chxn})_3]^{3+}$			42
$[Cr(\textit{meso}\text{-chxn})_3]^{3+}$			37
$[M(acac)_3]$ (M = Co, Al)	D-lactose	isopentane/ether	43, 44

Stereospecific reactions

Chemical interconversions may transfer the sense of chirality from a parent molecule to its reaction product. An illustrative example of synthesis in situ is the transformation of $[Co(en)_3]^{3+}$ into the "sepulchrate" complex $[Co(sep)]^{3+}$ by condensation with formaldehyde and ammonia [59]. An X-ray structure determination of absolute configuration confirms that the synthesis occurs with retention of the configuration of the $[Co(en)_3]^{3+}$ ion (Fig. 1).

Another type of stereospecific reaction is substitution in an organic chromophore situated in the coordination sphere of a transition metal ion as exemplified by halogenation and nitration of the acetylacetonato chromophore in $(+)_D$-$[Co(acac)(trien)]^{2+}$ occurring with retention of configuration [9].

Other stereospecific reactions are "simple" ligand substitutions such as the transformation of: $(-)_D$-*cis*-$[Co(en)_2(NCS)(Cl)]^{+}$ into $(+)_D$-*cis*-$[Co(en)_2(NCS)(NH_3)]^{2+}$ (ref. 7); $(+)_D$-$[Rh(en)_2(C_2O_4)]^{+}$ into $(+)_D$-*cis*-$[Rh(en)_2Cl_2]^{+}$ (ref. 13); $(-)_D$-$[Cr(N\text{--}N)_2OH]_2^{4+}$ into $(-)_D$-*cis*-$[Cr(N\text{--}N)_2Cl_2]^{+}$ (N--N being bipy [22], pic [23] or bispicen [24]); and $(+)_{365}$-$[Pt(en)_2Cl_2]^{2+}$ into $(+)_{312}$-$[Pt(en)_2(\text{L-dap})]^{4+}$ (ref. 58).

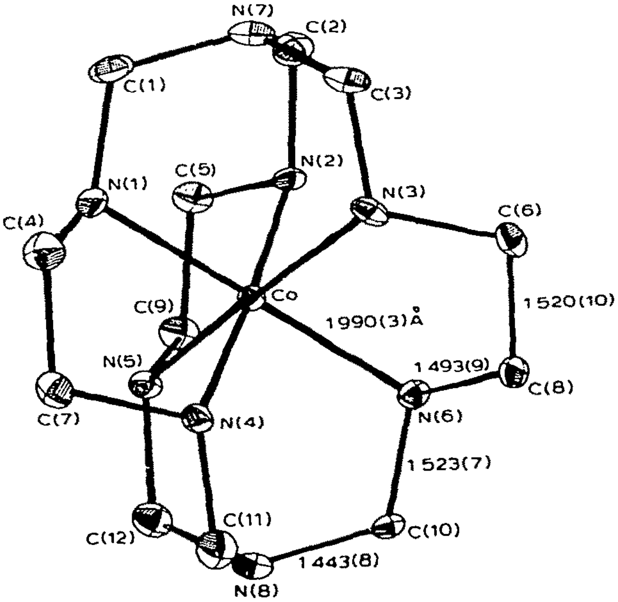

Fig. 1. (−)$_{589}$-[Co(sep)]$^{3+}$ (from ref. 59).

(ii) Elements of chirality

Although chirality is clearly a property of a structure in its entirety it may be advantageous to consider it as the result of contributions from distinct structural elements:

(1) the configurational element, i.e. the chiral arrangement of the chelate rings in a coordination entity (denoted by the symbols Δ, Λ [60,61]), or the chiral distributions of unidentate ligands;

(2) the conformational element, i.e. the chirality of a single chelate ring (denoted by symbols δ, λ [60,61]);

(3) the vicinal element, originating in either (a) induction from "asymmetric" ligand atoms, i.e. originating in central chirality (denoted by the symbols *R*, *S* [62]), or (b) induction from otherwise optically active ligands, i.e. originating in axial or planar chirality (denoted by the symbols *R*, *S* [62]), or helicity (denoted by the symbols *P*, *M* [62]).

The usefulness of this distinction depends on the validity of an additivity theorem for the contributions from each element to the overall rotatory strength. The case for such a theorem concerning *d*—*d* transitions was evaluated by Hawkins some years ago [63].

Tables 1 and 2 summarize mainly configurational and conformational chirality.

One of the major groups of complexes showing the vicinal effect is amino acid complexes. We may arrange these into two subgroups. In one the amino acids act as unidentate ligands, in the other as bi- or multidentate ligands either in themselves or in the form of derivatives of Schiff base type. In complexes with unidentate ligands we are faced with a pure vicinal effect, whereas in chelates this effect is superimposed by conformational and/or configurational effects.

Generally speaking the whole field of amino acidate complexes has been extensively investigated, and has now reached such a stage of documentation that theoretical calculations within a semi-empirical molecular orbital model [64,65] and within a dynamic coupling model [66] are feasible.

In order to indicate contemporary experimental work performed on amino acidate complexes we may add, to already cited papers [14,16,51,53], the following examples: platinum(II) and nickel(II) complexes of prochiral amino acids [67] or amino acid residues [68] and proline complexes of copper(II) showing induced Cotton effect in the spectral range of absorption due to a distant aromatic ligand as well as in the range of *d*—*d* and CT transitions [69].

The validity of the additivity theorem may be examined by comparisons between complexes which exhibit only one or two of the different effects with more complicated situations.

The sum of vicinal and conformational effects may be studied in complexes containing one bidentate chelate ring only, or two bidentate chelate rings *trans* to each other, but not with three rings. Thus tetracyanoferrate(II) and tetracyanocobaltate(III) complexes with (*R*)-1,2-diaminopropane and (*R*,*R*)-*trans*-1,2-diaminocyclohexane [70,71], *trans*-dichlorocobalt(III) complexes with chiral 1,2-diamines [72,73], square planar Ni(II) and Cu(II) complexes with chiral diamines such as bis-(*S*)-2-(aminomethyl)-pyrolidine [74] and bis complexes of Cu(II), Ni(II) and Pd(II) with N,N,N′,N′-tetramethyl-(*R*)-1,2-diaminopropane [75,76], have recently been investigated. It turns out that vicinal effects from "asymmetric" nitrogen atoms developed by chelation contribute significantly to the ligand field circular dichroism [73,74,76] and that "asymmetric" carbon atoms in a chelate ring contribute very little [70,71] although exceptions are known [72]. In connection with this general statement it has been of special interest to study specifically the pure vicinal effect from unidentate ligands. Formerly such inductions have been a subject of discussion (see p. 177 of ref. 63 and ref. 77). The tentative proposal, that chelation was necessary if the imposed Cotton effect should be measurable, has now been proven incorrect after the advent of very sensitive instruments [78—80].

Information extracted from simpler systems may be used in assigning chirality from sign of Cotton effect to complexes formed by complicated macrocyclic and/or multidentate ligands [81—83]. An especially interesting example connected to the question of specific selection of one of the various additive effects is that of the cobalt(III) complex of (*R*)-(—)$_D$-2-methyl-1,4,7-triazacyclononane ($[Co(R\text{-}MeTACN)_2]^{3+}$) [84] Fig. 2. In this complex the configurational effect is absent in the sense that no pairs of skew chelate rings are present. A catoptromer of the complex, therefore, owes its *d*-electron opti-

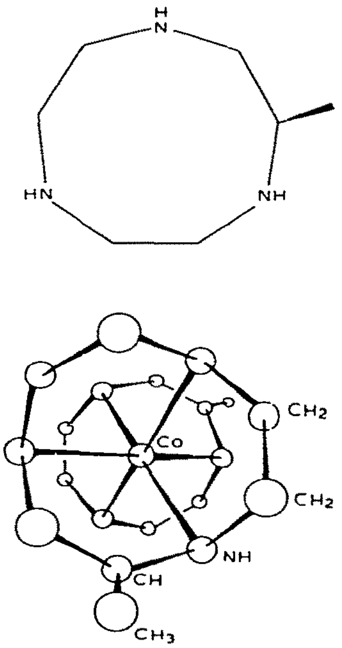

Fig. 2. *R*-MeTACN and its Co(III) complex (from ref. 84).

cal activity to the effect arising from six chelate rings with a common ring conformation. Accordingly it exhibits the largest conformational contribution to ligand field circular dichroism yet recorded ($\Delta\epsilon_{max}$ at 480 nm ca. 4 on a molar scale).

(iii) Stereoselectivity

One of the consequences of coordinating chiral ligands to transition metal ions is stereoselectivity, and high rigidity of the ligand in question is normally coupled with high stereoselectivity. Rigid chiral ligands may for example be produced through Schiff base condensation between amino acids and β-diketones. If the latter are chiral also, which of the two constituents is the stereochemically determining factor may be investigated spectroscopically [85,86].

Using Schiff bases prepared from diamines and β-diketones as coordination entities, stereoselectivity during oxidative expansion of the coordination sphere may be encountered [87], and specifically N,N'-1,2-cyclohexylenebis-(salicylideneimine) coordinated to Co(II) exhibits stereospecificity towards various amino acids [88,89].

The study of such compounds, which may be considered models for di- and tripeptide complexes, naturally inspires investigations into "the nature of enantioselectivity effects" [90], conformational analysis studies [91,92] and studies of polypeptide systems experimentally [93] as well as from a more theoretical point of view [64—66].

Chiral chelation is not a case for amino acids only, as numerous complexes of chiral synthetic ligands are known. Mentioning recent examples we may start with the type having, like amino acids, nitrogen as well as oxygen as coordinating atoms, e.g. synthetic amino acids (edda-type and others [69,94,95]), amino alcohols [96], and Schiff bases of amines and β-diketones [97—100]. Using the latter type of ligand, stereoselectivity and stereospecificity may be studied using exciton theory. Furthermore, knowledge about electronic structure may be gained using simple LCAO-MO theory and the assumption that the *d—d* transitions borrow electric transition moment for rotatory strength in the nearest allowed transitions, the $\pi \rightarrow \pi^*$ exciton couplets [100].

(iv) Chiral organometallic compounds

Until now we have been discussing Werner-type octahedral or square planar transition metal complexes. However, in the field of organometallic compounds chirality is also well known, and there are recent examples of the resolution of such racemates.

We may consider first Zeise-type complexes, where the coordinated olefin induces optical activity into the ligand field transitions due to an inherent planar chirality. Rh(I) complexes containing *trans*-cyclooctene [101], the resolution of which has been accomplished (Fig. 3) through stereospecific complexation, may be quoted as an example.

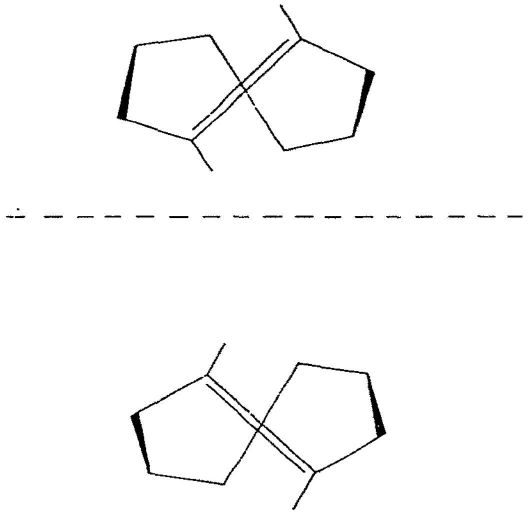

Fig. 3. Enantiomeric forms of *trans*-cyclooctene.

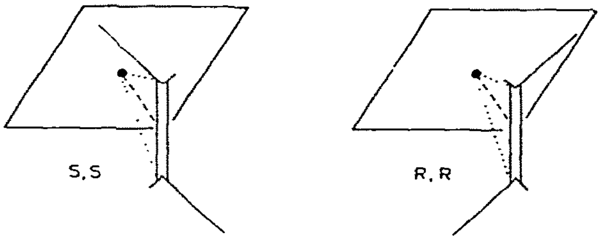

Fig. 4. Chiral coordination of *trans*-2-butene to a square planar Pt(II) complex (from ref. 104).

Compounds exhibiting configurational chirality may be obtained when an olefin or an acetylene is added oxidatively to a bis-chelated rhodium complex. If the olefin is prochiral we thus obtain four pairwise enantiomeric diastereoisomers [102]. The induction of chirality from prochiral olefins such as e.g. propylene, *trans*-2-butene and 1,2-dimethyl-2-butene has been studied specifically in square planar Pt(II) compounds [103—105], isomers of which are shown in Fig. 4. Optical activity of $d \rightarrow \pi^*$ (ethylene) transitions due to the chirality created through coordination of prochiral nitrogen atoms has also been studied [106].

Recently there has been a growing interest in chiral compounds with coordination geometries other than octahedral and square planar. Thus tetrahedral iron [107,108], manganese [109], cobalt [110], ruthenium [111], molybdenum [112] and tungsten [112] complexes have been described. As an illustrative example we mention manganese complexes of *para*-substituted triarylphosphine (Fig. 5) resolved through ester formation with sodium menthoxide. Subsequently, the diastereoisomers were separated through fractional crystallization and finally the enantiomers were obtained through cleavage with HCl and precipitation with NH_4PF_6 [109].

Square pyramidal complexes of the type $C_5H_5M(CO)_2(L^1—L^2)$, M being Mo or W, $L^1—L^2$ being a chiral bidentate ligand, may also exhibit optical activity [113—117]. Consider the example where $L^1—L^2$ is 1,2-diaminopropane (Fig.

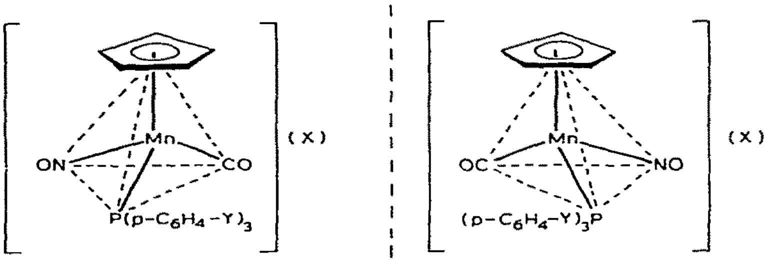

Fig. 5. Enantiomeric forms of a tetrahedral manganese complex (from ref. 109).

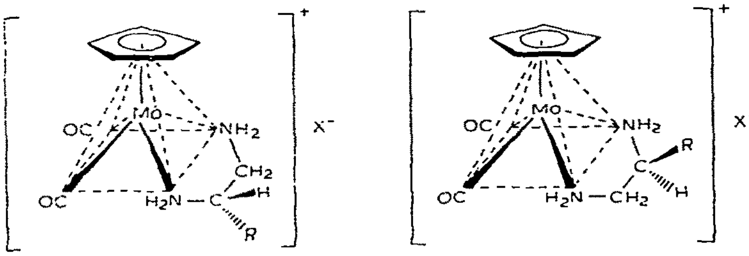

Fig. 6. Diastereoisomers of a square pyramidal Mo complex (from ref. 117).

6). This system has four pairwise enantiomeric diastereoisomers. The two racemates were separated by fractional crystallization but have not yet been resolved [117].

D. MICROSCOPIC INTERPRETATIONS

(i) X-ray structural analysis

Microscopic interpretations of chiral discrimination (including chiroptics) require detailed structural information, which may be obtained directly and most reliably from X-ray determinations of absolute configurations. Using Bijvoet's anomalous dispersion technique, a description of which is given in ref. 118, absolute configurations may be determined directly through a comparison between calculated and observed intensities [121,122,127,131—134]. However, introduction of an optically active counterion or ligand of known absolute configuration in the complex makes determination of the absolute configuration of the complex indirect as it becomes a matter of maintaining a known configuration [120,123,124,128—130,135—137].

Saito and co-workers have reviewed the subject of structural determinations employing the Bijvoet method [118,119], and the latter paper [119] is to the present authors' knowledge the most recent compilation of absolute configurations of metal complexes determined by X-ray analysis. As its latest entries are of November 1977, we supplement the compilation and include some determinations which did not qualify for it as they were based on indirect methods.

Bidentate complexes

$(+)_{589}$-$[Cr(en)_3]^{3+}$

(i) $Li(+)_{589}$-$[Cr(en)_3](d\text{-tart}_2 \cdot 3\ H_2O)$
monoclinic, $P2_1$; $a = 9.22$, $b = 16.99$, $c = 7.86$; $\beta = 100.4°$; $Z = 2$; $\Lambda(\delta\delta\delta)$ (ref. 120)

(ii) $(+)_{589}$-$[Cr(en)_3]Cl_3 \cdot 2\ H_2O$
monoclinic, $P2_1$; $a = 15.083$, $b = 11.137$, $c = 11.078$; $\beta = 109.36°$; $Z = 4$; $\Lambda(\lambda\delta\delta)$ and $\Lambda(\lambda\delta(60\%\delta, 40\%\lambda))$ (ref. 121)

$(-)_{589}$-$[Cr(en)_3]^{3+}$

(i) $(-)_{589}$-$[Cr(en)_3](SCN)_3$
orthorhombic, $P2_12_12_1$; $a = 14.753$, $b = 13.513$, $c = 9.202$; $Z = 4$; $\Delta(\lambda\delta\delta)$ (ref. 122)

$(+)_{589}$-$[Co(en)_3]^{3+}$
(i) $(+)_{589}$-$[Co(en)_3](d\text{-tart})Br \cdot 5\ H_2O$
triclinic, $P1$; $a = 8.50$, $b = 8.27$, $c = 8.16$, $\alpha = 95.3°$, $\beta = 101.0°$, $\gamma = 102.4°$; $Z = 1$; $\Lambda(\delta\delta\delta)$ (ref. 123)
(ii) $H(+)_{589}$-$[Co(en)_3](d\text{-tart})_2 \cdot 3\ H_2O$
monoclinic, $P2_1$; $a = 9.46$, $b = 16.89$, $c = 7.68$, $\beta = 99.4°$; $Z = 2$; $\Lambda(\delta\delta\delta)$ (ref. 124)

$(-)_{589}$-$[Co(R\text{-pn})_3]^{3+}$ R-pn = R-$(-)_D$-1,2-diaminopropane
(i) $(-)_{589}$-$[Co(R\text{-pn})_3]Br_3$
hexagonal, $P6_3$; $a = 11.012$, $c = 8.582$; $Z = 2$; $\Delta(\lambda\lambda\lambda)$ (ref. 125)

$(+)_{589}$-$[Co(bgH)_3]^{3+}$
(i) $(+)_{589}$-$[Co(bgH)_3]Cl_3 \cdot H_2O$
orthorhombic, $C222_1$; $a = 18.675$, $b = 14.086$, $c = 15.004$; $Z = 8$; Δ (ref. 126)

$(+)_{589}$-$[Co(S\text{-pea})_3]^{3+}$ S-pea = S-$(-)_{589}$-1-(2-pyridyl)ethylamine
(i) $(+)_{589}$-$[Co(S\text{-pea})_3](ClO_4)_3 \cdot 2\ H_2O$
monoclinic, $P2_1$; $a = 9.416$, $b = 18.122$, $c = 9.129$, $\beta = 92.16°$; $Z = 2$; $\Lambda(\delta\delta\delta)$ (ref. 127)

$(-)_{589}$-$[Co(L\text{-ala})_3]$
(i) $(-)_{589}$-$[Co(L\text{-ala})_3] \cdot H_2O$
orthorhombic, $P2_12_12_1$; $a = 5.247$, $b = 13.555$, $c = 19.351$; $Z = 4$; $\Delta(\delta\delta\delta)$ (ref. 128)

$(+)_{589}$-$[Co(C_2O_4)(en)_2]^+$
(i) $(+)_{589}$-$[Co(C_2O_4)(en)_2](H\text{-}d\text{-tart}) \cdot H_2O$
monoclinic, $P2_1$; $a = 8.27$, $b = 14.60$, $c = 7.02$, $\beta = 104.8°$, $Z = 2$; $\Delta(\delta\lambda)$ (ref. 129)

$(+)_{589}$-$[Co(en)_2Cl_2]^+$
(i) $(+)_{589}$-*cis*-$[Co(en)_2Cl_2](bcs)$
monoclinic, $P2_1$; $a = 13.76$, $b = 6.80$, $c = 12.08$, $\beta = 103.2°$; $Z = 2$; $\Lambda(\delta\lambda)$ (ref. 130)

$(+)_{589}$-$[Co(en)_2(N\text{-benzyl-gly})]^{2+}$
(i) $(+)_{589}$-$[Co(en)_2(N\text{-benzyl-gly})]Cl_2$
orthorhombic, $P2_12_12_1$; $a = 12.508$, $b = 22.970$, $c = 6.544$; $Z = 4$; Λ (refs. 131—133)

$(+)_{589}$-$[Co(CN)_2(mal)(NH_3)_2]^-$
(i) $(-)_{589}$-*cis*-$[Co(C_2O_4)(en)_2]$$(+)_{589}$-*cis*, *cis*-$[Co(CN)_2(mal)(NH_3)_2] \cdot 3\ H_2O$
orthorhombic, $P2_12_12_1$; $a = 16.709$, $b = 18.139$, $c = 7.569$; $Z = 4$; Δ (ref. 134)

Tetradentate complexes

Cu R-pn(acac)$_2$ R-pn(acac)H_2 is a Schiff base condensate between R-pn and acacH

(i) Cu *R*-pn(acac)$_2$
orthorhombic, $P2_12_12_1$; $a = 12.452$, $b = 21.032$, $c = 10.766$; $Z = 8$; Λ
(ref. 135)

(−)$_{546}$-[Co(C_2O_4)(*R*,*R*-2,3″,2-tet)]$^+$ *R*,*R*-2,3″,2-tet = (4*R*, 6*R*)-dimethyl-3,7-diazanonane-1,9-diamine

(i) (−)$_{546}$-[Co(C_2O_4)(*R*,*R*-2,3″,2-tet)]ClO_4
orthorhombic, $P2_12_12_1$; $a = 9.116$, $b = 25.010$, $c = 7.657$, $Z = 4$; Λ(δδ)
(ref. 136)

Hexadentate complexes

(−)$_{589}$-[Co(*S*,*S*-ebm)]$^+$ ebm = 6,9-diaza-2,13-dithiatetradecane-5,10-dicarboxylate

(i) (−)$_{589}$-[Co(*S*,*S*-ebm)]ClO_4
monoclinic, $C2$; $a = 12.34$, $b = 7.94$, $c = 9.46$, $\beta = 97.45°$; $Z = 2$; Λ(δλλ)
(ref. 137)

In connection with the compilation by Saito and co-workers mentioned above [119] we close this section by referring to another compilation performed by the same group giving a list of papers dealing with optically active coordination compounds studied in Japan [138].

(ii) Outer-sphere complexation

Although of paramount importance, information gathered through X-ray structural investigations is only valid for the solid state, and thus solution studies are necessary to investigate whether X-ray structural data are likely to predominate also in solution. A particularly interesting example is the work of Yoneda and co-workers, who studied the process of optical resolution through determination of absolute configuration of less soluble diastereoisomers [120,123,124,129,130] and coupled these investigations with studies of stereoselective ion-pair formation in solution [139].

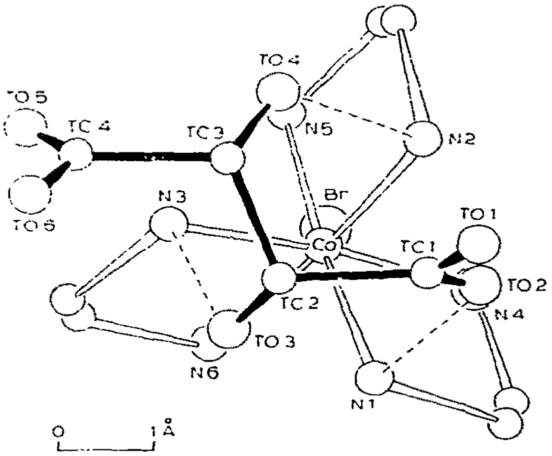

Fig. 7. Structure of Λ-[Co(en)$_3$]Br(*d*-tart) showing hydrogen bonds (- - - - -) (from ref. 123).

It was found from X-ray structural determinations that L-tartrate in Λ-[Co-$(en)_3$]Br(L-tart) · 5 H_2O [123] and in Li-Λ-[Cr$(en)_3$](L-tart)$_2$ · 3 H_2O [120] approaches the complex ion along the direction of the C_3 axis forming hydrogen bonds between three of its oxygen atoms and the three axial N—H hydrogen atoms of the complex ion (Fig. 7).

One might expect these structural features to play an important role for the stereoselectivity found in the formation of the diastereoisomeric salts from aqueous solution, and circular dichroism (CD) measurements are expected to serve as an effective means of investigating this in terms of association constants.

When this is done, indeed the structural features of the solid state, i.e. the number and length of hydrogen bonds, are reflected in the relative magnitudes of association constants of different diastereoisomeric pairs [139—141]. Conclusions such as those cited above depend on the additivity of induced circular dichroisms from various isomers. This however seems to be valid, as demonstrated recently for additions of malate, maleate and fumarate through hydrogen bond formation to Λ-$[Co(en)_3]^{3+}$ [142].

As a matter of fact formation of hydrogen bonds between diethyltartrate and simple Werner type complexes [143] or between equatorial prochiral N—H protons of chelated diamines and optically inactive substrates are subjects which have been focused on recently [144,145], but stereoselectivity also occurs by van der Waals attractive forces through hydrophobic interactions [146].

(iii) Pfeiffer effect

The Pfeiffer effect, which has recently been considered from a theoretical, thermodynamic point of view [147], is observed for example, when a chiral ion is added to a racemate of a labile metal complex. The resulting solution shows a Cotton effect directly attributable to the displacement of the equilibrium between the two enantiomers, and obviously the Pfeiffer effect can be utilized to study optical properties of chiral complexes which are difficult or impossible to resolve because of their lability [148].

Although the explanation offered by Schipper cannot be ruled out [147], the Pfeiffer effect is probably due to ion-pair formation, a hypothesis which is corroborated by the evidence given by Yoneda and co-workers [149—151]. Consequently the Pfeiffer effect has been used as a tool for the determination of absolute configuration of labile metal complexes [150,152]. However, the empirical nature of this application is born out by the recent demonstration that in the $[Cr(C_2O_4)_3]^{3-}$ and $[Co(C_2O_4)_3]^{3-}$ systems the Λ enantiomer is enriched using Λ-$[Co(phen)_3]^{3+}$ to produce a chiral environment [153] whereas the Δ enantiomer is enriched in the $[Co(acac)_3]^{-}$/Λ-$[Co(phen)_3]^{3+}$ system [154].

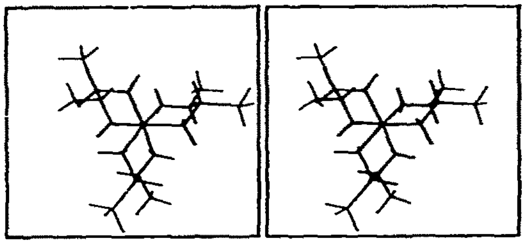

Fig. 8. Stereoscopic pair showing the equilibrium structure of lel$_3$-M(2*S*, 3*S*-bn)$_3$ superimposed on the lel$_3$-M(en)$_3$ structure. The rings have practically the same shape. Conformers depicted are those which are expected to predominate in an equilibrium in solution (from ref. 157).

(iv) Conformational analysis

Conformational analysis has been employed in order to obtain the structure of conformers as well as values of the free energy difference between them, and such values are needed in the assessment of the importance of conformational equilibria in solution. Sophisticated programs for this type of calculation have recently been documented [155] and calculations have been performed for tris(diamine) coordination compounds of 1,3-diaminopropane, 2,4-diaminopentane [156], 1,2-diaminoethane and 2,3-diaminobutane [157]. As an example of the results obtained it may be mentioned that chelate rings without methyl groups or with two equatorial ones are found to be highly puckered and they appear very rigid since both descriptors of the conformations have a very small range (Fig. 8). These conclusions are in agreement with crystal structure determinations [157]. Unfortunately, experimental thermodynamic data for the verification of results obtained through conformational analysis are rare [158] and difficult to gain. It is interesting to note that conformational equilibria are in fact also established in the solid state although only a few examples have been reported [121].

(v) Stereoselectivity

Combining stereochemical knowledge with investigations of kinetics of various stereoselective reactions we may learn about possible mechanisms and intermediates.

Recent investigations of an established mechanism deal with the concerted base hydrolysis of Λ-*cis*-dichlorobis(ethylenediamine)cobalt(III) [159] and Λ-*cis*-chloroamminebis(ethylenediamine)cobalt(III) complexes [160]. As far as intermediates are concerned the appearance of five coordinated species during the rapidly induced aquation of cobalt(III) pentammine complexes [161] has recently been documented further.

Information about kinetics and intermediates of a specific reaction involving a robust chiral complex may be found in the distribution of the various isomers produced [162—167]. However from work with labile complexes, information about mechanism and sources of stereoselectivity may only be obtained indirectly [168]. When the kinetics and thermodynamics of a series of reactions are known, one may design preparative procedures as was done for example for the production of $(-)_{589}$-Λ,Δ-$[(en)_2Cr(OH)_2Co(en)_2](ClO_4)_4$ [169].

Finally it should be mentioned that recently there has been a growing interest in the study of kinetics of catalysis and photolysis of chiral systems as exemplified by the racemization of $(+)_{589}$-tris(ethylenediamine)cobalt(III) in the presence of carbon-black [170] and by the enrichment of one of the enantiomers of a racemic mixture of complexes through irradiation with circularly polarized light [171,172].

(vi) Models

The comprehensive chiroptic evidence accumulated in the long tradition of studying cobalt(III) chelates has been exploited in the construction of models of the quantitative relation between molecular properties and chiroptic behaviour. The one-electron model has most often been chosen as the theoretical framework for such considerations since it embodies the basic concepts of crystal field theory. However, applications of the one-electron model to transition metal complexes are largely of a qualitative nature and have, as yet, underestimated the magnitude of the rotatory strengths of *d*-electron transitions in chiral coordination compounds. With this in mind, Mason and Seal [173] recently investigated the application of the complementary dynamic coupling model restricting themselves to the lowest-energy spin-allowed *d*-electron transition of the hexammine cobalt(III) chromophore, $T_{1g} \leftarrow A_{1g}$, in a series of chiral derivatives, notably the tris(diamine) chelate complexes.

The rotatory strength of a metal—ion excitation is given by

$$R_{0a} = -i\langle M_0L_0|\bar{\mu}|M_aL_0\rangle \cdot \langle M_aL_0|\bar{m}|M_0L_0\rangle \qquad \text{(eqn. 1 in ref. 173)}$$

Whereas the metal-ion excitations considered are allowed in a magnetic dipole radiation field, they are forbidden in an electric dipole radiation field and therefore the question of how to gain electric transition dipole moment for the production of a non-vanishing rotatory strength arises. To the first order, this may be done through mixing of forbidden and allowed electric dipole transitions at the metal ion centre under the perturbation of the static ground state charge distributions of the ligands (one-electron model), or through coulombic correlation of transient electric dipole moments in the ligands with the transitional charge distribution of the metal ion (dynamic coupling model).

In the second order perturbation the two models do not necessarily remain distinct and complementary, since magnetic dipole *d*-electron transitions may mix with electric dipole charge-transfer transitions.

Although the reader should consult the paper of Mason and Seal [173] for a detailed discussion of the power of the proposed model, the following calculated values of rotatory strengths of the Λ-[Co(en)$_3$]$^{3+}$ chromophore need to be quoted for the sake of the discussion in the next section

$R(A_2)$ 1st order	-43.0×10^{-40} c.g.s.
$R(A_2)$ 2nd order	-16.9×10^{-40} c.g.s.
$R(E)$ 1st order	42.0×10^{-40} c.g.s.
$R(E)$ 2nd order	21.9×10^{-40} c.g.s.

The model of Mason and Seal was tested by application to a specific transition of a specific set of compounds. Further theoretical approaches to the concept of optical activity of transition metal complexes may be found in work by Richardson and co-workers [64—66,174], Bunel et al. [175] and Schipper [176]. The latter [176] discusses the possibility of direct observation of electronic transitions which are either magnetic- or electric dipole-allowed using the so-called DICD-method (Dispersion Induced Circular Dichroism).

(vii) Crystal circular dichroism

Whatever model for optical activity may be proposed its evaluation depends inter alia on the availability of correct assignments of rotatory strength to particular transitions of known polarization direction and transition moment, data which can most reliably be obtained from circular dichroism measurements on crystals with known structure. Such measurements have formerly been considered feasible only along an optic axis in uniaxial crystals [177, 178], the existence of linear birefringence and linear dichroism otherwise presenting prohibitive complications.

The tris(diamine) cobalt(III) complex investigated in most detail is that of ethylenediamine. As pointed out by Mason and Seal [173] the crystal structure analyses of four different salts of the Λ-[Co(en)$_3$]$^{3+}$ chromophore show substantial agreements as also do five independent measurements of the axial single crystal CD spectrum of the complex, which, due to the orientation of the chromophores in the crystal, is an unperturbed measurement of the rotatory strength of the trigonal component $E \leftarrow A_1$ under the octahedral parent transition $T_{1g} \leftarrow A_{1g}$. Values obtained experimentally for $R(E)$ range from 43 [179] to 63 [177] in units of 10^{-40} c.g.s. which should be compared with the values reproduced in the previous section. Until very recently [179] the rotatory strength of the other trigonal component ($A_2 \leftarrow A_1$) in Λ-[Co(en)$_3$]$^{3+}$ has not been measured directly. Due to the existence of linear anisotropy perpendicular to the crystallographic *c*-axis (chromophoric C_3, optic axis), $R(A_2)$ has formerly been calculated assuming that the random circular dichroism in the $T_{1g} \leftarrow A_{1g}$ range was to be thought of as residual wing absorptions, i.e. that the sum rule $R(A_2) + R(E) = 0$ is obeyed.

Using a specialized mode of phase modulation spectroscopy and analysing the spectral response in terms of the Stokes-Mueller algebra, it has recently proven possible to overcome the difficulty presented by linear anisotropy

[180—183]. Briefly expressed, the attractive feature of the Mueller matrix for very complicated systems is that all the different experimental (phenomenological) effects (linear birefringence and dichroism, circular birefringence and dichroism, mean absorption) are separated into different elements of a differential matrix. Although exponential, this matrix may often be expanded, so that one has only to deal with linear superpositions of effects. As soon as this point is realized it is, at least to a certain extent, only a matter of electronics to measure specifically circular dichroism in the presence of linear anisotropies and vice versa.

Selective determination of circular dichroism in the presence of linear anisotropies has now been performed on several systems other than those containing the Λ-$[Co(en)_3]^{3+}$ chromophore. Thus the copper(II) complex of 4,4'-(*R*-1,2-propanediimino)di(3-pentene-2-one) (Cu *R*-pn(acac)$_2$) [135] was investigated both with respect to circular and linear dichroism [184] in order to verify independently earlier assignments of electronic transitions in the ligand field range based on a simple LCAO-MO treatment and a "borrowing" mechanism (ref. 100 and references cited therein).

An interesting case is presented by the Pt(II) and Pd(II) complexes *cis*-M(en)Cl_2. Crystals of *cis*-Pt(en)Cl_2 and *cis*-Pd(en)Cl_2 are isomorphous and belong to the orthorhombic system $C222_1$ (D_2^5). This space group symmetry requires that the ethylenediamine rings in a particular single crystal exhibit only one of the two possible conformations λ or δ, and a spontaneous resolution by crystallization has therefore been postulated. This has been verified by the direct measurement of crystal circular dichroism in the ligand field range [185].

NOTE ADDED IN PROOF

During the spring of 1979, the two following books of relevance to the present topic have appeared: S.F. Mason (Ed.), Optical Activity and Chiral Discrimination, Proc. NATO Adv. Study Inst. 1978, Reidel, 1979. Y. Saito, Inorganic Molecular Dissymmetry, Springer, 1979.

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