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Stereodynamics and degenerate ligand exchange in solutions of tetracoordinate chelate complexes of nontransition metals

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Abstract. Nontransition metal (d^0, d^{10}) chelate complexes possessing a tetrahedral configuration at the metal centre undergo fast intramolecular stereoisomerisation and intermolecular ligand exchange reactions in solution. Inversion of the stereochemical configuration is governed by two types of intramolecular reaction: (1) polytopal rearrangement (digonal twist) and (2) dissociation-recombination reaction due to the cleavage-formation of one of the metal–ligand bonds. The energetically preferred mechanism for the inversion is chiefly determined by the nature of the metal, but it also depends on the type of ligating atoms and their environment. The energy barriers to the inversion of the tetrahedral configuration vary in the range of 10–30 kcal mol^{-1}. The bibliography includes 175 references.

I. Introduction

As long as two or three decades ago, the structure of a molecule was regarded as fully described by its three-dimensional geometrical representation. Currently, such a description may be considered as inadequate if it is not complemented by data on the degree of stereochemical nonrigidity of the molecule. Stereochemical nonrigidity implies the ability of the molecule to undergo fast and reversible intramolecular isomerisation. The energy barrier to this is lower than that allowing for the preparative isolation of individual isomers at room temperature. Owing chiefly to the remarkable progress in the development of NMR spectroscopic technique and its wide application to the study of dynamic processses, the tendency of virtually all types of molecular structures to display stereochemical nonrigidity has been established. The degree of such nonrigidity is regulated by electronic and steric factors. It is the rigidity of the molecular structure (i.e. its association with a very deep minimum on the potential energy surface) that is to be regarded as a characteristic molecular property, whereas stereochemical nonrigidity—the ability of the molecule to fluctuate between several isomeric or topomeric forms separated by an energy barrier lower[1,2] than 20–25 kcal mol^{-1}—is a general property of the molecular structure. Thus the full structural description of a molecule must also include, in addition to three spatial dimensions, a fourth, time (or energy) dimension—the lifetime of the molecule in the given geometrical coordination.

The mechanisms of stereochemical nonrigidity are extremely varied. For metal coordination compounds, these may be categorised, in principle, into two main types: (1) rearrangements of compounds with multicentre bonds (π-complexes, organometallic clusters, polyhedral boranes and carbaboranes); (2) isomerisations and topomerisations (i.e. degenerate rearrangements) of the coordination poly-hedra formed by the central atom by means of two-centre two-electron bonds. In the terminology of the topological and graph-theoretical descriptions of the isomerisations of metal clusters and polyhedral structures, the two types are classified as globally delocalised and edge delocalised mechanisms respectively.[3]

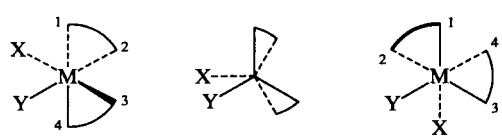
Formally, the rearrangements of coordination polyhedra may be thought of as permutations of the ligands in the central atom environment. The character of such a permutation defines the so called permutation mechanism[4,5] of the rearrangement. Nuclear magnetic resonance (NMR) spectroscopy serves as the most powerful tool for the differentiation of various permutational rearrangements including those of the degenerate type. It should be borne in mind, however, that in some cases certain types of permutation mechanisms are not NMR-distinguishable. In recent years, the potential of NMR spectroscopy in the study of the kinetics and selection of the mechanisms of chemical reactions has been substantially enhanced by the development of two-dimensional (2D) NMR spectroscopic methods.[6] The applications of 2D NMR in studies of chemical exchange reactions occurring in solutions of organometallic and metal coordination compounds have been reviewed.[7,8] Examples of the successful use of three-, four-, and even five-dimensional NMR spectroscopy in characterising the dynamics of organic and metal coordination compounds are known.[9]

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The determination of the permutation mechanism of the rearrangement is the initial stage of the investigation into the real (physical) mechanism of the processes determining the stereochemical nonrigidity. After the permutation mechanism has been elucidated, it must be assigned to a specific physical process involving the displacement of atoms and atomic groups within one or several interacting molecules, i.e. attributed to definite isomerisation or topomerisation reactions. Several different physical mechanisms can correspond to the same permutation mechanism. This general approach to the analysis of the mechanisms of stereochemical nonrigidity has been currently employed in the study of a wide range of metal complexes with central atom coordination numbers varying from 2 to 9.[10] As the number of ligands attached to the central atom grows, the number of possible permutation mechanisms increases rapidly and the types of the corresponding metal-centred intramolecular rearrangements become more diverse. Nevertheless, regardless of the complexity of the initial structure, the intramolecular rearrangements can be divided into two main classes in terms of the type of isomerisation: isomerisation (topomerisation) of the coordination centre without intermediate breakage of individual bonds (polytopal rearrangements[11]), and isomerisation via a dissociation-recombination mechanism. In the latter case, an intermediate with a reduced coordination number of the central atom usually arises in the course of the rearrangement.

The above mechanisms of the stereochemical nonrigidity have been most fully characterised in the case of pentacoordinate[1,12,13] and hexacoordinate[14–18] metal complexes. Depending on the structure of the complex and to a lesser extent on the nature of the medium, a particular mechanism predominates. Thus in the case of bischelate hexacoordinate complexes *cis*-$M(AB)_2XY$, a polytopal rearrangement of the trigonal twist type constitutes the only low energy barrier mechanism of the inversion of the octahedron for titanium(IV) dialkoxybis(β-diketonates)[17] and phenylchlorobis(benzoylacetonato)tin(IV).[16] One of the four rearrangement mechanisms, determined by the rotation relative to one of the four C_3 axes of the octahedron, is presented below.



1a **1c** **1b**

However, in the case of the (2,6-diisopropylphenoxy)titanium bischelate complexes based on 8-hydroxyquinoline or 8-hydroxyquinaldine[19] the rate-limiting stage of the configurational rearrangement involves the dissociation of one of the Ti–N bonds of the chelate ring, while in the case of dialkoxy(dimethyl phosophorodithioate)titanium(IV), the dissociation of the Ti–S bond assumes this role.[20] Pentacoordinate trigonal-bipyramidal structures arise as intermediates. Their importance for the mechanism of the stereoisomerisation of octahedral complexes was already predicted by Werner.[21]

Intermolecular associative mechanisms, involving the formation of intermediates with an increased coordination number of the central atom, are an alternative to the intramolecular stereoisomerisation mechanisms.[22–24] In those cases where nucleophilic catalysis of the stereoisomerisation is ruled out and a noncoordinating solvent is employed, the role of the nucleophilic species may be assumed by a second molecule of the complex, one (or two) donor atoms of which are coordinated to the central metal atom of the first molecule. The addition process is usually followed by a polytopal rearrangement in the intermediate with an increased coordination and then by a stage involving the splitting off of the leaving group (dissociation of one of the initial bonds). If the leaving ligand passes to the coordination environment of the metal in the second complex molecule (Scheme 1), such autosubstitution or degenerate ligand exchange reaction can be regarded as a manifestation of the stereochemical nonrigidity of the dimeric associated species.

Scheme 1

$$ML_n + M^*L_n^* \rightleftharpoons [MM^*L_nL_n^*] \rightleftharpoons \rightleftharpoons ML_{n-1}L^* + M^*L_{n-1}^*L$$

The present review deals with processes in which the stereochemical nonrigidity of tetracoordinate chelate complexes of nontransition metals (i.e. having unfilled d^0 or filled d^{10} electron shells according to IUPAC rules[25]) with a tetrahedral configuration in the ground electronic state is manifested. For comparison, data on intramolecular stereoisomerisation processes in solutions of tetrahedral chelate nickel complexes, occurring on the NMR time scale, are also considered. The identification and kinetic characteristics of the three fundamental types of rearrangement mechanisms (polytopal rearrangement, dissociation-recombination mechanism, and associative degenerate ligand exchange mechanism) are emphasised.

The stereoisomerisation of compounds of dicoordinate and tricoordinate nontransition elements (planar, pyramidal, and edge forms of inversion) are usually considered in the context of ideas concerning the stereochemistry of organic compounds (see, for example, Refs 26–28). The permutation and physical mechanisms of the stereochemical nonrigidity of pentacoordinate[12,13,29,30] and hexacoordinate[4,12–14,18,29] structures have been analysed in fair detail. Theoretical[29,31–33] and experimental[34,35] data on fluctuating hepta- and octa-coordinate metal complexes as well as complexes with higher (up to 12) coordination numbers[3,36,37] are rapidly accumulating. On the other hand, only short sections in an early review by Holm[1] and in a recent review[38] have been devoted, apart from the original communications, to the molecular dynamics of tetracoordinate metal complexes. The aim of the present review is to fill this gap.

II. Stereochemically nonrigid structures with tetracoordinate centres

The main type of dynamic rearrangements of stereochemically nonrigid structures of tetracoordinate transition and nontransition metal complexes is the interconversions of the tetrahedral and planar forms. The case of bischelate complexes based on asymmetric bidentate ligands (AB), which includes the interconversion of enantiomeric tetrahedral structures and the geometrical isomerisation of *cis*- and *trans*-planar structures, is fairly general. The scheme presented in Fig. 1 reflects two possible cases:† (1) the tetrahedral form corresponds to the most stable structure of the ground state (Fig. 1*a*) and (2) the planar (square) form is energetically more favourable (Fig. 1*b*). The latter version is more characteristic of transition metal complexes.

Not only the relative energies of the tetrahedral and planar structures but also the type of the stationary point on the potential energy surface corresponding to them depend critically on the nature of the central atom and the ligand structure. In the case of nontransition metal complexes of the type $M(AB)_2$, it has not been possible hitherto to detect reliably planar forms in equilibrium with tetrahedral forms‡ and, as follows from the results of

† The true symmetry of the coordination unit in the $M(AB)_2$ complexes (Fig. 1) is lower than the symmetry of the tetrahedron or square. However, it has become usual in the literature to designate these complexes as tetrahedral or square planar, emphasising the topological and not the geometrical characteristics.

‡ Individual communications concerning the existence in solution of equilibrium between the tetrahedral and planar tetracoordinate nontransition metal structures can be encountered in the literature. Thus, according to ^{1}H NMR data, magnesium(II) bisacetylacetonate exists[34] in solutions as two forms: tetrahedral (D_{2d}) and planar (D_{2h}).

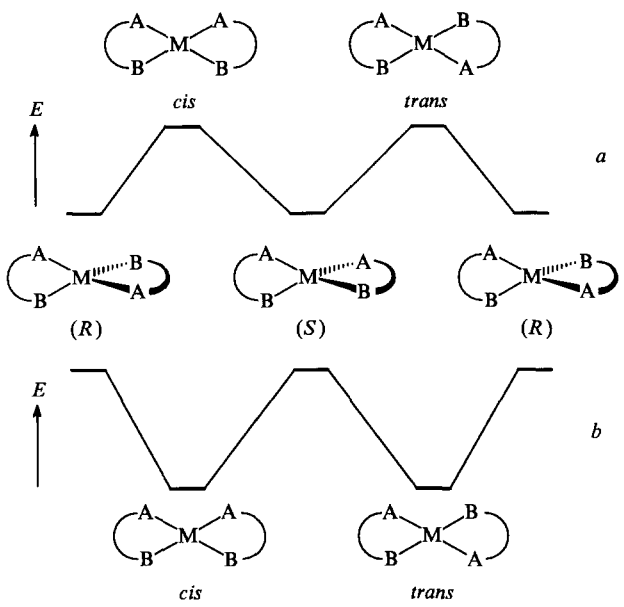


Figure 1. Schematic illustration of the configurational isomerisation of the tetrahedral structures of bischelate metal complexes: (*a*) M = non-transition metal; (*b*) M = transition metal.

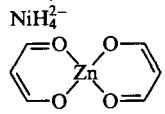
quantum-chemical calculations discussed below, they represent not metastable forms but the structures of transition states or even correspond to higher-order saddle points[39] in the interconversions of tetrahedral structures.§ The reverse situation, where tetrahedral structures correspond to transition states in the *cis–trans* isomerisation reactions of planar forms, is characteristic of Pt(II) and Pd(II) complexes.[35] The *trans*-planar and tetrahedral[41,42] or *cis*-planar and tetrahedral[43,44] forms of Ni(II) complexes may be stable and may coexist in solution. In the crystalline state, complexes of tetracoordinate Cu(II) and Ni(II) can assume configurations over a wide range, intermediate between planar and tetrahedral, depending on the structure of the ligands.[38,45]

The rate of the interconversions of the tetrahedral and planar structures of nickel(II) complexes in solution reaches 10^6-10^{13} s^{-1}.[1,46] In contrast to this, the tetrahedral structures formed by Group IVA elements possess a high degree of stereochemical rigidity. As can be seen from the data in Table 1, which presents the energy differences between the stable tetrahedral and square planar structures of the hydrides AH_4 calculated by nonempirical quantum-chemical methods, these quantities exceed the A–H bond dissociation energies, which implies that polytopal rearrangements of the type square ⇆ tetrahedron cannot be achieved.

Direct calculations and analysis based on allowance for the second-order Jahn–Teller effect[47-49] indicate the principal ways in which tetracoordinate structures can undergo a structural modification leading to a decrease in the energy gap between the tetrahedral and planar configurations. For the MX_4 structures with d^0 or d^{10} electronic configurations of the central atom, which is less electronegative than the carbon atom, the highest occupied molecular orbital of the square planar form has the b_{1g} symmetry, while the electronic ground state is $^1A_1(\delta)$. The lower the electronegativity of the central atom M and the higher the electronegativity of the ligand atoms X, the smaller the energy

§ A communication based on STO-3G calculations[40] concerning the possibility of the existence of a local minimum for the $C_{21}H_{28}$ (octaplane) structure, containing a planar tetracoordinate carbon atom between two chair-shaped cyclooctane rings, has appeared recently. However, the strain energy is ~15 kcal mol^{-1} per carbon atom for this hydrocarbon.

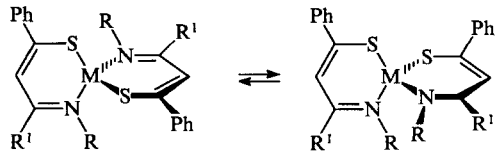
Table 1. The energy barriers to the planar inversion of the tetrahedral hydrides and fluorides MX_4 according to the results of nonempirical quantum-chemical calculations.

MX_4	Method of calculation	$\Delta(E_{D_{4h}}-E_{T_d})$ /kcal mol^{-1}	Ref.
CH_4	MP2/6-311+G**	141 [a]	47
SiH_4	3-21G*	95	47
SiH_3Cl	3-21G*	77 [b]	47
SiH_3NH_2	3-21G*	64 [b]	47
$Si(NH_2)_4$	3-21G*	53	47
BH_4^-	MP2/6-31G*	140	50
AlH_4^-	STO-3G*	76	50
CF_4	MP2/DZ+P	127	28, 51
SiF_4	MP2/DZ+P	63	28, 51
GeF_4	MP2/DZ+P	48	28, 51
SnF_4	MP2/DZ+P	37	28, 51
ScH_4^-	DZDH+P	28	48
TiH_4	DZDH+P	46	48
NiH_4^{2-}	8*S* 6*P* 3*d* (8*s*,6*p*,3*d*)	−26 [c]	52
	MINI	12	53

[a] The most rigorous of the currently available estimates[39] [MCSCF-6-31G(*d*,*p*), all the singly and doubly excited configurations are taken into account] is 159.5 kcal mol^{-1}.
[b] The energy difference between the C_{2v} and C_{3v} forms is presented.
[c] The planar D_{4h} form is stable.

difference between the planar and tetrahedral forms. Indeed, in the case of SnF_4 the energy difference expected on the basis of calculated data is close to the range of energy barriers for stereochemically nonrigid structures, while in the case of the bischelate Zn(II) complex with the ZnO_4 coordination unit it falls within this range.

The structure of the first stereochemically nonrigid transition metal complexes **2**, investigated in the pioneer study by Eaton and Holm,[54] corresponds fully to the criteria considered. These investigators observed for the first time that the tetrahedral bischelate Zn(II) and Cd(II) complexes of type **2**, containing electronegative nitrogen and sulfur atoms coordinated to the metal atom, undergo in solution the reversible enantiomerisation $(R) \rightleftarrows (S)$ associated with the inversion of the configuration of the tetrahedral metal atom occurring on the ^1H NMR time scale.

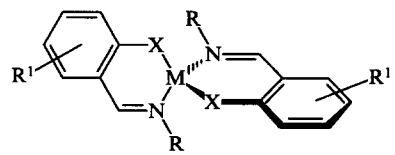


2(*R*) **2**(*S*)

M = Zn, Cd; R = Pr^i, CH_2Ph; R^1 = H, Me

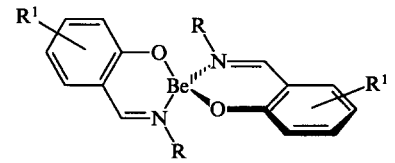
The presence of prochiral substituents R in dissymmetric chelate structures **2** makes it possible to detect the enantiomerisation process by NMR without resorting to the preliminary separation of the (*R*)- and (*S*)-enantiomers. The energy barriers to the enantiomerisation process, found from data for the temperature dependence of the diastereotopic averaging of the signals due to the methyl protons of the isopropyl group or the methylene protons of the benzyl group, amounted to ~21 kcal mol^{-1} for Zn(II) complexes and 12–15 kcal mol^{-1} for Cd(II) complexes.

It was soon shown that the tetrahedral bischelate Zn(II) and Cd(II) type **3** complexes[55] and Be(II) type **4** complexes[56,57] also exhibit stereochemical nonrigidity, whereas the kinetic and activation parameters of the enantiomerisation process $(R) \rightleftarrows (S)$ depend greatly on the nature of the donor atom X and the substituents R^1.



3

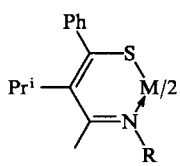
M = Zn, Cd; X = O, S, Se;
R = Pr^i, CH_2Ph
$\Delta G_{25}^{\neq}$ = 9.8–22.3 kcal mol^{-1}.



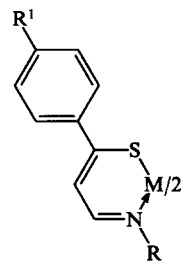
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R = Pr^i, CH_2Ph
$\Delta G_{25}^{\neq}$ = 22–24.5 kcal mol^{-1}.

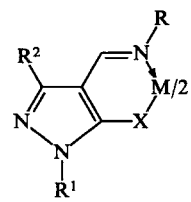
A fairly wide range of chelate complexes of nontransition (as well as transition) metals exhibiting stereochemical nonrigidity in solutions has now also been investigated. The principal structural types of such complexes are represented below by formulae **5**–**15**.



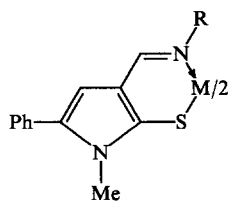
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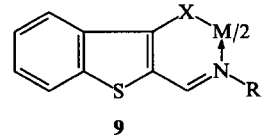
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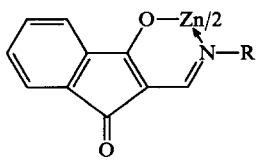
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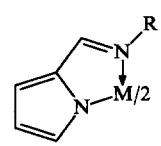
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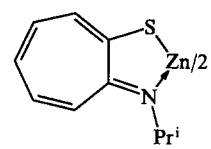
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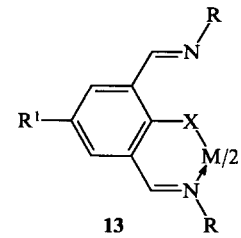
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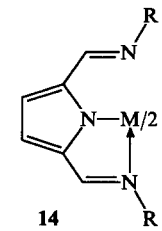
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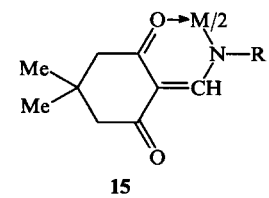
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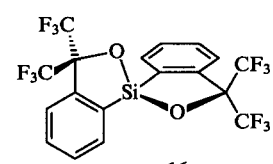
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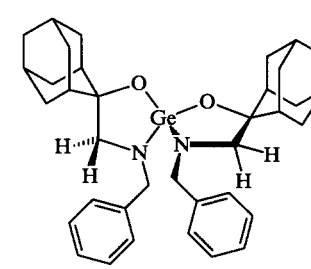
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M = Be, Zn, Cd, Hg, Pb; M/2 = BAr(Y);
Y = Ar′, OAlk, $GaMe_2$, $InMe_2$;
X = O, S, Se; R = Pr^i, CH_2Ph, Ar, Alk;
R^1 = H, Cl, Br, OMe, Me, NO_2, Alk, Ar;
R^2 = Me, Pr^i.

The tetrahedral configuration inversion processes have been studied in much less detail for compounds of Group IVA elements. Early communications stating that the bicyclic orthosilicic acid esters can have a preferred planar structure[58] or a low barrier to the conversion of the tetrahedral (D_{2d}) form into the planar form[59] were not subsequently confirmed. However, for another tetracoordinate silicon derivative (compound **16**), the energy barrier to the intramolecular inversion with transition through a planar structure, estimated as 28 kcal mol^{-1} from the data quoted by Martin et al.,[60] is close to the upper limit of the energy scale for stereochemically nonrigid structures.



16



17

Apparently the first true stereochemically nonrigid structure with a tetrahedral centre (a tetracoordinate Group IVA element) was the germanium spirane **17**.[61] The inversion barrier determined from data derived from the temperature dependence of the ^1H NMR spectrum in the region of the signals of the diastereotopic methylene protons (toluene-d_8) amounted to 22.2 ± 2.5 kcal mol^{-1}.

III. The mechanisms of the stereochemical nonrigidity of tetracoordinate structures

An important question arising in the study of inversion processes is that of the choice of the energetically preferred reaction pathway. Three principal mechanisms, capable of leading to the inversion of the configuration of the central atom of the coordination polyhedron, were indicated above. They are presented in Fig. 2 for a specific case—the inversion of the configuration of the central atom in the tetrahedral bischelate complexes of Group IIA–IVA elements, to which all the compounds of types **2**–**17** belong.

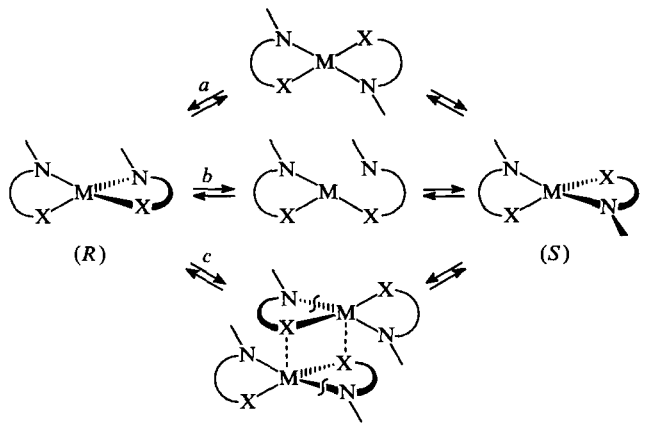


Figure 2. General scheme of the inversion mechanisms for tetrahedral bischelate complexes **2**–**17**: (*a*) polytopal rearrangement of the digonal twist type involving passage through a planar *trans*-structure; (*b*) intramolecular process determined by the dissociation-formation of one of the M–N bonds; (*c*) intermolecular degenerate ligand exchange process.

The intramolecular processes include, apart from the polytopal rearrangement occurring via the digonal twist mechanisms without the dissociation of the metal–ligand bonds (see, for example, Muetterties[11]) with formation in the transition state (or as intermediates) of *trans*- or *cis*-structures (the latter are not shown in Fig. 2) (pathway *a*), also a mechanism involving the dissociation of one of the metal–ligand bonds. The dissociation of this bond leads to the formation of an intermediate tricoordinate achiral structure, which then rapidly recyclises (pathway *b*). The third mechanism leading to the inversion of the configuration of the tetrahedral metal atom is associated with intermolecular ligand exchange proceeding via the formation of a dimeric structure via pathway *c* or *b*+*c*.

Studies have shown that all three types of mechanisms considered operate in thermal reactions involving the inversion of the configuration of the tetrahedral centre in metal chelate complexes. The choice of the preferred pathway in the inversion process is dictated mainly by the nature of the metal, but it depends significantly also on other structural features of the complex.[38] The general methodology, widely applied in various studies, is based on the following four effective approaches: (1) the introduction into the structures of the stereochemically nonrigid complexes **2**–**15** of prochiral groups R as substituents at the nitrogen atoms as well as into other parts of the molecules of the complexes; (2) the introduction of 'spin labels', usually magnetic ($S = ½$) isotopes of the metal atoms and the ligating atoms; (3) structural modelling of the dissociation-recombination mechanism in complexes of types **13**–**15** based on alterdentate ligands, i.e. ligands in which the number of structurally equivalent donor centres exceeds the coordination capacity of the metal;[62] (4) the determination of the kinetic orders (n) of the observed degenerate transformations by investigating the dependence of the lifetime (τ) of the exchanging states on the solute concentration and using the relation

$$\tau^{-1} = kc^{n-1} , \qquad (1)$$

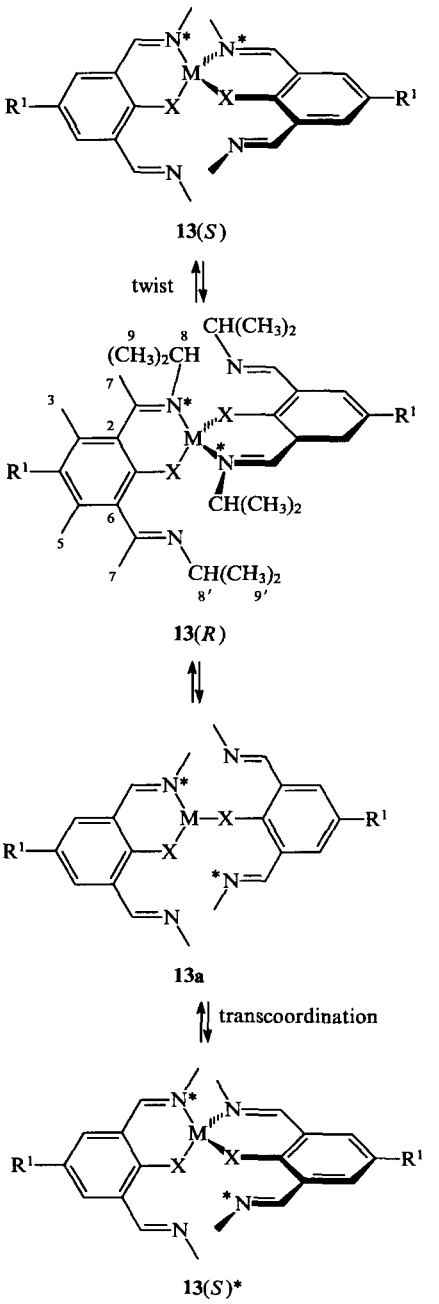
where k is the rate constant for the reaction of kinetic order n and c is the concentration of the solute.

We shall consider briefly what information about the mechanism of the inversion process can be extracted when each of the above approaches is employed.

1. The standard procedure for the introduction of prochiral groups such as Pr^i or CH_2Ph into an asymmetric or dissymmetric structure and analysis of the temperature-dependent diastereotopic averaging[24,63–65] makes it possible to detect the interconversion of enantiomers, by-passing the operation involving their preliminary separation, under conditions of unrestricted monitoring of the reversibility and reproducibility of the experiment. The dynamic process recorded in this way does not, however, permit the differentiation of the possible ways in which the molecule can undergo a structural reorganisation, leading to the inversion of the tetrahedral configuration of the central metal atom.

2. The introduction into the molecular structure of a 'spin' label — a metal isotope with a half-integral spin ($^{111,113}Cd$, ^{199}Hg, ^{207}Pb) linked by spin–spin coupling to the ligand nuclei — makes it possible to observe directly the metal–ligand bond dissociation-formation processes via pathways *b*, *c*, or *b* + *c* (Fig. 2). These processes can be detected both by investigating the temperature dependence of the line forms of the corresponding spectral multiplets (the disappearance of the metal–ligand nucleus spin–spin coupling constant on dissociation of the bond) and with the aid of two-dimensional NMR spectroscopic methods.

Scheme 2



If, however, the lifetime of the intermediate structure [the tricoordinate intermediate on pathway *b* (Fig. 2)] is shorter than the relaxation time of the metal and ligand nuclei linked by spin–spin coupling, the correlation of the spins of these nuclei is retained, while the spin–spin coupling is manifested in the spectrum despite the occurrence of an intense intramolecular dissociative process.[66] In this admittedly rare case, the observation of a temperature dependence of the spin–spin coupling constant is not diagnostic in the study of the inversion process mechanism.

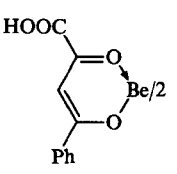
3. The dissociative type *b* inversion mechanism (Fig. 2) has been detected, for example, in the study of the structural nonrigidity of complexes **13** with bischelate rings based on alterdentate ligands, i.e. ligands providing the metal with two equivalent imine donor centres. In view of the steric hindrance, the alternative donor centres in complex **13** cannot participate simultaneously in intramolecular coordination. However, in the presence of dissociative processes (modelling pathway *b* in Fig. 2), the recombinations of the metal–nitrogen bond on recyclisation of the intermediate tricoordinate structure **13a** with participation of each of the unoccupied donor centres are equally probable. The intramolecular transcoordination (bond switching) process occurring under these conditions, illustrated in Scheme 2, has been reliably detected by the NMR method from the averaging of the signals due to the nuclei, separated by the effective plane of symmetry, under the conditions of rapid exchange.

4. The observation of a concentration dependence for the exchange processes detected by NMR spectroscopy is a clear indication of the intermolecular nature of the reaction and of the inclusion of degenerate ligand exchange processes in the overall stereochemical result of the reaction. The importance of taking this process into account (pathway *c* in Fig. 2) had been already indicated in the pioneer study of Eaton and Holm,[54] who noted that, in the case of Cd(II) chelates (complex **2**), the rate of associative processes involving the inversion of the tetrahedral configuration of the metal atom is very close to the rate of the intramolecular reaction. Careful allowance for the associative reactions proceeding via the ligand exchange mechanism (Scheme 1) is essential, particularly in the light of data[67] indicating the appreciable association of the chelate complexes in solutions in noncoordinating solvents.

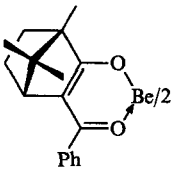
The combination of the above approaches to the study of the kinetics of processes involving the inversion of the tetrahedral configuration of metal chelate complexes, with specific structural modelling of the latter, has made it possible to penetrate to a considerable extent details of the mechanisms of structural nonrigidity in solution and also to establish the principal characteristics of the influence of the nature of the metal atom, the donor atoms, and substituents in the ligands on the kinetics of the inversion process $(R) \rightleftarrows (S)$ and the possible ways of achieving it. The data obtained are presented and discussed in the present review in conformity with the type of metal, starting with beryllium and boron complexes and ending with heavy metal (lead and mercury) complexes. The review also contains a section on the dynamic tetrahedral configuration inversion processes in bischelate Ni(II) complexes. Reactions whose rates permit their direct observation on the NMR time scale are discussed. Although nickel in its usual oxidation state Ni(II) is a typical transition metal, the nature of the stereodynamic processes in solutions of its complexes is extremely close to that of the processes determining the inversion of the configuration of the central nontransition metal atom in complexes **2**–**15**.

IV. Beryllium complexes

In the early experiments on the preparative separation of optical isomers of bischelate Be(II) complexes — bis(benzoylpyruvato)-beryllium **18** and bis(benzoylcamphorato)beryllium **19** — based on the crystallisation of the diastereoisomeric salts with brucine, an enrichment of the racemic mixture in one of the enantiomers was already achieved and mutarotation was observed in solution at the usual temperature.[68,69] The energy barriers to the racemisation reaction, calculated later[56] from the polarimetric data presented in the above studies,[68,69] are 21–25 kcal mol^{-1} depending on the solvent.



18



19

Energy barriers to the $(R) \rightleftarrows (S)$ enantiomerisation of beryllium bis(*N*-alkyl-5-R^1-salicylaldiminates) **4** close to the above values were found from the temperature dependence of the change of line shape of the signals due to the diastereotopic methyl and methylene groups of the Pr^i and CH_2Ph substituents at the nitrogen atom.[56,57,70]

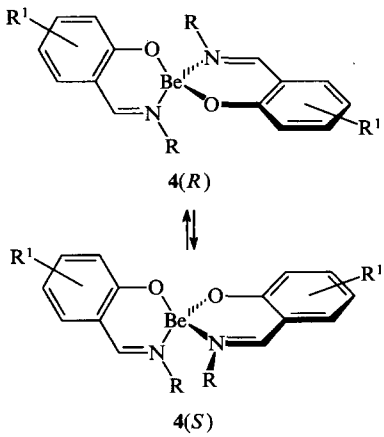
Table 2 presents the results of the kinetic studies on processes involving the inversion of the tetrahedral configuration of beryllium in complexes **4** (Scheme 3), obtained with the aid of the dynamic ^{1}H NMR method.

Table 2. Kinetic and activation parameters of the enantiomerisation of type **4** Be(II) bischelate complexes (solvent — nitrobenzene).[56,57,70]

R	R^1	$10^4 k_{25}$/s^{-1}	$\Delta H^{\neq}$/kcal mol^{-1}	$\Delta S^{\neq}$/cal mol^{-1} K^{-1}	$\Delta G^{\neq}_{25}$ [a]/kcal mol^{-1}
Pr^i	H	3.6	24.0	6.4	22.1 (22.2/143 °C)
CH_2Ph	H	5.8	22.0	−3.9	23.2
Pr^i	5-Br	3.6	24.9	6.4	22.1 (22.4/147 °C)
Pr^i	5-NO_2	7.9	30.0	18.8	24.4 (23.4/167 °C)
Pr^i	5,6-C_6H_4	1.4	26.8	13.8	22.7
Pr^i	3-NO_2	2.2	21.2	−3.2	22.4
Pr^i	5-OMe				(22.4/131 °C)
Pr^i	5-Me				(21.7/139 °C)
Pr^i	5-Cl				(22.1/144 °C)

[a] The free energies of activation estimated[56,70] at the temperature corresponding to the coalescence of the signals of the diastereotopic groups are presented in brackets.

Scheme 3



The energy barriers increase with increase in the electron-accepting capacity of the substituent R^1 and are satisfactorily correlated with Hammett's σ constants.[70]

$$\Delta G^{\neq}_{T_c} = 1.81\sigma + 21.96 \text{ (kcal mol}^{-1}\text{)} \quad (2)$$

The variation of the concentrations of solutions of complexes **4**, listed in Table 2, in the range $10^{-3}-10^{-1}$ M is not reflected in the rate of isomerisation. This indicates the absence of a contribution by degenerate ligand exchange intermolecular processes (pathway *c* in Fig. 2) to the observed kinetics of the inversion of the configuration of the tetrahedral beryllium atom: **4**(*R*) ⇄ **4**(*S*).

In order to choose between the alternative intramolecular pathways *a* and *b* (Fig. 2), a study was made of the thermal enantiomerisation of the bischelate type **13** (X = O) beryllium complexes obtained from alterdentate ligands (Scheme 2).[71,72]

The ^{1}H NMR spectra of beryllium complexes **13** at room temperature include two sets of signals due to nonequivalent protons of the chelated and nonchelated aldimine fragments [(7,7′), (8,8′), and (9,9′)] and the benzene ring (3,5) (for the numbering of the atoms, see Scheme 2). The protons of the diastereotopic methyl groups 9 and 9′ are anisochronic and are represented by doublets of doublets in the spectra. If the stereoisomerisation occurred solely via the digonal twist mechanism *a*, the chemical exchange process would reduce to the temperature-dependent exchange-induced broadening and coalescence of the signals due to the diastereotopic groups of the prochiral substituents. In contrast to this, the dissociative mechanism *b*, which involves the formation and recyclisation of the tri-coordinate intermediate **13a** (M = Be), should lead not only to diastereotopic averaging but also to averaging of the signals due to the ^{1}H and ^{13}C nuclei in the 3,5-, 2,6-, 7,7′-, 8,8′-, and 9,9′-positions.

The observed temperature-dependent evolution of the line shapes of the indicator signals of all the type **13** beryllium complexes corresponds to the transcoordination of the metal atom with dissociation of the M–N bonds and enantiomerisation involving both possible types of reactions: **13**(*R*) ⇄ **13**(*S*) and **13**(*R*) ⇄ **13a** ⇄ **13**(*S*)′.

It has been found[71,72] that, within the limits of the usual experimental errors, the energy barriers to the dynamic processes detected from exchange averaging of the (7,7′) and (3,5) pairs of indicator signals and the signals due to the diastereotopic 9,9′-groups, calculated using the full analysis of the line shape, are the same. Variation of the concentrations of the solutions hardly affects the kinetics of the observed reactions, which agrees with the first-order kinetics of the reaction (n = 1) in Eqn (1). The rate constants and activation parameters for the enantiomerisation of complexes **13** (M = Be) in solution in nitrobenzene-d_5 are presented in Table 3.

Table 3. Kinetic and activation parameters of the enantiomerisation of type **13** (X = O, R = Pr^i) Be(II) bischelate complexes (solvent — nitrobenzene-d_5).[71,72]

R	$10^5 k_{25}$/ s^{-1}	$\Delta H^{\neq}$/ kcal mol^{-1}	$\Delta S^{\neq}$/ cal mol^{-1} K^{-1}	$\Delta G^{\neq}_{25}$/ kcal mol^{-1}
H	7.2	23.7	2.3	23.1
Me	4.2	27.3	13.3	23.4
Br	46	23.8	5.5	22.2
OMe	52	23.8	6.3	21.9
NO_2	0.16	28.8	11.8	26.3

Comparison with the data on the kinetics of the enantiomerisation of complexes **4** (Table 2) shows that the free energies of activation for the dynamic processes involving both types of complexes with analogous substitution are very similar. This serves as a basis for the hypothesis that the enantiomerisation **4**(*R*) ⇄ **4**(*S*) (Scheme 3) also takes place via a dissociative mechanism (pathway *b*, Fig. 2) and not via the alternative pathway *a* involving a polytopal rearrangement.

The results of theoretical modelling with the aid of the MNDO method of the mechanism of the inversion of the tetrahedral configuration of the Be atom in the bis(*N*-methylaminopropenoato)beryllium complex, differing from complex **4** by the absence of condensed benzene rings, fully agrees with this conclusion. The energy barrier calculated for the dissociation-recombination inversion mechanism is lower by 8–10 kcal mol^{-1} for the stereoisomerisation involving transition through planar *trans*- or *cis*-tetracoordinate structures.[73]

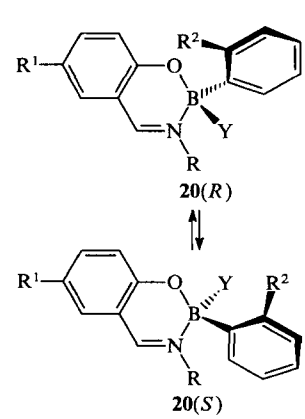
An attempt[74] to investigate by dynamic ^{1}H NMR the inversion process in Be(II) and Zn(II) β-diketonates containing a prochiral isopropyl group in the 2-position was unsuccessful. The diastereotopic methyl groups in these complexes remained isochronic up to −80 °C.

Since, as mentioned above, the bischelate Be(II) complexes with the analogous type of chelate unit BeO_4 can be separated into optical isomers by a preparative procedure (see also Ferroni and Cini[75]), Ronsisvalle et al.[74] attribute this fact to the extremely small diastereotopic splitting in the prochiral substituent which is more remote from the stereogenic centre in these complexes than in complexes **4**.

V. Complexes of boron, gallium, and indium

The thermal inversion of the configuration of the tetrahedral boron atom was first investigated quantitatively in 2,2-diaryl-5,6-benzo-1,3,2-oxazaborines **20** — chiral monochelates formed by the imine derivatives of aromatic *o*-hydroxyaldehydes and asymmetric diarylborinic acids incorporating an asymmetric boron atom (Scheme 4). The tetrahedral configuration of the bonds at the boron atom was characterised by X-ray diffraction of

Scheme 4



R = Pr^i, CH_2Ph; Y = Ar, OAlk.

Table 4. Kinetic and activation parameters of the enantiomerisation of type **20** boron chelates.[78,79]

R	R^1	R^2	Y	Indicator group	k_{25}/s^{-1}	$\Delta H^{\neq}$/ kcal mol^{-1}	$\Delta S^{\neq}$/ cal mol^{-1} K^{-1}	$\Delta G^{\neq}_{25}$/ kcal mol^{-1}
Pr^i	H	H	*o*-$MeOC_6H_4$	Pr^i	9.3×10^{-3}	20.6	1.1	20.2
Pr^i	Br	H	*o*-$MeOC_6H_4$	Pr^i	1.3×10^{-2}	21.6	5.5	20.0
Pr^i	H	H	1-$C_{10}H_7$	Pr^i	1.1×10^{-2}	22.5	6.3	20.1
Pr^i	Br	H	1-$C_{10}H_7$	Pr^i	7.9×10^{-3}	22.3	6.6	20.2
Pr^i	NO_2	H	1-$C_{10}H_7$	Pr^i	1.5×10^{-3}	23.8	8.6	21.3
Pr^i	H	MeO	1-$C_{10}H_7$	Pr^i	1.1×10^{-2}	22.4	7.6	20.1
Pr^i	Br	MeO	1-$C_{10}H_7$	Pr^i	3.0×10^{-2}	21.0	4.8	19.5
Pr^i	NO_2	MeO	1-$C_{10}H_7$	Pr^i	3.8×10^{-3}	23.9	10.5	20.8
CH_2Ph	H	MeO	1-$C_{10}H_7$	Pr^i	8.6×10^{-4}	23.6	6.8	21.6
Me	H	H	OPr^i	Pr^i	4.2×10^{-1}			17.9
CH_2Ph	H	H	OPr^i	Pr^i	6.7×10^{-2}			19.0
				CH_2Ph	6.9×10^{-1}			17.7
Pr^i	H	H	OMe	Pr^i	5.0×10^{-1}			17.8
Pr^i	NO_2	Me	OCH_2Ph	Pr^i	7.1×10^{-1}			17.5
				CH_2Ph	2.5			16.9
Pr^i	H	Me	OCH_2Ph	Pr^i	6.2×10^{-1}			17.8
				CH_2Ph	3.0			16.8
Me	5,6-C_6H_4	Me	OCH_2Ph	CH_2Ph	7.7×10^{-2}			19.0
Pr^i	5,6-C_6H_4	Me	OCH_2Ph	Pr^i	7.2×10^{-2}			19.0
				CH_2Ph	1.1			17.4
CH_2Ph	5,6-C_6H_4	Me	OMe	CH_2Ph	8.8×10^{-1}			17.6

Note. *o*-Dichlorobenzene was the solvent in the first nine cases and bromobenzene in the remaining cases.

certain compounds of this type.[76,77] The presence of prochiral isopropyl and benzyl groups in compound **20** (Y = Ar) makes it possible to investigate the dynamics of the enantiomerisation in accor-dance with Scheme 4 by means of dynamic ^1H and ^{13}C NMR without enriching the racemate in one of the enantiomers. The energy barriers to the inversion process (Table 4) are in the range 19.6–21.5 kcal mol^{-1} [78–80] which is lower by 1–2 kcal mol^{-1} than the barriers observed in the enantiomerisation (Scheme 3) of beryllium complexes **4** based on the analogous salicylaldimines.

The energy barriers listed in Table 4 depend only slightly on the nature of the substituents R, R^1, R^2, and Y. However, as in the series of type **4** beryllium compounds, in complexes **20** the maximum barrier is attained when the electron-accepting NO_2 group is present in the *para*-position relative to the oxygen of the salicylaldiminate fragment.

Change in solvent polarity and increase in solute concentration from 0.1 to 3 M do not exert an appreciable influence on the stereoisomerisation kinetics. The intermolecular degenerate ligand exchange processes were modelled by mixing in solution various pairs of boron chelates **20** containing different substituents. The reaction proceeds at an appreciable rate only at temperatures above 90–100 °C. Thus, in the above temperature range the contribution of the intermolecular degenerate ligand exchange process to the inversion mechanism is insignificant, which makes it possible to make a choice between the intramolecular variants *a* and *b* (Fig. 2).

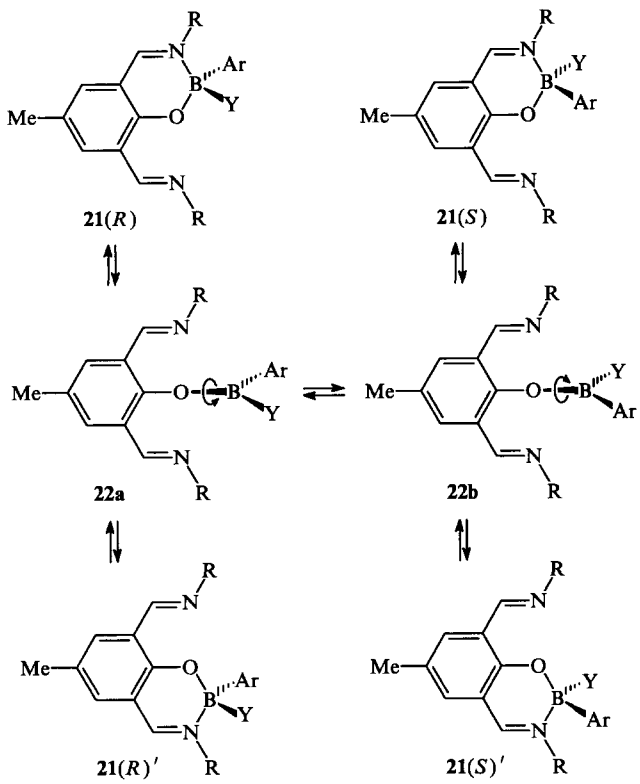
The hypothesis was put forward initially[80] that the digonal twist type polytopal rearrangement mechanism is more probable. This mechanism is favoured, in conformity with predictions,[59,81] by the presence at the boron atom of π-donor (O) and σ-acceptor (O, N) ligating centres, which stabilise the planar structure with a tetracoordinate boron atom. However, MNDO calculations carried out by Schleyer and Würthwein[82] for the model 1,3,2-oxazaborine led to the conclusion that structures with a tetracoordinate planar or pyramidal boron atom are in general unstable and cannot correspond to the transition states in the tetrahedral inversion reaction. The calculations[82] revealed another structure of the transition state, incorporating a tricoordinate boron atom with a single ruptured B–N bond. The calculated activation energy for the inversion of the configuration of the boron atom via this mechanism proved to be extremely close to the experimental values obtained for compound **20** (Table 4). Subsequent calculations[83] carried out with a higher degree of approximation (*ab initio*, 4-31G) yielded a different structure of the transition state in the tetrahedral inversion process, corresponding to the digonal twist type with a planar tetracoordinate boron atom, but its energy relative to the structure of the ground state (95 kcal mol^{-1}) was found to be much higher than the experimental inversion barriers.

Boulton and Prado[84] were the first to draw attention to the possibility of using the specific features of the spectroscopic behaviour of chiral chelate boron complexes of type **13**, based on alterdentate ligands, as a test which makes it possible to separate the intramolecular stereoisomerisation processes $(R) \rightleftarrows (S)$ via pathways *a* and *b* (Fig. 2). By analysing the temperature-dependence of the ^1H NMR spectra of a series of type **13** monochelates of diarylboron (M/2 = BArAr′, X = O, R = CH_2Ph, R^1 = Me), obtained from 2,6-bis(*N*-benzylideneamino)-4-methylphenol, the above investigators estimated the energy barriers to the B–N bond dissociation-formation reaction in these compounds at the temperatures corresponding to the coalescence of the signals due to the methylene protons of the benzyl groups in solutions in $CD_3OC_6H_4Cl$-*p* (~20 kcal mol^{-1}), which proved to be comparable with the energy barriers to the enantiomerisation of the boron chelates **20**. On this basis, it was concluded that the inversion of the tetrahedral configuration of the boron atom in compound **20** also proceeds via a dissociative mechanism involving the dissociation of the B–N bond.

However, a direct comparison of the dissociative reaction and the polytopal twist rearrangement (which should have been reflected by the diastereotopic averaging of the signals due to the methylene protons of the benzyl group) proved to be impossible for the type **13** compounds investigated in the above study.[84] As a result of the considerable temperature drift, the AB multiplet of the methylene protons of the benzyl group is transformed on raising the temperature into an average singlet virtually without intermediate broadening. For the same reasons, it proved impossible to characterise quantitatively the inversion processes for some of the compounds **20** with substituents R = CH_2Ph described by Korobov et al.[78]

A better justified identification of the mechanisms of the inversion of the configuration of the tetrahedral boron atom in chelate complexes was achieved in the study of compounds **13** (M/2 = BArAr′, R = Pr^i) and 2-alkoxy-5,6-benzo-1,3,2-azaborines of types **20** and **21**, containing a second prochiral substituent Y at the boron atom.[79]

Scheme 5



The tetrahedral inversion of the chelates **21** (Y = OPr^i, OCH_2Ph) is independent of concentration. It was characterised quantitatively on the basis of the diastereotopic averaging of the signals of the *N*- and/or *O*-isopropyl and the corresponding benzyl substituents. The energy barriers to the inversion reaction (Table 4) were found to be slightly lower (by 1–2 kcal mol^{-1}) than those found for the diarylboron chelates **20**.

The dynamic ^{1}H NMR spectra of compounds **21** (Nos. *1–3* in Table 5) reveal separately the occurrence of two dynamic processes. The inversion of the enantiomers (*R*) ⇄ (*S*), which reflects overall both possible reaction pathways, *a* and *b* (Fig. 2), is detected from the diastereotopic averaging of the signals due to the Pr^i and $PhCH_2$ groups in the substituent Y. The dissociative reaction involving the dissociation-formation of the B–N coordinate bonds is detected from the dynamic averaging of the chemical shifts of the signals due to the protons of the chelated and non-chelated aldimine fragments and also from the averaging of the ^{1}H and ^{13}C signals from the benzene ring linked to the aldehyde fragments.

The overall mechanism of the stereodynamic processes in compounds **21** (Nos. *4–7* in Table 5) is reflected by the reactions presented in Scheme 5. Two parallel reaction pathways, which rule out the inconversion of the intermediates (**22a** ⇄ **22b**), correspond to the interconversion–transcoordination processes in the temperature range below 110 °C detected in the dynamic ^{1}H NMR spectra of compounds of this type. The stereoisomerisation mechanism presented in Scheme 5 is clearly visualised by 2D exchange ^{1}H NMR spectra. The dissociation of the B–N bond and the formation of intermediates are detected from the appearance of four multiplet cross-peaks for compound **21**, (R = Y = OCH_2Ph, Ar = Ph), with which the frequencies of the downfield and upfield components of the doublets of doublets due to the methyls of the isopropyl groups at different nitrogen centres are correlated.

Rotation about the B–O bond in complexes **22a–b** requires an additional energy expenditure and takes place at a higher temperature. The energy barriers to the interconversion (*R*) ⇄ (*S*) and transcoordination in compounds **21** (Table 5) as well as the inversion processes in complexes **20** (Table 4) are extremely similar, which shows that the dissociative mechanism of the inversion of the tetrahedral configuration of the boron atom in the types of complexes indicated is preferred.

The dissociation of the B–N bond is the rate-limiting stage also in a number of other stereoisomerisation reactions of tetracoordinate boron compounds. It has been shown by dynamic ^{1}H and ^{13}C NMR methods that the inversion of the configuration of the tetracoordinate nitrogen atom in the chelate boron complex **23** involves the opening of the 1,3,2-oxazaborolidine ring and its subsequent closure at the hydroxyethyl group accompanied by proton transfers (Scheme 6).[85]

Scheme 6

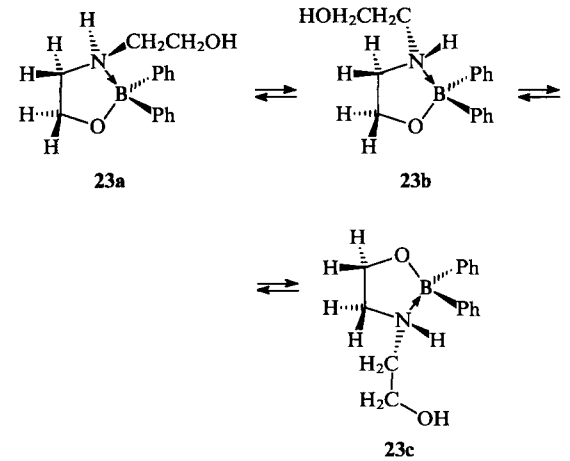


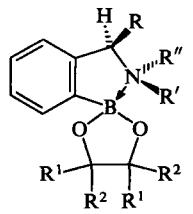
Table 5. Kinetic and activation parameters of the B–N bond dissociation and of the rotation of the boron-containing B(Ar)Y fragment about the B–O bond in type **21** compounds (solvent—nitrobenzene-d_5).[79]

No. of compound	R	Ar	Y	Indicator group	k_{25}/s^{-1} for:		$\Delta G^{\neq}_{25}$/kcal mol^{-1} for:	
					B–N bond dissociation	rotation about B–O bond	B–N bond dissociation	rotation about B–O bond
1	Me	*o*-$MeOC_6H_4$	OPr^i	Pr^i	1.4×10^{-1}		18.8	
2	Me	*o*-$MeOC_6H_4$	OCH_2Ph	CH_2Ph	2.7×10^{-1}		18.2	
3	cyclo-C_6H_{11}	*o*-$MeOC_6H_4$	OCH_2Ph	CH_2Ph	1.1		17.4	
4	Pr^i	*o*-$MeOC_6H_4$	OMe	Pr^i	7.9×10^{-2}	4.6×10^{-4}	18.9	22.0
5	Pr^i	*o*-$MeOC_6H_4$	OCH_2Ph	Pr^i	4.9×10^{-1}	5.4×10^{-3}	17.9	21.4
6	Pr^i	Ph	OCH_2Ph	Pr^i	1.5	4.5×10^{-6}	16.9	24.5
7	Pr^i	Ph	*o*-$MeOC_6H_4$	Pr^i	3.0×10^{-2}	–	19.6	>30

The energy barrier in the reaction (in solution in CD_2Cl_2) is 14.7 ± 0.3 kcal mol^{-1}, which is close to 12.9 kcal mol^{-1} found for the barrier in the dissociation of the B–N bond in the trimethylamine–trimethylboron complex.[86]

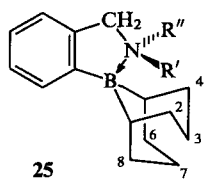
The asymmetric transformation, which makes it possible to obtain individual diastereoisomers of optically pure tetracoordinate boron complexes (oxazaborolidinones) by crystallisation from a suitable solvent, also includes a slow stage—the dissociation of the B–N bond, similar to that presented in Scheme 6.[87]

The intramolecular stereotransformations of [2-(dialkylaminomethyl)phenyl]boronates **24**,[88,89] 9-[2-(dialkylaminomethyl)phenyl]-9-borabicyclo[3.3.1]nonanes **25**,[90] and 9-[2-(ethylthiomethyl)phenyl]-9-borabicyclo[3.3.1]nonanes (**26**)[91] have been investigated in fair detail.



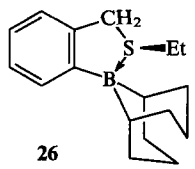
24

R = H, Me;
R′ = R″ = Me, Et;
$\Delta G_{25}^{\neq}$ = 11.5–11.6 kcal mol^{-1}.



25

R′ = R″ = Me, Et;
$\Delta G_{25}^{\neq}$ = 14.1–18.3 kcal mol^{-1}.



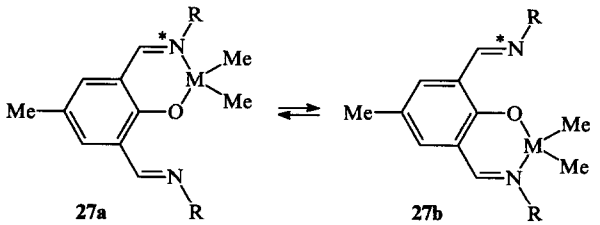
26

$\Delta G_{25}^{\neq}$ = 11.6 kcal mol^{-1}.

Depending on the type of substitution at the stereogenic centre—nitrogen, sulfur, and boron, the thermal dissociation of the B–N bonds in complexes **24** and **25** and of the B–S bond in compound **26** leads to the stereoisomerisation or topomerisation of the above centres. It has been found[89] that the energy barriers corresponding to the averaging of the signals due to the ^{13}C 3(7)-, 2(4)-, and 6(8)-atoms in compounds **25** are lower by 1.2 kcal mol^{-1} than those corresponding to the averaging of the signals due to the diastereotopic protons of the methylene group. This is because the first process reflects the dissociation of the B–N bond, whereas the averaging of the signals due to the methylene protons is attained after the inversion of the nitrogen atom following dissociation of this bond.

Particular attention has been devoted[89,90] to the quantitative determination of the contribution of the entropy of activation to the free energy of activation for the stereoisomerisation. The value of $\Delta S^{\neq}$ is regarded as an important diagnostic test of the mechanism and of the structure of the transition state of the reaction. The large positive values of $\Delta S^{\neq}$ found in the stereoisomerisation reactions of the intrachelate complexes **24**–**26** (15–20 e.u.) indicate[89–91] a significantly lower polarity of the transition state in the B–N bond dissociation reaction compared with the structure of the ground state. It follows from the kinetic data in Table 4 that positive activation entropies are likewise characteristic of the inversion of the configuration of the boron atom in the chelates **20**, which takes place via the dissociation of the B–N bond.

There are so far few quantitative data on the configurational lability of tetrahedral chelate Ga(III) and In(III) complexes. The enantiotopomerisation reactions of dimethylgallium and dimethylindium derivatives **27** have been investigated[92] on the basis of the temperature-dependent evolution of the line shape of the signals due to the nonequivalent protons of the phenyl and azomethine fragments in the dynamic ^1H NMR spectra.

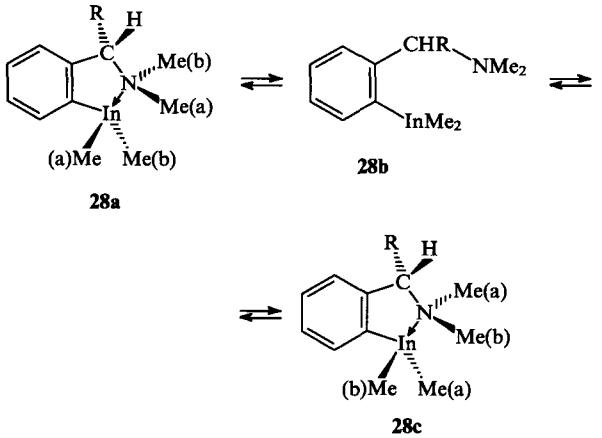


27a **27b**

R = Pr^i; M = Ga; k_{25} = 0.44 s^{-1}; $\Delta G_{25}^{\neq}$ = 17.9 kcal mol^{-1}.
M = In; k_{25} = 7.3 × 10^3 s^{-1}; $\Delta G_{25}^{\neq}$ = 12.2 kcal mol^{-1}.

Another known example of the enantiotopomerisation of a tetracoordinate indium atom is provided by the configurational dynamics of *o*-dimethylaminomethylphenyl(dimethyl)indium **28** (Scheme 7).[93]

Scheme 7



28a **28b** **28c**

R = H, Me.

The prochiral tetrahedral centres—nitrogen and indium atoms—in the chelated inner complex **28a** are responsible for the diastereotopic splitting of the methyl group signals (R = Me), which vanishes at room temperature owing to the dissociation of the In–N bond.

With increase in the atomic number of the central atom, the strength of the M–N bond diminishes and the energy barriers in the transcoordination reaction (Schemes 5 and 7), associated with the thermal dissociation of these bonds, diminish in the sequence B > Ga > In.

VI. Zinc complexes

The Zn(II) ion in complexes is known to be able to adapt its configuration and coordination capacity readily to the structural features of the ligands linked to it.[94–96] As a result of this ability, induced to a large extent by the absence of stabilising crystal field effects, the zinc atom is incorporated in the macromolecules of many enzymes functioning as active catalysts of biological processes.[97,98] It is not surprising that the stereochemical nonrigidity of the coordination compounds of tetracoordinate Zn(II) is determined (depending on the ligand environment) by all the types of mechanisms presented in Table 2 and also by certain others which will be considered in this section.

The most complete data concerning the influence of various structural factors on the kinetics and mechanisms of the processes determining the stereochemical nonrigidity of the tetrahedral configuration of the tetracoordinate nontransition metal atom have been obtained for the bischelate Zn(II) complexes of types **2**, **3**, and **5**–**15**.[54,55,70,99–110] The influence of the following structural factors has been studied: (1) the nature of the chelating centre X = O, S, or Se; (2) the nature of the substituents R and R^1 in complexes **6** and **7** and also of the condensed arene and heteroarene rings in complexes **3** and **5**–**15**; (3) the steric and electronic characteristics of the substituents R attached to the coordinated nitrogen atoms in complexes **5** and **7**.

Some of the results of such investigations are compiled in Table 6. The observed energy barriers are in the range from 10 to 24 kcal mol^{-1}, while the rate constants are from 10^3 to 10^{-5} s^{-1} (at the usual temperature). Analysis of the data in Table 6 makes it possible to differentiate the following principal trends in the changes in the energy barriers to enantiomerisation as a function of the characteristics of the ligand structure:

1. When the nature of the donor centre X in isotypical series of compounds **3** and **7**–**9** is varied, the activation energies increase in the sequence O < Se < S.

2. The condensation of the benzene, benzothiophene, and benzocyclopentene rings with the chelate ring in type **2** complexes and their oxygen analogues (X = O) (complexes **3**, **9**, and **10**) diminishes $\Delta G_{25}^{\neq}$ [for complex **6** (R = Pr^i, R^1 = H), it amounts to 20.6 kcal mol^{-1} [54]], whereas the condensation of five-membered nitrogen-containing heterocycles — the pyrrole (compound **8**) and pyrazole (compound **7**) rings — increases the energy barrier to the inversion of the tetrahedral Zn(II) atom.

3. The differences between the electronic and steric characteristics of the substituents at the coordinated nitrogen atom in the series of compounds **5** have little effect on the inversion barriers.

4. In contrast to the beryllium complexes **4**, the introduction of electron-accepting substituents into the benzene rings of the analogous zinc complexes **3** (X = O) reduces the inversion barrier. The negative sign of the reaction constant in the correlation equation obtained by Bottino and Finocchiaro[70] is consistent with this [cf. Eqn. (2)].

$$\Delta G_{T_c}^{\neq} = -2.48\sigma + 15.44 \text{ (kcal mol}^{-1}\text{)}$$

This difference reflects in all probability the inversion mechanism of enantiomerisation in Zn(II) complexes for which the reaction pathway associated with the type *a* polytopal rearrangement (Fig. 2), proceeding without the preliminary dissociation of the Zn–N coordinate bond, becomes energetically preferred. This hypothesis is supported also by the negative entropies of activation for the inversion of the tetrahedral configuration of Zn(II) with the N_2O_2 ligand environment (Table 6).

Clear-cut evidence indicating that the digonal twist mechanism (a) (Fig. 2), not involving the dissociation-formation of coordinate bonds, is energetically preferred has been obtained in a study of the dynamic ^1H NMR spectra of bischelate zinc complexes **13** (X = O) with alterdentate ligands.[107]

Table 6. Kinetic parameters of the inversion of the configuration of the tetrahedral Zn(II) in bischelate complexes with a ZnN_2X_2 coordination unit.

Type of complex	R^1, R^2	X	R	Solvent	k_{25}/s^{-1}	$\Delta H^{\neq}$/ kcal mol^{-1}	$\Delta S^{\neq}$/ cal mol^{-1} K^{-1}	$\Delta G_{25}^{\neq}$/ kcal mol^{-1}	Ref.
3	5-OMe	O	Pr^i	$CDCl_3$	–	–	–	16.0/33 °C[a]	70
	H	O	Pr^i	CD_2Cl_2 ($CDCl_3$)	51	9.3	−19.6	15.1 (15.5/19 °C)[a]	55, 70
	5-Br	O	Pr^i	$CDCl_3$	–	–	–	14.9/12 °C[a]	70
	5-NO_2	O	Pr^i	$CDCl_3$	–	–	–	13.3/−21 °C[a]	70
	3,4-C_6H_4	O	Pr^i	Bromobenzene-d_5	2.8	15.3	−5.2	16.8	108
	4,5-C_6H_4	O	Pr^i	"	14.9	13.0	−9.7	16.0	108
	5,6-C_6H_4	O	Pr^i	"	3.1×10^3	9.0	−12.5	12.7	108
	5-OMe		Pr^i	"	7.3	15.1	−3.8	15.3	72
	H		Pr^i	"	2.3	17.7	2.7	16.9	72
	5-Br		Pr^i	"	2.1	18.0	3.3	17.0	72
	5-NO_2		Pr^i	"	0.5	17.7	−0.5	17.8	72
	3,4-C_6H_4		Pr^i	"	1.3	23.8	21.8	17.4	108
	4,5-C_6H_4		Pr^i	"	3.8	22.0	18.0	16.6	108
	5,6-C_6H_4		Pr^i	"	43.9	13.1	−7.1	15.2	108
5	–	–	CH_2Ph	Chlorobenzene	0.6	20.1	8.1	17.7	99
	–	–	Pr^i	"	1.5	17.1	−0.2	17.2	99
	–	–	Bu^t	"	4.1	14.7	−6.3	16.6	99
	–	–	Ph	"	4.7	13.3	−10.9	16.5	99
	–	–	2,4,6-$C_6H_2Me_3$	"	0.1	25.6	22.5	18.8	99
7	Ph/Pr^i	O	Pr^i	*o*-Dichlorobenzene	2.3×10^{-2}	20.0	1.2	19.7	100
	Ph/Pr^i		CH_2Ph	"	5.1×10^{-5}	26.2	9.7	23.3	100
	Ph/Pr^i		CH_2Ph	"	4.0×10^{-3}	19.7	−3.3	20.7	100
	Ph/Me		Pr^i	"	1.3×10^{-3}	23.3	6.4	21.4	100
9	–	O	Pr^i	"	8.2	11.4	−15.8	15.9	109
10	–	O	CH_2Ph	CH_2Cl_2	5.1×10^3	8.2	−14.2	12.4	109
12	–	–	Pr^i	Nitrobenzene	2.7×10^{-1}	15.7	−8.4	18.2	109

[a] The quantity $\Delta G^{\neq}$ was determined from the coalescence of the signals due to the diastereotopic methyl groups at the temperature indicated.

Table 7. Kinetic and activation parameters of the enantiomerisation reactions of the zinc complexes **13** (R = Pr^i, X = O, S) (solvent—bromobenzene-d_5).[71,107]

X	R^1	Digonal twist				Transcoordination			
		k_{25}/ s^{-1}	$\Delta H^{\neq}$/ kcal mol^{-1}	$\Delta S^{\neq}$/ cal mol^{-1} K^{-1}	$\Delta G^{\neq}_{25}$ [a]/ kcal mol^{-1}	k_{25}/ s^{-1}	$\Delta H^{\neq}$/ kcal mol^{-1}	$\Delta S^{\neq}$/ cal mol^{-1} K^{-1}	$\Delta G^{\neq}_{25}$/ kcal mol^{-1}
O	OMe	110	13.3 ± 1.1	−4.6 ± 4.1	14.6	0.15	18.0 ± 0.2	−1.9 ± 0.6	18.4
O	Me	100	9.1 ± 0.5	−18.1 ± 1.2	14.7	0.18	14.9 ± 0.4	−11.9 ± 1.7	18.4
O	H	83	9.0 ± 0.6	−22.8 ± 3.8	14.8	0.18	14.8 ± 1.9	−12.2 ± 6.2	18.4
O	Br	130	13.4 ± 0.5	−9.9 ± 1.6	14.6	0.14	16.7 ± 1.1	−6.3 ± 3.0	18.5
O	NO_2	470	4.2 ± 0.5	−32.3 ± 1.9	13.8	0.48	16.6 ± 0.9	−4.4 ± 2.6	17.8
S	OMe	–	–	–	–	14.4	15.3 ± 0.8	−2.0 ± 0.3	15.8
S	Me	–	–	–	–	9.0	13.6 ± 0.7	−8.6 ± 0.8	16.1
S	Br	–	–	–	–	9.1	12.0 ± 0.5	−14.0 ± 1.7	16.1
S	NO_2	–	–	–	–	3.5	13.0 ± 0.4	12.4 ± 1.6	16.7

[a] For sulfur-containing compounds, $\Delta G^{\neq}_{twist} > \Delta G^{\neq}_{transcoord}$

In contrast to beryllium complexes, both types of dynamic transformations have been detected in the dynamic ^{1}H and ^{13}C NMR spectra of zinc complexes **13** (X = O) (Scheme 2): the digonal twist and the transcoordination process occurring at a higher solution temperature and detected from the complete averaging of the spectrum relative to the X–C(R^1) axes. The kinetic sequence of the above transformations is retained for all the complexes **13** (M = Zn, X = O) investigated regardless of the nature of the substituents R^1. The rate of the polytopal rearrangement is three orders of magnitude higher than the rate of the simultaneous dissociation-recombination reaction.

Variation of the solvent polarity and of the concentrations of the solutions hardly affects the kinetics of the observed dynamic reactions, which indicates their intramolecular nature. The kinetic parameters of the processes investigated are presented in Table 7.

The energy barriers to inversion via the digonal twist mechanism for zinc complexes **13**, presented in Table 7, are close to the values characterising the enantiomerisation of zinc bis-salicylaldiminates **3** (M = Zn) with identical substituents R^1 (Table 6), which confirms that this stereoisomerisation pathway is likewise preferred for complexes **3** (X = O).

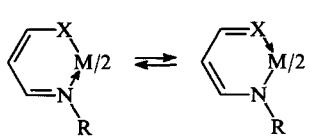
The modification of the structure of the alterdentate ligand in zinc complexes **13** by replacing the donor oxygen atom by a sulfur atom alters radically the energy sequence of the enantiomerisation mechanisms. The dissociative mechanism of the inversion of configuration of the tetrahedral centre becomes preferred, as for the beryllium and boron chelates **13** considered previously. The barriers in the dissociation-recombination mechanism found in zinc complexes **13** (X = S) are significantly lower than those detected for the similar process in the analogous complexes with (X = O) (Table 7).

The difference between the mechanisms of the enantiomerisation of the Zn(II) complexes with the N_2O_2 and N_2S_2 chelate environments is reflected in the difference between the activation entropies for the enantiomerisation of complexes **3** of this type and also in the nature of the effect of the substituents R^1 on the free energies of activation. For the majority of complexes **3** (M = Zn, X = S), the activation entropies are positive or have low negative values (Table 6), which is characteristic of reactions proceeding with dissociation of metal–ligand bonds[91] (in this case, the reactions of complexes **13** in accordance with Scheme 2 are not quite so characteristic in view of the superposition of a number of secondary processes involving rotation about the M–N and M–X bonds). The correlation equation,[72] linking the inversion barriers in zinc complexes **3** (X = S) to the parameters of the 5-R^1 substituents, has a form similar to that of Eqn. (2) for the analogous Be(II) complexes.

$$\Delta G^{\neq}_{25} = 1.41\sigma + 16.74 \text{ (kcal mol}^{-1}\text{)}; \quad r = 0.984.$$

Such changes in the mechanisms of the inversion processes can be attributed to the lengthening of the Zn–N bonds (2.036–2.112 Å for three compounds of this type) and hence to their weakening in the six-membered chelate ring ZnN_2S_2 com-pared with the ZnN_2O_2 analogues (1.981–2.017 Å for the eight examples described in the literature).[38,110–114]

In type **3** complexes and their analogues, there is, in principle, a possibility of the dissociation-recombination mechanism involving the rupture of the M–X (X = O, S) and not M–N bonds, since the structure of the chelate ring is evidently reflected by the resonance of canonical structures of type **29**,[115] the relative contribution of which may vary greatly depending on the type of metal and of the substitution in the ligand.



29a **29b**

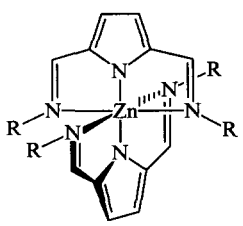
However, hitherto all attempts to observe the enantiomerisation of bischelate complexes with the MN_2X_2 coordination unit, where M is a main subgroup metal, proceeding via the M–X bond dissociation mechanism have been unsuccessful. The resultsof the study of the stereodynamics of chelate complexes **15** (M = Zn, R = Pr^i) with alterdentate ligands, the structure of which was selected in such a way that the transcoordination process involving the dissociation of the Zn–O bond can be modelled, are instructive. The tetrahedral configuration of Zn(II) is inverted via the intramolecular digonal twist mechanism ($\Delta G^{\neq}_{T_c} = 11.8$ kcal mol^{-1} in CD_2Cl_2, $T_c = -55$ °C). Transcoordination with dissociation of the Zn–O bond is not observed in solution in nitrobenzene-d_5 on heating to 150 °C ($\Delta G^{\neq}_{150} > 22$ kcal mol^{-1}), above which the decomposition of the complex begins.

The wide variety, characteristic of the Zn(II) central ion, of coordination types—ranging from planar tricoordinate in anionic complexes, for example in $Zn(SR)_3^-$,[116,117] to hexacoordinate, which occurs preferentially in cationic complexes[118]—in reactions of tetracoordinate zinc should be manifested respectively by tendencies to undergo dissociative or associative reactions. Examples of the stereoisomerisation of complexes of the first type were examined above.

At high concentrations of the solutions, the degenerate ligand exchange mechanism (pathway c in Fig. 2), involving the formation of dimeric association complexes with pentacoordinate zinc atoms [characteristic of many tetrahedral Zn(II) complexes in the

crystalline state[96]], actually begins to compete with mechanisms *a* and *b*. For the pyrrole complexes **11**, the degenerate ligand exchange mechanism is energetically preferred for the inversion of the configuration of tetrahedral Zn(II) even at very low concentrations (when the dynamic NMR method is used).

The associative mechanism of the enantiomerisation of tetrahedral Zn(II) complexes can be made also to operate intramolecularly by means of an appropriate design of the alterdentate ligands. Whereas the steric structure of the ligand in type **13** complexes rules out the possibility of an increase in the coordination number of the central metal atom as a result of the intramolecular interaction with the excess donor centres in the ligand with 6,6′-aldimine groups, in type **14** complexes, based on 2,5-diformylpyrrole bisimines, the formation of both pentacoordinate **30** and hexacoordinate **31** structures of the complexes is sterically unhindered.



31

The dynamic ^1H and ^{13}C NMR spectra of complexes **14** (R = Pr^i, cyclo-C_6H_{11}) are fully averaged in solution in CD_2Cl_2 even at −80 °C (f_0 = 300 MHz), which corresponds to an effective D_{2d} symmetry. Of the two possibilities — the stable octahedral structure **31** or the very rapid dynamic inversion of the configuration of the tetrahedral Zn(II) centre (Fig. 3) — the latter is actually realised.[106] This conclusion is supported by the following evidence: (a) nonzero dipole moments of complexes **14** (3.17 D for R = cyclo-C_6H_{11} in benzene), (b) X-ray diffraction data for this complex [pentacoordinate trigonal-bipyramidal structure with the central Zn(II) atom delocalised over two unequally populated positions], and (c) the deaveraging of the ^{15}N NMR spectrum of the ^{15}N=CH isotopomer occurring in solution in CD_2Cl_2–Et_2O at −110 °C. The energy barrier to the tetrahedral inversion estimated from the ^{15}N NMR spectroscopic data is 8.6 kcal mol^{-1} at −70 °C.

VII. Cadmium complexes

In solutions of cadmium(II) complexes **3**,[53] **5**,[119,120] **2**,[121] **7**,[100] **8** and **9**,[122] and **13**,[123] it is possible to follow separately and characterise quantitatively the kinetics of both intramolecular and intermolecular stereoisomerisation processes. The study of the dynamic behaviour of the ^{111}Cd ($S = \frac{1}{2}$) isotopomers of the above complexes has been widely used in the above investigations. The manifestation of the spin–spin coupling of the ^{111}Cd nuclei with ^{13}C nuclei and protons enriches significantly the spectroscopic information. Thus the dynamics of metal–ligand bond dissociation processes can be followed directly from the temperature dependence of the constants $^nJ_{^{111}Cd-H}$ and $^nJ_{^{111}Cd-^{13}C}$ as well as $^nJ_{^{111}Cd-X}$ (X = other nuclei). The dynamic pattern in the ^1H NMR spectrum of complex **5** (R = Pr^i), for example, is extremely characteristic.[119] Below −30 °C (CD_2Cl_2), all the exchange processes are 'frozen' — the methyl groups in both prochiral isopropyl substituents are anisochronic and we have the constant $^3J_{^{111}Cd-N=CH}$ = 30 Hz.[119] An increase in the solution temperature leads initially merely to a concentration-independent diastereotopic averaging of the signals due to the methyls of the isopropyl groups, which reflects the intramolecular inversion of the configuration of the tetrahedral Cd(II) (at T_c = −1 °C, the inversion rate constant is k = 115 s^{-1}).

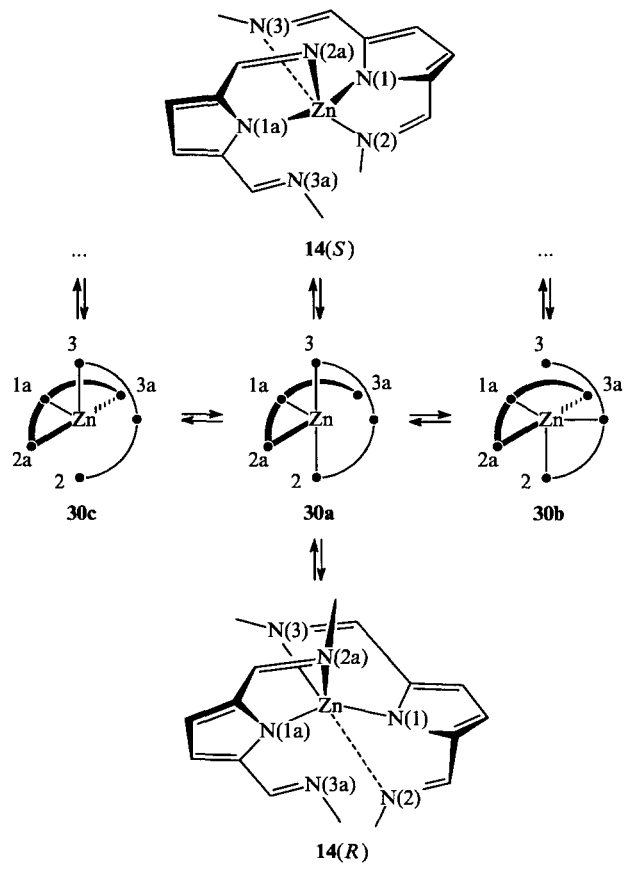
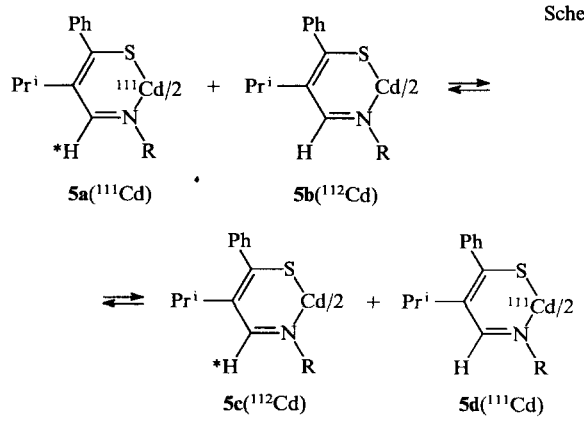


Figure 3. The associative (S_N2 type) mechanism of the intramolecular inversion of the tetrahedral configuration of Zn(II) in complexes **14** according to NMR and X-ray diffraction data.[106]

Above T_c, exchange processes, leading ultimately to the disappearance of the constant for the spin–spin coupling of the proton in the azomethine fragment of the ligand with the ^{111}Cd nuclei, begin to be manifested in the spectra. In contrast to the higher-temperature dynamic transformation observed for the first process, a linear relation has been established between τ and c^{-1}, showing that the process is kinetically second order and indicating the occurrence of a bimolecular degenerate ligand exchange reaction [n = 2 in Eqn. (1)] in the type **2** complex (pathway *c* in Fig. 2).

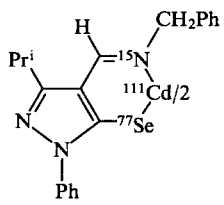
The intermolecular character of the degenerate ligand exchange processes is illustrated particularly clearly by the temperature-dependent two-dimensional ^1H NMR spectra of a mixture of the ^{111}Cd ($S = \frac{1}{2}$) and ^{112}Cd (S = 0) isotopomers of the type **5** complex (R = cyclo-C_6H_{11}) in the resonance region

Scheme 8

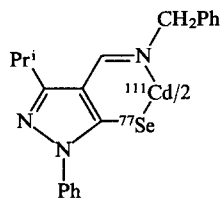


of the CH = N protons.[124,125] At temperatures below 10 °C, only diagonal (auto) peaks are present in the ^{1}H NMR spectra (f_0 = 100 MHz). The two extreme peaks among them correspond to the azomethine protons of the ^{111}Cd ($^3J_{^{111}Cd-N=CH}$ = 30 Hz) isotopomer, while the central peak corresponds to the ^{112}Cd isotopomer. An increase in the solution temperature to 33 °C leads to the appearance of six cross-peaks, two of which induce, at the resonance frequencies of the extreme auto-peaks, chemical exchange in the ^{111}Cd isotopomer, while the remaining four induce the intermolecular ligand exchange of the ^{111}Cd and ^{112}Cd isotopomers. This form of the spectra corresponds directly to the form of the exchange matrix for the reaction (Scheme 8). At a temperature above 53 °C, the coalescence of all the diagonal peaks and cross-peaks is observed in the ^{1}H NMR spectrum as a consequence of the intense ligand exchange.

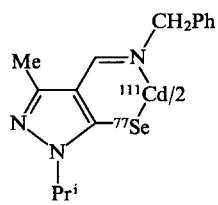
It has been suggested that observation of the temperature dependence of the spin–spin coupling constants for the ^{111}Cd atom in the isotopomeric type **7** complexes, incorporating the ^{15}N and ^{77}Se magnetic nuclei in the coordination unit, would make it possible to answer the question which of the bonds (Cd–Se or Cd–N) in these and structurally similar complexes is the most labile in the ligand exchange reaction (Scheme 1).



7a



7b



7c

However, analysis of the dynamic ^{111}Cd, ^{77}Se, and ^{1}H NMR spectra of the series of complexes **7a–c** showed that the rate constants and activation barriers for the dissociation of these bonds, indicated by the dynamics of the disappearance of the spin–spin coupling constants $^3J_{^{111}Cd-N=CH}$ in the ^{1}H NMR spectra and $J_{^{111}Cd-^{77}Se}$ in the ^{77}Se{H} NMR spectra, are identical within the limits of the usual experimental errors.[126] The synchronous nature of the Cd–N and Cd–X (X = S, Se) bond dissociation-formation steps in the ligand-exchange reactions is also demonstrated by data indicating the thermoinduced disappearance of the spin-spin coupling constants for the ^{111}Cd nucleus of the ligand: $^4J_{^{111}Cd-N=C-CH}$ = 3.5 Hz and $^3J_{^{111}Cd-N=CH}$ = 22 Hz in the spectra of complex **6** (R = Pr^i, R^1 = Br), $^nJ_{^{111}Cd-^{13}C}$ for the α,β-carbon atoms and the carbon atoms of the benzene ring in the ^{13}C{H} spectra of the bischelates **5** (R = Pr^i) and **6** (R = Pr^i, R^1 = H), as well as $J_{^{111}Cd-^{77}Se}$ and $J_{^{111}Cd-^{15}N}$) in the dynamic ^{111}Cd NMR spectra of the triply labelled compound **7a**.

Selected kinetic parameters of the observed dynamic reactions of the bischelate cadmium [^{111}Cd(II)] complexes are presented in Tables 8 and 9. Analysis of these and other data obtained in the study of type **6** complexes shows that, at solution concentrations in the range 10^{-1}–10^{-2} M, the intramolecular enantiomerisation reaction proceeds in all cases at a rate 1–2 orders of magnitude higher and the energy barriers are then lower by 2.5–4 kcal mol^{-1} than the values characteristic of the degenerate ligand exchange process.[100,119,120]

Comparison of the data in Tables 6 and 8 shows that the energy barriers to the intramolecular enantiomerisation of the bischelate cadmium(II) complexes are lower by 4–7 kcal mol^{-1} than that observed for a series of isoligand zinc(II) complexes. The calculated entropies of activation have higher negative values both for the intramolecular inversion process and for the bimolecular association reaction. The influence of structural factors on the barriers in the intramolecular inversion of the tetrahedral configurations of Cd(II) and Zn(II) in isoligand complexes is largely of the same type. The significantly more marked dependence of the configuration inversion barrier in the intermolecular reaction (the energy barriers increase approximately in parallel with increase in the bulk of the

Table 8. Kinetic parameters of the intramolecular inversion of the configuration of the tetrahedral Cd(II) in bischelate complexes with a CdN_2X_2 coordination unit (solvents—$CDCl_3$, *o*-$Cl_2C_6H_4$).

Type of complex	R^1, R^2	X	R	k_{25}/s^{-1}	$\Delta H^{\neq}$/kcal mol^{-1}	$\Delta S^{\neq}$/cal mol^{-1} K^{-1}	$\Delta G^{\neq}_{25}$/kcal mol^{-1}	Ref.
3	H	O	Pr^i	8.1×10^3	5.5	−22.1	12.1	55
	H	S	Pr^i	1.2×10^4	5.4	−21.7	11.9	55
5		S	CH_2Ph	2.1×10^4	8.2	−10.7	11.5	120
		S	Pr^i	5.5×10^2	9.9	−12.7	13.7	120
		S	Bu^t	9.7×10^2	12.8	−1.8	13.4	120
		S	Ph	8.2×10^3	6.5	−18.9	12.1	120
		S	C_6H_4OMe-*p*	1.3×10^4	6.5	−17.6	11.8	120
		S	C_6H_4Cl-*p*	1.0×10^4	6.6	−17.9	11.9	120
7	Ph, Pr^i	S	CH_2Ph	4.7×10^2	5.8	−26.8	13.8	100
	Pr^i	S	cyclo-C_6H_{11}	1.6×10^1	13.6	−26.6	15.9	100
	Ph, Pr^i	Se	cyclo-C_6H_{11}	4.7×10^2	5.8	−26.8	13.8	–
	Pr^i	S	CH_2Ph	7.5×10^2	9.5	−13.5	13.6	100
	Pr^i, Me	Se	CH_2Ph	2.1×10^2	6.0	−22.9	12.9	100
	CH_2Ph, Pr^i	S	Pr^i	1.6×10^1	14.4	−4.8	15.8	100
		Se	Pr^i	3.8×10^2	10.0	−13.3	13.9	100
9		S	Pr^i	3.0×10^3	5.9	−23.0	12.7	122

Table 9. Kinetic parameters of the degenerate ligand exchange reaction (Scheme 8) in solutions (in $CDCl_3$ or CD_2Cl_2) of Cd(II) bischelate complexes obtained from the temperature variation of the $^3J_{^{111}Cd-N=CH}$ for the isotopomeric complexes **5** and **7** (95% enrichment in ^{111}Cd).

R	X	k_{25} [a]/s^{-1}	$\Delta H^{\neq}$/kcal mol^{-1}	$\Delta S^{\neq}$/cal mol^{-1} K^{-1}	$\Delta G^{\neq}_{25}$/kcal mol^{-1}	Ref.
Complex **5**						
CH_2Ph		4.1×10^2	10.6	−11.2	14.0	120
Pr^i		5.7	19.6	−10.7	16.4	120
Bu^t		6.7	12.3	−13.5	16.3	120
Ph		1.6×10^3	8.5	−15.3	13.1	120
C_6H_4OMe-*p*		5.5×10^2	9.8	−13.1	13.7	120
C_6H_4Cl-*p*		4.1×10^3	8.5	−15.3	13.1	120
Complex **7** ($R^1 = Pr^i$, $R^2 = Me$)						
Et	S	1.0×10^2	8.9	−9.6	14.7	126
CH_2Ph	S	4.2	15.5	−3.8	16.6	–
cyclo-C_6H_{11}	S	6.7×10^{-3}	19.3	−3.6	20.4	126
Bu^t	S	2.7×10^{-2}	17.2	−7.9	19.6	126
Me	Se	7.6×10^3	9.9	−7.5	13.6	126
Ph	S	1.7×10^2	6.1	−27.8	14.3	126
C_6H_4Me-*p*	S	8.2	10.8	−18.0	16.0	126
CH_2Ph	Se	2.7	7.4	−3.2	16.8	126

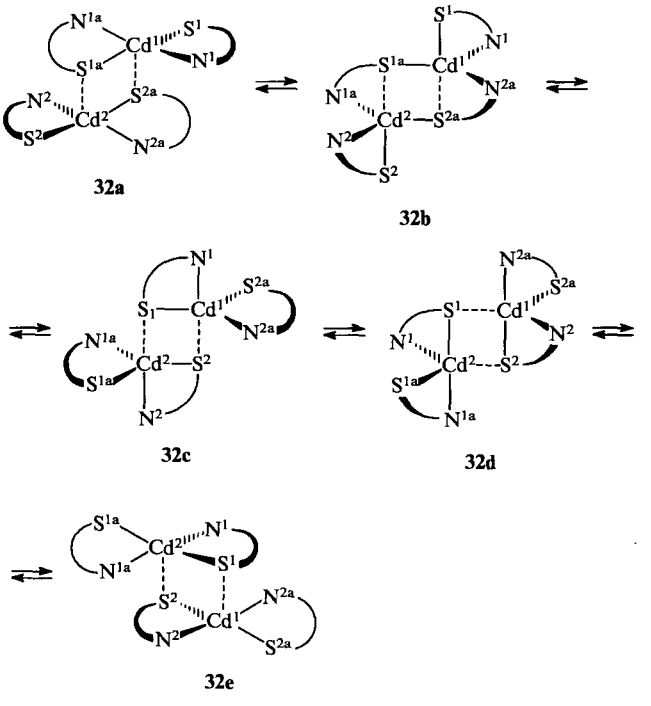
[a] All the reactions investigated are kinetically second order. For comparison with the kinetic parameters of the intramolecular inversion of configuration of Cd(II) (Table 8), the rate constants were assumed to be pseudofirst order, i.e. $k = k_2 c$ for $c = 3 \times 10^{-2}$ M.
[The second entry of the table appears to be in error (Ed. of Translation)]

substituent: Et < Ar < CH_2Ph < Bu^t < cyclo-C_6H_{11}) compared with the intramolecular process constitutes an exception. The ligand exchange reaction mechanism (Scheme 8), which makes it possible to account for the synchronisation of the Cd–N and Cd–S bond dissociation-formation processes, is presented in Scheme 9, which presupposes the formation in solution of fairly stable dimeric intermediates with four-membered Cd_2S_2 rings.[119,121,124]

The formation of dimeric structures with planar M_2X_2 (X = O, S, Se, Te) metallocycles is extremely characteristic of zinc[117,127] and cadmium[128,129] phenoxides, thiophenoxides, selenoxides, and telluroxides. The configuration of the bonds at the metal atom in the dimeric intermediates **32a** is then close to the trigonal-bipyramidal configuration for the Zn(II)[95] and Cd(II)[130,131] complexes according to X-ray diffraction data. Intermolecular coordination leads to partial loosening of one of the metal–ligand bonds and promotes its dissociation with subsequent binding to the cadmium atom of another chelate complex. The series of concerted metal–ligand bond dissociation-formation processes, including the rearrangements of pentacoordinate structures of the Berry pseudorotation type, in the stages **32b** ⇄ **32c** ⇄ **32d** ensures the exchange of cadmium atoms between the two units of the dimer, i.e. degenerate ligand exchange. It has been shown[117,129] that a ligand exchange of this type does indeed occur in solutions of zinc and cadmium thiophenoxides via the dissociation and formation of M–S bonds in the dissociation and formation of the dimers respectively.

The energetically preferred mechanism of the intramolecular enantiomerisation of the bischelate complexes with the CdN_2X_2 coordination unit most probably involves the dissociation-formation of Cd–N bonds (pathway *b* in Fig. 2) and not a digonal twist (pathway *a*). This has been confirmed by the results of a study of the temperature dependence of the ^1H and ^{13}C NMR spectra of the bischelate cadmium complex **13** (M = ^{111}Cd, X = S, R = Pr^i, R^1 = Me) based on 2,6-diformyl-4-methylthiophenol bisalkylimine.[123] Fig. 4 shows that the ^{13}C {H} NMR spectrum of this compound at −90 °C does not reveal the occurrence of the chemical exchange reaction but does indicate $^{111}Cd-^{13}C$ spin–spin coupling for certain carbon nuclei of the ligand. An increase in solution temperature leads to the dynamic averaging of the signals due to the carbon atoms of the diastereotopic methyl groups in each of the isopropyl substituents and at the same time to the averaging of the ^{13}C chemical shifts of

Scheme 9



both groups as well as the ^{13}C nuclei in the 3,5-, 7,7′-, and 8,8′-positions. Examination of the dynamic ^1H NMR and two-dimensional exchange (2D EXSY) spectra of this complex leads to the similar conclusion that the intramolecular processes involving the inversion of configuration and the switching of coordination (Scheme 2) are synchronous. The observed disappearance of the constants for the spin–spin coupling of the ^{111}Cd nucleus with the C(1), C(2), and C(6) atoms of the ligand, observed in the temperature-dependent ^{13}C spectra (Fig. 4), is caused by the activation of the intermolecular degenerate ligand exchange process with a relatively higher barrier. Thus the inversion of the configuration of the tetrahedral Cd(II) atom in the given compound is determined by the intramolecular bond dissociation-formation process leading to the (*R*) ⇄ (*S*) inversion (the transcoordination pathway is indicated in Scheme 2).

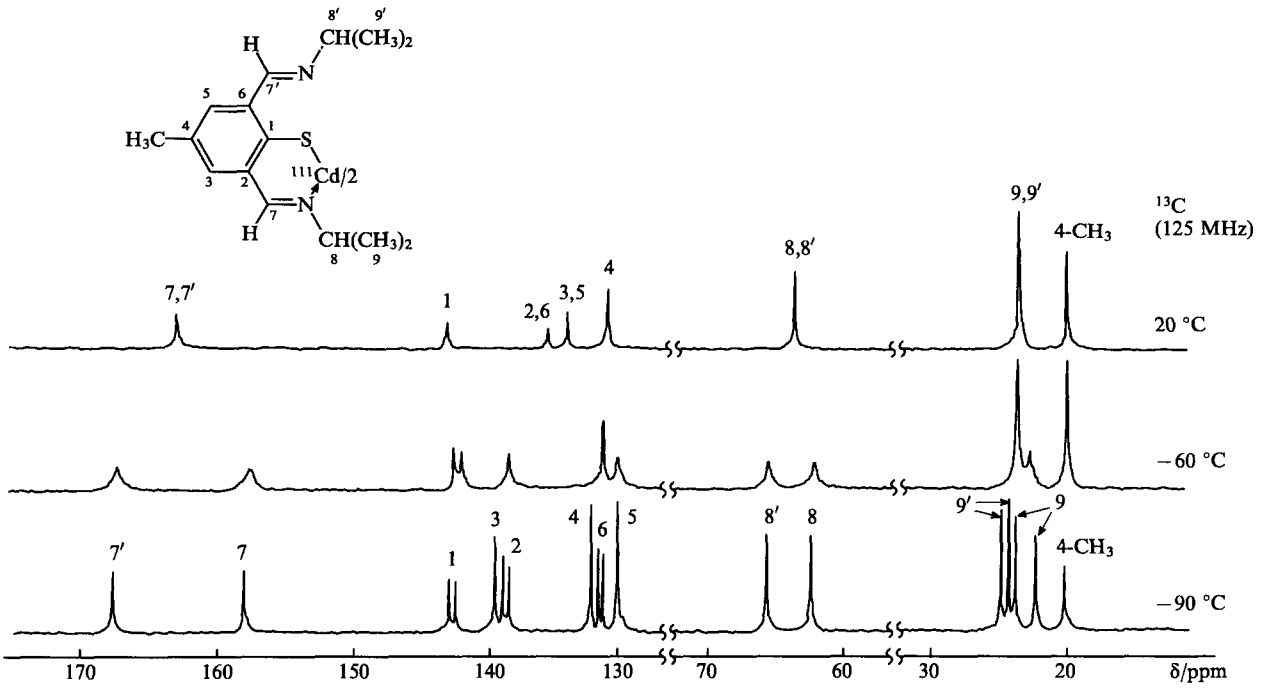


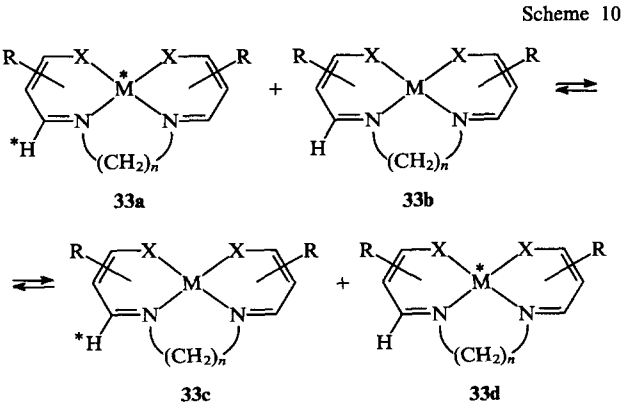
Figure 4. Temperature variation of the ^{13}C NMR spectra (125 MHz, CD_2Cl_2) of the type **13** (X = S, R^1 = CH_3) ^{111}Cd (95%) complex[123]. $J_{^{111}Cd-^{13}C}$ (Hz): 13.3 for C(1), 28.5 for C(2), and 15.6 for C(6); $\Delta G_{25}^{\neq}$ = 12.8 kcal mol^{-1}.

The free energy of activation for the process (12.8 kcal mol^{-1}) is very close to the corresponding value for the intramolecular inversion process in cadmium bis(*N*-isopropylthiosalicylaldiminate) **3**. This is evidence in support of the operation of a similar dissociative mechanism of the enantiomerisation (*R*) ⇄ (*S*) in Cd(II) complexes of types **5**, **7**, and **9** (Table 8).

The retention of the spin–spin coupling constants for the ^{111}Cd nucleus of the ligand in the temperature range in which the intramolecular dissociative process is detected in the cadmium complex **13** (M = ^{111}Cd, X = S, R = Pr^i, R^1 = Me) and in the cadmium complexes of types **3**, **5**, **7**, and **9** (Table 8), based on the usual bidentate ligands, may be justified by the argument that the lifetimes of the intermediate tricoordinate structures linked by spin–spin coupling of the ^{111}Cd and ligand nuclei are shorter than the relaxation time (Fig. 1 and Scheme 2).

Evidently, this is the reason why it is impossible to detect the operation of the intramolecular metal–ligand bond dissociation-formation mechanism in solutions of the sterically strained bischelate ^{111}Cd (and ^{207}Pb) complexes **33** with an enforced (*n* = 2) *cis*-planar configuration at the metal centre (Scheme 10).[103,124]

Scheme 10



X = S, Se; M = Cd, Pb; *n* = 2, 4, 6.

Only the degenerate ligand exchange process, occurring at unexpectedly high rates and having energy barriers only 2.5–4.0 kcal mol^{-1} higher than in the analogous complexes with a tetrahedral configuration based on bidentate ligands, could be detected in the dynamic ^1H NMR spectra of these compounds.

With increase in the length and mobility of the polymethylene bridge in the tricyclic complexes **33**, the cadmium ion assumes (starting with *n* = 4) a tetrahedral configuration and these complexes exhibit, like their analogues **5** and **6**, two types of reactions in solutions: intramolecular inversion of the configuration of the tetrahedral centre and intermolecular degenerate ligand exchange also accompanied by the inversion of the configuration at the metal atom (Scheme 10).

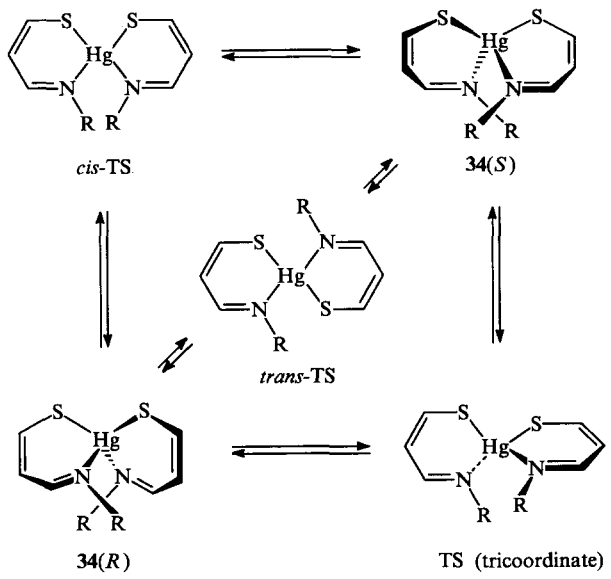
VIII. Complexes of mercury and lead

Both the intramolecular and intermolecular exchange processes occurring in solutions of Hg(II) bischelate complexes are much faster than for the zinc and cadmium analogues and the determination of quantitative data is difficult in view of the small separations between the diastereotopic indicator signals. For these reasons, there are fairly limited data on the stereochemical lability of Hg(II) complexes. For complex **7** (M = Hg, X = S, R = cyclo-C_6H_{11}, R^1 = Pr^i, R^2 = Me), the rate of the inversion process, detected from the diastereotopic averaging of the signals due to the methyls of the isopropyl substituent R^1 ($\Delta\delta$ = 0.01 ppm in CD_2Cl_2) is independent of the solution concentration and the type of solvent employed, which indicates its intramolecular nature (k_{-80} = 4 s^{-1}, k_{25} = 1.9 × 10^3 s^{-1}, $\Delta G_{25}^{\neq}$ = 12.9 kcal mol^{-1}).[132]

A theoretical modelling of the possible mechanisms of the intramolecular enantiomerisation has been carried out[133] using the MNDO method for the tetrahedral bischelate complex **34** (Scheme 11), which serves as a model of complexes **7** (M = Hg).

The MNDO method reproduces satisfactorily the highly distorted tetrahedral configuration of the bonds at the mercury atom in complex **34**, which agrees with the X-ray diffraction data[132] for the pyrazole complex **7** (R = cyclo-C_6H_{11}, R^1 = Pr^i, R^2 = Me) having the identical chelate unit (the SHgS and NHgN bond angles are 141° and 103.2°, and the Hg–S bond length is

Scheme 11



2.39 Å). The greater SHgS bond angle indicates that the Hg–S bonds are highly covalent, while the Hg–N bonds in this complex are predominantly dative.[115]

Calculations revealed three structures of the transition state (TS), which are presented in Scheme 11.

As can be seen from the calculated data (Table 10), one may expect the energy barriers to depend fairly strongly on the steric bulk of the substituent R. For R = H, the digonal twist (*trans*-TS) is energetically preferred, while the replacement of hydrogen by the more bulky methyl group (R = Me) results, as expected, in the dissociative mechanism of the inversion of the configuration with dissociation of the Hg–N bond being preferred. For the type **7** complex, the calculated activation energies are fairly close to the experimental inversion barrier for mercury. They also illustrate clearly the extremely fine balance between the principal mechanisms of the intramolecular inversion of the configuration of the pseudotetrahedral mercury atom, providing evidence on the whole in support of the dissociation-recombination pathway *b* in the enantiomerisation of the type **7** Hg(II) chelates (Fig. 2).

Table 10. Modelling of the mechanisms of the intramolecular enantiomerisation of Hg(II) bischelate complexes by means of the MNDO method (with parameters taken from Minkin et al.[133]).

Parameter	**34**	Transition state		
		cis	*trans*	tricoordinate
R = H				
$\Delta\Delta H^{\neq}$/kcal mol^{-1}	0	12.5	8.2	16.0
Hg–N/Å	2.16	2.19	2.18	3.30
$\upsilon_{im}^{\neq}$ /cm^{-1}	–	61	52	64
R = Me				
$\Delta\Delta H^{\neq}$/kcal mol^{-1}	0	24.4	16.1	9.2
Hg–N/Å	2.23	2.27	2.40	3.01
$\upsilon_{im}^{\neq}$/cm^{-1}	–	141	129	94

The gradual decrease in the energy barriers in the dissociative configuration inversion reaction involving the dissociation of the M–N bonds in the type **13** and **7** chelate complexes in the sequence Zn > Cd > Hg correlates with the decrease in the energies of these bonds in the same sequence. According to calorimetric measurements[136] of the heats of hydrolysis of zinc, cadmium, and mercury bis(trimethylsilyl)amides M[N(SiMe$_3$)]$_2$, the M–N bond energies are (kcal mol^{-1}) 50.0 (Zn–N), 34.4 (Cd–N), and 25.8 (Hg–N).

The rate of the degenerate ligand exchange for the type **7** bischelate complexes of mercury is 2–3 orders of magnitude lower than the rates of the intramolecular inversion processes. The intermolecular ligand exchange processes, which are kinetically second order, have been detected in solution from the temperature dependent changes in $^3J_{CH=N-^{199}Hg}$ in the ^{1}H NMR spectra and in $J_{^{199}Hg-^{15}N}$ the ^{199}Hg NMR spectra. The corresponding kinetic data are presented in Table 11.

In the series of the bischelate lead complexes **7** (X = Se), the protons of the diastereotopic grounds remain isochronic (^{1}H NMR) when the solutions in CD_2Cl_2 are cooled to −80 °C, which may be associated with the extremely high rates of the inversion process ($\Delta G_{25}^{\neq} < 7$ kcal mol^{-1}). However, for a series of compounds of this type (Table 11) enriched in ^{207}Pb, it is possible to detect an intermolecular degenerate ligand exchange process, which is indicated by the disappearance of the spin–spin coupling constant $J_{^{207}Pb-^{77}Se}$ in the ^{77}Se{H} NMR and $^3J_{^{207}Pb-N=CH}$ in the ^{1}H NMR spectra. This is also found with the aid of two-dimensional ^{1}H NMR spectroscopy.[135] As in the case of the isoligand cadmium complexes, the reaction is kinetically second order and the Pb–N and Pb–Se bond dissociation-formation processes are synchronous. The rate of reaction diminishes with increase in the bulk of the substituent at the coordinated nitrogen atom.

IX. Complexes of copper, silver, and gold

In the +1 oxidation state, copper, silver, and gold have the d^{10} valence electron shell, like the zinc, cadmium, mercury, and lead complexes in the +2 oxidation state examined above. For this reason, their bonds at the metal centre have a tetrahedral configuration in the tetracoordinate structures.

The Cu(I), Ag(I),[137] and Au(I)[138] bischelate complexes with neutral bidentate ligands of type **35** and having the general formula $[ML_2]^+PF_6^-$ (**36**), where L represents bis(tertiary arsines) and bis(tertiary phosphines), have been investigated in fair detail.

Table 11. Kinetic and activation parameters of the degenerate ligand exchange in type **7** Hg(II) and Pb(II) complexes [solvents—$CDCl_3$, $(CHCl_2)_2$, toluene-d_8].[132,135]

M	R	$^3J_{M-N=CH}(S=\frac{1}{2})$/Hz	k_{25}/s^{-1}	$\Delta H^{\neq}$/kcal mol^{-1}	$\Delta S^{\neq}$/cal mol^{-1} K^{-1}	$\Delta G_{25}^{\neq}$/kcal mol^{-1}
Hg	cyclo-C_6H_{11}	33.0	5.75	7.3	−30.7	16.4
	Bu^t	45.0	17.7	3.4	−41.3	15.8
	Pr^i	12.0	22.8	5.1	−35.1	15.6
	C_6H_4Me-*p*	13.0	13.5	6.2	−32.3	15.9
Pb	cyclo-C_6H_{11}	14.0	7.1×10^2	8.2	−17.9	13.6
	CH_2Ph	16.5	2.7×10^3	10.3	−8.3	12.8
	C_6H_4Me-*p*	16.0	4.3×10^3	5.76	−16.2	10.6

Note. In the mercury complexes, X = S, R^1 = Pr^i, R^2 = Me; in the lead complexes X = Se, R^1 = Pr^i, R^2 = Me.

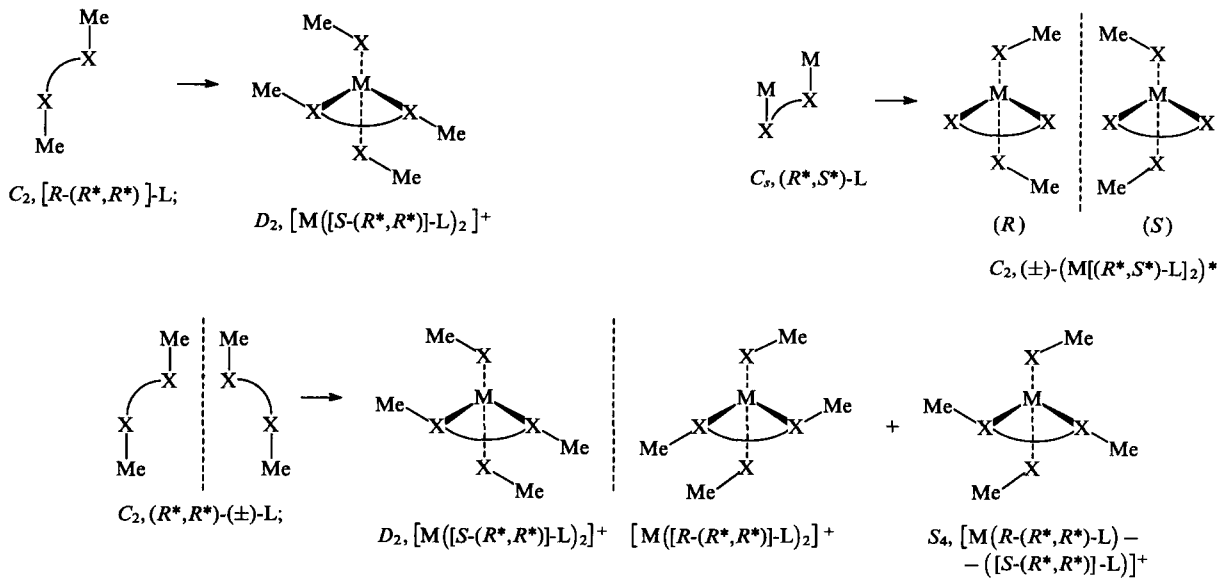
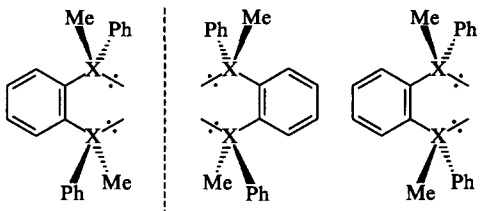
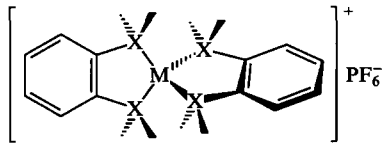


Figure 5. Stereochemical representation, according to the data of Salem et al.,[137] of the tetrahedral complexes **36** using the nomenclature of Cahn et al.[140] for the stereochemical descriptors.

When the donor centres in these ligands are chiral, as in 1,2-phenylenebis(methylphenylphosphines) and the corresponding arsines,[139] the complexes formed by them constitute a complex mixture of diastereoisomers (Fig. 5).





36

X = PMePh, AsMePh;
M = Cu, Ag, Au

The optically active forms of the dissymmetric ligands **35** (C_2-symmetry) give rise to discrete enantiomers of the complexes with D_2 symmetry, in which the PMe or AsMe groups are equivalent. The (R^*,R^*)-forms afford a mixture of chiral (D_2 symmetry) and achiral (S_4 symmetry) chelate complexes. Evidently, the interconversion of these diastereoisomeric forms is possible only as a result of the intermolecular ligand exchange. The achiral (R^*,S^*)-diastereoisomers of the ligand **35** form complex cations with C_2 symmetry in which the PMe or AsMe groups are diastereotopic. The possibility of detecting the intramolecular inversion of configuration in complexes **36** appears in those cases where the tetrahedral metal complex, produced by the (R^*,R^*)-(±)-form of the ligand, is stable in relation to the ligand redistribution reaction between different metal centres.

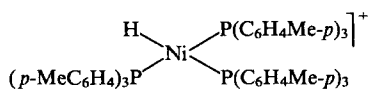
Both types of processes involving the inversion of the configuration of the metal centre have been observed in solutions of the bischelate complexes **36**. For example, when the mirror enantiomers of the phosphinecopper complex **36** are mixed in solution in CH_2Cl_2, the signals due to the PMe groups of the achiral diastereoisomer (S_4-symmetry) gradually appear in the ^{1}H NMR spectrum. The equilibrium ratio is $D_2 : S_4 = 1 : 6$ (at 20 °C). The time of attainment of equilibrium between the above diastereoisomers, induced by the intermolecular liquid exchange reactions in solution in CD_2Cl_2, is between 1 and 20 min for the copper complexes **36** at the usual temperature and between 1 min and 1 month for the gold(I) complexes.[137,138] Since the ligand exchange reactions are fairly slow under these conditions for all the complexes investigated, there is a possibility of the independent detection of the intramolecular inversion of the tetrahedral configuration of the metal centre in complexes **36** from the diastereotopic averaging of the signals due to the XMe (X = P, As) groups. Table 12 presents the free energies of activation for the inversion process determined at the coalescence temperatures. The observed values are very close to those listed in Tables 7, 8, and 11 for the Zn(II), Cd(II), Hg(II), and Pb(II) bischelate complexes. Although Salem et al.[137] were unable to obtain definite evidence in support of one of the two possible intramolecular inversion mechanisms, they suggest that the reaction follows the digonal twist mechanism without involving the intramolecular dissociation of the bonds between the central atom and ligating atoms.

Table 12. Free energies of activation at the coalescence temperatures (f_0 = 200 MHz) for the intramolecular inversion of the tetrahedral configuration of the metal centre in type **36** complexes (±)-(M[(R^*,S^*)-L]$_2$)PF_6 (L = compound **35**).[137,138]

M	X	Solvent	T_c/°C	$\Delta G^{\neq}_{T_c}$/kcal mol^{-1}
Cu	P	$C_6D_5NO_2$	>120	20.5
Cu	As	CH_2Cl_2	5	13.1
Ag	P	CH_2Cl_2	5	11.9
Ag	As	CH_2Cl_2	−55	10.4
Au	P	$C_6D_5NO_2$	120	18.7
Au	As	CH_2Cl_2	−29	11.7

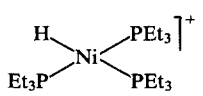
X. Complexes of nickel and other transition metals

The principal cause of the instability of the planar configuration of the complexes of d^{10} metals — the filling of the antibonding b_{1g} molecular orbital with electrons — is eliminated for the complexes of d^8 metals.[141-143] The planar configuration is therefore energetically preferred for the 16-electron valence shell of the Ni(II), Pd(II), Pt(II), Au(III), etc. complexes. In a number of instances, the stable configuration in the crystalline state for Cu(II) and especially Ni(II) complexes is intermediate between the planar and tetrahedral configurations and the dihedral angle, which determines the transition from planar (θ = 0°) to tetrahedral (θ = 90°) coordination, can vary within very wide limits (see the references in the review of Garnovskii et al.[38]). The situation where tetrahedral structures play the role of the reaction transition states in the isomerisation or topomerisation of the planar forms is more general (Fig. 1).[35,144] In a number of instances, the relative energies of these structures — transition states in the isomerisation reaction — are fairly low and the planar complexes of the tetracoordinate metals are then fluctuating molecules and the isomerisation itself is recorded on the timescale of NMR spectra. Certain examples of such complexes (compounds **37-39**) are given below (the free energies $\Delta G_{25}^{\neq}$ for the *cis-trans* isomerisation are indicated).



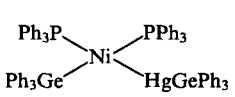
37

$\Delta G_{25}^{\neq}$ = 14.6 kcal mol^{-1}
(Eaton et al.[145])



38

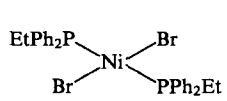
$\Delta G_{25}^{\neq}$ = 12.0 kcal mol^{-1}
(English et al.[146])



39

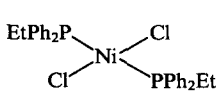
$\Delta G_{25}^{\neq}$ = 12.3 kcal mol^{-1}
(Grishin et al.[147])

In some cases, the tetrahedral structures are isomeric in relation to the planar forms and exist in solution in equilibrium with them. The barriers to the interconversion of the planar and tetrahedral structures are usually very low (see the Introduction), but for certain complexes (compounds **40-42**) the barriers reach values which can be determined with the aid of the dynamic NMR method.



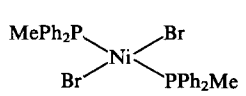
40

$\Delta G_{25}^{\neq}$ = 10.4 kcal mol^{-1}
(LaMar and Sherman[148])



41

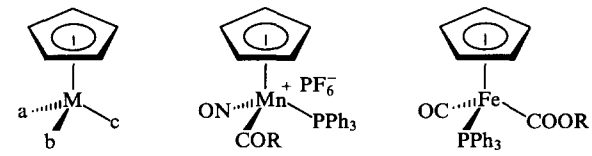
$\Delta G_{25}^{\neq}$ = 9.3 kcal mol^{-1}
(LaMar and Sherman[148])



42

$\Delta G_{25}^{\neq}$ = 9.2 kcal mol^{-1}
(Pignolet et al.[149])

Within the framework of the present review, transition metal complexes for which the tetrahedral forms correspond to the structures of the ground states and the tetracoordinate metal centre is itself chiral are of special interest. A wide range of such complexes of the general type **43** are now known.



43 **43a** **43b**

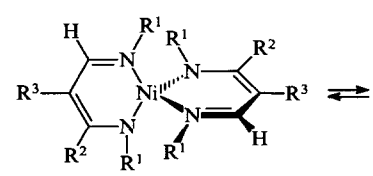
M = Mn, Fe, Ru, Cr, Mo, W, Co.

Some of them, for example, complexes **43a** and **43b**, are configurationally stable compounds which can be resolved into their optical isomers on a preparative scale.[150,151] The mechanisms of the inversion of the tetrahedral configuration of the metal atom in type **43** complexes have been subjected to a careful kinetic analysis and have also been investigated by a computational method.[152] The most probable is the dissociative mechanism involving, for example in complex **43a**, the splitting off of the phosphine ligand and the formation of a chiral intermediate with a tricoordinate pyramidal metal atom undergoing rapid inversion.

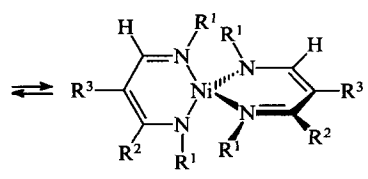
Knorr and coworkers[153-156] obtained the bischelate and configurationally stable nickel complexes **44** and **45** with high barriers to tetrahedral inversion.

The inversion process in complex **44** (Scheme 12) has been investigated from the temperature-dependent diastereotopic averaging of the signals due to the methylene groups of the ethyl substituent (R^3) or the methyl group of the *o*-tolyl substituent (R^3). The energy barriers to the inversion process at the temperatures of the coalescence of the indicator signals (at 95-180 °C in cyclohexane or tetralin) are in the range 17.2-23.8 kcal mol^{-1}.[153,155]

Scheme 12



44(*R*)



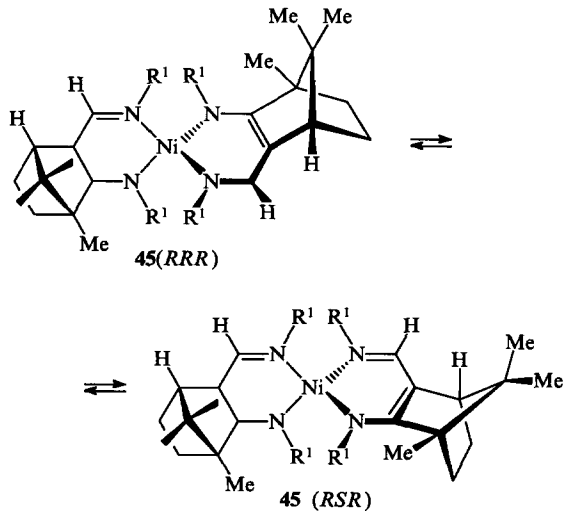
44(*S*)

R^1 = Me, Ph; R^2 = Me, Pr; R^3 = Et, C_6H_4Me-*o*.

The bischelate complexes **45** contain an additional chiral unit — the (*R*)-camphor fragment, so that the inversion of the tetrahedral Ni(II) (Scheme 13) (see over) represents not enantiomerisation but diastereoisomerisation, both diastereoisomers being chiral. It has been established[154] that this process is purely intramolecular. The kinetics have been investigated both by integrating the signals due to the pairs of hydrogen atoms involved in the exchange (in view of the paramagnetism of complexes **44** and **45**, the chemical shifts of their protons were very large) and polarimetrically (slow mutarotation). The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ ($\Delta H^{\neq}$ = 22.5 ± 0.8 kcal mol^{-1} and $\Delta S^{\neq}$ = −15 ± 3 cal mol^{-1} K^{-1} in tetralin) found for complex **45** (R^1 = Ph) indiate the possibility of the preparative separation of the enantiomers of tetrahedral paramagnetic bischelate Ni(II) complexes. For complex **45** (R = Me), the height of the barrier corresponds to $\Delta G^{\neq}$ = 17 ± 1 kcal mol^{-1}.

The possibility of the operation of the dissociative intramolecular mechanism of the enantiomerisation of the bischelate complexes of type **44** with the NiN_4 chelate unit and involving the

Scheme 13

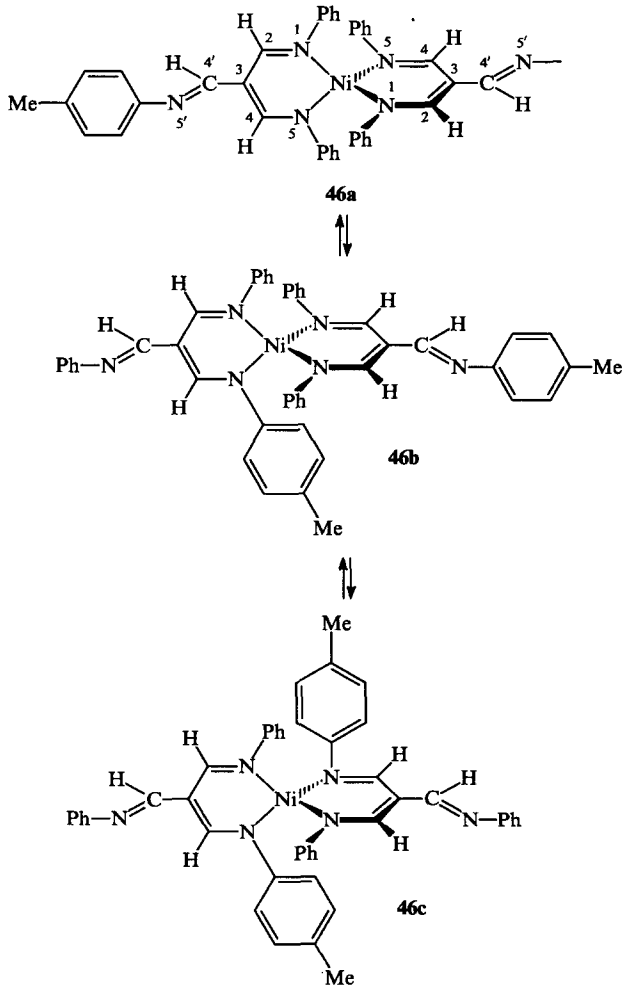


45(*RRR*)

45 (*RSR*)

dissociation of the Ni–N bond has been demonstrated in a study of the transcoordination of the metal atom in complex **46** (Scheme 14).[156] It was established that the transcoordination reaction is very slow [$k = (38 \pm 5) \times 10^{-8}$ s^{-1} at 24.5 °C in solution in the 3 : 1 $CCl_4/CDCl_3$ mixture] and cannot therefore make an appreciable contribution to the observed inversion transformations.

Scheme 14



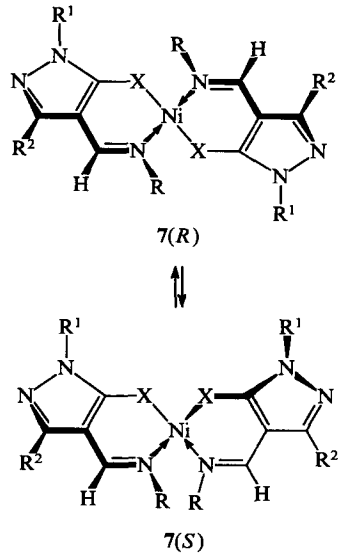
46a

46b

46c

The possibility of the intramolecular tetrahedral inversion of Ni(II) with a fairly high barrier in the series of metal chelates with a NiN_2X_2 (X = O, S, Se) coordination unit, the rate of which corresponds to the characteristic time scale of dynamic ^{1}H NMR, was first demonstrated for type **7** complexes of the pyrazole series (Scheme 15).[157–160]

Scheme 15



7(*R*)

7(*S*)

The condensation of the pyrazole ring with the chelate ring in complexes **7** stabilises sharply the tetrahedral configuration relative to the planar structure,[43,157,161–163] which can be explained by the steric strain in the chelate ring induced by the condensation of the five-membered heterocycle with it.[164] The pseudotetrahedral structure of complexes **7** in the solid state has been confirmed by X-ray diffraction studies.[38,111,165]

The inversion of the tetrahedral configuration (Scheme 15) has been investigated from the temperature-dependent diastereotopic averaging of the signals due to the corresponding groups of prochiral substituents (Pr^i, CH_2Ph) at the coordinated nitrogen atom and in the 1- and 3-positions in the pyrazole ring. Although the multiplet structure of the signals due to the protons of the diastereotopic groups is not resolved in the spectra owing to the broadening of the signals ($\Delta\nu_{1/2}$ = 12 Hz) typical for paramagnetic complexes, the difference between their chemical shifts at low rates of the exchange processes is 25–500 Hz (f_0 = 100 MHz), which explains the adequate accuracy of the determination of the rate constants and energy barriers for the inversion process at temperatures corresponding to coalescence of the indicator signals.

The energy barriers to the inversion of the tetrahedral configuration of Ni(II) in the bischelate complexes **7** are presented in Table 13. It is seen that the barriers increase with increase in the steric bulk of the substituent R, the increase being particularly notable for R = Bu^t. This effect is fully consistent with a feature well known for complexes of tetracoordinate Ni(II) with NiN_2X_2 chelate units (complexes of types **2**, **3**, **5**, **9**, and **11**)—the shift of the square–tetrahedron equilibrium to the right in the series of substituents R: n-alkyl < *sec*-alkyl < *tert*-alkyl.[1,27,28]

It follows from data of Nivorozhin and coworkers[158,159] that the observed inversion process proceeds via the digonal twist mechanism (pathway *a* in Fig. 2) with formation in the transition state of the planar achiral *cis*-structure typical for the complexes NiN_2S_2 and NiN_2Se_2.[157,160,167–169] It may be expected that, in connection with the rapid development of the NMR methods for the investigation of the kinetics of reactions of paramagnetic compounds,[170] the available information on the dynamics of the stereoisomerisation of tetrahedral Ni(II) complexes will soon expand significantly.

Table 13. Energy barriers to the inversion of the tetrahedral configuration of Ni(II) in type **7** bischelate complexes (solvent—$CDCl_3$).[158, 159]

X	R	R^1	R^2	T_c/°C	$\Delta G^{\neq}_{T_c}$/kcal mol^{-1}
S	Me	Pr^i	Me	−50	10.2
S	Pr^i	Pr^i	Me	−20	12.1
S	Bu^t	Pr^i	Me	100	17.6[a]
Se	Me	Pr^i	Me	−25	11.5
Se	Pr^i	Pr^i	Me	−10	12.5
S	$C_6H_4NMe_2$-*p*	Pr^i	Me	−20	12.3
S	C_6H_4Me-*p*	Pr^i	Me	−40	11.4
S	$C_6H_4NO_2$-*p*	Pr^i	Me	−50	11.0
Se	C_6H_4Me-*p*	Pr^i	Me	−20	12.3
S	Pr^i	CH_2Ph	Me	−20	11.6
Se	Pr^i	Ph	Me	−5	12.4
S	Pr^i	Ph	Pr^i	−43	11.1
S	Bu^t	Ph	Pr^i	60	16.9
Se	Pr^i	Ph	Pr^i	−48	11.1

[a] Solvent—DMSO-d_6.

XI. Conclusion

The data presented in this review show that all the theoretically possible types of mechanisms of the inversion of the tetrahedral configuration operate in the enantiomerisation reactions of dissymmetric chelate complexes of transition metals. The majority of these compounds have stereochemically nonrigid structures and the energy barriers to the tetrahedral inversion fit within the characteristic time scale of NMR spectroscopy. In the presence of suitable prochiral substituents in the complexes, the stereoisomerisation processes can be investigated and characterised quantitatively by means of the dynamic NMR method without the preliminary separation of the enantiomeric forms, while with the aid of structural modelling of the ligand, especially when alterdentate ligands are used, it is possible to differentiate reliably the different intramolecular stereoisomerisation mechanisms.

Table 14 summarises the principal results of the studies carried out in this field. For comparison, it also includes the energy barriers to the intramolecular inversion of the tetrahedral configuration of the sp^3-carbon centres. The preferred enantiomerisation pathway is determined mainly by the nature of the centre undergoing inversion.

The data available hitherto on the kinetics and mechanisms of the processes involving the inversion of the tetrahedral configuration in nontransition metal complexes, examined in this review, are still far from complete. Nevertheless, they are already sufficient to reveal certain general trends in the behaviour of the stereochemically nonrigid complexes of this type and to compare them with the much more detailed results obtained in the study of the stereodynamics and ligand exchange reactions for transition metal complexes.

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Table 14. Energy barriers (kcal mol^{-1}) to the inversion of the tetrahedral configurations of the tetracoordinate d^0 and d^{10} metals and Ni(II).

M(R^1,R^2,R^3,R^4)	Digonal twist	Dissociation-formation of M−R bonds	Intermolecular associative mechanism
C(IV)	Not found[a]	18−28[b]	$(RR^1CHLi)_4$[c]
Be(II)	"	18−25	20−27
B(III)	"	20−22	22−25
Ga(III)	Not investigated	18	$(RR^1R^2Ga)_n$[d]
In(III)	"	12	$(RR^1R^2In)_n$[d]
Zn(II)	9−20	>15	17−22
Cd(II)	9−14[e]	>11	11−17
Hg(II)	11−13[e]	13	14−17
Pb(II)	Not investigated	10	9−14
Cu(I)	13−20	No data	[f]
Ni(II)	3−18	>26	14−20

[a] See Table 1.

[b] The energy barriers were determined by dynamic NMR for the intramolecular isomerisations of indolinospirobenzopyrans and 2-oxaindanospirobenzopyrans involving the thermal dissociation of the C_{sp^3}−O bonds.[170−173]

[c] This mechanism operates readily at the usual temperature in solutions of associated organolithium[174] and other organometallic compounds.

[d] This mechanism operates readily in solutions of dimers and polymeric associated species of organogallium and organoindium compounds.[175]

[e] The choice between the digonal twist intramolecular mechanism and the intramolecular mechanism involving the dissociation-formation of the M−N bond is not unambiguous.

[f] When enantiomers of Cu(I) complexes are mixed with type **35** ligands, racemisation takes place with a half-life $\tau_{1/2}$ = 1−20 min in solution in CH_2Cl_2 at 25 °C.[137, 138]

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