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Enantioselective effects in coordination compounds

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ABSTRACT. The information that has appeared during the last 15 years relating to enantioselectivity in the formation and reactions of kinetically inert and kinetically labile complexes is classified in the present review. Attention is mainly given to chiral discrimination of ligands that are exchanged in the internal or external coordination spheres of the complexes. The occurrence of enantioselective effects has also been recorded in reactions of coordination compounds that occur without ligand exchange, in particular, in photochemical processes. The variety of forms in which enantioselectivity is displayed is shown and methods for studying it are described.

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I. Introduction

Enantioselective effects may be encountered in very different regions of chemistry and biochemistry. These are the enantioselective effect of enzymes on racemic substrates, the enantioselective polymerisation of chiral monomers, photochemical processes involving circularly polarised light, etc. The variety of areas in which the reactions of enantiomers have been studied has resulted in the fact that up to the present time no single stereochemical terminology on selective and specific processes has developed. This literature review contains material that is selected in accordance with that definition of enantioselectivity which we gave in our first review[2] devoted to this subject—processes in which one out of the two enantiomeres present in a system is mainly involved are enantioselective. This type of discrimination can naturally only occur in a reaction with a particular chiral reagent (discriminator, selector), so in the general case enantioselectivity is the difference in the reaction of two enantiomeres with some third chiral structure.[1,2]

II. Enantioselective effects that accompany ligand exchange in the internal coordination sphere of kinetically inert complexes

Enantioselective processes that accompany ligand exchange in the internal coordination sphere of kinetically inert complexes were some of the first to be found in coordination chemistry. The most intensive studies of these processes were carried out at the end of the 1960's and the beginning of the 1970's. Enantioselectivity in kinetically inert systems may be both kinetic and thermodynamic in nature and in many cases it is no easy task to separate the contributions of these effects. It is assumed that a state of equilibrium between possible isomers of an inert complex is catalysed by the addition of active carbon, and this method is frequently used to achieve "thermodynamic" enantioselectivity.

Tatechata[3] studied the formation of $[Co(phen)_2(S\text{-aa})]^{2+}$ complexes (phen = phenanthroline, aa = amino-acid) from racemic Δ,Λ-*cis*-$[Co(phen)_2Cl_2]^+$ and *S*-amino acids (Ala, Leu, Ile, Val, and Phe were studied). The resulting diastereomeric complexes were separated by chromatography on Sephadex. The ratio of their Δ- and Λ-isomers was determined. The Λ-isomer was mainly formed in the systems studied, and the enantioselectivity increases significantly with an increase in branching of the α-substituent of the amino acid. Having studied the ^1H NMR spectra of the complexes, Tatechata[3] established that the amino acid in $[Co(phen)_2(S\text{-aa})]^{2+}$ has an equatorial configuration of the α-alkyl substituent. Enantioselectivity occurs as a result of the different degree of nonbonded interactions between the α-alkyl group of the amino acid and the aromatic ligands in Δ- and Λ-structures.

In a series of studies Vagg and Williams[4–11] studied similar reactions for racemic ruthenium complexes Δ,Λ-$[Ru(phen)_2Cl_2]$ or Δ,Λ-$[Ru(bipy)_2Cl_2]$, where bipy = bipyridyl, and since the reaction was carried out using excess *S*-amino acid, no enantioselectivity was found. However, the authors subsequently determined the equilibrium constants for isomerisation of the form:

$$\Delta\text{-}[Ru(am)_2(S\text{-aa})]^+ \rightleftarrows \Lambda\text{-}[Ru(am)_2(S\text{-aa})]^+,$$

where am = bipy or phen. The constants proved to be different from unity. The Λ-diastereomer is more stable for *S*-Phe, *S*-Tyr, *S*-His, and *S*-Pro.[5] At first glance these results do not have any bearing on enantioselectivity. But it follows from them that if the authors had used an insufficient quantity of *S*-amino acid, the Λ-isomer of the initial racemic complex would have mainly undergone reaction with *S*-Trp, *S*-Phe, *S*-Tyr, *S*-His, and *S*-Pro in reaching thermodynamic equilibrium. The reverse pattern would have occurred with *S*-Glu, *S*-Ala, and *S*-Ser.

In a series of studies by Yoshikawa et al.[12–17] the enantioselectivity and enantiospecificity of processes involving the formation of cobalt tetramine complexes was investigated. The coordination of tetramines is stereospecific and the *cis*-β-isomer is

mainly formed, its absolute configuration being clearly (100% enantiospecificity) determined by the optical configuration of the tetramine. For those tetramines studied—3(*S*),8(*S*)-Me_2-trien, 5(*R*)-Me-trien, 2(*S*),10(*S*)-Me_2-trien, 3(*S*),9(*S*)-Me_2-trien, and 1(*R*),2(*R*)-baetchxn, where trien = 1,4,7-triazaheptane, baetchxn = *N*,*N*′-bis(β-aminoethyl)diaminocyclohexane—the optical configuration of the cobalt complex was found to be Λ.[13,14] When this complex coordinates an amino acid molecule on to the two remaining free coordination sites to form $[Co(am)(aa)]^{2+}$, the coordination is again stereospecific with the Λ-β_2-structure mainly formed.

When the amino acid has an *N*-alkyl substituent (*N*-Me-Ala was the most widely studied), with such an amino acid fragment there will be two asymmetric centres in the complex—the carbon atom with a configuration that is determined by the configuration of the amino acid and the nitrogen atom which becomes asymmetric on coordinating. For most of the systems studied coordination of the nitrogen atom of an *R*-amino acid is not enantiospecific and the corresponding diastereomers are in equilibrium (which is rapidly established even at pH 7) in equal quantities. Only in the case of 3(*S*),8(*S*)-Me_2-trien and *N*-Me-Ala is there a ratio of 3:1 for diastereomers with *R*- and *S*-configurations of the N atoms. On the other hand, in complexes with *S*-amino acids the coordination of the N atom is 100% enantiospecific and only the *R*-diastereomer is formed. It was also shown that the ratio of diastereomers (on the nitrogen atom) is independent of the pH of the medium since equilibrium is reached even in neutral solution.[16]

At the same time, racemisation of the asymmetric carbon centre of the amino acid residue occurs in alkaline solution, resulting in the equilibrium:

$$\Lambda\text{-}\beta_2\text{-}[Co(am)(S\text{-}aa)]^{2+} \rightleftarrows \Delta\text{-}\beta_2\text{-}[Co(am)(R\text{-}aa)]^{2+},$$

where *R* and *S* denote the configuration of the C atom of the amino acid. Yamaguchi et al.[17] determined the ratio of the respective diastereomers in the equilibrium solution. These results, just as the results for the Ru complexes reported above, characterise not only the enantiospecificity of the complex formation process but also the enantioselectivity of the reaction:

$$\Lambda\text{-}\beta_2\text{-}[Co(am)]^{3+} + R,S\text{-aa} \rightleftarrows \Lambda\text{-}\beta_2\text{-}[Co(am)(R\text{- or }S\text{-aa})]^{2+}.$$

The enantioselectivity of this reaction depends both on the type of amine and on the structure of the amino acid. The introduction of an *N*-alkyl substituent has a particularly marked influence as does the ability of the α-alkyl substituent of the amino acid to form hydrogen bonds with the nitrogen atoms of the tetramine. The authors consider that the reason for enantioselectivity occurring lies in the difference between nonbonded interactions of both an interligand and intraligand type in the diastereomers. Conformational calculations were carried out in order to determine the most stable conformations of some complexes.[15] According to these calculations, $\{Co[2(S),10(S)\text{-}Me_2\text{-}tet]_2(R\text{-}Ala)\}^{2+}$, where tet = 1,4,7,10-tetraazadecane, is no different in energy from $\{Co[2(S),10(S)\text{-}Me_2\text{-}tet](S\text{-}Ala)\}^{2+}$, but $[Co(S,S\text{-}pyht)(S\text{-}Ala)]^{2+}$, where pyht = 1,7-bis(2-pyrrolidyl)-2,6-diazaheptane, is 3.15 kJ mol^{-1} more stable than $[Co(S,S\text{-}pyht)(R\text{-}Ala)]^{+}$. The latter value is quite close to the difference between the energies of the diastereomers (3.95 kJ mol^{-1}) found experimentally. At the same time, a value of 1.72 kJ mol^{-1} in favour of the diastereomer with (*S*)-Ala was found experimentally for the first system.

Yamaguchi et al.[16] subsequently carried out a more detailed conformational analysis of $[Co(am)(R\text{- or }S\text{-}N\text{-Me-Ala})]^{2+}$ complexes that took into account the contribution from the asymmetric nitrogen atom, and they obtained values for the conformational energy that agreed quite well with the experimental values. This is an indication of the correctness of the chosen model, from which it follows that the main contribution to enantioselectivity in this system is made up by distortions of the torsion and bond angles resulting from nonbonded interligand interactions. The system studied by Yoshikawa et al.[12–17] displays quite a small difference in conformational strain energies for two comparable diastereomers.

In a similar manner Brubaker and Massura,[18] by minimising the energy of nonbonded interactions in cobalt complexes with *N*,*N*′-bis(2-picolyl)-1,2-(*S*)-propylenediamine and alanine enantiomers, found that the difference in conformational strain energies between the two diastereomers was 2.5–3.5 kJ mol^{-1}, and they managed to detect both diastereomeric forms of the complex in an equilibrium solution.

The search for highly selective systems constitutes one of the areas of research on the stereochemistry of coordination compounds. A group of Japanese research workers led by Fujii[19–26] has had considerable success in this field. The authors studied heteroligand complexes of cobalt with Schiff bases and amino acids such as [Co(SB)(aa)], where SB = bis(salicylideneamino)ethylene (sal_2en) and its methyl derivative ($Me\text{-}sal_2en$) or bis(2-hydroxynaphthylideneamino)ethylene ($bsal_2en$). These Schiff bases coordinate stereospecifically with a Co atom to form exclusively the *cis*-β_2-structure.[19] Subsequent reaction of $[Co(sal_2en)]^{+}$ or $[Co(Me\text{-}sal_2en)]^{+}$ complexes with an *S*-amino acid (the reaction is carried out until thermodynamic equilibrium is reached) results in the formation of two diastereomers in unequal proportions; the ratio varies from 1.5:1 for *S*-Ala to 17:1 for *S*-Trp in favour of the $(-)_{435}$-diastereomer.[20] Correctly assuming that if racemic amino acid and optically active complex were reacted separation of the racemate could be achieved, Fujii et al.[21,22] used the enantiospecific coordinating ligand (1*S*,2*S*)-*N*,*N*′-1,2-cyclohexane-bis(salicylideneamine) (sal_2chxn), which forms complexes exclusively with a Λ-β_2-structure, in this reaction. In this case they achieved the following degree of enantiomeric enrichment remaining in the excess amino acid: Ala 6–8% (*R*), Leu 6–8% (*R*), Met 6–8% (*R*), Ser 10–12% (*R*), Thr 27–30% (*R*), Asp 16–18% (*R*), Glu 6–8% (*R*), Phe 39–41% (*R*), Trp 41–43% (*R*), Pro 48–50% (*S*). The results obtained agree quite well with the data from the determination of thermodynamic enantioselectivity in the same complexes in dimethylformamide:water (1:4) solution,[23] where the structure containing the *S*-enantiomer of the amino acid (Ala, Val, Leu, Phe, Trp were studied) proved to be the most stable. Thus, the Λ-complex preferentially contained an *S*-amino acid. Only proline, whose *R*-enantiomer proved more active, constituted an exception.

In this connection the $[Co(Me\text{-}sal_2en)(S\text{-Pro})]$ system was studied in greater detail.[24] It was found that when starting from *S*-proline and $[Co(Me\text{-}sal_2en)]^{+}$ the less stable diastereomer, which has a negative rotation at 435 nm, is initially formed, but subsequently it is slowly converted to the $(+)_{435}$-diastereomer. The rate constant of isomerisation *k* is equal to 7.95×10^{-5} s^{-1},[24] and according to the ^1H NMR spectra, only one isomer is present in the final solution. A similar transformation was subsequently also found for $[Co(Me\text{-}sal_2en)(S\text{-Hyp})]$ and $[Co(Me\text{-}sal_2en)(S\text{-}a\text{-Hyp})]$. The degree of kinetic enantioselectivity, determined from the ratio of diastereomers $(-)_{435}$:$(+)_{435}$ at the initial moment in time, was lower in these complexes (56% for *S*-Hyp and 23% for *S*-*a*-Hyp) than for proline (87%).[25] However, in this case, just as for proline, a gradual conversion to the more stable $(+)_{435}$-diastereomer occurs.

Fujii et al.[26] subsequently succeeded in finding a system in which kinetic enantioselectivity occurs for other amino acids, in particular for valine and isoleucine. $[Co(bsal_2en)]^+$ complexes had this property. A considerable effect from the solvent on the ratio of diastereomeric structures in solution was reported.

The *N*-alkyl substituent in the amino acid residue of the complex has a very considerable effect on the degree of enantioselectivity. Thus, if the complex $[Co(Me\text{-}sal_2en)]^+$ is reacted not with *S*-alanine (ratio $\Lambda/\Delta \approx 2$) but with its *N*-methyl derivative, the content of Λ-isomer in the equilibrium mixture is as high as 93% while for the *N*-benzyl derivative it is 100%.[19] Correspondingly, if Λ-*cis*-β_2[Co(*S*,*S*-sal$_2$chxn)]$^+$ is used, racemic *N*-benzylalanine reacts with almost 100% enantioselectivity, leaving the *R*-enantiomer unreacted. The ratio of the resulting complexes for the system [Co(Me-sal$_2$en)(*R*- or *S*-*N*-Bzl-Ala)] was used to establish the following relative stability of diastereomeric complexes (configuration of the complex, configuration of the N atom in the amino acid molecule, and configuration of the amino acid are given): $\Lambda(S,S) = 19.5$; $\Delta(R,S) = 11.3$; $\Delta(S,S) = 8.2$; $\Lambda(R,S) = 0$ kJ mol^{-1}. This corresponds to the following ratio of $\Delta(R,S):\Delta(S,S)$ diastereomers at equilibrium of 96.5 : 3.5.[11] For comparison we can indicate that for the {Co[3(*S*),8(*S*)-Me$_2$-trien](*N*-Me-Ala)}$^{2+}$ system reported above the three complexes $\Lambda(R,S)$, $\Delta(S,S)$ and $\Delta(R,S)$ are in equilibrium in the ratio 60 : 20 : 20, which corresponds to a considerably lower selectivity for the system.

The high enantioselectivity for formation of complexes based on quadrivalent Schiff bases was also confirmed by Okawa,[27] who synthesised complexes of cobalt with Schiff bases obtained from 1,2-diaminopropane or *trans*-1,2-diaminocyclohexane and 1(*S*)-menthyloxy-3-benzeneacetone. If a Schiff base obtained from a racemic diamine is reacted, there is the sole formation of the Λ-*cis*-β_1-structure of the complex, containing only *R*-propylidenediamine or *S*-cyclohexanediamine residues.

The enantioselectivity found in complexes of cobalt with trimethylene-bis(pyrrolidine-2-carboxylic acid) is just as high.[28] This ligand coordinates enantiospecifically and stereospecifically, giving an asymmetric Λ-structure. Subsequent reaction of this complex with *R*,*S*-proline or *R*,*S*-pipecolinic acid results in the formation of a heteroligand complex that contains only the *R*-enantiomers of the amino acids.

The majority of the studies described above had octahedral complexes of trivalent cobalt as the subject of their research; these complexes were and remain a favourite topic in stereochemical studies. At the same time other kinetically inert complexes, and particularly other coordination polyhedra, in relation to enantioselectivity remain almost unstudied. There is no doubt that the study by Payne and Stephan[29,30] on square planar platinum complexes proved very interesting in this respect. Complexes with this type of stereochemistry were regarded as unfavourable subjects for the study of enantioselectivity. Since the ligands in these structures are situated at a considerably greater distance from each other compared to octahedral complexes, the occurrence of interligand interactions — the basis of enantioselectivity — seemed improbable. However, this study disproved these predictions. Platinum complexes that contained a chiral diphosphine ligand, methyl group, and chlorine atom reacted with a racemic monoamine or monophosphine to give diastereomers in a ratio which quite frequently differed from 1 : 1, which was an indication of the enantioselective course of the reaction.

Equally, Shinoda et al.[31] found that for the reaction of *trans*-{Pt(Cl$_2$)(SR$_2$)[(*R*,*S*)-Val-OMe]} with *R*- or *S*-phenylethylamine there were quite noticeable differences in the equilibrium constants, which indicate the preferential replacement by phenylethylamine of the amino acid ligand belonging to a configurational series opposite to that of the amine itself.

Studies on enantioselectivity in reactions of organometallic compounds should also be mentioned. Although research into the preparation of diastereomeric organometallic compounds was started a long time ago (see, for example, the study by Brunner[32] and the references in it), the question of the ratio of concentrations of the resulting diastereomers or the ratio of their rates of formation has generally not been raised. In the studies of Kane-Maguire et al.[33–35] it was shown that $[Fe(CO)_3(1\text{-}5\eta\text{-}2\text{-}MeOC_6H_6)]^+$ reacts with optically active phosphines[33,34] or phenylethylamine,[35] exhibiting both kinetic and thermodynamic enantioselectivity. Pearson and Yoon[36] reported that the reaction of iron dienyl complexes of the type $(\eta^4\text{-COD})Fe(CO)_2[P(OEt)_3]$ with optically active enolates stabilised with sulphoximine is enantioselective (about 50% enrichment) and may be used to obtain an organometallic derivative in an optically active form. They noted a considerable effect of the nature of the enolate cation on the degree of enantioselectivity (Li exhibits a considerably lower enantioselectivity than K).[36] A system in which the enantioselectivity is close to 100% is described in a study by Tsyryapkin et al.[37] The reaction of racemic $[Mn(CO)_3(\eta^5\text{-}1\text{-}N\text{-}Me_2\text{-}2\text{-}CHO\text{-}C_5H_3)]$ with optically active dipeptides in the presence of Cu^{2+} ions takes place in such a manner that only the $(-)_{435}$-enantiomer of the complex forms a Schiff base, while the $(+)_{435}$-isomer remains unreacted and can be isolated by extraction from the reaction mixture. Subsequent study of this reaction showed that the enantioselectivity depends to a considerable degree on the structure of the dipeptide.[47] Thus for Gly-(*S*)-Ala the ratio of diastereomeric complexes is 41 : 1 but for (*S*)-Ala-Gly or (*S*)-Val-Gly it is close to the statistical average.

It was found quite unexpectedly that organometallic compounds can act as substrates for enzyme reactions.[39] Although the enantioselectivity of the hydrolysis of (2-ethoxycarbonylbuta-1,3-diene)iron tricarbonyl with pig liver esterase was not so high (an optical purity of about 85% for the acid isolated), with a subsequent single-stage crystallisation a product with an optical purity of >98% could be obtained.

III. Enantioselective effects that accompany ligand exchange in the internal coordination sphere of kinetically labile complexes

In contrast to kinetically inert complexes with an octahedral structure, kinetically labile complexes did not originally attract a great deal of attention from research workers. The two main reasons for this situation may be stated here. Firstly, the majority of kinetically labile complexes have a square planar or tetrahedral structure of the coordination polyhedron which were not considered conducive for the display of enantiomeric effects. Secondly, in contrast to kinetically inert complexes, where each diastereomer can be isolated and characterised in a pure state, with kinetically labile complexes the researcher is compelled to work with an equilibrium mixture of all possible forms, whose individual properties can only be obtained by calculation. This naturally complicates the investigation.

The increased interest in this class of coordination compounds is due to the development of ligand-exchange chromatography,[1] which is based on the use of enantioselective effects in labile systems.

Even in the initial studies carried out by Davankov et al.[2] relating to the simulation of processes in ligand-exchange chromatography, considerable enantioselective effects were found in square planar complexes of Cu^{2+} with bidentate *N*-alkyl-α-amino acid ligands.[2] These investigations were subsequently extended in studies by other scientists.

Ritsma[40] studied bis-complexes of bivalent Co, Ni, Cu, and Zn with *N*-(*o*-hydroxybenzyl)alanine. From his results it is clear that the addition of a second ligand (chiral amino acid) to the metal is enantioselective. In the case of Co and Ni the formation of structures that contained ligands of the same optical configuration proved more favourable. Ritsma accounts for the occurrence of enantioselectivity by the fact that Co and Ni ions form octahedral complexes. On the other hand, in Cu complexes (square planar configuration) or Zn (tetrahedral configuration) there was no enantioselectivity. The difference between the stability constants of log 0.3 reflects only a statistical preference for the *meso* structure compared with an equal-paired one.

Ritsma subsequently studied[41] a further series of tridentate amino acid ligands: histidine, α-*N*-methylhistidine, α-*N*,*N*-dimethylhistidine, α-*N*-benzylhistidine, aspartic acid, glutamic acid, and their complexes with Co(II), Ni(II), Cu(II), and Zn(II) ions. In this case enantioselectivity was found not only for octahedral Co(II) and Ni(II) complexes but also for some Cu(II) and Zn(II) complexes. Moreover, as detailed studies of copper complexes showed,[40] enantioselectivity depends to a considerable extent on whether the amino group of histidine is protonated or not; protonation causes a change in enantioselectivity so that the formation of an equal-paired structure is preferred.

These results were subsequently confirmed by Pettit et al.[42] In a potentiometric study of the stability of complexes of Co(II), Zn(II), Ni(II), Pb(II), and VO(II) with histidine in unprotonated complexes, enantioselectivity was only found for Co, Ni and Zn, but in monoprotonated complexes it also occurred for Cu.

The study of histidines was extended by Pettit[43] to imidazolyl-substituted derivatives. In the ternary complexes M(*N*-imidazolyl-substituted histidine)(*R*- or *S*-histidine), the formation of M(*R*)(*S'*) complexes was more favourable for Ni and Zn. For Cu there was no enantioselectivity in the unprotonated complex while in the monoprotonated complex formation of an M(*R*)(*R'*) structure was more favourable.

However, in studies on ternary complexes containing histidine (or its *N*-substituted derivative) and bidentate amino acid ligands, results were obtained that differed from those described above. In this case selectivity occurred as a rule in unprotonated complexes but in protonated complexes it was absent.[44–46] Moreover, substituents in the imidazole ring affected the degree of enantioselectivity much less than did substituents on the α-amino group. An even more unexpected result was that there was no enantioselectivity in the analogous Ni(II) complexes.[45] It was also not found in heteroligand complexes of copper with histidine when the second amino acid ligand was threonine, serine, proline, or methionine.[46]

In order to elucidate the mechanism of enantioselectivity, Pettit et al.[45,47,48] undertook a potentiometric study of ternary complexes of bidentate amino acids. In most of the systems studied the enantioselectivity was insignificant or absent but for the system Cu–proline–tryptophan the Cu(*S*)(*S'*) structure proved more stable than the Cu(*R*)(*R'*) complex by a factor of log 0.26.[45]

For complexes of Cu with serine and threonine there is very little difference between the stability constants of the diastereomeric structures but, on the other hand, there is a distinct difference in the enthalpy of formation of these structures, as determined by calorimetry.[47] The Cu(*R*)(*R'*) structure was preferred. However, its enthalpy advantage is completely balanced by the entropy contribution, so the free energies of formation of *meso* and equal-paired structures become the same. A similar ratio of enthalpy and entropy contributions in the formation of *meso* and equal-paired structures of the complexes was also found in the system Cu-*N*-benzylproline.[49] But there was not a complete balance of the contributions in this system and as a result of the predominance of the entropy contribution, the formation of a *meso* structure was preferred. At the same time, in a complex of Ni(II) with methionine both the enthalpy and entropy contributions favour the formation of a *meso* structure; it proves to be 2.72 kJ mol^{-1} more stable than the equal-paired structure.[48]

With an improvement in the process for calculating the stability constants of complexes and methods for studying equilibrium systems, research workers have repeatedly directed their attention to complexes of copper(II) with bifunctional α-amino acid ligands, trying to find enantioselectivity in this most simple system. Thus, Olin et al.[50–52] again studied the formation of complexes with optically active and racemic ligands for the following α-amino acids: valine,[50] proline, serine, threonine, tryosine,[51] and aspartic acid.[52] In the majority of the systems, according to the findings of earlier studies,[2] enantioselectivity was not found, but for valine and tyrosine complexes it was possible to detect slight enantioselectivity. In the case of valine the equal-paired structure was preferred (log β_2^{RR} = 14.698, log β_2^{SS} = 14.699, log β_2^{RS} = 14.690), while in the case of tyrosine the meso structure was preferred (log β_2^{RR} = 14.355, log β_2^{RS} = 14.360). However, the differences occurring in this case probably lie within the limits of experimental error for determination of the constants.

Enantioselectivity was recorded with much greater reliability in a study of heteroligand complexes of proline with a number of other bidentate amino acid ligands,[53] where formation of a Cu(*S*)(*S'*) structure proved to be more favourable. As was mentioned above,[45] enantioselectivity of the same sign was also found in a complex of copper(II) with proline and tryptophan, so that this effect can be regarded as typical in proline complexes. From this point of view, and this was stressed by Olin et al.,[53] it is surprising that there is no enantioselectivity in the homoligand bis-complex of proline with Cu(II).

Sakurai et al.[54–56] tried to detect enantioselectivity in copper complexes that contained amino acids with functional groups carrying different electrical charges or forming hydrogen bonds between themselves. It was suggested that in one of the diastereomeric structures of the complex, interactions between the functional groups will occur more readily than in the other. The systems copper(II)–(aspartic acid or glutamic acid)–(lysine, ornithine, or asparagine),[54] copper(II)–(histidine)–(asparagine, homoserine, glutamine, citrulline, serine, threonine, alanine, or valine)[55,56] were studied, but enantioselectivity was not found at all. The resolution of the amino acid enantiomers that occurs on crystallisation of the ternary complexes[57–59] is probably due to the enantioselectivity of the process for crystallising diastereomeric salts, which has been known since the time of Pasteur.

It should be mentioned that in other studies[60,61] enantioselectivity was in fact found in a system of ternary complexes containing histidine and an amino acid ligand. For diaminocarbonyl ligands the formation of complexes containing ligands of a single

configurational series was more favourable,[60] while for a Zn(histidine)(threonine) complex the Zn(*S*-His)(*R*-Thr) form was more stable.[61]

Angelici et al.[62] studied enantioselectivity in complexes of Co(II), Ni(II), Cu(II), and Zn(II) with β-(2-pyridyl)-α-alanine and β-(6-methyl-2-pyridyl)-α-alanine, regarding them as analogues of the histidine ligand. They found that for Co(II), Ni(II), and Zn(II) the formation of *meso* structures was more favourable (difference in stability constants of the diastereomers reaches almost log 1), while for Cu, as in the case of histidine, there is no enantioselectivity. The authors also showed that introduction of a methyl substituent into the pyridine part of the ligand molecule reduces the difference in stability between the diastereomeric forms of the complexes. They attribute this effect to the reduction in coordinating ability of the 6-methyl-substituted pyridine compared to the unsubstituted ligand.

No appreciable selectivity was found either in the formation of heteroligand complexes of copper(II) with *N*-carboxymethyl-β-(2-pyridyl)-*S*-α-alanine and valine. On the other hand, in ternary complexes of nickel with the pyridyl ligand, noticeable differences in the stability of diastereomers occurred for a whole series of amino acids (ratio of log K_2^{RS} to log K_2^{SS} was 0.25:1 for Ala, 0.21:1 for Ser, 0.56:1 for Val, and 0.26:1 for Phe).[63] The different behaviour of the copper and nickel complexes was attributed to the different structure of the coordination polyhedron in these metals — square planar in Cu(II) and octahedral in Ni(II).

Enantioselective formation of complexes often has an effect on the course of processes that take place in coordination compounds. Kitagawa et al.[64] described nickel complexes with 1,2-bis[2(*S*)-2-aminomethyl-1-pyrrolidinyl]ethane and its *N*-methyl-derivative that had the ability to catalyse enantioselectively the hydrolysis of α-amino acid methyl esters. At the same time these complexes were able to coordinate enantioselectively amino acid ligands, where in the case of the unsubstituted ligand *R*-enantiomers of alanine and valine were more strongly bonded while in the case of the *N*-methyl derivative it was the *S*-enantiomers of these amino acids and also proline that were more strongly bonded.[64,65] Kitagawa et al.[64,65] noted that there is a direct correlation between the enantioselectivity of the amino acid ligand coordination and the enantioselectivity for hydrolysis of their methyl esters. A similar mechanism for enantioselectivity also occurred for a copper complex of 2-[hexadecyl-*N*,*N*-(2-hydroxypropyl)aminomethyl]pyridine.[66] Micelles formed by this complex were used as a catalyst for the hydrolysis of *p*-nitrophenyl esters of amino acids. The authors maintain that by using micelles they were able to achieve a more than tenfold difference in the rates of hydrolysis of the enantiomers.

In a number of studies[1,67–86,90–95] investigation of enantioselective effects was carried out directly in conjunction with ligand-exchange chromatography. The authors tried to establish a relationship between the degree of enantioselectivity in forming model complexes in solution and the exit order of enantiomers in ligand-exchange chromatography of corresponding racemates on a chiral sorbent. Such studies were first carried out by Davankov et al.[1] in the case of copper complexes of *N*-benzylproline which simulated the coordination compounds formed in the sorbent phase that was obtained from a chloromethylated polystyrene matrix and proline. Subsequently Kurganov et al.[67–73] studied a large number of homo- and hetero-ligand coordination compounds of copper with α-amino acid,[67–70] 1,2-diamine,[71,72] and 1,3-dicarbonyl[73] types of ligands and demonstrated that enantioselectivity occurs in a number of systems. This included the detection of enantioselectivity for the first time in complexes containing diamine ligands.

Considerable attention was given in the studies of Kurganov et al.[67–83] to the mechanism for the occurrence of enantioselectivity. With this purpose the circular dichroism spectra of these coordination systems were studied in detail,[67,73–80] the molecular structures of a number of model complexes were established,[81,82] and a conformational analysis of complexes of copper with alanine and its *N*-methyl derivative was carried out.[83] It follows from conformational calculations[83] that in equilibrium solution as methyl derivatives are introduced on to the nitrogen atom in the ligand molecule the proportion of complexes with a *trans*-structure of the chelate bonding increases and the proportion of *cis*-structures decreases; so for *N*,*N*-dimethylalanine the latter can be ignored. At the same time the difference in conformational energy between the respective diastereomeric forms of the complexes increases in favour of the structure that contains ligands of a single configurational series. These results are in good agreement with the data of crystallographic studies in which both *trans*- and *cis*-structures were found for unsubstituted ligands (amino acids or diamines) but for *N*-alkyl derivatives all of the structures studied were of the *trans* type.[81,82] At the same time, calculated results should be supplemented with data on the entropy component of free energy since, as was mentioned above, the enthalpy (one of the components of which is the conformational energy) and entropy often provide opposing contributions to the total enantioselective effect.

Similar calculations were carried out by Simeon et al.[84–86] for a wide range of conformers of copper(II) complexes with *N*,*N*-dimethyl-valine or *N*,*N*-dimethylleucine (only the *trans*-structure of the chelate bonding was considered). According to their results each chelate ring (for example, *N*,*N*-dimethylvaline) has six local minima of conformational energy, one of which lies considerably apart ($\approx$10 kJ mol^{-1}) from all the others (this conformation is similar to that used in calculations on *N*,*N*-dimethylalanine complexes[83]). If the chelate rings are considered to be independent, a copper bis-complex of this ligand can exist in the form of 21 conformers, from which only three display noticeable enantioselectivity, all three containing the above-mentioned minimum-energy conformation at least for one of the chelate rings. The maximum enantioselectivity occurs for conformers in which both rings are in this favourable conformation. However, while for a complex containing *R*,*S*-ligands 98% of the conformers belong to this type, in complexes with *R*,*R*-ligands only 70% of the complexes have such a conformation since the conformational range is substantially greater in them than in complexes with *R*,*S*-ligands. This slightly reduces the enantioselectivity for the preferred formation of a *meso* structure.

From a detailed analysis of the structure of complexes and equilibria occurring in solution, it was later possible for Davankov et al.[87] to formulate a number of general rules for enantioselectivity to occur in square planar complexes with bidentate organic ligands. At the same time there was shown to be no clear correlation between the enantioselectivity of complex formation in solution and the enantioselectivity for separation of enantiomers by ligand-exchange chromatography in related systems. The reason for this proved to be that interactions between the complexes and the achiral stationary chromatographic phase play an active role in determining the enantioselectivity of chromatographic separation.[88] This follows from such an obvious example as the reversal in sign of enantioselectivity of the chromatographic system containing the same

chiral resolving agent and enantiomers being separated by simply changing the type of achiral stationary phase.[88] Moreover, it transpired that chromatographic separation of enantiomers is only possible when the enantioselectivity for the formation of complexes with a chiral selector in solution and on the surface of the stationary phase are different in magnitude (or even better, different in sign).[89]

In more recent studies[90–95] it was suggested that there must be a correlation between the enantioselectivity of formation of model complexes in solution and the enantioselectivity of a chromatographic system. Thus, Tsuchida et al.[90] compared the enantioselectivity of complex formation in the system Cu(II)–(*N*-benzyl-*S*-leucine)–(alanine, valine, or leucine) with the enantiomeric separation of these amino acids on a chiral sorbent obtained by the reaction of *S*-leucine with a chloromethylated copolymer of styrene and divinylbenzene. French research workers[91–95] examined systems of complexes that simulated sorbents, obtained by the reaction of *S*-proline with chloromethylpolystyrene[91,92] or polyacrylamide[93,94] and *S*-phenylalanine with chlorosulphonated polystyrene.[95] In a number of cases qualitative agreement was obtained between the exit order of the enantiomers from the chromatographic column and the enantioselectivity of complex formation in model systems. In the cases where it was absent the authors suspected that the models used were inadequate. In actual fact a model cannot be adequate if it does not transmit the essential adsorptive interactions between the diastereomeric complexes and the achiral surface or matrix of the sorbent.[88,89]

Enantioselectivity in labile complexes with other types of ligands has been studied much less than for amino acid ligands. Pettit and Swash[96] studied the enantioselectivity of complex formation between $[VO]^{2+}$ and tartaric acid ($tartH_2$). They found quite a large number of polynuclear structures in this system, from which a noticeable difference in the stability complexes with racemic and optically active ligands was only found for $[VO]_2(tart)_2(OH)_4$. The structure containing two ligands with opposing optical configurations is more stable.

The same type of relationship of the stabilities of diastereomeric structures of complexes was found for coordination compounds of Cu(II) with tartaric acid.[97] In this case the complex Cu(*l*-tart)(*d*-tart) is approximately twice as stable as the Cu(*l*-tart)$_2$ complex. While enantioselectivity is insignificant for hydroxo complexes present in the system, equal-paired structures are more stable for polynuclear structures with the composition $Cu_2(tart)_2$, the difference in the stability constants being so great (4×10^8 and 0.2×10^8) in an equilibrium solution of a racemic ligand, complexes with the composition Cu_2(*l*-tart)(*d*-tart) are virtually absent (less than 1%).

Petit-Ramel et al.[98] found enantioselectivity in the formation of heteroligand complexes of copper(II) with *N,N'*-dimethyltartramide and mandelic acid. In this case the complex containing *d*-tartaric acid amide and *l*-mandelic acid proved to be more stable ($\log \beta_{111} = 17.78$). The stability constant of the complex containing *d*-tartaric acid amide and *d*-mandelic acid was lower by a factor of log 0.72.

The reasons for enantioselectivity to occur in these systems, which have a large number of various polynuclear forms, were examined by Tapscott.[99] He wrote a review[100] of the studies on complexes of tartaric acid, in which there is a section devoted to enantioselectivity and a discussion on the thermodynamics of the disproportionation of the complexes $(VO)_2$(*l*-tart)$_2(OH)_4$ and $(VO)_2$(*d*-tart)$_2(OH)_4$ to $(VO)_2$(*l*-tart)(*d*-tart)$(OH)_4$.[101] The enthalpy of this reaction is equal to 1.46 kcal mol^{-1}, which is an indication of the greater stability of the *meso* structure, with a content of not less than 96% in the equilibrium solution, compared to the equal-paired form.

The enantioselectivity of formation of gadolinium and dysprosium complexes with the tartaric acid analogue—α-hydroxysuccinic acid—was studied.[102] The stability constant of the complex with an optically active ligand was less than the stability constant of the complex with racemic hydroxysuccinic acid. Enantioselectivity occurs here in the formation of tris- as well as bis-complexes.

In contrast to α-hydroxysuccinic acid, *O*-phosphoserine did not show any noticeable enantioselectivity in complex formation with Co(II), Ni(II), or Cu(II), but for Zn(II) the equal-paired structure proved more stable than the *meso* structure (by a factor of log 0.28).[103] Enantioselectivity was found[104] in the coordination of histidine with the complex triaqua-tribenzo[*b,f,j*][1.5.9]triazacyclodecylnickel(II). The respective constants for formation of ternary complexes for *S*-His and *R*-His were 7.26 and 7.42. By using this difference in the stability of the heteroligand complexes, Erno and Jordan[104] were able to separate the initial homoligand complex into optical isomers and use it subsequently for the resolution of racemates of a number of other amino acids. However, in the latter case successful resolution is only achieved when two or three recrystallisations of the heteroligand complexes are used, and therefore the question of enantioselectivity occurring in them cannot be regarded as conclusive.

IV. Enantioselective effects in kinetically inert and kinetically labile coordination compounds that accompany outer-sphere ligand exchange

Enantioselective effects of outer-sphere complex formation are known in the chemistry of coordination compounds as the Pfeiffer effect (PE).[105–107] The latter first observed the following phenomenon: there is a change in the angle of rotation of (+)-α-bromocamphor-π-sulphonic acid when it is added to a solution of a racemic $Zn(phen)_3$ complex.[108] With the development of chiro-optical methods for studying PE, circular dichroism spectroscopy started to be used instead of optical rotation measurement.

The first explanation for PE was given by Dwyer,[109] who proposed that in placing a racemic compound in an optically active medium, the equilibrium between the enantiomeric forms is displaced in favour of one of them. He noted at the same time that associates (outer-sphere coordinate compounds) also contribute to PE, those involving enantiomers of the complex and an optically active component of the solution. The resulting associates are no longer enantiomeric but diastereomeric and hence they can have an unequal stability and occur in solution in unequal quantities. Moreover, their molar chiro-optical properties also cannot have the same absolute value.

A further reason for PE was disclosed by Mason,[110] who showed that electronic transitions not only for racemic complexes (i.e., chiral by nature) but also for achiral compounds can be optically active from the effect of a chiral medium. This effect was found by him in the case of the complex $[Co(NH_3)_6]^{3+}$ in a solution of tartaric acid. The extensive occurrence of this phenomenon was subsequently demonstrated.[111–114]

By correlating the results of different authors, Schipper[107,115] proposed two main mechanisms for the occurrence of PE:

associative and nonassociative (inductive). The latter, in essence, is similar to the chiral induction mechanism of Mason. The associative mechanism, according to Schipper, involves three types of equilibria:

$$\Delta\text{-antipode} + S\text{-inductor} \rightleftarrows \Delta\text{-antipode}.S\text{-inductor} \quad (1a)$$
$$\Lambda\text{-antipode} + S\text{-inductor} \rightleftarrows \Lambda\text{-antipode}.S\text{-inductor} \quad (1b)$$
$$\Delta\text{-antipode}.S\text{-inductor} \rightleftarrows \Lambda\text{-antipode}.S\text{-inductor} \quad (2)$$
$$\Delta\text{-antipode} \rightleftarrows \Lambda\text{-antipode} \quad (3)$$

The first of these equilibria represents the formation of diastereomeric associates, while the second and third represent a displacement of the equilibria between associates or enantiomers. All of these equilibria occur simultaneously:

$$\begin{array}{ccc} \Delta + S & \overset{(1a)}{\rightleftarrows} & \Delta\cdot S \\ {\scriptstyle(3)}\downarrow\uparrow & & \downarrow\uparrow{\scriptstyle(3)} \\ \Lambda + S & \underset{(1b)}{\rightleftarrows} & \Lambda\cdot S\,. \end{array}$$

The following equilibrium constants relate to these processes:

$$K^{1a} = \frac{[(\Delta\cdot S)]}{[(\Delta)]\,[(S)]},\quad K^{1b} = \frac{[(\Lambda\cdot S)]}{[(\Lambda)]\,[(S)]},$$
$$K^{2} = \frac{[(\Lambda\cdot S)]}{[(\Delta\cdot S)]},\quad K^{3} = \frac{[\Delta]}{[\Lambda]}.$$

In the case of kinetically labile complexes the equilibria are established rapidly and the observed PE is the total result of all these processes. For kinetically inert complexes the situation is complicated by the slowness in establishing equilibrium and the occurrence of additional kinetic enantioselective effects. On reaching equilibrium, the relationship $K^{1b}/K^{1a} = K^3/K^2$ will be fulfilled for all types of coordination compounds. Thus, PE can be characterised either by the difference in the stability constants of the resulting diastereomeric adducts or by the difference of the epimerisation constant of the resulting adduct from unity (the racemisation constant of the enantiomers). The latter case, according to Dwyer,[109] indicates the shift in chiral equilibrium between enantiomers in an optically active medium.

The occurrence of PE is usually monitored from the change in chiro-optical properties of the system, namely, from the change in angle of rotation or solution ellipticity of the chiral inductor in the presence of a coordination compound. In general, in accordance with the scheme given above, the chiro-optical property of an equilibrium solution can be represented in the following manner:[116]

$$\alpha = \alpha_S[S] + \alpha_\Delta([\Delta] - [\Lambda]) + \alpha_{\Delta\cdot S}[\Delta\cdot S] + \alpha_{\Lambda\cdot S}[\Lambda\cdot S], \quad (4)$$

where α_S, α_Δ, $\alpha_{\Delta\cdot S}$, and $\alpha_{\Lambda\cdot S}$ are the molar characteristics of the chiro-optical properties of the inductor, complex, and adducts respectively.

By analysing equation (4), Ogino and Kumagai[116] came to the conclusion that PE can occur even when there is no redistribution in the concentrations of enantiomers (i.e., $K^{1a} = K^{1b}$) or the chiro-optical properties of the diastereomeric associates appear to be enantiomeric ($\alpha_{\Delta\cdot S} = -\alpha_{\Lambda\cdot S}$). Usually these values differ from each other and the observed PE constitutes the change in chiro-optical properties of the solution both from the change in concentrations of the optically active components already in solution and from the appearance of new ones.

Mason et al.[117] studied PE in a system of racemic complexes $M_3[Cr(ox)_3]$ (ox = oxalate) in optically active esters of α-hydroxy-acids and found that the complex undergoes "antiracemisation" to the extent of 70% whatever the type of M and the configuration of the ester. The effect is completely eliminated by the addition of an equivalent of a crown ether to the solution. Miyoshi et al.[118,119] interpreted PE in a similar manner for $[Co(ox)_2(phen)]^-$ [118] or $[Cr(ox)_3]^{3-}$ and $[Co(phen)_3]^{3+}$ [119] complexes in solutions of quinine, quinidine, cinchonidine, or their derivatives. The same authors studied PE in the case of $[Cr(ox)_2(phen)]^-$ and $[Cr(ox)_2(dipy)]^-$ complexes in the presence of *N*(1)-methyl and 9-acetyl derivatives of the same alkaloids.[120] They showed that the magnitude of the shift of the chiral equilibrium mainly depends on the configuration of the C(8) and C(9) atoms of the alkaloid and that it is greater for acetyl derivatives than for unsubstituted alkaloids. Out of the complexes studied the greatest shift was achieved in $[Co(ox)_2(phen)]^-$ in the presence of 9-acetoxyquinidine (28.3% of enrichment with the Λ-isomer), 9-acetoxyquinine (22.4% of enrichment with the Δ-isomer), and *N*(1)-methyl-9-acetoxyquinine (23.8% of enrichment with the Δ-isomer). The rate constants of racemisation of the Δ- and Λ-isomers of $[Co(ox)_2(phen)]^-$ were also determined in the presence of the same alkaloids, and it was shown that an accumulating isomer in this system had a lower rate of racemisation. Miyoshi et al.[121] demonstrated the possibility of using coordination compounds as a chiral inductor and examined in detail PE for $[Co(ox)_3]^{3-}$ in the presence of optically active *cis*-[M-diamine)$_2$(X)(Y)] complexes, where M = Cr or Co; diamine = ethylenediamine (en) or diethylenetriamine (tr); X, Y = Cl^-, NH_3, NO_2^-, $C_2O_4^{2-}$, and acac. In order to confirm the possibility of a shift in the equilibrium between Δ- and Λ-enantiomers of $[Co(ox)_3]^{3-}$, the authors determined the rate of their racemisation in the presence of $[Co(en)_2(NO_2)_2]$Br enantiomers. Since the rate of racemisation in the Δ−Δ-system proved to be somewhat lower than in the Δ−Λ-system, the authors assumed that in a solution of Δ,Λ-$[Co(ox)_3]^{3-}$ when Δ-$[Co(en)_2(NO_2)_2]$Br is added, Δ-$[Co(ox)_3]^{3+}$ will accumulate. It is evident however that these conclusions are not completely correct. Firstly, while the oxalate complex undergoes racemisation, the chiral inductor will also racemise. Moreover, in many cases equilibrium is established in the system more rapidly than racemisation of $[Co(ox)_3]^{3-}$ takes place even in the presence of the optically active [M(diamine)$_2$(X)(Y)], which is an indication that it is not racemisation that is the rate-determining stage for PE.

A whole series of studies by Japanese authors[122–133] is devoted to the effect of different factors (the ionic strength of the solution, the presence of the organic solvent, the type of optically active inductor) on the magnitude of PE. In several studies[125,126,134–138] data on the structure of the associates formed in solution are given. According to these data, various interactions — ionic, hydrophobic, van der Waals — can cause the formation of adducts.[131] Even when the same charges occur on a complex and inductor it does not exclude the possibility of their association.

In the majority of cases the formation of associates occurs through hydrogen bonding. This conclusion is supported by the results of studying the structure of associates by both indirect methods[125–127,139] and the direct findings of X-ray diffraction analysis.[140–143]

Bosnitch and Watts[144] calculated the thermodynamic parameters of the shift in chiral equilibrium for a $Ni(phen)_3$ complex in (−)-2,3-butanediol: $\Delta H = -119$ cal mol^{-1} and $\Delta S = -0.28$ cal K^{-1} mol^{-1}. They also determined the rate constants of racemisation of (+)- and (−)-$Ni(phen)_3$ in this solvent and detected a difference in the rates of racemisation of the enantiomers which was in good agreement with the magnitude of the shift of the chiral equilibrium in the system (+)-$Ni(phen)_3$ − (−)-2,3-butanediol.

Mayer[145] had previously reported some results for the system (+)-$Ni(phen)_3$ − *L*-Glu that were not in such good agreement; the time of half-racemisation of the complex in this system was 14 h

while the PE equilibrium was reached after only 25 min. In order to overcome this contradiction, Mayer[145] proposed a new mechanism for PE—the mechanism of asymmetric modulation. Gillard et al.[146] suggested that the possibility of hydration of the phenanthroline or dipyridyl ligands (it is complexes of these ligands which are most widely used for studying PE), which results in the formation of new asymmetric sites, should be taken into account.

These studies indicate that in a number of cases PE can include specific processes inherent in individual systems, but these processes should not be regarded as general principles of the PE mechanism, especially as all the contradictions mentioned above can readily be eliminated if the enantioselectivity of association is taken into account.

Barton et al.[147] explain the phenomenon of PE in deoxyribonucleic acid (DNA) with $[Zn(phen)_3]^{2+}$ from these points of view, while Bartery et al.[148] use the same explanation for the change in peroxidase activity of an enzyme in the presence of Fe^{3+} chelates. It was subsequently shown[149] that enantioselective association of DNA also takes place with the $[Ru(phen)_3]^{2+}$ complex, with the right-hand spiral of DNA containing mainly the Δ-isomer of the complex. Yamagishi[150] confirmed these observations in the case of other tris-chelate complexes of transition metals.

It is interesting to note that if a $[Ru(phen)_2Cl_2]$ complex is used instead of $[Ru(phen)_3]^{2+}$ and hence there is a change from outer-sphere complex formation to inner-sphere (Cl ions are replaced), the Λ-structure of $[Ru(phen)_2Cl_2]$ will mainly be contained in the DNA spiral,[151] with one $[Ru(phen)_2]^{2+}$ species for every 11 pairs of nucleic bases. Thus, the enantioselectivity of inner- and outer-sphere coordination in these very similar systems proved to be directly opposite. A review was published by Barton[152] on the studies of enantioselective coordination of DNA with transition metal complexes, and the mechanism of the interaction of DNA with ruthenium complexes is discussed in detail in another study.[153]

Hemmes and Lee[154] studied PE for a complex of $[Zn(phen)_3]^{2+}$ with adenosine monophosphate and related compounds. They found quite considerable optical activity brought into this system, and they related it to the formation of associates with the following composition: 1 molecule of $[Zn(phen)_3]^{2+}$ to 2 molecules of adenosine monophosphate. The strength of these associates is mainly achieved through electrostatic interactions.

Association processes have also been studied in a fairly detailed manner for kinetically inert complexes.[136,155–167] In a number of systems thermodynamic enantioselectivity has been reliably detected. Formation constants of associates were not determined for some complexes but it has been clearly established by indirect methods[168,169] that they differ. In other cases the difference between the constants is within the limits of experimental error or absent altogether,[170,171] and hence PE is solely due in this case to the difference in chiro-optical properties of the diastereomeric associates.

Attempts have been made over a long period of time to establish a correlation between the absolute configuration of a chiral compound and the sign of PE occurring for it.[106,121,172–176] Definite progress was made in this direction but, as is noted by Miyoshi et al.,[177] it is first of all necessary to make an accurate assignment of the transition in the circular dichroism spectrum on which the correlation is carried out, and this is not always possible. Moreover, the occurrence of PE is due to a whole number of processes, the relative importance of which can vary significantly from system to system. Moreover, the suggestion put forward by Kirschner and Ahmad[176] that the observed PE reflects the spectroscopic characteristics of that enantiomer of the complex with which the solution is enriched gives rise to doubt.

Brittain et al.[178–187] studied the induced optical activity of tris-complexes of Eu(III) and Tb(III) with pyridine-2,6-dicarboxylic acid or 4,4,4-trifluoro-1-(2-thienyl)butane-1,3-diol in the presence of amino acids,[178,179] optically active chromium complexes,[180] amino alcohols,[181,182] ascorbic acid,[183] hydroxyphenyl derivatives of amino acids,[184] *N*-substituted amino acids,[185,186] and sugars.[187] Thus, the study of PE was extended to lanthanide complexes. The results obtained in these studies[178–187] are of considerable significance for the determination of the optical purity of organic compounds using a chiral shift reagent. In fact, in this case the formation of an outer-sphere complex (and perhaps an inner-sphere one) also takes place, and since an optically active lanthanide complex and a racemic (or enantiomerically enriched) organic ligand take part in reaction, the reaction can be enantioselective. Therefore the intensity of the signals from the two diastereomeric associates can depend, in addition to other factors, on the enantioselectivity of this process. Although NMR is extensively used to determine optical purity (see, for example, two studies[188,189] and subsequent reports[190–194]), its use for studying the enantioselectivity of complex formation has not been widely applied so far (see the study of Krasutskii et al.[195] and the references in it).

A very special case was reported in 1978 by Garvey and Pope.[196] The authors found PE in the heteropolyanions $[P_2Mo_{18}O_{62}]^{6-}$ and α-$[P_2W_{18}O_{62}]^{6-}$ in the presence of *l*-brucine. Another similar system—$[MnMo_9O_{32}]^{6-}$—was later found by Nomija et al.[197] Since the structure of a heteropolyanion rules out the possibility of its racemisation, PE occurs here solely as a result of the difference in the association constants and the differences in the chiro-optical properties of the adducts [equilibria (2) and (3) in the scheme given above do not occur].

In conclusion we should mention the study of Shigematsu et al.,[198] in which the formation of an axial adduct between a trifluoroacetyl-*d*-camphor copper(II) complex and phenylethylamine was studied. The formation constant of the adduct with the *d*-amine was approximately 2.5 times higher than with the *l*-amine. Formally this system can be classed as a complex with inner-sphere ligand exchange, since direct binding between the amine and the metal atom occurs in the adduct, and also as an outer-sphere complex, since the axial ligands are bonded to the copper atom much more weakly than the ligands of the main coordination sphere.

V. Enantioselective effects in the reactions of coordination compounds that occur without ligand exchange

A typical example of a potentially enantioselective reaction that takes place without involving a chiral chemical compound is the action of circularly polarised light on complexes (similar reactions are known for racemic organic compounds).[199] The essence of this effect is that enantiomers absorb light energy to a different degree when they are irradiated with right-handed and left-handed circularly polarised light.[200,201] This can lead to an unequal degree of photodestruction or other photochemical processes and hence to an accumulation in solution of that enantiomer which absorbs light energy to a lesser extent. Of course, for this effect to occur it is essential that racemisation of the complex without irradiation takes

place very slowly or not at all. Enantioselective photolysis was demonstrated experimentally in the case of complexes of Cr(III) with acetylacetone or its derivatives,[201–206] oxalic acid,[207,208] and phenanthroline,[209] in which the fundamental rate constant of racemisation has a value of the order of 10^{-6} s^{-1}. In all cases the observed enantiomeric enrichment did not exceed 5%, which is an indication of the small degree of enantioselectivity of such processes.

Approximately the same degree of enantiomeric enrichment also occurred in systems where linearly polarised light was used rather than circularly polarised light, but irradiation was carried out in an optically active medium.[209] The difference in the absorption of light in this case was due to the formation of diastereomeric associates. Yoneda et al.[210] studied these processes in greater detail in $[Cr(ox)_3]^{3-}$, $[Cr(ox)_2(phen)]^-$, $[Cr(ox)(phen)_2]^+$, and $[Cr(phen)_3]^{3+}$ complexes in the presence of *d*-cinchonine or *l*-cinchonidine. They established that a solution on irradiation is enriched with the same enantiomer of the complex which accumulates as a result of dark PE.

Less conclusive results were obtained by Norden[211] by irradiation of a solution of Cr(III) in the presence of racemic tartaric acid with circularly polarised light. In this solution a large number of isomeric forms of complexes can be formed and it is not clear towards which isomers the equilibrium is shifted on irradiation. Norden[211] suggests that the occurrence of optical activity in solution is mainly due to the isomerisation

$$\Lambda\text{-Cr}(R\text{-tart})_3 \rightarrow \Delta\text{-Cr}(R\text{-tart})_3$$
and
$$\Delta\text{-Cr}(S\text{-tart})_3 \rightarrow \Lambda\text{-Cr}(S\text{-tart})_3.$$

The question of enantioselectivity occurring in electron-transfer reactions between complexes also proved to be controversial. It was reported[212] that if the racemic complex $[Cr(phen)_3]^{2+}$ is oxidised by $\Lambda\text{-}(+)_D\text{-}[Co(phen)_3]^{3+}$, 92% $\Delta\text{-}(-)_D\text{-}[Cr(phen)_3]^{3+}$ and 8% $\Lambda\text{-}(+)_D\text{-}[Cr(phen)_3]^{3+}$ is formed. However, Kane-Maguire et al.,[213] having checked these results, could not detect any noticeable optical activity in the resulting $[Cr(phen)_3]^{3+}$. She then studied a further 13 different systems in which electron transfer occurs and in which enantioselectivity could be expected to occur, but her endeavours were unsuccessful. She concluded from these results that enantioselectivity is not present in outer-sphere redox processes.

Geselowitz and Taube,[214] having examined the results of previous studies,[213] came to the conclusion that the required ratio of the rates of oxidation to racemisation was not fulfilled, so enantioselectivity could not be detected. Having chosen as their research topic the reaction between $\Delta,\Lambda\text{-}[Co(edta)]^-$ and $\Delta\text{-}[Os(bipy)_3]^{3+}$, they demonstrated that this reaction leads to the formation of $[Co(edta)]^-$ that is 3% enriched with the Δ-isomer. Similarly, when $\Lambda\text{-}[Os(bipy)_3]^{3+}$ was used, the same excess of $\Lambda\text{-}[Co(edta)]^-$ was obtained. Subsequently, these and a number of other electron-transfer reactions were studied in detail by Lappin et al.[215–219] They confirmed that enantioselectivity occurred in these processes and noted the important role of the conformation of the ligands[215] and the structure of the complex[219] for enantioselectivity to take place. They also showed that there was a correlation between the enantioselectivity for formation of outer-sphere associates between oxidising agent and reducing agent and the enantioselectivity of electron-transfer.[216,217] The important role of the solvent in these processes was studied by Geselowitz et al.[220]

In studying energy transfer (from emission spectra) between terbium and europium ions, Brittain[221] found that complexes of terbium with racemic aspartic acid transfer their energy to a europium ion more effectively than complexes with optically active aspartic acid. It is worthy of note that all attempts to find any difference in the properties of complexes of terbium with *R*- or *S*- and *R,S*-aspartic acids by other methods (potentiometric titration, spectrophotometry) were unsuccessful.

Enantioselectivity was shown to occur in processes involving electrochemical oxidation/reduction of complexes when this process is carried out using an optically active electrolyte. Thus, the reduction of $Co(acac)_3$ in the presence of trimethyl-(–)-menthylammonium results in optical activity in the unreduced complex.[222,223] The enantioselectivity of this process was small, but Ohkubo et al.[222,223] were confident of increasing it through the choice of a suitable supporting electrolyte.

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