Coordination Chemistry Reviews, 126 (1993) 1–69

Ligand environment and the structure of Schiff base adducts and tetracoordinated metal-chelates

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(Received 12 December 1991; revised 11 September 1992)

CONTENTS

A. INTRODUCTION

Since the seminal works by Ettling, Schiff and Pfeiffer (see ref. 1 and the references cited therein) metal-chelate Schiff base complexes have continued to play the role of one of the most important stereochemical models in main group and transition metal coordination chemistry due to their preparative accessibility, diversity and structural variability.

For example, the reactions (1) and (3) of *ortho*-hydroxy(thio-, seleno-, amino-)

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0010-8545/93/$24.00

Schiff bases **1**, **4** (LH) with the metal salts MA_n proceed through the elimination of the corresponding acid HA, resulting in the formation of metal-chelate complex **2**, **5** (ML_2) (Fig. 1). The methods of synthesis and the structure of tetracoordinate Schiff base metal-chelates **2** have previously been amply reviewed [1–23]. However, the most relevant full-length review papers [1,2] are already outdated whereas subsequent ones [3–23] are essentially concentrated on various special properties of those complexes **2** which contain as ligating centres only oxygen and nitrogen atoms (X = O, NR). Much less attention was paid to the chalcogen analogs of **2** (X = S, Se) since most preparative and particularly structural data on these complexes have been accumulated during the last decade. It was the first goal of the present review to systematize this structural information (see Table 1) as well as those related to the whole set of metal-chelates **2** (X = O, NR, S, Se) and to stress the drastic changes in configuration of the metal centre caused by replacement of ligating oxygen atoms by chalcogens; we also consider the role of structural modifications in more distant parts of the ligand moieties. The structural variations in more rigid Schiff base metal-

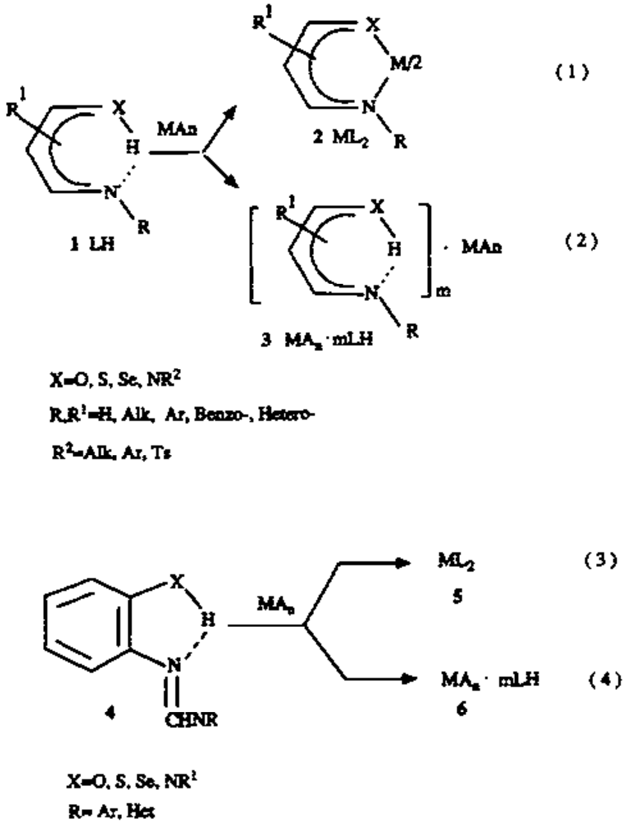


Fig. 1. Interaction of Schiff bases with Lewis acids.

chelates derived from *N*,*N'*-bridged tetradentate ligands are examined, focusing on the geometrical tuning imposed on the metal centre by systematic variations in the length and flexibility of the available strap.

A separate section of the present review is devoted to the relatively poorly studied five-membered ring metal-chelate compounds **5**. Some novel results on their preparation and structure are generalized, allowing us to elucidate distinguishing features of five-membered metal-chelates **5** compared with their six-membered ring analogues **2**, both possessing identical ligating atom environments.

In the sixties, it was discovered that, apart from formation of metal-chelate complexes **2**, **5** other pathways, (2) and (4), may occur which yields the adducts **3**, **6** $MA_n \cdot m$LH containing the intact ligand moieties [24–26] (Fig. 1). There is growing interest in the development of preparative methods for, and study of the bonding and structure of type **3**, **6** complexes [27–30]. Some early conclusions were ambiguous and need to be reconsidered. Our task in this part was to survey critically these problems mentioned previously which had not been treated comprehensively.

We include a brief section dealing with the structure and tautomerism of Schiff base ligands **1** from an angle of consideration different from that in an earlier review [18]. The ability of ligand **1** (LH) to retain the acidic hydrogen atoms when reacting with Lewis acids and affording complexes **3** depends upon structural peculiarities, the nature of the coordinate bond and reaction conditions. The role of those factors is thoroughly analyzed.

Thus this review discusses the current state of study of different structural factors (nature of ligating centres, size of chelate ring, different structural modifications) affecting (1) the configuration at the metal centre in metal-chelate complexes **2**, **5** (X = O, NR, S, Se) and (2) the tendency of certain ligands **1**, **4** to form, with Lewis acids, not chelate but rather molecular adduct-type complexes.

The literature is covered to the beginning of 1992 with emphasis on studies carried out during the last decade.

B. LIGANDS

The structures of Schiff bases and their analogues have been thoroughly summarized [18,31,32]. For this reason, we will confine our consideration to the principal conclusions from these data and discuss some previously omitted results which may be important for understanding the complexation of Schiff base ligands.

(i) Tautomerism

In principle, the tautomeric equilibrium of three prototropic tautomers is possible for Schiff base compounds of type **1** (Fig. 2) [18,31,32]. The enamine **7b** is the energetically favourable form for the β-aminopropenones (thiones) **7** (X = O, S; R, R^1 = H, Alk, Ar) and Schiff bases of *ortho*-hydroxy(thio, seleno) heteroaromatic

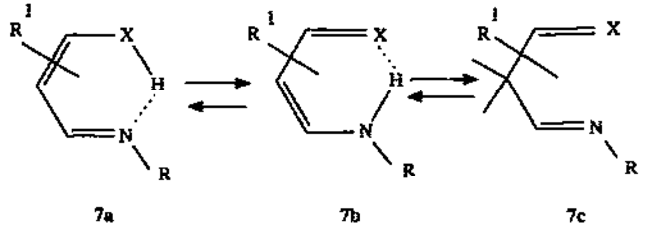
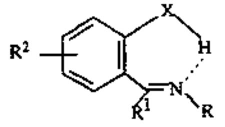


Fig. 2. Tautomeric forms of Schiff bases.

aldehydes such as pyrrole-, thiophene-, furan- and their benzoannelated derivatives, and azoles [33–40]. This enamine form dominates in both solution and the solid state irrespective of the substituent R, R^1, type of solvent and temperature.

Benzoannelation to the aminoenone moiety essentially shifts the tautomeric equilibrium towards type **7a** tautomers such that arylimines of salicylaldehyde **8** ($R = Ar$; $R^1 = R^2 = H$; $X = O$) and aryl(alkyl)imines of 2-hydroxy-3-naphthalenealdehyde **8** (R, $R^1 = H$, Alk, Ar; $R^2 = 4,5$-benzo; $X = O$) possess hydroxyimino structure **7a** in solvents of various polarity [31].



8

X=O,S,Se

R,R^1=H,Alk,Ar; R^2=H, 4,5-benzo, 3,4-benzo

The structural variations in **8** involving substitution of the *N*-aryl group by alkyl, the substitution of $X = O$ for sulphur or selenium and 3,4-benzoannelation increase the relative stability of the tautomeric form **7b** whereas alkyl and aryl substituents at the azomethine carbon atom (R^1 = Alk, Ar) and electron-withdrawing groups in the aldehyde moiety R^2 [41,42] favour the benzenoid tautometer **7a** [28]. The position of the tautomeric equilibrium (Fig. 2) is strongly affected by the solvent; protonic and aprotonic solvents with high dielectric constants shift the equilibrium towards the quinonoid tautometer **7b**.

The tautomeric form **7c** is insignificant for compounds of type **1** but it was found in measurable amounts in the case of β-diketones and arylimines of β-ketoethers used as ligands for the synthesis of metallocomplexes [30,43–45].

Additional basic centres conjugated with the azomethine group involve the occurrence of other tautomeric forms of Schiff bases apart from those shown in Fig. 2. The tautomeric form of type **9a** was established for imines of 3-formyl-2(1H)quinolinethione and selone which could display a tautomeric equilibrium between the structures **9a**–**9c** [46], while other forms, **10a**–**10d**, may be conceivable in the case of substituted *ortho*-indophenols (Fig. 3) [47].

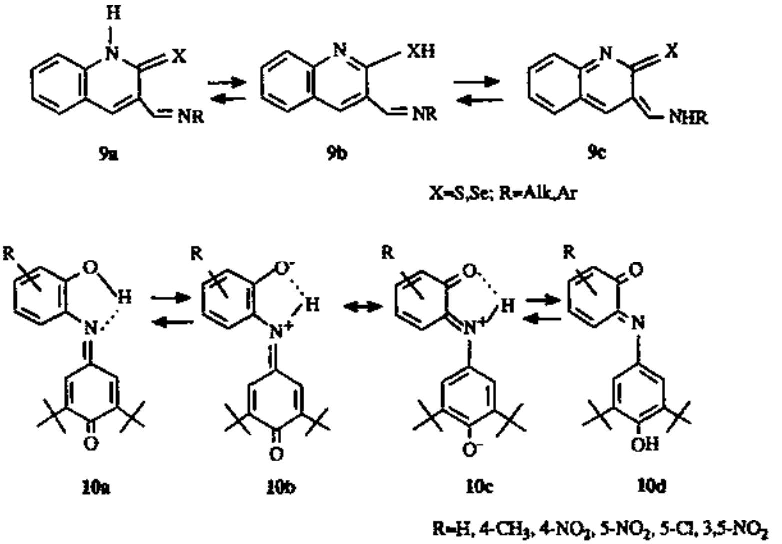


Fig. 3. Tautomeric equilibria for imines of 3-formyl-2(1H)quinolinethione(selone), **9** and imino-phenols, **10**.

(ii) Hydrogen bond

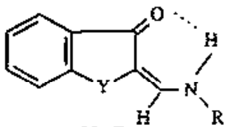
Intramolecular hydrogen bonds in Schiff bases may form six- or five-membered cycles exemplified by the structures of types **1** and **4**. The hydrogen bonds participating in six-membered rings are essentially stronger than those of five-membered rings due to the acquisition of a quasi-aromatic type in the former case [3,48]; this is supported by spectroscopic data.

As seen from IR spectra, the stretching vibrations of the −OH group for **1** occur as broad bands in the range 2300–3400 cm^{-1} [18], unlike **4** where these bands appear as sharp peaks at 3400–3470 cm^{-1} [3,49,50]. The frequencies characteristic for −OH groups play an important role as a prognostic test for monitoring whether or not deprotonation occurs upon complexation, resulting in the formation of a chelate complex [51] or adduct [52] (see later).

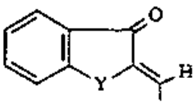
In some cases the formation of intermolecular hydrogen bonds is an alternative to the formation of intramolecular hydrogen bonds [35]. Indeed, X-ray data of several heterocyclic enamines **11** have confirmed the existence of Z-isomers [53]. A dimeric structure with an intramolecular hydrogen bond was found for the indophenolic compound **10a** ($R = 4\text{-}NO_2$) [50]; the mechanism of the $Z \rightleftharpoons E$ isomerization around the C=N bond in these compounds was shown to be dependent upon the strength of the hydrogen bond [47,50].

(iii) Stereochemistry

The energetically preferred conformations of Schiff bases are non-planar [18,54–72]. As the structure **12** shows, the nitrogen aryl substituents are usually



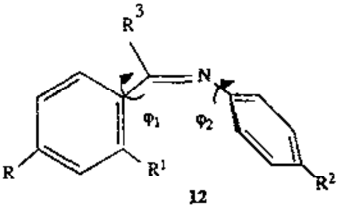
11 E-



11 Z-

R=Ph, 1-Pyperidyl
Y=O, S

twisted along the C—N axis by the angle ϕ_2, while the aromatic rings of the aldehyde moieties are practically coplanar with the azomethine group ($\phi_1 \approx 0°$) [18,54–58]. These conformations were predicted by quantum mechanical calculations [54–56,59–63] and have been found in the solid state [18,58,64], in solution [54–56,66,70–72] and in the gas phase [18,65]. Compounds of type **12** were shown to display atropisomerism [54–56].



12

R,R^2=H,Alk,Ar,OAlk,Hal,NO_2,COOH,CN,$N(CH_3)_2$,OCF_3
R^1=H,OH R^3=H,Alk,Ar

The nature of the non-planar structure of Schiff bases is accounted for by the sum of steric and electronic effects [54,57]. For example, electron acceptor substituents in the imine fragment R^2 as well as the alkyl and aryl substituents R^3 [61] increase the value of angle ϕ_2, while donor substituents R^2 decrease them. Nevertheless, these simple correlations are not accurate [18,58], especially in the crystalline state where various mesomorphic modifications may be revealed [58].

Ortho-hydroxy substituents R^1 in **12** affect only slightly the overall conformation of the molecule [18,67–72], e.g. the angle ϕ_2 for *N*-phenylbenzaldimine ($R = R^1 = R^2 = R^3 = H$) is equal to 55.2° and 49° in the case of the related *N*-phenylsalicylaldimine ($R = R^2 = R^3 = H$, $R^1 = OH$) [18].

From the study of Kerr constants, the value of ϕ_2 in solution is close to that in the solid state. For *N*-phenyl-2-hydroxy-1-naphthaldimine in the crystalline state, ϕ_2 equals 41.3° [28] and 48° in dioxane solution [71].

The trends in ϕ_2 behaviour described above can be extended to *β*-aminopropenones, as the corresponding value of 47.9° has been found for *N*-(4-bromophenyl)-acetylacetoneimine by X-ray structural investigation [27]. An essentially twisted conformation of the CH=N—Ar moiety was recently revealed [72] both in solution and in the solid for 2-TeR (R = Hal, Alk)-substituted *N*-arylbenzaldimines.

Thus, the lability of Schiff base molecular structure is determined by possibilities for tautomeric transformations, formation of different types of hydrogen bond as well as by conformational effects. These properties, as illustrated in the next section, are also responsible for the subtle balance of factors influencing the structure of Schiff base adducts.

C. ADDUCTS

The capacity to form adducts with Lewis acids such as **3** and **6** is a characteristic feature of a large group of compounds containing the −XH function (X = O, N, S, Se) involved in an intramolecular hydrogen bond. In addition to Schiff bases, these include *β*-diketones, 8-hydroxy-(thio)quinolines, formazanes and others. A comprehensive survey [29] covering different aspects of the synthesis and structure of adducts of all these ligand structural types has recently been published; thus we consider here only the relevant Schiff base adducts in more detail with the emphasis on recent developments in the field.

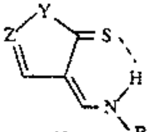
(i) Synthesis

Schiff base adducts of type **3** were initially reported [24] in the reaction of *N,N'*-ethylene-bis(acetylacetoneimine) (H_2Acacen) with Zn(II) and Sn(II) chlorides and the nitrates of Ag(I), Ca(II) and Sr(II) followed by investigation [25,26] of the adducts of salicylaldimines with $Th(NO_3)_4$ and different Group IV metal chlorides. Subsequently [29], the directed synthesis of adducts with various Schiff bases of types **1** and **4** and Lewis acids (mainly halides and pseudo-halides of the elements of Groups III–V) were accomplished; these are commonly carried out by the direct interaction of Schiff base and Lewis acid in aprotic solvents with low dielectric constants such as hydrocarbons and chlorinated hydrocarbons. To complete this general situation, we consider some representative examples involving the use of modified ligand systems, other Lewis acids and preparative methods.

Schiff bases and their analogues containing additional donor centres in the imine part of the molecule as well as at the ligand periphery have been extensively studied. These include hydrazones (derived from both non-substituted [73,74] and monoaryl-substituted hydrazines [75]), tridentate ligands formed by monocondensation of diamines with *β*-dicarbonyl compounds [76], Schiff bases prepared from heterocyclic amines incorporating azole and azine rings [29,77,78], iminoalcohols [29,79], imines of types **1** and **4** derived from *o,o'*-diamino-, and *o,o'*-diformyl- and diarylditellurides [80,81], enaminothiones **13** ($R = C_6H_5Cr(CO)_3$-η^6) [82] bearing the π-bound organometallic d-base [83,84] fragment.

So far, few data are related to adducts with Schiff bases of type **4** and those of type **1** containing donor atoms other than oxygen (X in formulae **1**), e.g. X = S

[85,86] and X = NTs [87], the former being reported for heterocyclic enaminothiones **13** containing furan (Y = O), thiophene (Y = S) and pyrazole (Y = NR) rings [29].



13

Y=O, S, NR; Z=N, CPh; R= Alk, Ar

To outline the body of Lewis acids employed, one could also add halides of Co(II), Co(III) [88]; Fe(II), Fe(III) [89]; W(VI) [90,91]; Mo(VI) [27,92,93] and lanthanide metals [29,94,95], nitrates of Ag(I) [94] and Ca(II) [96], sulphates of Zn(II), Cd(II) and Hg(II) [97].

Selection of the appropriate solvent to carry out the transformations (2) and (4) (Fig. 1) depends on the necessity to create conditions for avoiding hydrolysis or solvolysis of the Lewis acid (particularly, in the case of the elements of Groups III–VI) and suppressing dissociation of the hydroxy group. Indeed, the interaction of $NbCl_5$ with **7** in methanol or ethanol yielded the complexes $NbCl_3(OR)_2 \cdot LH$ ($R = CH_3, C_2H_5$) with alcohol residues [98]; alcoholysis was also observed for the adducts of MoO_2Cl_2 [92]. In this connection, the reported synthesis of $SnCl_4$ and Ph_3SnCl adducts with **7** in ethanol is uncertain [99]. Nevertheless, in view of the low solubility in hydrocarbons or chlorinated hydrocarbons of metal halides or nitrates of elements of Groups I, II, VII, and VIII, the following solvents were used with varying success: absolute alcohols [25,88,92,94–104], acetone [105], acetonitrile [73–80], ethers [25,92], tetrahydrofuran [29,106] and mixtures of solvents [29,86]. When the reactions are conducted in solvents possessing the ability to coordinate, they may afford solvated complexes of type $(MA_n \cdot mLH)_p \cdot Solv$ which is particularly typical for tetrahydrofuran [106].

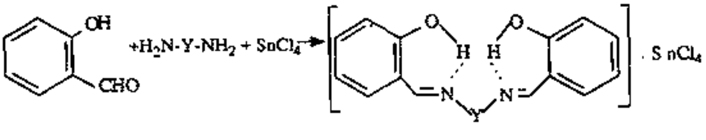
Thus, the direct interaction of Schiff bases with Lewis acids is not always an adequate synthetic strategy for the preparation of adducts. Other synthetic routes yielding the Schiff base adducts, viz. ligand exchange reactions and template synthesis, have been reported in several cases.

Ligand exchange reactions were used in the case of weakly soluble Lewis acids. For example, complexes of $NbCl_5$ with **7** were obtained by reaction of benzene solutions of the $NbCl_5$ adduct with ethylacetate (EA) with Schiff base ligands under cooling (eqn. (5)) [107,108]. A similar procedure (eqn. (6)) was employed for the high yield preparation of Schiff base adducts of $NbOCl_3$ [109] and WO_2Cl_2 [110] utilizing, in the latter case, the adduct of WO_2Cl_2 with triphenylphosphineoxide.

$$NbCl_5 \cdot EA + LH \xrightarrow{C_6H_6} NbCl_5 \cdot LH + EA \qquad (5)$$

$$\mathrm{WO_2Cl_2 \cdot R_3P{=}O + 2LH \xrightarrow[70-80\%]{CH_2Cl_2} WO_2Cl_2 \cdot 2LH + R_3P{=}O} \qquad (6)$$

Synthesis of the adducts of $SnCl_4$ with Schiff base **14** was reported by the template condensation of ligand precursors and Lewis acid without solvent [111].



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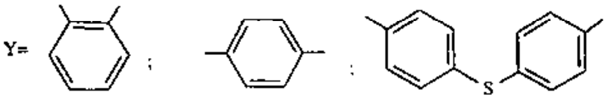


Another representative synthesis involves the preparation of salicylaldimine adducts with $PdCl_2$ [112] from the corresponding metal-chelate complex by the action of mineral acid. However, the direct synthesis of adducts from Schiff base ligands and Lewis acids continues to be the most general and appropriate method for the preparation of Schiff base adducts with various ligands and Lewis acids.

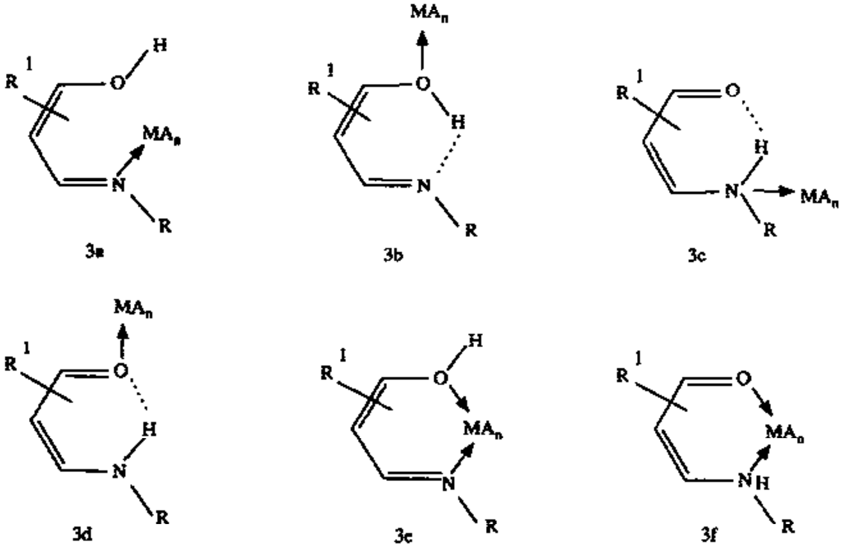
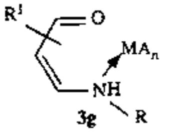


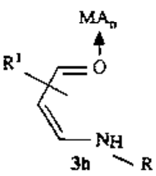
Fig. 4. Structural types of Schiff base adducts 3.

(ii) Structure, tautomeric forms of the ligands, coordination modes, stereochemistry

Analysis of the literature data reveals that six principal structures (Fig. 4) are used to describe the Schiff base adducts of type **3**. These structures differ as follows. (1) The tautomeric form of the ligand is hydroxyimino in the case of **3a**, **3b**, and **3e** and ketoamino for **3c**, **3d** and **3f**; (2) in adducts **3a–3d**, the ligands are monodentate, being coordinated either through nitrogen or oxygen ligating centres whereas in **3e** and **3f** they display bidentate nature; (3) the ligand hydrogen bond is retained in complexes of type **3b**, **3c** and **3d**, while in **3a**, **3e** and **3f** it is broken. In addition, there could exist two conceivable structures of type **3g** and **3h** possessing monodentate bonding via N— (**3g**) or O— (**3h**) atoms without intramolecular hydrogen bonds.

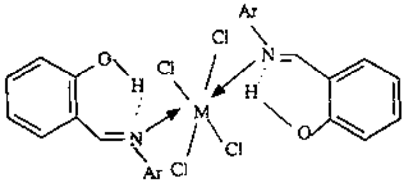


3g



3h

Schiff base adduct **3** structural assignments were originally treated in ref. 26. Evaluation of the IR spectral data on $TiCl_4$ and $SnCl_4$ adducts, supposedly with structure **15**, showed that these involve *N*-coordination and the presence in the ligand moiety of an intramolecular hydrogen bond.



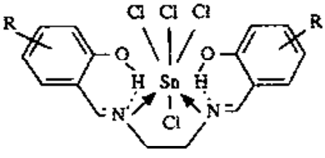
15

M=Sn, Ti

Ar=C_6H_5, 4-$CH_3C_6H_4$, 4-$NO_2C_6H_4$,3-$NO_2C_6H_4$

Coordination by the nitrogen atom is suggested for ligands with six-membered hydrogen-bonded rings **1** [25,26,73,92,107,111,113,114] and those with five-membered rings, **4** [52,92,107,109]. In the former case, the hydrogen bond in the coordinated ligand is either retained in the structure, e.g. **15** [26], **16** [115] or broken, e.g. **17** [116], **18** [79], **19** [76], **20** [79]. For adducts of type **4** structures without a hydrogen bond **21** [52] and **22** [117] are preferable.

Comparison between structures of types **15** and **16** and those of types **17–20** shows rupture of the hydrogen bond in the case of ligands containing additional donor groups coordinated to the metal (e.g. hydroxy group incorporated in the iminoalcohol residue [118,119]); however, the occurrence of the latter structures is not well documented and is particularly doubtful for **19** and **20** in view of the unusual coordination numbers for silicon and tin.



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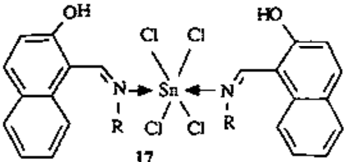
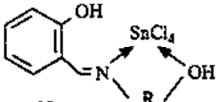


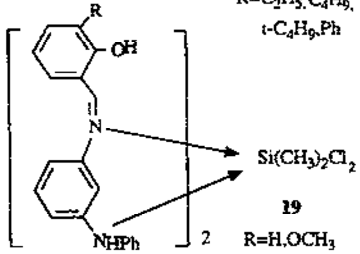
17

R=C_2H_5, C_4H_9, t-C_4H_9,Ph



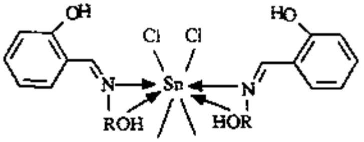
18

R= $-(CH_2)_2-$, $-(CH_2)_3-$, $-\underset{C_2H_5}{CH}-CH_2-$



19

R=H,OCH_3



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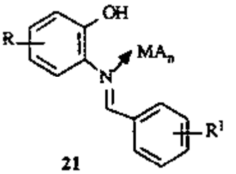

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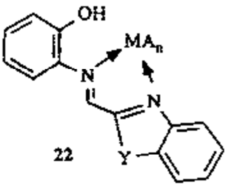


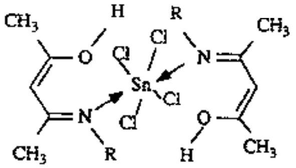
22

R=H, 3-NO_2, 4-NO_2
R^1=H, 4-NO_2, 4-$N(CH_3)_2$, Hal, Alk

Y=S, NR; R=CH_3, C_2H_5

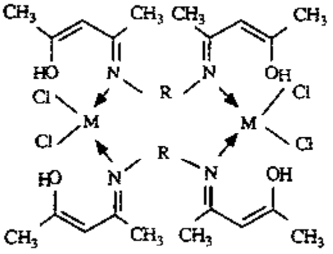
Coordination by nitrogen atoms is inferred for adducts of β-aminopropenones [104,116] and β-aminopropenethiones [85]. The tautomeric form of the ligand was assigned to be hydroxyimino for complexes **23** and **24** [104,116].

However, one of the first X-ray structural determinations of a Schiff base adduct of type **3** [120] revealed the importance of the O-binding mode found in the polymeric complex **25** of $(CH_3)_2SnCl_2$ with H_2Salen where the metal is coordinated to a phenolic oxygen. Although the hydroxy group proton has not been localized, the distance 2.62 Å of N ··· O corresponds to the occurrence of the hydrogen bond N ··· HO. Similar ligation is known for a large number of tin derivatives of the general type R_nSnCl_{4-n} (R = CH_3, C_4H_9, C_8H_{17}, Ph; n = 1, 2) with H_2Salen [121] investigated by means of IR and Mössbauer spectroscopy. The structure **3d** was also



23

R=C_2H_5, C_3H_7, C_4H_9



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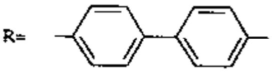
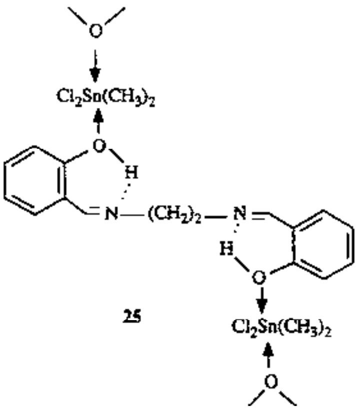


M= Zn, Cd, Hg

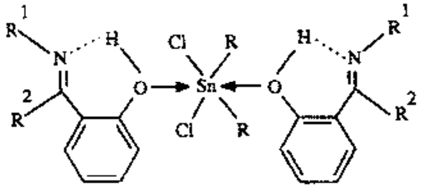
suggested for adducts of H_2Salpn with chlorides and nitrates of lanthanides [122] and those of WCl_6 [90,91].



25

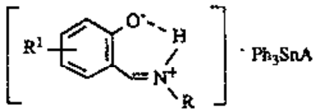
In spite of that, the IR spectra of organotin chloride complexes with **8** show a higher frequency shift for the C=N group stretching vibrations, 1620–1660 cm^{-1}, compared with those in the free ligand, apparently revealing N-coordination [26,93]; their structure was attributed to **26a** [123] and **27b** [124] with coordination also from oxygen.

Analogous structures were suggested for adducts of Ca(II) [96], Zn(II), Cd(II), Hg(II) [97] and lanthanide metals salts [94] with *N,N'*-bridged ligands of the H_2Salen type. The use of X-ray structural and IR spectral data in ref. 97 led to conclusions about the contribution of the mesomeric zwitter-ionic form **3d**. The predominance of zwitter-ionic forms in O-bonded Schiff base adducts was later reported for the complexes of Zn(II), Cd(II) and Hg(II) salts with imines of salicylic aldehydes [97]; adducts of Ph_3SnCl and Ph_3SnNCS with **8** of type **27** and imines of 2-hydroxy-1-naphthaldehyde [101]; for the adducts of tetyrachlorides (bromides) of Sn(IV), Ti(IV) and V(IV) of type **28** [125].



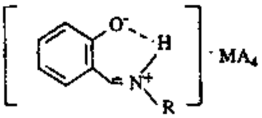
26 a R,R^1=CH$_3$, C$_2$H$_5$, C$_4$H$_9$; R^2=H

b R=CH$_3$, C$_2$H$_5$, C$_4$H$_9$, Ph;
R^1=C$_3$H$_7$, C$_4$H$_9$, Ph; R^2=H



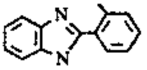
27

R=Alk, Ar, -(CH$_2$)$_2$OH
R^1= 3-OC$_2$H$_5$, 4-OCH$_3$
A= Cl$^-$, NCS$^-$



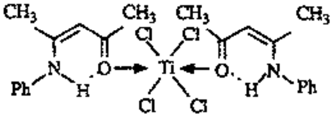
28

R =



M= Sn, Ti, V; A=Cl$^-$, Br$^-$

The coordination of oxygen to metal atom is reported for adducts of β-aminopropenones with structure **3d** [85,126–128]. This type of coordination was suggested for the first time for complex **29** on the basis of IR spectral data [126].

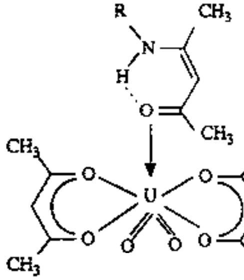


29

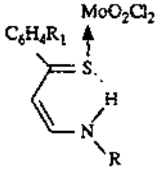
The structure **3d** was claimed for axially coordinated adducts of β-aminopropenones with β-diketonates of uranyl **30** [43] and lanthanide metals, and, in the case of the adducts of MoO_2Cl_2, with β-aminopropenethiones **31** [86].

The possibility for chelate-type ligation in adducts **3** is apparent. Chelate structures were supposed for adducts of Ag(I), Ca(II), Sr(II) nitrates and Sn(II) and Zn(II) chlorides with H_2Acacen [24]. N,O-chelate bonding and the hydroxyimino tautomeric form of the ligand was also found for the salicylaldimine adducts with lanthanide metals [95]; $UO_2(NO_3)_2$ **32a** [108], **32b** [100] and those of $SnCl_2$ and $SnCl_4$ **33** [102], **34** [78].

Structure **3f** was assigned to adducts of Schiff bases derived from salicylic aldehydes with metal halides such as **35** [88] and **36** [29]. The presence of the quinonoid form of the ligand in these compounds is supported by the appearance in the UV spectra of absorption bands at 400 nm and the fluorescence of adducts



30



31

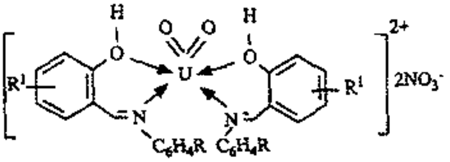
R= -(CH$_2$)$_2$-, C$_7$H$_{15}$, 4-C$_6$H$_4$Y
(Y=H, CH$_3$, OCH$_3$, Br, N(CH$_3$)$_2$)
R^1= H, 4-Br

characteristic of ligand tautomers containing the type **3f** moiety [29]. The structure of type **3f** was also suggested for the β-aminopropenones adducts **37** [29].

It appears from data considered above that structural conclusions for **3** adducts have mostly been proved with IR spectral data. However, in some cases these are controversial. Changes in frequency of the following stretching vibrations in the free ligand compared with the bound ligand are usually considered characteristic of adduct formation (ν (cm^{-1}) for the free ligand): C=N (1600–1670), Ph–O (1280–1300) and NH $\cdots$ O (N $\cdots$ HO) (2700–3200). In adducts, the C=N band is shifted to a higher frequency by 10–70 cm^{-1} while Ph–O and –OH (–NH) vibrations remain practically unchanged, the last possibly with a higher intensity. By comparison, for metal-chelate complexes, the C=N vibration bands undergo a shift to lower frequency by 10–30 cm^{-1}, the value of $\nu_{\mathrm{Ph-O}}$ increases by as much as 50 cm^{-1}, and the –OH (–NH) stretching vibrations are not observed. Nevertheless, the type of tautomeric form of the ligand, and assignment of coordination site in adducts is not certain since bands in the range 1580–1700 cm^{-1} may correspond either to C=N bond vibration of increased frequency (N-coordination of hydroxyimino tautomer) or to C=O group vibrations of decreased frequency compared with those vibrations in the uncoordinated ligand (O-, N,O-coordination of ketoamino tautomer). IR spectral data for Schiff base adducts with ligands of type **4** containing five-membered hydrogen-bonded rings are also largely uniformative due to possible formation of intermolecular rather than the intramolecular hydrogen bonds OH $\cdots$ N (see Sect. B(ii)).

In some cases, Schiff base adduct structure has been judged from electronic spectra. Where longwave bands in the range of 400–450 nm, characteristic of the quinonoid tautomeric form, are present assignment to structural type **3d** [122] or the related mesomeric structures [99,101] is possible.

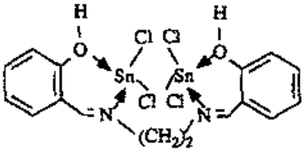
Several structural assignments [98,99,101,114,123] were made using ^{1}H NMR spectral data; however this is often complicated by the rather small proton signals shifts associated with complexation and low solubility of the adducts. According to refs. 98, 99, 101, metals are attached to ligand through the oxygen atoms since the



32

a R=H, R^1=H, 3-NO$_2$, 4-NO$_2$

b R=2-CH$_3$, 3-CH$_3$, 4-CH; R^1=H



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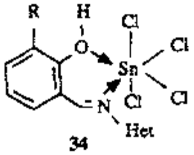
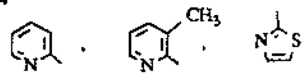
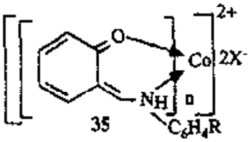


34

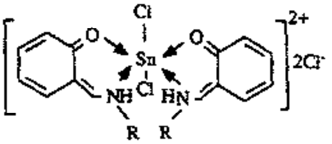
R=H, OCH$_3$; Het=





35

R=H, 2-CH$_3$, 3-CH$_3$, 4-CH$_3$, 2-OCH$_3$; X=Cl$^-$, Br$^-$; n=2, 3



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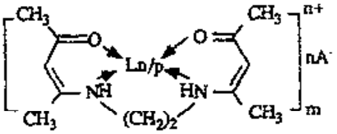
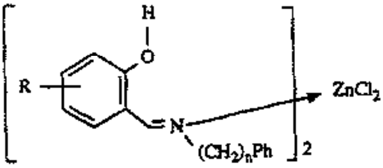


37

Ln=La, Ce, Pr, Nd, Sm, Gd, Dy, Y, Er

A=Cl$^-$, NO$_3^-$, SCN$^-$; m=2,3; n=3,6; p=2, 3 / 2

–OH group signals appear as broadened singlets at 12.2–14.8 ppm while those of CH=N protons at 8.2–8.7 ppm remain unshifted in the adducts compared with the free ligands. The opposite conclusion for coordination via imine nitrogen was reported for complex **38** [114].



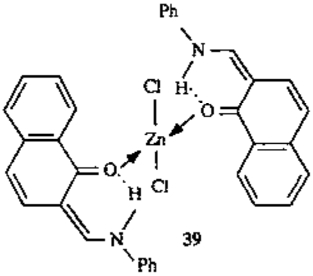
38

R=H, 3-OCH$_3$, 3-NO$_2$, 5-NO$_2$

Thus, spectral studies alone do not usually permit one to distinguish between the various Schiff base adduct structural types **3a–3h**.

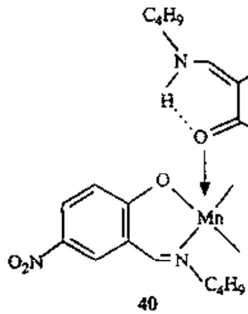
On the other hand, X-ray structural determinations are obviously informative. The structure **3d** with M←O coordination and an intramolecular hydrogen bond NH···O occurs with Schiff base adducts of salicylic and hydroxynaphthoic aldehyde [28,96,101,106,120], and *β*-aminopropenones [27,43,127,128]. The X-ray studies [27,43,129] identified the −OH (−NH) protons.

For example, in complex **39**, obtained by reaction of $ZnCl_2$ with *N*-phenyl-2-hydroxy-1-naphthaldimine, the zinc atom is coordinated by oxygen atoms, the Zn−O bond length lying in the range 1.96–2.00 Å [28]. The ligand in complex **39** undergoes tautomeric transformation from the hydroxyimino form, which is the case of the uncoordinated Schiff base, to the quinonoid form in the complex. This is seen from the corresponding bond lengths, C=O 1.29 Å (shortened by 0.045 Å compared with free ligand), and C−N 1.35 Å (lengthened by 0.057 Å). The O···H distance of 1.65–1.74 Å indicates the absence of the O−H valent bond. A similar tautomeric form of the ligand was found in the adduct **40** [129] with N−H bond lengths of 1.14 Å and an NH···O distance of 2.19 Å. A manganese atom is bonded to the oxygen centre with an Mn−O bond distance of 2.19 Å.



39

In adducts **41**, the mobile protons are also localized at the nitrogen atoms [96]. The N−H bond lengths are 0.91 and 0.99 Å; the H···O distances were 1.78 and 1.88 Å (somewhat larger than those for typical hydrogen bonds). The analogous O→N proton transfers were revealed in Ph_3SnNCS adducts with *N*-phenyl-2-hydroxy-1-naphthaldimine [101]. For these two complexes, the ligand has a zwitterionic structure which is mesomeric to the quinonoid tautomeric form. Similar structural peculiarities are characteristic of MoO_2Cl_2 complexes, e.g. **42** [27,128]. In adducts **42** (R = Ph [128], C_7H_{15} [27]), the corresponding bond distances are 1.07, 1.03 Å (N−H); 1.28 Å (C=O); 2.20, 2.179 Å (Mo−O); 1.76, 1.84 Å (NH···O). A quinonoid tautomeric form with an intramolecular hydrogen bond was found in axially coordinated uranyl acetylacetonato adducts with *β*-aminopropenones **30** [43]. Participation of oxygen atoms in coordination with metals is also supported by the structure of O-bonded adducts **43** derived from metal-chelate complexes



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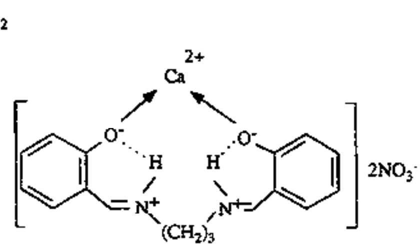

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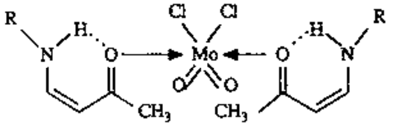
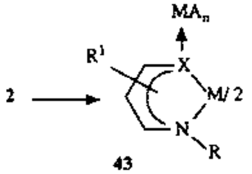


42

R=C_7H_{15}, Ph

[10,130–136]. Although the mode of coordination described by structure **43** is accepted in most papers, alternative structural types are also discussed [130,131].

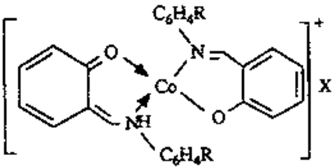


43

X=O, NR^2

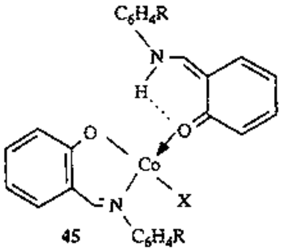
Ligands with additional donor centres bind Lewis acids according to the Pearson concept of soft and hard bases and acids [130,131] so that soft acids ($HgCl_2$, $AgNO_3$, $PtCl_2$) are bound to the soft tellurium atom in Schiff base ligands containing the ditelluride moiety [80,81] and chromium atoms of the $Cr(CO)_3$ moiety in **13** [82] whereas hard acids, e.g. BF_3, $SnCl_4$, $SbCl_5$ are coordinated by oxygen. Structural assignment in the latter cases follow from IR spectral data for C=N and $Cr(CO)_3$ groups and also from available [84] X-ray structural data for arenechromiumtricarbonyl complexes with Lewis acids.

The ability of metal centres to display different coordination numbers as well as a variety of coordination modes makes it difficult to establish the corresponding stereochemical peculiarities of Schiff base adducts. In tetracoordinated $ZnX_2 \cdot 2LH$, the metal centre has a tetrahedral configuration. X-ray data are available for two complexes, bis(acetylacetone-*N*-propyliminato)Zn(II)I_2 [127] and **39** [28] with OZnO′ valence angles of 104° and 110.3°, respectively. A tetrahedral structure could also be assigned to the salicylaldiminato complexes **44** given their magnetic moments of 4.06–4.44 B.M. [88]. However, in this case, the alternative structure **45**, also containing a tetrahedral metal centre, seems more reasonable.



44

R=H, 4-CH_3; X=Cl^-, Br^-



45

Among adducts containing pentacoordinated metals, Ph_3SnCl and Ph_3SnNCS complexes with salicylic aldehyde Schiff bases **27**, and those of 2-hydroxy-1-naphthaldehyde [99,101] were considered in detail. According to X-ray structural [101] and Mössbauer spectral investigations [99], these complexes have a trigonal bipyramidal structure in which three phenyl groups form a triangular core with axially coordinated Schiff base and chlorine (isothiocyanato) ligands. A square pyramidal structure containing an O-coordinated salicylaldimine as an apical ligand was reported for the Mn(II) complex **40** [129] with a magnetic moment of 5.96 B.M.

An octahedral configuration is also characteristic of MoO_2Cl_2 adducts with acetylacetoneiminato ligands of the type $MoO_2Cl_2 \cdot 2LH$ [27,128]; it is also typical of other Mo(VI) dioxohalide complexes [135]. An octahedral configuration was suggested [88] for the salicylaldimine adduct **35** ($R = H$, $X = Cl^-$, $n = 3$) with a magnetic moment of 4.7 B.M. However, the composition of the complex could also correspond to a pentacoordinate structure with two bound chloride ions and three monodentate salicyaldimino ligands due to the proneness of Schiff base ligands to display monodentate behaviour (see, for example, refs. 28, 114 and 120).

X-ray structural determination of adduct **41** [96] indicates a hexagonal bipyramidal structure with octacoordinated calcium, CaO_8. The metal ion is coordinated via oxygen atoms of the nitrate and μ-nitrate groups, and phenolic oxygen centres.

Coordination affects Schiff base conformations so that they become practically planar (see Sect. B.(iii)). For example, the dihedral angle between the naphthalene moiety and benzene rings in the Schiff base formed by aniline and 2-hydroxy-1-naphthaldehyde is 41.3° [28], whereas in its adduct with $ZnCl_2$, **39**, this angle decreases to 5.9–10.8° [28]. This structural transformation was also confirmed by quantum mechanics calculations [62,63]. This planarity effect is not observed in the metal-chelate complexes (see Sect. D.).

In summary, among the eight conceivable structures **3a–3h** suggested for Schiff base adducts, only type **3d** is unequivocally proved. In this structure, the ligand possesses a quinonoid tautomeric form with an $NH \cdots O$ intramolecular hydrogen bond retained, while the metal is coordinated by oxygen. The occurrence of this particular structural type is confirmed by X-ray structural as well as IR spectral data. The adducts derived from *N,N'*-bridged Schiff bases such as H_2Salen and H_2Acacen may form either monomeric or oligomeric structures, depending on the type of Lewis acid. In the case of Schiff base adducts **6** derived from *o*-aminophenol imines, lack of structural information still prevents any decisive conclusions on their structure. We wish to stress again that Schiff base adduct structural assignments based exclusively on IR spectral investigations are not reliable and even when found in current publications (see, for example, refs. 76, 95 and 114) should be treated critically.

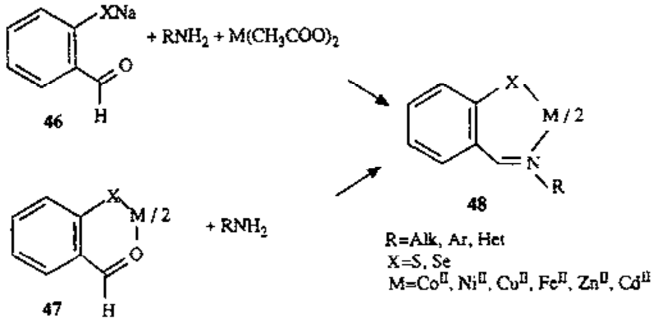
D. TETRACOORDINATED METAL-CHELATE COMPLEXES WITH SIX-MEMBERED METALLOCYCLES

(i) Synthesis

The usual methods for preparation of metal-chelate complexes with an MN_2O_2 or MN_4 coordination sphere include (a) direct interaction of the Schiff base with the metal salts, (b) template condensation of aldehydes (ketones), primary amines and metal salts and (c) reaction of aldehydato complexes with amines [1,5]. Electrochemical reactions based on anodic oxidation of metals in non-aqueous solvents were also successfully used for the preparation of several salicylaldiminato bis-chelate complexes [137–141] whereas other reactions may result in the formation of MLA-type complexes. Zero-valent metals, e.g. nickel and copper, are reported [142] to interact with salicylaldimines with the formation of type **2** complexes in tribochemical reactions by grinding the metal powders and ligands with a small amount of alcohol or polymethylsiloxane. However, yields are rather low.

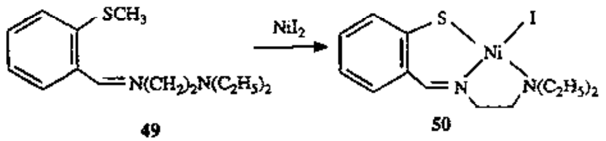
In contrast to MN_2O_2 metal-chelates, synthesis of their $MN_2S_2(Se_2)$ analogues must be carried out with the precautions necessary to avoid facile oxidation of the mercapto and seleno ligand groups. The first syntheses of thiosalicylaldiminato Ni(II) [143,144] and Co(II), Cu(II), Zn(II) [144] complexes **46**→**48** were reported as the template condensation of amines, metal acetates and the sodium salt of thiosalicylic aldehyde accessible through the reduction of *N*-methylanilide of thiosalicylic acid [143] or via the reaction of *ortho*-thiocyanobenzaldehyde with sodium sulphide [144,145]. The complexes with various substituents, R, attached to the coordinated nitrogen atom (M = Co(II) [146], Ni(II) [147–150], Cu(II) [150] and Zn(II) [147,148,150]) were later prepared by the reaction **46**→**48**, in which stepwise addition of amine and then metal acetate to an ether solution of thiosalicylic aldehyde led to isolation of the corresponding Ni(II) and Co(II) complexes of type **48** (X = S) [151]. The former approach had been used in the synthesis of the first representatives of selenosalicylaldiminato metal-chelates [152,153].

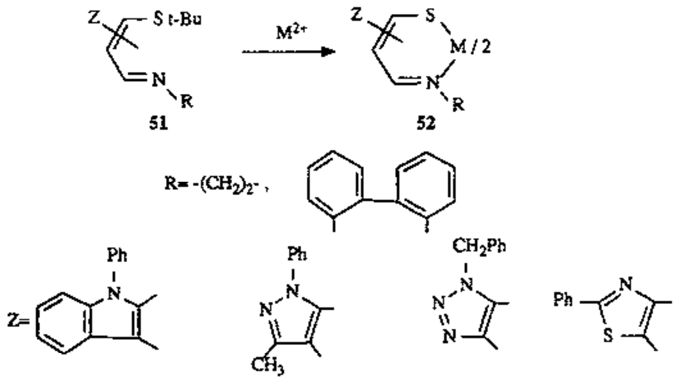
The reaction of stable thiosalicylaldehydato complex **47** with amines was used for the synthesis of metal-chelates **48** (Co(II) [154], Fe(II) [155,156]) and related complexes with ligands in which the azomethine moiety incorporated such functional groups as hydrazono-, oximo-, iminoalcohol- and *S*-alkylthiosemicarbazido-

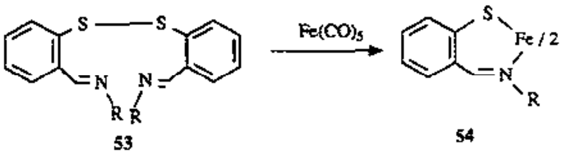


[157–159]. Reaction of the Ni(II) complex of monoselenoacetylacetone with amines gave the corresponding Schiff base metal-chelates [160].

Some methods are based on the dealkylation of the alkylthio- group, e.g.







49→**50** [161], **51**→**52** [162–164], and the scission of the disulphide bridge **53**→**54** [165].

As mentioned in Sect. B, imines of *ortho*-thio(seleno)heteroaromatic aldehydes as well as β-aminopropenethiones possess the stable enaminothione form and may usually be isolated and used as ligands for the synthesis of type **2** metal-chelates with R^1 = Alk, Ar; X = S [166–176] and X = Se [177]; R^1 = Hetero-, X = S, Se [8,178–189].

Metal acetates are considered to be the most convenient substrates for complexation with Schiff bases due to their solubility in alcohols and to their being the salts of a weak acid. The application of metal nitrates or chlorides is possible when the ligand solution is first treated with sodium or potassium hydroxide, acetate or alcoholate in order to convert the neutral ligands into their respective phenolates. Thallium salts of thiosalicylaldimines were employed for the synthesis of pentacoordinate Fe(III) complexes [190]. Sometimes, milder reaction conditions may be provided by the use of tetraalkylammonium salts of metal tetrahalides in ethanol [191,192] or tetrahydrofuran [1,2,5]. A facile oxidation of Cu(I) to Cu(II) was used for the synthesis of Cu(II) complexes from $[Cu(CH_3CN)_4]BF_4$ by virtue of cleavage of the *t*-Bu—S bond in **51** [162–164].

(ii) Stereochemistry

Tetracoordinate Schiff base metal-chelates of type **2** may form trans and cis planar or tetrahedral (R and S enantiomeric where the entire molecule is dissymmetric) structures which, in principle, are able to undergo stereo (inversion of tetrahedral configuration at the metal centre) and geometrical (interconversion of cis and trans planar structures) isomerizations. These are shown schematically in Fig. 5. The low-energy structure may correspond to either tetrahedral (Fig. 5(a)) or planar (Fig. 5(b)) configurations. The following order of increasing ability of the metals to form

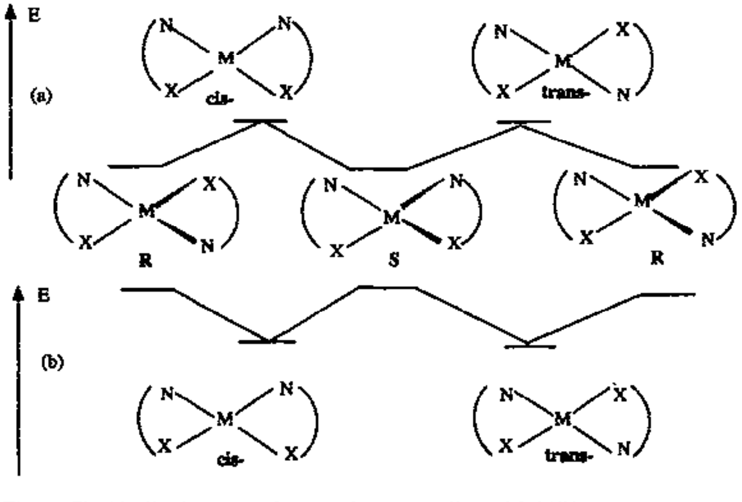


Fig. 5. The idealized structural types of tetracoordinated Schiff base complexes and their possible interconversion pathways. The low-energy structure corresponds to the tetrahedral (a) and planar (b) configuration.

tetrahedral structures in Schiff base complexes in an approximation of the isosterical ligand environment has been reported [14]: Pd < Cr < Cu ≈ Ni < Co < Fe < Zn < Cd < Be.

With the d^0, and d^{10} metals, the planar structure generally represents only the transition state in interconversion reactions of tetrahedral enantiomeric or enantiotopomeric forms although quantum mechanical calculations [193,194] showed that the energy difference between planar and tetrahedral structures decreases for the less electronegative metals and more electronegative donor atoms. A tetrahedral structure may be a conceivable transition state in the reactions of cis$\rightleftharpoons$trans isomerization of essentially planar tetracoordinate complexes such as those of Pd(II); however, the latter rearrangements have not yet been observed with Schiff base metal-chelates.

For some transition metal complexes, especially those of Ni(II) and Co(II), the energy gap between planar and tetrahedral structures is very low resulting in the existence of planar$\rightleftharpoons$tetrahedral equilibria with very high interconversion rates in solution and slightly distorted planar or pseudo-tetrahedral configuration in the solid. Cu(II) complexes also display lability of molecular configuration steered by minor variations in ligand environment since the entire continuity of structures, varying from strictly planar to tetrahedral species, is revealed in the solid state, although only a single structural form seems to be represented in solution [195].

In the present survey, we consider mainly static distortions, however, these would also be referred to the corresponding dynamic parameters, viz. the barriers against R$\rightleftharpoons$S interconversion obtained experimentally for many asymmetric tetrahedral Schiff base complexes by use of dynamic NMR spectroscopy and which are assumed [194] to reflect the stability of the tetrahedral configuration at the metal centre relative to its square-planar configuration provided no competitive dissociative mechanisms operate in this reaction.

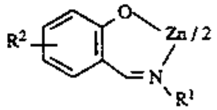
The occurrence of different structural types related to tetracoordinate Schiff base complexes with various ligand environment was revealed by pioneering work in the 1960s and was summarized in a comprehensive review paper by Holm and O'Connor [2]. At that time, the structural features were mainly assessed within several types of complex containing MN_2O_2 and MN_4 coordination sites and derived from salicylaldimines, β-aminopropenones and β-aminopropeneimines. It was esablished that: (1) the formation and relative stability of the preferred configurations at the metal centre is determined by the steric volume of the R substituent attached to the coordinating nitrogen atom so that the stability of planar geometry decreases as the bulkiness of R increases; and (2) conformational features defined by puckering of the metallocycle along the $N \cdots X$ axis resulting in the occurrence of a stepped conformation may also be important in defining configurational peculiarities. Novel structural data related to the above-mentioned complexes found during the last two decades substantially developed these conclusions. Later results showed that, in addition, drastic structural changes caused by variations in the steric properties of R may be induced by (1) the incorporation of chalcogen centres (X = S, Se) bound to the metal and (2) annelation of five-membered heteroaromatic rings to metallocycles. Thus, in the present survey, the complexes were primarily classified with respect to donor atom set followed by gradation to those derived from non-annelated, benzoannelated, and then heteroannelated ligands.

(a) MN_2O_2 complexes

A strictly planar or slightly distorted trans configuration is characteristic for transition metal complexes of Co(II), Ni(II), Cu(II) and Pd(II) with an MN_2O_2 coordination sphere, e.g. salicylaldiminato and β-aminopropenoneato metal-chelates in the case of less bulky R substituents at the coordinating nitrogen atoms, R = H, CH_3, *n*-Alk and Ar [1,5,14,16]. Recently, such a structure was revealed for the usually less stable Cr(II) and Mn(II) complexes bis(*N*-butylacetylacetoneiminato)Cr(II) [196] and bis(*N*-butyl-5-nitrosalicylaldiminato)Mn(II) [129].

The incorporation of α-branched alkyl substituents, and particularly the *t*-Bu group, destabilizes the planar configuration and leads, in the case of Cu(II) complexes, to a gradual distortion of a planar structure towards a tetrahedral one, whereas for Ni(II) complexes, these changes result in the shift of the planar⇌tetrahedral equilibrium to the right in solution, and stabilization of tetrahedral structures in solid state. The Co(II) ion is more inclined to form a tetrahedral configuration, the planar occurring only in the case of R = H.

In contrast to transition metal complexes, the ligand environment affects only slightly the structure of d^0 and d^{10} metal complexes. For example, valence angles and bond lengths of bis(salicylaldiminato)Zn(II) complexes **55a–55e** [197] are virtually independent of the variations of both R^1 and R^2, whereas the angle θ, defined as the angle between OZnN and O(1)ZnN(1) planes belonging to different metallocycles, lies within the range 84–89°.



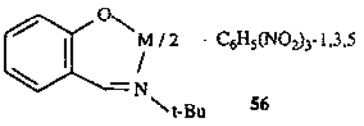
55a-e

	R^1	R^2	θ*
a	C_2H_5	H	88.6; 88.3°
b	i-C_3H_7	H	84.1°
c	C_4H_9	H	87.6°
d	$C_2H_5S(CH_2)_3$-	H	86.1°
e	C_3H_7	4-OCH_3	89.1°

* The angle between OMN and O(1)MN(1) planes belonging to different metallocycles if not otherwise specified

Comparison of these data with the geometry of the isoligand complexes **56** [198] shows that variations in the metal centre in complexes with a similar ligand environment increase the tetrahedral angle in the order Cu < Ni < Co < Zn, in parallel with the trend of increasing relative stability of a tetrahedral structure [14].

It is worth noting that the molecular structure of a metal chelate may be influenced by formation of an adduct with a strong electron acceptor molecule, e.g. trinitrobenzene. The angle θ of the Cu(II) adduct **56** compares with the θ value 53.6° in bis(*N*-*t*-buthylsalicylaldiminato)Cu(II) [199]. Hydrogen bonding to donor oxygen atoms may also alter molecular geometry [14].

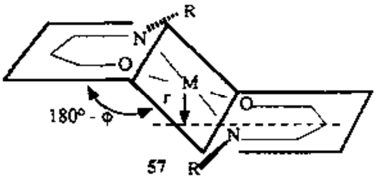


56

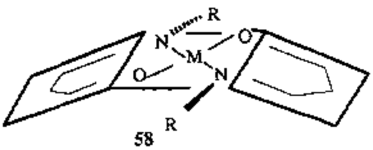
M	Pd*	Cu	Ni	Co
θ	0°	61.4°	78.5°	81.3°

* without solvent

Pd(II) complexes do not adopt any planar-to-tetrahedral distorted configuration, even in the case of the bulky *tert*-butyl group. To minimize steric crowding, the molecule acquires a stepped conformation **57** due to puckering of the metallocycles along the N ··· O axis in opposite directions. This arises through steric requirements because the bending angle ϕ considerably decreases with the less bulky R [200].



57
stepped

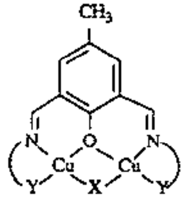


58
umbrella

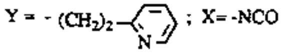
The structural features of Pd(II) salicylaldiminato complexes [200] may be helpful in understanding that most Schiff base complexes with a planar configuration, e.g. those of Ni(II) and Cu(II), form a stepped **57** rather than an entirely planar conformation. Should this be attributed to the relief of steric interactions in an otherwise unfavourable planar conformation, the effects of crystal packing or inherent properties of the molecule? Pseudo-tetrahedral complexes usually display rather small puckering, whereas metals with a labile molecular configuration, e.g. Cu(II), show a tendency to decrease the puckering with increase of tetrahedral torsion. The Pd(II) complexes example shows that steric interactions may certainly be decreased by out-of-plane distortions. However, this does not explain the occurrence of this conformation for sterically less bulky substituents present in the structures of complexes with a planar configuration. Puckering of metallocycles may originate, to some extent, from crystal packing phenomena. This is demonstrated, for example, by the established mesomorphism of Cu(II) complexes [2,14] as well as other numerous cases of unequal bending angles for different metallocycles within the same molecule. However, Kerr constants of tetrahedral salicylaldiminato Be(II), Zn(II) and Co(II) complexes [201,202] showed the presence of puckering in solution, the values of ϕ angles falling within the range of 7–25°, close to those observed in solid, thus showing the similarity in conformation features in solution compared with the solid. The umbrella conformation **58** found for some bridged complexes derived from Schiff bases of diamines (see Sect. F) is a conceivable alternative to the stepped form **57**.

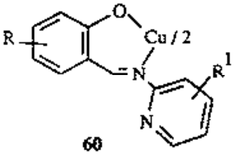
Even though it is not typical for crystalline bis-chelate complexes, it may exist in solution either as the dominating form or in dynamic equilibrium with the stepped form [203].

To elucidate more thoroughly the relationship between ligand environment and the structure of tetracoordinate Schiff base complexes, it is relevant in the context of the present survey, to present several recent examples of complexes possessing coordination numbers higher than four, i.e. penta- and hexa-coordinated species retaining the basic MN_2O_2 framework. These may arise either as a dimeric species bound by two intermolecular metal-phenolate oxygen bonds or in an intramolecular fashion where additional functional groups exist in the ligand structure with the capacity to coordinate to the metal centre. The positions preferred for intramolecular coordination are the β and γ carbon atoms of the =NAlk or $-NAlk_2$ group and the ortho positions of the =NAr moiety in the case of a $-OCH_3$ substituent [5,14,204]. Pyridine nitrogen atoms are also good potentially coordinating groups bound to the metal centre in the dinuclear Cu(II) complex derived from the diimine of 2,6-diformylphenol with 2-(2′-pyridyl)ethylamine **59** [205] and tetrameric [(Salα-Py)-$CuNO_3 \cdot H_2O]_4$ [206]. However, the Cu(II) metal-chelates **60a** and **60b** [140] and **61** [207] are tetracoordinate according to X-ray data, although in the latter case, UV and ESR data confirm additional coordination in THF solution, illustrating the fact that such binding is usually weak and labile.



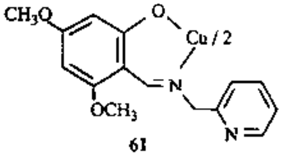
59





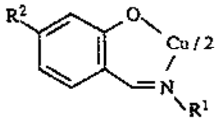
60

	R	R^1
a	5-OCH_3	3-CH_3
b	H	6-CH_3

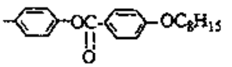


61

The occurrence of a dimeric square-pyramidal structure through intermolecular binding of copper with a phenolato oxygen may be induced by designing a long alkyl chain attached to the coordinating nitrogen atom or at the ligand periphery. This provides for a regular orientation of the molecule in the solid state and results in the emergence of liquid crystalline properties. These properties are not necessarily associated with formation of dimeric structures as indicated by X-ray data available for series of mesogenic salicylaldiminato Cu(II) complexes **62a–62f** [208–213]. However, the lifetime and temperature range for the existence of a smectic phase were reported [212] to correlate with the stability of dimers. Axial coordination was also assumed for analogous mesogenic Ni(II) complexes [214]. The choice of the metal centre is reported [214] to be important for the thermal stability of the nematic phase. This increases for Ni(II) compared with Cu(II) complexes, rationalized as a consequence of the higher susceptibility of Cu(II) complexes to static tetrahedral distortion than in the case of Ni(II).

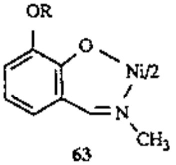


62a-f

	R^1	R^2	Structural type	Ref.
a	$C_6H_4OCH_3$-p	$C_7H_{13}O$-	Pl. + Tetr.*	208
b	C_6H_4F-p	$C_7H_{13}O$-	Dimer	209
c		$C_8H_{15}O$-	Pl.	210
d	C_6H_4CN-p	$C_7H_{13}O$-	Dimer	211
e	$C_6H_4CH_3$-p	$C_7H_{12}O$-	Dimer	212
f	$C_6H_4C_6H_{11}$-p	$C_6H_4COOC_4H_9$-p	Dimer	213

* Two symmetrically independent monomeric molecules with different configuration at metal centre, trans-square planar (θ=0°, φ=21.7°) and pseudo-tetrahedral (θ=113°) were revealed in solid within the same unit cell.

Notable examples of intermolecular self-organization were recently reported [215–217] for *N*-methylsalicylaldimiinatoNi(II) complexes, **63**, containing a polyether pendant arm next to a phenolato oxygen atom. These complexes were found to be monomeric and planar both in solution and in the solid. They displayed an unexpectedly high affinity towards alkali metals to form Ni_2Na_2 clusters. An initially suggested [215] pseudo-crown cavity arising as binding site for the alkali metal anions in a conceivable cis planar configuration was disproved [216] by X-ray data of the adduct with sodium picrate showing complicated unsymmetrically bound clusters containing two six-coordinate nickel centres. Additional four-coordinate bonds at two nickel atoms are formed by binding to a water molecule, two picrate oxygen atoms and one ether oxygen atom (from another salicylaldimine subunit). The presence of the picrate anion does not seem to be a key requirement for encapsulating the alkali metals since encapsulation also readily occurs with perchlorates. In this case, the structural unit responsible for ionophoric properties is supposed [217] to be composed of dimers made up by nickel to phenolate oxygen intermolecular bonds and containing a trans planar N_2O_2 core around metal centre.



63

R= $-CH_3$, $-CH_2CH_2OCH_3$

Although salicyladiminato and β-aminopropenoneato bis-chelates still continue to be one of the most ubiquitous types of tetracoordinate Schiff base complexes with an MN_2O_2 coordination site, metal-chelate complexes containing other ligands have recently attracted much attention.

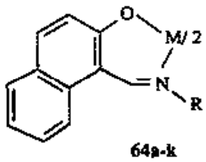
The annelation of a benzene ring to the salicylaldimino aromatic moiety in the case of naphthaldiminato complexes does not confer any essential structural changes as indicated by structural data for Schiff base complexes **64a–64k** of Cu(II), Ni(II), Pd(II), Zn(II) and Be(II) [218–224] derived from imines of 2-hydroxy-1-naphthaldehyde. The notable difference between the geometry of the Cu(II) complex **64f** ($\theta =$ 138°) [221] derived from the paramagnetic Schiff base of 4-amino-2,2,6,6-tetramethylpiperidyl-1-iminoxyl radical as compared with its salicylaldiminato analogue ($\theta =$ 152°) [225] may occur due to structural reorganization in the solid in the former case, since magnetic moment determinations as well as ESR data reveal an ensemble of three interacting spins belonging to two iminooxyl radicals and the Cu(II) centre of three different molecules, even though the complex **64f** is monomeric in the crystalline state. Comparison of the structural features of Ni(II) complexes incorporating salicylaldimino, 2-hydroxy-1-naphthaldimino and 2-hydroxy-3-naphthaldimino moieties shows [222] the common slightly stepped ($\phi < 12.9°$) molecular conformation and the trans square planar configuration at the metal centre in two series of complexes containing 2,2-diethoxyethyl [222(a)] and (1,3-dioxolan-2-yl)-methyl [222(b)] substituents at the coordinating nitrogen atom. It was expected [222] that the tautomeric form displayed by the free ligand (see Sect. B(i)) might influence the structural properties.

The structural features of bis(pyridoxaldiminato)Cu(II) complexes **65a–65e** [226–229] incorporating an annelated pyridine ring are important in illustrating the influence of the six-membered heteroaromatic moiety. These closely resemble the structural peculiarities of salicylaldiminato and 2-hydroxy-1-naphthaldiminato complexes, i.e. an increase in the steric volume of R increases tetrahedral distortion and diminishes puckering along the $N \cdots O$ axis. The crystalline structure of **65** is polymeric due to the formation of intermolecular hydrogen bonds between the hydroxy group and the pyridine nitrogen atom.

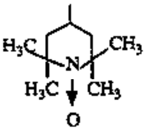
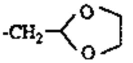
In contrast, the stabilization of a tetrahedral configuration was reported for complexes with annelated five-membered heterocyclic rings, viz. pyrazole and benzofuran Schiff base complexes of type **66** [180] and **67** [230]. Although this is not studied in particular detail and not confirmed by X-ray structural data, extensive investigations of related MN_2S_2 complexes surveyed in the following section reveal the same tendency; this analogy is also indicated in the retention of a planar configuration for complexes **68** with a benzothiophene fragment [231].

(b) $MN_2S_2(Se_2)$ complexes

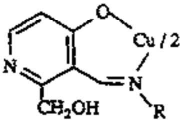
Schiff base complexes of the type $MN_2S_2(Se_2)$ have been extensively studied since the end of the 1970s when convenient methods for the preparation of sulphur- and selenium-containing ligands were developed. In recent years, many X-ray struc-



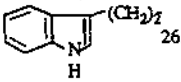
64a-k

	M	R	θ	φ(r, Å)	Ref.
a	Cu	C_6H_5	180°*	15.9°	218a
b	Cu	$C_6H_4N(CH_3)_2$-p	180°*	18.2° 6.5°	218b
c	Cu	CH_3		(0.1)	219
d	Cu	1-Adamantyl	124.2°		220
e	Cu	2-Adamantyl	153.9°		220
f	Cu		138°		221
g	Ni	$-CH_2CH(OC_2H_5)_2$	180^0*	12.9^0 (0.94)	222a
h	Ni		180^0*	(0.073)	222b
i	Pd	C_6H_5	180^0*	4^0	223
j	Zn	C_6H_5	88^0	(0.408) (0.15)	224
k	Be	C_6H_5	89^0	(0.39) (0)	224

* Molecular strucnires are reported to be close to trans-square planar configuration at metal centre although the particular values of θ are not given in original papers

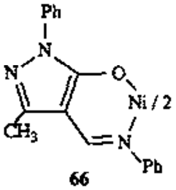


65a-e

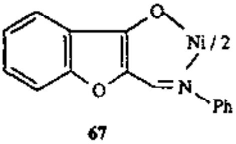
	R	θ*	φ	Ref.
a	CH_2Ph	26°	46.5°	226
b	n-C_4H_9	15.9°	24.8°	227
c	t-C_4H_9	52.9°	19.8° 13.3°	228
d**	t-C_4H_9	47.1°	24.4°	228
e		26.0°	46.5°	229

* θ =0° refers to trans-square planar configuration .

** **65d** · 1/3 CH_3OH .



66



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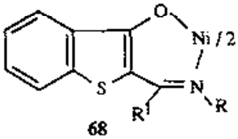


68

R=C_4H_9, CH_2Ph, Ar
R^1=H, CH_3, Ph

tural studies of these complexes **69–109** have been reported [164,232–258] and are summarized for the first time in Table 1.

The structural features of β-aminopropenethionato and thio(seleno)salicylaldiminatoNi(II) complexes probed in early studies [259] by investigation of magnetic and dipole moments revealed their low-spin electronic state and unexpectedly high polarity (within the range 5–6 D) contrasting with the corresponding low polarity of MN_2O_2 complexes. Similar Cu(II) complexes were also found to be highly polar. These peculiarities of the MN_2S_2 and MN_2Se_2 complexes were accounted for by the stability of their cis planar form in distinction to the trans planar non-polar structure known for their MN_2O_2 analogues. Dipole moments of Schiff base complexes and their use for structural assignment has been previously reviewed in ref. 259.

Apparently, the fully planar cis structure is sterically crowded due to the repulsive interaction of the substituents at the coordinating nitrogen atom. This repulsion may be decreased in the stepped conformation analogous to those of type **57** with puckering of the metallocycles along the $N \cdots S$ axis. This kind of distortion seems to be ubiquitous for the crystalline state (Table 1).

As a possible explanation for the preference of a cis MN_2S_2 structure, a specific attractive sulphur–sulphur interaction was suggested [16] which is favoured by shortened intramolecular $S \cdots S$ distances compared with the sum of the van der Waals radii (3.68 Å). Such a shortening has been revealed for the bis(2-mercaptophenylazobenzolato)Ni(II) complex [260,261] and for planar dithiobiuretoNi(II) and Pd(II) complexes [5]. This interaction, perhaps, may be considered as a specific example of hypervalent bonding, well-known for organic compounds of sulphur [262,263] and selenium [264]. It should also be mentioned that most of the pseudotetrahedral MN_2S_2 structures are distorted towards the cis ($\theta < 90°$) rather than the trans ($\theta > 90°$) donor atom arrangement.

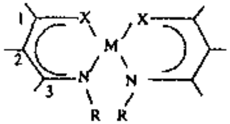
Another distinguishing feature of $MN_2S_2(Se_2)$ complexes with respect to their MN_2O_2 analogues is the relative stability of the planar form compared with the tetrahedral form [5]. Several examples given in Table 2 show that the replacement of the oxygen atom by sulphur results in a shift of the planar$\rightleftharpoons$tetrahedral equilibrium in Ni(II) complexes towards the planar structure [149,190,265].

Considering the structural properties of MN_2S_2 Schiff base complexes together with sulphur-containing β-diketonato and azobenzolato metal-chelates, Kogan et al. [16] introduced a concept of "specific cis planarity influence" that sulphur atoms in the MN_2S_2 bis-chelate complexes render on their structure.

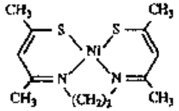
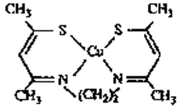
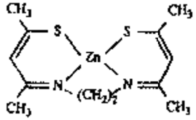
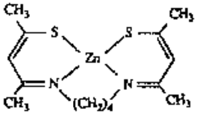
Recently, in addition to the frequently studied β-aminopropenethionato complexes, **110** [266], metal-chelates derived from 1,2-, 2,1- and 2,3-mercaptonaphthaldimines, **111**, [267] and complexes of Schiff bases of (1R)-3-hydroxy-methylenebornane-2-thione [34] have been reported and characterized. Intramolecular rearrangements where the metal atom "switches" the coordination site from one imino nitrogen atom to another were studied in the complexes, **112**, derived from alterdentate ligands, diimines of 2,6-diformylthiophenol [268].

TABLE 1

Bond lengths of chelate rings (Å); angles between NMX and N'MX' planes, θ, deg, angles of bending of chelate rings along the N ⋯ X axis, ϕ (deg), and exit of metal atoms from the best metallocyclic plane, r (Å), for Schiff base complexes of the type MN_2X_2 (X = S, Se)



θ = 90° refers to an undistorted pseudo-tetrahedral configuration, whereas θ = 0° corresponds to cis and θ = 180° to trans square planar.

No	Compound	C(1)=N	C(1)–C(2)	C(2)=C(3)	C(3)–X	M–X	M–N	θ	ϕ(r)	Ref.
69		1.311 1.315	1.445 1.420	1.329 1.365	1.703 1.671	2.163 2.139	1.923 1.917ᵃ	0		232
70		1.275 1.338	1.421 1.386	1.338 1.366	1.723 1.731			27.8	(0.36) (−0.22)	233
71		1.303	1.435	1.351	1.735	2.293	2.027	55.7	(0.617)	234
72		1.329	1.420	1.369	1.736	2.277	1.997	74.5	(0.75)	235

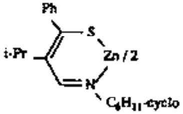
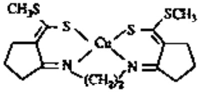
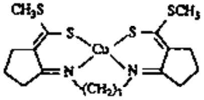
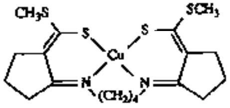
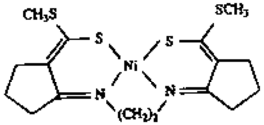
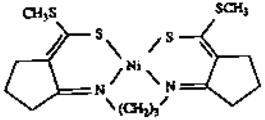
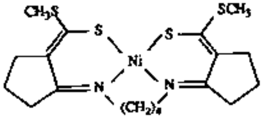
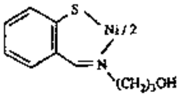
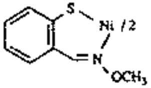
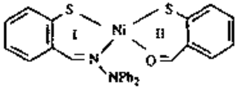
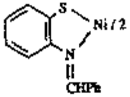
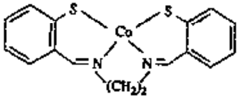
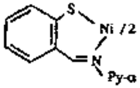
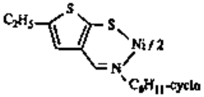
73		1.288 1.280	1.445 1.446	1.356 1.358	1.733 1.732	2.283 2.275	2.036 2.031	81.7	17.7 17.4	236
74		1.370 1.388	1.360 1.398	1.395 1.433	1.728 1.680	2.243 2.258	1.966 1.925	20[b]		237
75		1.310	1.429	1.359	1.723	2.222	1.950	52.8[b]		238
76		1.310	1.448	1.365	1.722	2.221	1.955	57.1[b]		239
77		1.312	1.439	1.351	1.730	2.174	1.893	3.4[b]		240
78		1.305	1.428	1.358	1.716	2.160 2.173	1.910 1.916	18.9[b]		240
79		1.311	1.440	1.363	1.716	2.162 2.161	1.919 1.923	38.6[b]		240

TABLE 1 (*continued*)

No.	Compound	C(1)=N	C(1)–C(2)	C(2)=C(3)	C(3)–X	M–X	M–N	θ	φ(r)	Ref.
80								19.2	32.6^{c,d} 40.2	241
81		1.275 1.284	1.425 1.445	1.408 1.409	1.732 1.747	2.167 2.143	1.891 1.899	30.3	0^{d}	241
82		1.287	1.442	1.400	1.762	1.869 2.149	1.931	11.9	39.4^{Id} 19.5^{II}	241
83		C=N 1.29 C–N 1.42	C=C 1.36		1.76	2.182	1.923	24.1	37.0^{e}	242
84						2.206	1.915	21.4^{f}		243
85		1.29 1.31	1.46 1.42	1.39 1.40	1.767 1.747	2.162 2.146	1.92 1.94	13.5	21.4^{d} 44.7	244
86		1.280 1.285	1.446 1.436	1.402 1.405	1.748 1.729	2.244 2.255	2.010 2.010	85		245

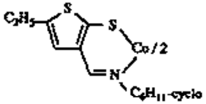
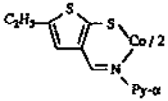
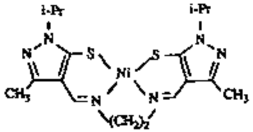
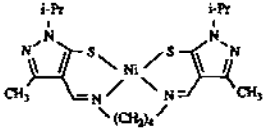
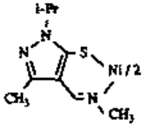
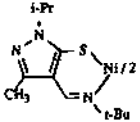
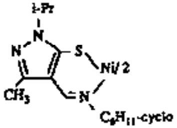
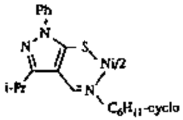
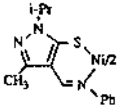
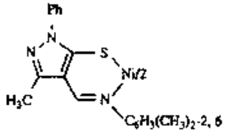
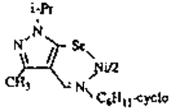
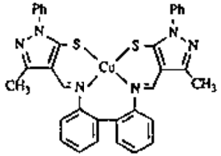
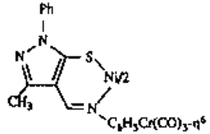
87		1.31 1.30	1.45 1.45	1.38 1.37	1.707 1.740	2.271 2.258	1.995 2.010	85		245
88		1.32 1.34	1.42 1.45	1.39 1.38	1.73 1.69	2.241 2.341	2.028 1.986	83.1[g]		246
89		1.287 1.281	1.423 1.405	1.395 1.399	1.708 1.706	2.185 2.183	1.902 1.916	5.7	2.8 5.8	247
90		1.295 1.293	1.402 1.435	1.399 1.388	1.718 1.716	2.173 2.211	1.943 1.917	18.3	16.5 42.5	247
91		1.28 1.28	1.43 1.43	1.41 1.41	1.715 1.726	2.237 2.247	1.975 1.985	81.9 82.4	0[h] 1.4	248
92		1.288 1.289	1.427 1.413	1.396 1.416	1.697 1.694	2.254 2.253	1.984 1.995	96.3	1.4 3.8	248
93		1.276 1.290	1.436 1.417	1.389 1.392	1.720 1.724	2.243 2.258	1.975 1.992	85.5	0	249

TABLE 1 (*continued*)

No.	Compound	C(1)=N	C(1)—C(2)	C(2)=C(3)	C(3)—X	M—X	M—N	θ	ϕ(r)	Ref.
94		1.306	1.420	1.382	1.720	2.251	1.990	85.3	13.1	250
95		1.300	1.412	1.403	1.708	2.229	1.984	68.7	2.1[d]	248
96		1.365	1.398	1.408	1.706	2.211	1.962	180	32.4	251
97		1.295	1.412	1.388	1.866	2.341	1.973	76.3	19.2[d]	250
98		1.292			1.721	2.245 2.185	1.984 1.927	51.9[b,d] 35.7[i]		164 252
99		1.31 1.30	1.39 1.43	1.44 1.39	1.72 1.74	2.257 2.223	2.02 1.95	86.5	20 0	253

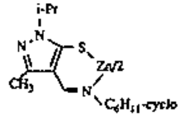
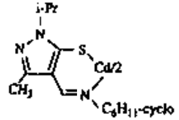
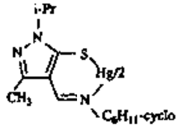
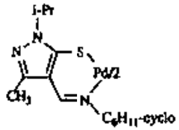
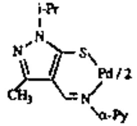
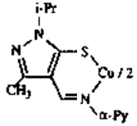
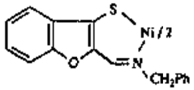
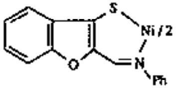
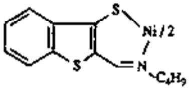
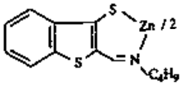
100		1.290	1.420	1.400	1.725	2.291	2.049	80.2	21.3	249
101		1.276 1.287	1.430 1.426	1.400 1.410	1.738 1.732	2.469 2.481	2.256 2.240	90.7	5.1 22.4	249
102		1.279	1.42	1.41	1.727	2.391	2.398	95.6	6.8[j] (0.188)	254
103		1.288	1.410	1.404	1.717	2.324	2.059	173	40.0	255
104		1.31	1.41	1.41	1.728	2.289	2.089	5	35	256
105		1.33	1.49	1.37	1.73	2.23	1.95	57.0	0	244
106		1.294	1.400	1.367	1.706	2.254	1.980	80.6	16.6	257

TABLE 1 (*continued*)

No.	Compound	C(1)=N	C(1)–C(2)	C(2)=C(3)	C(3)–X	M–X	M–N	θ	φ(r)	Ref.
107		1.347 1.324	1.426 1.423	1.348 1.356	1.727 1.713	2.238 2.248	1.974 1.991	74.4	6.7 5.3	257
108		1.282 1.289	1.402 1.396	1.334 1.409	1.715 1.710	2.19 2.16	1.92 1.92	14	37 25	258
109		1.25 1.33	1.42 1.46	1.38 1.38	1.80 1.81	2.28 2.28	2.11 2.02	92	29(0.83) 19(0.44)	258

[a] For different metallocycles within the same molecule.

[b] The angle between SMS′ and NMN′ planes.

[c] The structure was not fully solved due to the uncertain position of the $-(CH_2)_3OH$ substituent.

[d] Shortened intramolecular S ··· S distances (Å): 2.94 (**80**), 2.971 (**81**), 2.949 (**82**), 2.864 (**85**), 3.388 (**95**), 3.667 (**97**); Se ··· Se 3.105 (**98**).

[e] Phenyl groups of the N=CHPh moiety lie in trans positions with respect to the neighbouring phenylene rings.

[f] Dimeric square pyramidal structure with a Co ··· S intermolecular distance of 2.44 Å.

[g] Pentacoordinated structure with Co ··· N_{pyr} intramolecular bond of 2.448 Å.

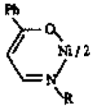
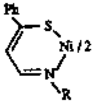
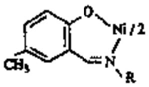
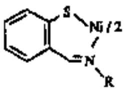
[h] For two molecules occupying different positions within the same unit cell.

[i] For isoligand Ni(II) complex.

[j] The valence angle SHgS′ of 141.0° exhibits a tendency for the mercury atoms towards linear coordination of sulphur atoms.

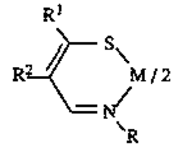
TABLE 2

Thermodynamic parameters of the planar⇌tetrahedral equilibrium for Ni(II) Schiff base complexes of the type MN_2O_2 and MN_2S_2

No.	Compound	R	ΔG^0_{298}[a] (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (kJ mol^{-1})	N^t_{298}[b]	Ref.
1		s-C_4H_9 active meso	 −4.0 −3.7	 0.4 1.3	 14.7 16.9	 0.83 0.82	190
2		s-C_4H_9 active meso	 2.4 0.9	 16.7 14.9	 48.1 46.9	 0.28 0.41	190
3		s-C_4H_9 active meso	 0.5 1.0	 4.6 5.9	 13.6 16.5	 0.45 0.40	265
4		n-C_4H_9	5.9	8.0	7.1	0.12	149

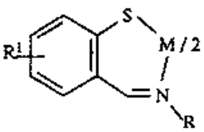
[a] Negative values correspond to the less stable planar form.

[b] The fraction of tetrahedral form.



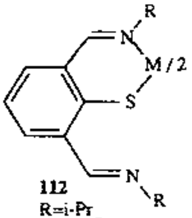
110

R= Alk, Ar
$R^1=C_6H_4Y$-p (Y=H, Br, OCH_3, NO_2)
R^2= H, i-Pr



111

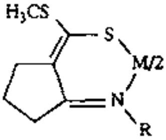
R= Alk, Ar
R^1= 1,2-; 2,1-; 2,3-benzo



112

R=i-Pr
M= Zn^{II}, Cd^{II}

2-Aminocyclopentenedithiocarboxylato Cu(II) and Ni(II) complexes of type **113** have recently been studied [269,270] by means of UV, NMR and ESR spectroscopy. These display structural features resembling those of β-aminopropenethionato and thiosalicylaldiminato metal-chelates. NMR data of Ni(II) complexes with alkyl substituents R, diamagnetic in the solid, reveal the typical equilibrium pattern between planar ($S=0$) and tetrahedral ($S=1$) forms with the latter amount at room temperature being about 22.1% ($R=CH_3$), 42.4% ($R=C_2H_5$), 14.4% ($R=C_3H_7$) and 15.3% ($R=C_4H_9$). Of the three Cu(II) compounds investigated with $R=H$, CH_3, C_2H_5, only the one complex containing the ethyl group exhibits, in parallel with stabilization of the tetrahedral form in the corresponding Ni(II) complex, a planar-to-tetrahedral distorted structure with a θ value estimated from ESR parameters of about 60°.



113

R= H, Alk

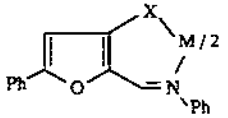
Few X-ray structurally characterized β-aminopropenethionato and thiosalicylaldiminato complexes with bidentate ligands (for consideration of Schiff base complexes with tetradentate ligands see Sect. F) are known. In the case of the Zn(II) complex **73**, tetrahedral coordination around zinc was shown ($\theta=81.7°$) with moderate puckering of the metallocycles along the N···S axis [236]. Bis(thiosalicylaldiminato)Ni(II) complexes **80** [241], **81** [241] and **85** [244] have a markedly distorted cis planar structure. Although all contain additional potentially coordinating groups, no intermolecular nor intramolecular interactions were found in the solid state, as seen with analogous MN_2O_2 complexes.

Metal-chelate complexes derived from *N*-alkyl(aryl)imines of heterocyclic thio(seleno)aldehydes confirmed that, in addition to the bulkiness of substituents attached to the ligating atom, and the origin of the latter, annelation of heterocyclic rings to the metallocycle drastically affects the configuration at the metal atom.

The structural features of complexes containing thiophene and benzothiophene moieties are close to those of parent β-aminopropenethiolato metal-chelates and their benzoannelated derivatives. X-ray data [245] for Ni(II), **86**, and Co(II), **87**, complexes with a cyclohexyl substituent R at the nitrogen centre show a tetrahedral structure, whereas the Ni(II) complex **108** [258] containing the less bulky *n*-butyl group is planar. Magnetic moments are in accord with these findings. For example, for Ni(II) complexes such as **108**, magnetic moments in the solid state are equal to 3.32 ($R = t\text{-}C_4H_9$) and 3.65 ($R = CH_2Ph$) B.M. Planar (21%) and tetrahedral (79%) forms of **108** were found to coexist in a rapid equilibrium in DMSO solution at 304 K [184]. The Zn(II) complex of type **109** [258] has a tetrahedral structure. The pentacoordinate MN_3S_2 mode was reported for the bis(5-ethyl-3-α-pyridylalidimino-2-thienylthionato)Co(II) complex **88** [246], displaying a metal centre with a basically tetrahedral environment but with an additional weaker intramolecular coordinate bond with the pyridine nitrogen, $Co \cdots N_{pyr}$ 2.448 Å.

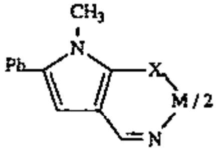
The replacement of a sulphur atom by oxygen in the annelated heterocyclic rings brings about stabilization of tetrahedral geometry similar to MN_2O_2-type complexes. Two structurally characterized Ni(II) complexes, **106** and **107**, derived from enamines of 3-formyl-2-benzo[*b*]furanthione [257] have a tetrahedral structure even though they contain benzyl and phenyl R substituents which usually form a planar structure. The magnetic moments of these [257] and analogous Ni(II) species with different R [185] in the solid state were in the range 3.1–3.6 B.M., consistent with a tetrahedral configuration. The same structural assignment stems from magnetic moments of Co(II) and Ni(II) 3-*N*-phenylaldimino-2-furanthionato metal-chelates, **114**, [183] with R = Ph. Study of the magnetic and dipole moments of Schiff base complexes with a pyrrole moiety, **115** [183] and **116** [186], unambiguously shows the preference of tetrahedral structures in the solid state. In this case, the geometry around the metal centre seems again controlled by annelation since these compounds contain a phenyl group at the coordinated nitrogen atom.

Among bis-chelate complexes derived from ligands containing heterocyclic



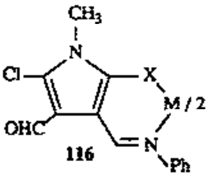
114

M	X	μ_{eff}, B.M.
Ni	S	3.33
Ni	Se	3.28
Co	S	4.53
Co	Se	3.93



115

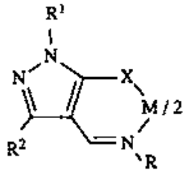
M	X	μ_{eff}, B.M.
Ni	S	3.10
Ni	Se	3.12
Co	Se	4.42



116

M	X	μ_{eff}, B.M.
Ni	S	2.79
Co	S	4.12
Ni	Se	2.98
Co	Se	4.27

moieties annelated to chelating units, special attention has been paid to pyrazolealdiminato metal-chelates **117a–117d**. Ni(II) complexes of type **117** were originally assigned a tetrahedral structure based on magnetic moments (3.0–3.5 B.M. in solid) measured for a few compounds of type **117a** [180,181]. This assignment was later extended to a broad series of analogous complexes of type **117a** [188,271] and **117b–117d** [272,273] in solution. The contact ^{1}H NMR shifts arising from partial delocalization of the unpaired electron density to the ligands displayed a linear vs. $1/T$ dependence in accordance with Curie's law, whereas the effective magnetic moments of 3.21–3.55 B.M. in chloroform (within a large series of about 30 complexes with different R) remained unchanged over the accessible temperature intervals 218–330 K. This is an additional indication that no appreciable amounts of diamagnetic planar form appear through a shift of the equilibrium with the stable tetrahedral isomer. Inversion of the tetrahedral configuration at the metal centre R$\rightleftharpoons$S in **177a**–**117d** was followed by ^{1}H NMR spectra, the coalescence of several pairs of diastereotopic protons being studied [188,273]. The activation barriers span the range from 41 to 74 kJ mol^{-1}. The bulky R substituents at the aldimine nitrogen give rise to a significant increase in the energy barriers to enantiomerization owing to steric hindrance in the intermediate square planar form.



117 a-d

	R^1	R^2
a	CH_3	Ph
b	Ph	i-Pr
c	CH_2Ph	CH_3
d	i-Pr	CH_3

R=Alk, Ar
X=S, Se

X-ray data are available for Ni(II) complexes **91** [248], **92** [249], **93** [250], **94** [250], **95** [248], **96** [251], **97** [250] and **99** [253] (Table 1) with various R substituents, while bridged complexes **89** and **90** [267], and **98** [164,252] will be considered in Sect. F.

Complexes **91–96** and **99** have a cis distorted (except for **92**, R = *t*-Bu, with a small trans distortion) pseudo-tetrahedral structure which is close to a tetrahedral configuration ($\theta > 80°$) for **91–94** and **99** whereas a higher degree of tetrahedral-to-planar distortion was observed for complexes **95**, R = Ph ($\theta = 68.7°$) and **96** ($\theta = 76.3°$), the latter representing the only structurally characterized Schiff base metal-chelate of type **2** with an MN_2Se_2 coordination site. These two complexes display shortened intramolecular contacts between the sulphur and selenium atoms, respectively, being less than the sum of van der Waals radii, S $\cdots$ S, 3.338 Å, and Se $\cdots$ Se, 3.667 Å.

The key exceptional example in the series is represented by complex **96** [251] displaying a trans square planar structure according to the X-ray structural investigation. This distinctive case points to a subtle balance between interfering trends in ligand environment to determine particular geometrical features at the metal centre. In this compound, a strong tendency to adopt a tetrahedral configuration by annelation of the pyrazole fragment is overcome by the crowding in this form caused by the presence of two methyl groups in the ortho positions of the aromatic rings attached to the coordinating nitrogen atom [259]. However, the preferred cis square planar form is also sterically strained; hence the unusual trans configuration is adopted. The energy difference between all three forms may be very small in solution since NMR investigation showed the presence of the characteristic rapid planar$\rightleftharpoons$ tetrahedral equilibrium of Ni(II) complexes shifted to the right.

To clarify whether a correlation exists between tetrahedral-to-planar distortion and energy barriers to R$\rightleftharpoons$S interconversion, trends in $\Delta G^{\neq}$ and θ changes were compared [248]. For complexes with R alkyl substituents, activation barriers, indeed, increase with an increase in steric volume in the order $CH_3 < C_6H_{11}$-cyclo $< t$-Bu, which is reflected by corresponding steric constants E_s (Table 3). In the case of a similar complex with R = Ph, the θ value falls appreciably but is not accompanied by a change in $\Delta G^{\neq}$. Another structural parameter reflecting steric strain in the molecule, viz. valence angle NNiN′ is in good agreement with $\Delta G^{\neq}$ variations for all four complexes (Table 3).

Substituents remote from the metal centre in pyrazolealdiminatoNi(II) complexes do not significantly affect their geometry. For example, all main structural parameters are very similar for complexes **93** and **94** with the same R and varied R^1 and R^2. Typical structural parameters and the absence of any metal–metal interactions are also displayed in complex **99** [253] containing an η^6-phenylchromiumtricarbonyl substituent R with strong π-electron acceptor properties. The R$\rightleftharpoons$S interconversion barriers were also similar to those of complexes with conventional aryl substituents [308].

Schiff base Cu(II) complexes with a N_2S_2 coordination sphere are usually stable only with tetradentate ligands [274,275] or where there is additional coordination to the copper centre [276] due to the easy Cu(II)$\rightarrow$Cu(I) reduction. Complex **105** [244] is the first example of a structurally characterized Cu(II) metal-chelate of type **2** (X = S) derived from a bidentate ligand. By analogy with NiN_2S_2 pyrazoleal-

TABLE 3

Selected structural parameters and activation barriers of R$\rightleftharpoons$S interconversion of Ni(II) pyrazolealdiminato metal-chelates **117d**

R	CH_3(**91**)	C_6H_{11}-cyclo(**93**)	t-Bu(**92**)	Ph(**95**)
θ degrees	81.9; 82.4	85.3	96.3	68.7
∠ NNiN′ (degrees)	100.9; 101.2	115.0	133.0	104.3
$\Delta G^{\neq}$ (kJ mol^{-1})	42.7	49.5	73.7	45.2
E_s[a]	0.00	−0.79	−1.54	

[a] Steric constant of substituent.

diminato complexes, annelation of the pyrazole ring favours a pseudo-tetrahedral geometry around the metal centre, $\theta = 57.0°$. ESR parameters for **105** in $CHCl_3$–toluene glass, $A_{\parallel} = 13.1 \times 10^{-3}\ cm^{-1}$, $g_{\parallel} = 2.149$, $g_{\perp} = 2.036$ [244] are very similar to those reported for the pseudo-tetrahedral complex **98** [164] $A_{\parallel} = 13.7 \times 10^{-3}\ cm^{-1}$, $g_{\parallel} = 2.155$, $g_{\perp} = 2.036$, treated as a synthetic model mimicking the active site of blue copper proteins.

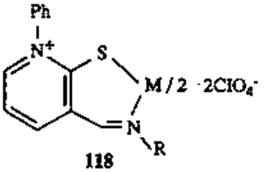
Zn(II) and Cd(II) pyrazolealdiminato complexes form more stable tetrahedral structures compared with Ni(II), as shown by the increasing order Ni < Cd < Zn of the energy barriers $\Delta G^{\neq}$ against interconversion through the planar intermediate or transition state structures. The magnitude of the barriers amounts to 89–98 and 55–66 kJ mol^{-1} [189] for Zn(II) and Cd(II) complexes, respectively. A slightly distorted tetrahedral structure was reported for the Cd(II) complex **101** [249], $\theta = 90.6°$. The deviation from tetrahedral geometry towards a cis planar arrangement of sulphur atoms is as much as 9.1° in the isoligand Zn(II) complex **100** [249], $\theta = 80.9°$. A distortion of similar magnitude towards the trans planar arrangement of donor atoms was found, in contrast, for the analogous Zn(II) complex with X = O (**117b**, $X = C_6H_{11}$-cyclo), $\theta = 101.7°$.

An X-ray crystal study of the Hg(II) metal-chelate **102** [254] reveals some interesting structural features, most important of these being substantial enlargement of the SHgS′ valence angle to 141.0°. In accordance with the Haaland approach [277] to the description of the coordinate bond, such a large value of the valence angle proves almost purely covalent character in the Hg–S bonds. By contrast, the Hg–N bonds in this complex are dative bonds in accord with the magnitude of Hg–S and Hg–N bond lengths of 2.391 and 2.397 Å, respectively.

The unique example of a trans planar MN_2S_2 structure has recently been reported [255] for the Pd(II) complex **103**. The appearance of this unusual geometry could perhaps be accounted for by the presence of bulky $N-C_6H_{11}$ substituents preventing the formation of cis structure due to strong sterical constraints. Indeed, the replacement of this group by the less bulky N–Py-α results in a cis planar configuration for **104** [256]. Note the atypical umbrella molecular conformation in **103** with bending along the $N \cdots S$ axis, $\phi = 40°$, leading to the appearance of a high dipole moment of 4.01 D in dioxan [278].

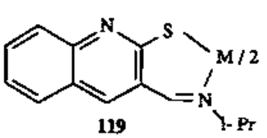
Several MN_2S_2 Schiff base complexes containing annelated six-membered metallocycles with heteroaromatic pyridine **118** [279,280] and quinoline **119** [46] fragments have recently been reported. According to X-ray data [329], the Cu(II) adduct **118** ($R = -(CH_2)_2-$) possess a chelate-type $[CuLClO_4^-]^+ClO_4^-$ square pyramidal structure. The barrier against inversion of the tetrahedral bond configuration for the Zn(II) complex **119** [46] was determined to be 13.6 kcal mol^{-1}. This value is significantly lower than interconversion barriers in the corresponding Zn(II) pyrazolealdiminato complexes (19.7–22.9 kcal mol^{-1} [188]), perhaps reflecting the higher stability of a transition planar structure.

To summarize the structural features pertaining to MN_2S_2 Schiff base com-



118

R= Ar, -(CH$_2$)$_n$-
M=Cu^{II}, Zn^{II}



119

M= Zn^{II}, Cd^{II}

plexes, two essential peculiarities mostly related to Ni(II) complexes are established: (1) occurrence of cis in contrast to trans square planar structure characteristic of MN_2O_2 complexes and (2) significant stabilization of tetrahedral configuration for complexes containing five-membered heterocyclic fragment annelated to a metallocycle.

At the present, there is no appropriate theoretical quantitative model to account for the contribution of a conceivable sulphur–sulphur interaction as the driving force in the occurrence of experimentally observed shortened intramolecular $S \cdots S$ contacts. On the other hand, semiempirical quantum mechanical calculation [16,281] demonstrated the cis planar MN_2S_2 structure to be energetically preferable relative to the trans form. The same conclusion is reached on a simple electrostatic model of the coordination sphere taking into account the metal polarizability [282]. MNDO calculations of reaction pathways for inversion of tetrahedral configuration at Be(II) and Hg(II) complexes of type MN_2S_2 [283] revealed the energy preferable trans square planar structure as a transition state of intramolecular reaction, however, the alternative cis form was also found to correspond to the stationary point at the energy profile.

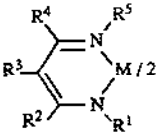
The importance of annelation was recently studied from the viewpoint of a simple conformational approach [281], which accounts for a single contribution to a total conformational energy of the molecule from valence angle deformation energy. In this concept, the occurrence of a particular molecular configuration is deeply related to intrinsic molecular conformation features determined by a particular donor atom set and ligand periphery. The ubiquitous envelope conformation of six-membered metallocycles found in complexes with a planar configuration is supposed to be the inherent property of molecular structure caused by requirements to adopt optimal valence angles for all atoms. For example, semiempirical quantum mechanical calculations of the model idealized metallocycle containing all atoms with their typical valence angles reveal a puckering along the $N \cdots S$ axis 35°. When this occurs, steric repulsion between substituents attached to a coordinated nitrogen atom is diminished and the planar arrangement of donor centres promoted. Otherwise, to minimize steric interference, the metal centre will adopt a planar-to-tetrahedral distorted configuration. Annelation of the five-membered heterocyclic fragment essentially raises adjacent valence $\alpha_{C=C}$ angles of the metallocycle compared with any aromatic or heteroaromatic six-membered ring so that the preferable conformation is planar, thereby destabilizing the planar configuration due to increasing steric interactions between nitrogen substituents. The exceptional behaviour of complexes containing a thiophene ring which remain planar may similarly be explained by the smaller thiophenic sulphur valence angle of 91° compared with that of, for example, sp^2-nitrogen atom (120°) compensating the influence of annelation.

The validity of the above approach may further be considered in relation to MN_4 complexes.

(c) MN_4 complexes

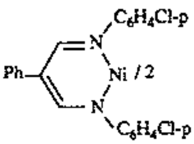
Of complexes derived from imines of *ortho*-amino unsaturated, aromatic and heteroaromatic aldehydes and previously reviewed in refs. 4, 5, and 21–23, the structural features of β-aminopropeneiminato metal-chelates have been studied in particular detail.

NMR and UV spectral investigations as well as magnetic moment measurements of Ni(II), Co(II) and Cu(II) complexes of type **120** show the configuration at the metal centre to be tetrahedral both in solution and in the solid state regardless of the character of the R^1–R^5 substituents, the only exception being the case of smallest steric volume substituents $R^1 = R^5 = H$, which give rise to the planar structures [5,23]. X-ray studies of Ni(II) **121** [284] and Cu(II) **122** [285] complexes reveal tetrahedral distortion θ angles of 68.5° and 67°, respectively, consistent with the above assignment. Another distinctive structural feature characteristic of these complexes is the planar conformation of the metallocycles in both cases. In addition to the initially investigated complexes derived from symmetrically substituted ligands ($R^1 = R^5$, $R^2 = R^4$), in subsequent studies [192,286–291] asymmetrical complexes with different combinations of R^1–R^5 substituents were reported and the barriers against the inversion of tetrahedral configuration at the nickel centre $R \rightleftharpoons S$ were determined by use of dynamic ^1H NMR spectroscopy. These were found to fall in the range 72–100 kJ mol^{-1} [192,291].

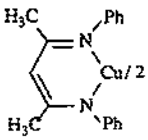


120

R^1, R^5=H, Alk, Ar;
R^2, R^4=H, CH_3; R^3=H



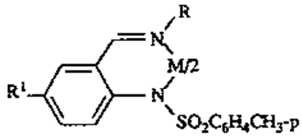
121



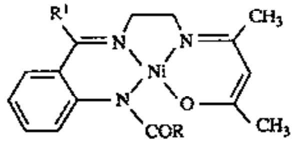
122

Complexes based on imines of *o*-aminobenzaldehyde with definite composition were isolated only with *N*,*N*′-bridged tetradentate ligands [292–297]. Otherwise, complexation affords compounds of unestablished structure, presumably due to possible side reaction of ligand self-condensation [298,299].

An intriguing structural problem is presented by complexes **123** obtained from imines of *N*-tosylaminobenzaldehyde [22,300–302]. Magnetic moments of Ni(II), 3.2–4.1 B.M., and Co(II) complexes, 4.2–4.4 B.M., correspond to the high-spin electronic state. According to X-ray structural data for the Ni(II) complex **123** (R = i-Pr, $R^1 = H$) [22], the coordination geometry may be described as a tetrahedral core supplemented with two weaker intramolecular bonds of the nickel atom with oxygen centres of two neighbouring tosylamino groups, N ··· O 2.48 Å. A tetracoordinate metal centre is supposed [302] to be present in an unsymmetrical bridged Schiff base complex **124** containing an N-acyl group, whereas the trifluoromethyl analogue ($R^1 = CH_3$, $R = CF_3$) displays, according to X-ray data, a square-pyramidal coordination site by virtue of axial intramolecular Ni ··· F binding, the corresponding Ni ··· F distance being 2.724 Å.

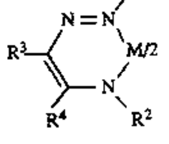


123
R=Alk, Ar; R^1=H, NO_2
M=Co^{II}, Ni^{II}

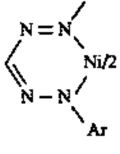


124
R=CH_3, CF_3; R^1=H, CH_3

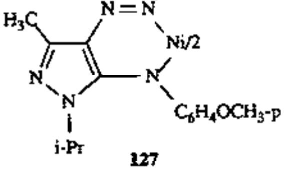
Incorporation of the azo instead of the azomethine group in the MN_4 metal-chelates **125** [22,303,304] drastically affects the structure of the complexes. While the Cu(II) complexes retain a pseudo-tetrahedral configuration in solution as well as in solid state, e.g. with $R^1 = Ph$, $R^2 = R^4 = CH_3$, $R^3 = -COPh$ ($\theta = 58°$; $\phi = 4.0$, $10.4°$; ESR parameters in solution: $g_{\parallel} = 2.188$, $A_{\parallel} = 13.2 \times 10^{-3}$ cm^{-1}) the analogous Ni(II) complex ($R^3 = COCH_3$) possesses a planar structure both in the solid state ($\theta = 0°$, $\phi = 46.6°$) and in solution [304]. Thus, the steric demands of four aryl groups neighbouring the metal centre may be circumvented by forming a stepped conformation and thereby retaining an intact planar configuration at the metal centre, which is otherwise unfavourable. This is also the case of planar formazanatoNi(II) complexes such as **126** [305].



125
R^1=Ar; R^2, R^4=H, Alk, Ar
R^3=H, -COPh, -COCH$_3$



126



127

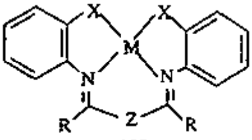
The predominance of conformational versus configurational changes associated with the incorporation of the azo group was ascribed [281] to the fact that valence angles pertaining to uncoordinated sp^2 nitrogen atoms (120°) in the metallocycle are less labile to deformations compared with those of sp^2 carbons capable of enlargement to as much as 125–130° in Schiff base complexes. Therefore, this may result in a different conformation of the metallocycle being more puckered in the latter case. Nevertheless, one may again tune the tetrahedral configuration by annelation of a pyrazole ring to the metallocycle. The X-ray study [306] revealed a tetrahedral structure of a Ni(II) complex **127** ($\theta = 90°$) containing planar metallocycles ($\phi = 4°$ and 7°). The tetrahedral form is also represented in solution as indicated by the value of the corresponding magnetic moment, 3.25 B.M., being practically constant at different temperatures.

In conclusion, the influence of annelation of a five-membered heterocyclic ring on the structural features of Schiff base complexes is also traced in metal-chelates with an MN_4 coordination site in addition to those of MN_2O_2 and MN_2S_2 structural types. To assess the origin of structural variation, the conformation peculiarities should also be taken into account. It may be supposed that recent achievements in conformational analysis of coordination compounds in the frame of molecular mechanics calculations [307] could lay a firmer basis for discrimination of different contributions steering the structural features of tetracoordinate Schiff base complexes.

E. TETRACOORDINATED METAL-CHELATE COMPLEXES WITH FIVE-MEMBERED METALLOCYCLES

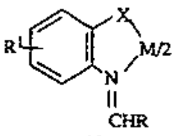
(i) Synthesis

Complexes with five-membered metallocycles of the type MN_2X_2 include the metal-chelates derived from Schiff bases of *ortho*-amino(thio, seleno)phenols, substituted *ortho*-phenylenediamines and aliphatic, aromatic and heteroaromatic aldehydes, dialdehydes and ketones **128,129** [1,3] and the complexes of Schiff bases of 2-formylpyrrole(azoles) **130** and aminotroponoiminates **131** [5].



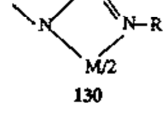
128

R=H, Alk, NR^1; R^1=H, Ts;
X=O, S; Z=Alk, Het



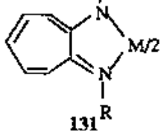
129

R=Ar, Het;
R^1=H, 3-NO_2, 4-OCH_3;
X=O, S, Se, NTs



130

X, Y, Z=N, CR, Benzo-
R=Alk, Ar



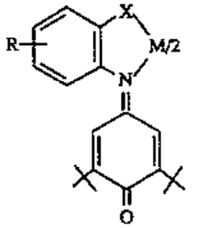
131

R=Alk, Ar, $-(CH_2)_n-$

The synthesis and structure of complexes **128** and **129** were reviewed earlier [1–3,5]. The general reaction scheme for the synthesis of complexes **129** is shown in Fig. 6.

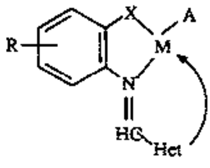
Complexes of Cu(II) [2,51,308,309], Ni(II) [309,310], Co(II) [309], Mn(II) [309,311], Zn(II), Cd(II) and Pb(II) [309,312] were obtained by coupling ligands **132** with metal acetates. In the case of Cu(II), hydrolysis of the azomethine bond may lead to isolation of *ortho*-aminophenolato complexes **133** (X = O) [51,308,313]. An excess of aldehyde was used in several cases to avoid side reactions [51,308]. Cleavage of the azomethine bond during complexation is confirmed in the crystal structure of Mn(II) [313] and Pd(II) [314] complexes containing the coordinated *ortho*-aminophenol molecules. The reaction of ligands and metal salts was also used for the synthesis of MN_4 complexes of type **129** (X = NTs) [315] and metal-chelates of *ortho*-indophenols **134** [314,316].

Complexes with Schiff bases of heterocyclic aldehydes prepared using the reaction portrayed in Fig. 6 can have two different structures, **129** or **135**, with the anion A bound to the metal centre. Many of the latter examples were prepared from vicinal hydroxyazomethines of furfural [3], azoles and azines [3,317].



134

R=H,4-CH_3,4-NO_2,5-NO_2,5-Cl
X=O,NTs
M=Co^{II},Ni^{II},Cu^{II},Zn^{II},Pd^{II},Pt^{II}



135

R=H,5-NO_2; X=O,S
A=CH_3COO^-,Cl^-
M=Co^{II},Ni^{II},Cu^{II},UO_2

The composition of the complexes is also affected by reaction conditions and the nature of the anion. For example, the reaction of **132** (X = O) HL with Mn(II) acetate yields, depending on pH, metal-chelates of type ML_2 [311] or tetrameric complexes $Mn_4L_6Ac_2$ [313] containing hexacoordinate manganese centres, whereas the reaction with the corresponding metal chloride gives the mixed-ligand complex

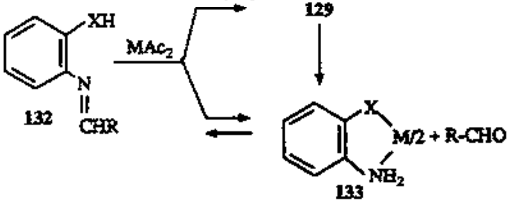
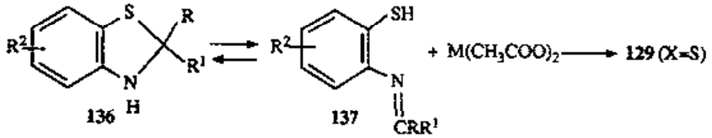


Fig. 6. Synthesis of metal-chelates of type **129**.

$Mn_4L_4L'_2Cl_2 \cdot 2H_2O \cdot 2CH_3OH$ (L′ being the anion of *ortho*-aminophenol) with pentacoordinate metal centres [313].

Schiff bases of aromatic and heteroaromatic aldehydes with *ortho*-aminothiophenols **137** for which the cyclic thiazoline structure **136** is preferred [2,318,319] were used for the synthesis of various complexes of type MN_2S_2 **129** (X = S) [317,320–325].



R=H,Alk,Ar,Het,COAr; R^1=H,Ar
R^2=H,Hal,NO_2

The formation of complexes derived from tridentate ligands of type **135** has also been reported in this reaction [317,323,324,326]. The transformation **129** → **135** (R = α-Py, $R^1 = R^2 = H$, X = S) via the reaction with $NiCl_2$ could also occur [323].

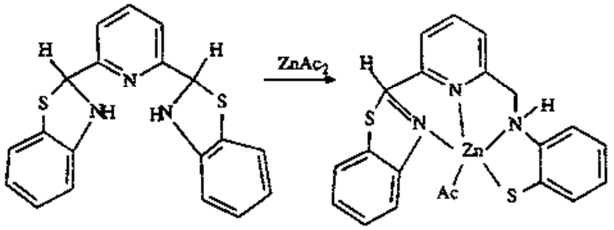
Another method for the synthesis of complexes of type **129** with X = S is the reaction of *ortho*-aminothiophenolato metal-chelates with aldehydes (Fig. 6) [317,320,323,325]. This reaction was also used for the preparation of the first complexes with an MN_2Se_2 coordination sphere (X = Se, R = Ph, 2-benzothiazolyl; R^1 = H; M = Zn(II)) [327]. Attempts to prepare complexes of type MN_2Te_2 by this reaction did not succeed, resulting in formation of 2,2′-diaminodiphenyl ditelluride [328].

Electrochemical reductive cleavage of the disulphide bond in Schiff bases formed by salicylic or 2-pyrrole aldehyde and 2,2′-diaminodiphenyl disulphide performed in a cell with Ni, Cu, Zn or Cd anode, resulted in the formation of the corresponding metal-chelate thiolato complexes [329,330].

The bridged metal-chelates of type **128** (X = S) were prepared with Schiff bases of malon-, succin-, (M = Cd(II)) [331], 2,6-pyridine- (M = Zn(II)) [332] and 2,5-furan- (M = Cu(II), Zn(II), Cd(II), Pb(II)) [333] dialdehydes. Due to the cyclic structure of the ligands and the presence of the additional donor centres, some unusual structures occur, e.g. the 2,6-bis(2-benzothiazolinyl)pyridine **138** gives complexes of type **139** [334]. Similar complexes were prepared from 2,5-bis(2-benzothiazolinyl)thiophene [333]. A ligand transformation associated with self-redox was reported [335] for macrocyclic Schiff base complexes incorporating a template unit like that in **138**.

(ii) Stereochemistry

To outline the structural features appropriate to complexes with the coordination mode portrayed in formulae **128** and **129**, one must take into account that this particular structural type is often complicated due to ease of ligand hydrolysis and redox transformations, the binding of anionic residues and the formation of oligo-



138 **139**

meric structures. Thus, an unequivocal structural assignment is not always straightforward and, perhaps, requires revision of some previous results, particularly those not confirmed by X-ray data.

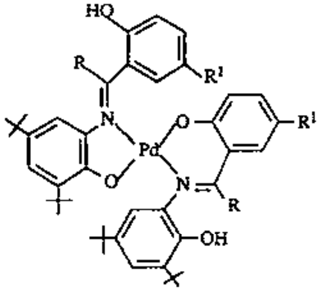
The tetrahedral structure was assigned to Cu(II) complexes of type **129** (X = O) and also confirmed by magnetic and dipole moments for Ni(II) [309,310] and Co(II) [309] complexes. The same configuration was attributed to Mn(II) [311], Zn(II), Cd(II) and Pb(II) [309,312] complexes.

Complexes of type **129** NiN_2S_2 are cis planar, resembling those of thiosalicylaldiminato metal-chelates. This was inferred for the bis[2-benzaldimine(2-thiophenolato)]Ni(II) complex **83**, which proved to be diamagnetic and polar ($\mu \approx 7.5$ D) [320] and subsequently verified by an X-ray determination [242]. A tetrahedral structure was revealed by X-ray structural investigation of bis[2-pyrrolealdimino(2-thiophenolato)-N,S]Zn(II) complex in which the pyrrole nitrogen atoms are not coordinated; this structure may be also assigned to the Co(II) complexes **129** (X = S) [330].

The mechanisms of $Z \rightleftharpoons E$ interconversion of the azomethine bond in complexes **134** were studied in ref. 336. Pd(II) complexes forming rather strong coordinate bonds undergo rearrangement through rotation around the C=N bond whereas in the case of Hg(II) metal-chelates, with weaker metal–ligand bonds, the mechanism of planar inversion at the nitrogen atom dominates.

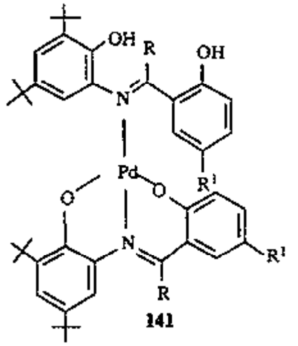
Chelate complexes with a structure incorporating five- and six-membered metallocyclic moieties with the same metal centre were prepared from Schiff bases of salicylic aldehyde and *ortho*-aminophenol [314]. In the case of Pd(II) complexes derived from Schiff bases formed by salicylic aldehyde or *ortho*-hydroxyacetophenone and 3,5-di-*t*-butyl-2-aminophenol, an unsymmetrical ligand environment **140** or **141** has been found. An X-ray study of the compound isolated from solution revealed structure **142** of a partially hydrolysed complex, which is assumed to be formed from **141** rather than from **140** [314]. Tetracoordinate square planar {1-[(2-hydroxyphenyl)iminomethyl]naphthalen-2-olato-O,O′,N}Ni(II) complexes containing bound piperidine or diethylamine molecules with a coordination site similar to that in **142** were recently revealed by X-ray structural investigations [337,338].

The synthesis of metal-chelates of type **128** and their application for analytical purposes has been reported [322,331]. For the structure of the complex containing a bridged thiophene fragment, no coordination of the sulphur atom to the metal

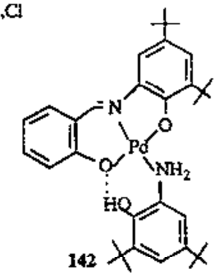


140

R=H,CH$_3$; R^1=H,Cl



141



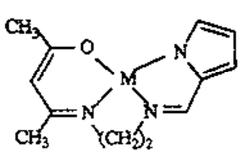
142

centre has been implicated [333]. However, this conclusion was opposed in a recent review [339].

An increased stability of the planar structures relative to their tetrahedral counterparts is characteristic of complexes of types **130** and **131** [2,5,21,22]. For Ni(II) [2,5] and Cu(II) [2,5,340,341] complexes of type **130** with R = H, *n*-Alk, Ar, the planar forms were found to be preferable both in solution and in the solid state. In the case of R = s-Alk, the Ni(II) complexes display an equilibrium between planar and tetrahedral structures in solution. Structural data are available for the bridged complexes (see Sect. F) and isoligand series of Ni(II) [342], Co(II) [343], Cu(II) [344] and Zn(II) [345] metal-chelates **130** with R = *t*-Bu, their structures being close to tetrahedral, $84.7° \leqslant \theta \leqslant 89.6°$.

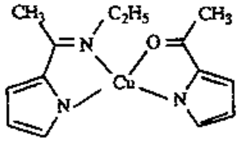
An X-ray study of mixed-ligand complexes **143** [346] and **144** [347] justified their planar structure. The X-ray crystal structure of **145** [348] with a tetradentate β-aminopropenone core shows the preferred formation of six-membered MN_2O_2 metallocycles instead of involving pyrrole nitrogen atoms coordinated to copper as in **143** and **144**.

To summarize the structural features of Schiff base complexes containing five-membered metallocycles and represented by structural types **129**, **130** and **131**, as in complexes incorporating six-membered metallocycles, there is stabilization of the cis planar configuration when oxygen ligating atoms are replaced by sulphur. In contrast to the usually tetrahedral Ni(II) and Cu(II) β-aminopropeneiminato complexes, the corresponding metal-chelates with five-membered metallocycles **130** and **131** show a

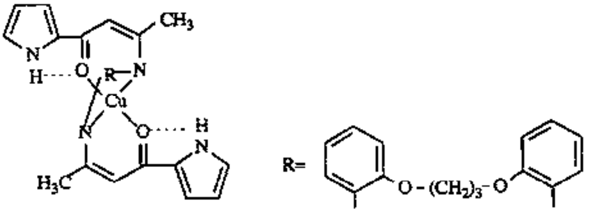


143

M=Cu^{II},Ni^{II}



144



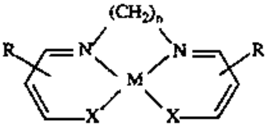
145 trans-

θ=151.8°

molecular configuration strongly dependent on the steric properties of the substituents carried by the coordinated nitrogen atoms.

F. BRIDGED METAL-CHELATE COMPLEXES

In bridged Schiff base complexes of type **146**, the imino nitrogen atoms are bound together with polymethylene chains which, through variation of their length, allow tuning of the geometry around the metal centre.

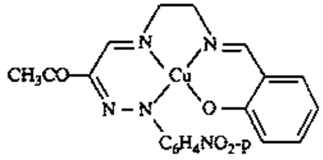


146

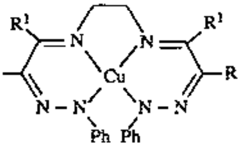
R=Alk, Ar, Benzo-, Hetero-
X=O, S, Se, NR

The structure and properties of complexes possessing the shortest admissible bridge ($n = 2$), e.g. derived from N,N'-ethylene-bis(salicylaldimino) and N,N'-ethylene-bis(β-acetylacetoneimino) ligands [M(Salen)] and [M(Acacen)] have been repeatedly reviewed [1,5,7,18], special attention being paid to their properties as efficient oxygen carriers [349]. The ethylene bridge enforces complexes **146** to adopt a cis planar configuration at the metal centre, in some rare cases slightly distorted towards the tetrahedral form. An important exception is, however, the Zn(II) complex **71** for which significant tetrahedral distortion is evident, $\theta = 55.6°$ [234]. Sterically interacting groups placed in close proximity to each other in the planar arrangement can also provide for substantial tetrahedral distortions. The planar geometry around the central metal atom is kept in the case where one of the imino nitrogen atoms is substituted by oxygen bearing no substituents. This is exemplified by **147** [350], whereas a tetrahedral distortion as great as 35.8° occurs for **148** [351] containing two −NPh groups in close steric contact. By contrast, **149** [352] possesses a planar configuration at the nickel atom.

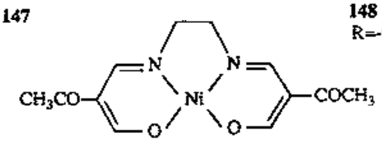
The molecular conformation of the essentially planar ethylene-bridged complexes involves an umbrella or stepped form **57**, **58** due to puckering of the six-membered metallocycles along the N ··· X axis, while the metal atom may move out of the plane formed by the donor atoms. Structural data [7] indicates that the umbrella conformation occurs in dimeric pentacoordinated complexes and in those complexes containing solvent molecules or other ligands in axial sites. Recent structural data including μ-bridged complexes [353–357] are generally consistent with this trend. The stepped conformation has been reported for dimeric [{Cu(Salen)}$_2$] [358], [{Co(II)(Salen)}$_2$] [353] and [{Fe(III)(Salen)}Cl] [359] complexes. Umbrella-type distortions, although not so great, were found for monomeric tetracoordinated complexes derived from Schiff bases of *o*-aminobenzaldehyde of Co(II) [338] and Cu(II) [339], and [Cu(Acacen)] [360]. The energy difference between possible conformations is probably not very high. For example, the Co(II) complex derived from the Schiff base of salicylic aldehyde and *o*-phenylenediamine crystallizes as planar and umbrella conformational isomers within the same unit cell [361].



147

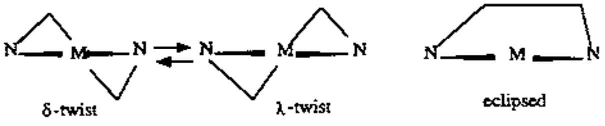


148
R=-COPh, R^1=CH$_3$

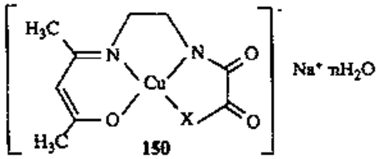


149

The conformation of the ethylenediamine bridge is closely connected with the molecular configuration. Usually, the twist conformation (δ or λ) occurs. The eclipsed conformation may be found for fully planar complexes, e.g. [{Cu(Acacen)}·(CH$_3$NH$_3$)$^+$ClO$_4^-$] [362] with distortion increasing proportionally to the overall deviation from planarity. An eclipsed conformation was also reported for the pseudo-tetrahedral complex **150a** [363] while in the related **150b** and **150c**



[363], the twist conformation is observed. The frequency of the $\delta \rightleftharpoons \lambda$ interconversion is supposed to be very high on the ^{1}H NMR time scale since methylene protons were found to be equivalent in NMR spectra (see, for example, ref. 302). However, it may be frozen for complexes incorporating a fifth axially ligating group [302,364].



150

a X=O
b NH
c NCH_3

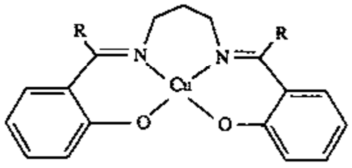
The substitution of a methylene hydrogen by an alkyl group allows one to distinguish between δ and λ conformations. The λ conformation with an axial methyl group was shown to be preferable both in solution and in the solid state, whereas the relative stability of the δ conformation increases if the azomethine carbon atoms bear a methyl group instead of hydrogen [14].

The possibility to tune the configuration at the metal centre in bridged Schiff base complexes has been extensively investigated [296,365–368] using UV spectroscopy and magnetic moment measurements. As expected, the flexibility in the molecular structure grows as the number of methylene groups in the *N*,*N*′-bridge increases. However, to date few examples of structurally characterized complexes are available with $n > 2$.

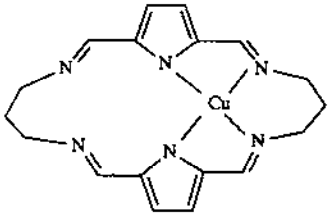
The Cu(II) complexes demonstrate significant deviations from planarity, even in the case of $n = 3$, e.g. **151a** and **151b** [369,370] ($\theta = 19.1°$ and $34.4°$, respectively), **152** [371] ($\theta = 30.3°$), **75** [238] (52.8° between NCuN′ and SCuS′ planes) with the exception of the planar complex **153** [372] and analogous planar $[Cu(Naphthen)]_2$ [373]. High values of θ were also reported for aminoazo complexes **148** ($R^1 = CH_3$) with propylene bridge 58.0° ($R = -COPh$) [351], 43.1° ($R = -COCH_3$) and 45.1° ($R = H$) [374]. Further increase of the length of the polymethylene chain, $n = 4$, does not significantly change the magnitude of distortion for aminocyclopentenedithicarboxylato and aminoazo complexes. In the former case, **76** [239] possesses a corresponding dihedral angle of 57.1°, which is 4.3° larger than for $n = 3$. In the latter case, values of θ are 53.3° (**148**, $n = 4$, $R = -COPh$, $R^1 = H$) [351] and 121° (**148**, $n = 4$, $R = -COPh$, $R^1 = CH_3$) [374], indicating transformation from cis to trans distorted structure.

Ni(II) complexes with $n = 3$ formed by the Schiff base of *o*-aminobenzaldehyde [296], **153** [372] and pyrrolealdiminato metal-chelate with 1,3-dimethylpropylene bridge [375] are planar. Structural data for five Ni(II) complexes of type **148** ($n = 2$–4) with different substituents R, R^1 have also been reported [374]. The values of θ lie within the range 2.2–28.3° with no regular influence of bridge length on the degree of distortion.

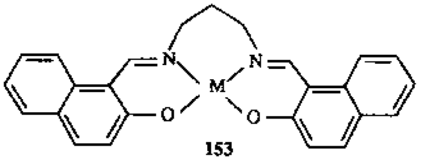
A comprehensive study of the variations in polymethylene chains was carried out for macrocyclic Cu(II) and Ni(II) aminotropocoronands **154** [376,377]. Whereas



151a,b
a R=H θ = 19.1°
b R=CH$_3$ θ = 34.4°

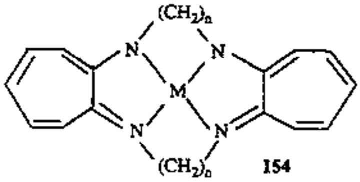


152 θ=30.3°



153
M=Cu^{II}, Ni^{II}

for Cu(II) complexes values of θ gradually change from zero to 61.3° for $n,n = 5/5$, with Ni(II) a stepwise transformation is observed from $n,n = 4/5$ ($\theta = 27.1°$) to $n,n = 5/5$ ($\theta = 70.1°$) accompanied by a change in total spin of the complex $S(0) \rightarrow S(1)$ ($\mu = 3.18$ B.M.).



154

	θ					
n,n	3/3	4/4	4/5	5/5	2O/2O*	6/6
M=Ni^{II}	8.3	28.9	27.1	70.1	74.5	85.2
M=Cu^{II}	0	36.6		61.3		

* n,n= -CH$_2$CH$_2$OCH$_2$CH$_2$-

A similar spin transformation was observed for pyrazolealdiminatoNi(II) complexes **155a** with change of n from 4 to 5 [378]. This complex with an ethylene bridge **89** [247] is planar and diamagnetic both in solution and in the solid state. A slightly distorted ($\theta = 18.3°$) cis planar structure was found for **90** with $n = 4$, X = S

155a,b
a R=i-Pr; X=S, Se; n=2-5
b R=Ph; X=NH; n=2-4

[303]. In CHCl$_3$ solution, an equilibrium mixture of planar low-spin and tetrahedral high-spin forms was observed with the relative amount of the latter N_t of 0.33 (X = S) and 0.28 (X = Se) at 298 K calculated from effective magnetic moments 1.9 and

1.7 B.M. The averaged ^{1}H and ^{13}C NMR spectra for these complexes indicate a rapid interconversion $S(0) \rightleftharpoons S(1)$. Lowering the temperature of the solution to 248 K, the inequivalence of the isopropyl methyl and methylene protons is achieved in the 100 MHz spectrum, indicating freezing out of inversion at the metal centre. Apparently, inversion of the seven-membered diaza cycle is a rate-limiting process, analogous to observations for Schiff base complexes containing an *o,o′*-diphenyldiamine bridge [379]. Possible dynamic rearrangements are shown in Fig. 7. They include interconversion of the planar and tetrahedral forms without inversion of the tetrahe-

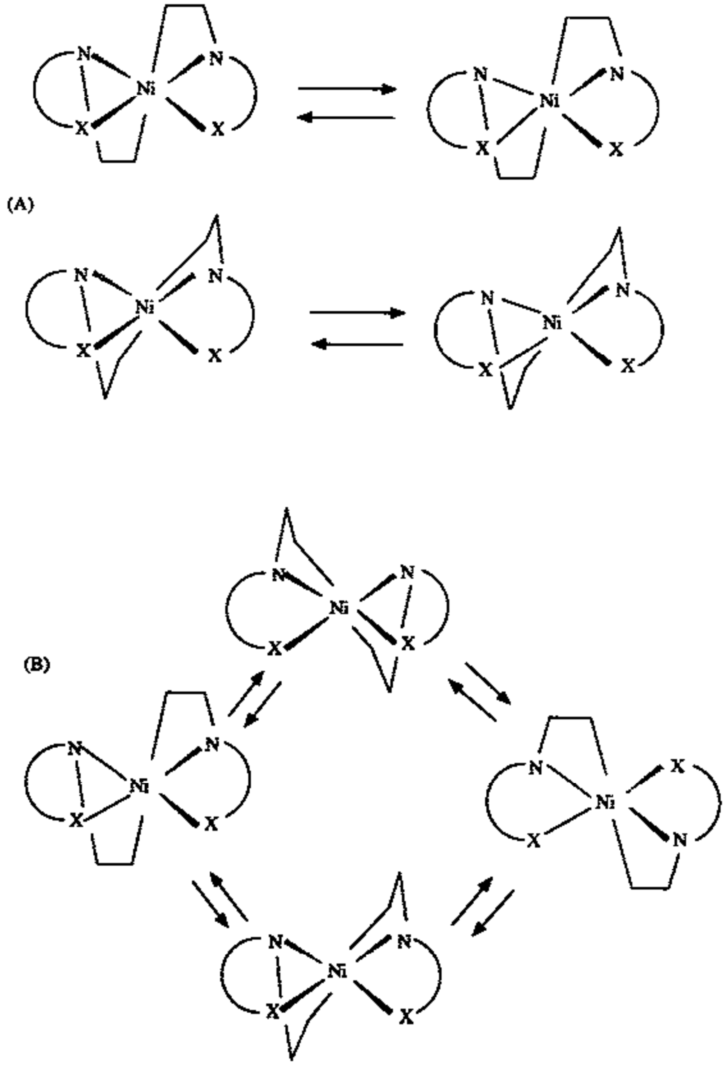
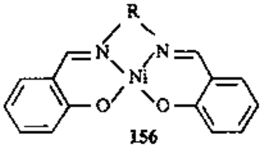


Fig. 7. Stereodynamic rearrangements in complexes **155** ($n = 4$) at $T < -50$°C (A) and $T > -50$°C (B).

dral configuration at low temperatures and R⇄S enantiomerization accompanied with inversion of metallocycle at higher temperatures, $\Delta G^{\neq} = 48–50$ kJ mol^{-1} [247]. Similar behaviour is characteristic of analogous complexes **155b** ($n = 4$) with an MN_4 coordination site ($N_{t,303\,K} = 0.385$; $\Delta G^{\neq}_{213\,K} = 42.8$ kJ mol^{-1}) [380]. This contrasts with 2-aminocyclopenetenedithiocarboxylatoNi(II) complexes **113** ($R = -(CH_2)_n-$; $n = 2–5$) [269] which display in solution only trace amounts of a high spin form (3% for $n = 4$ and 4% for $n = 5$), illustrating the important contribution associated with annelation of the pyrazole ring in stabilizing the tetrahedral form, in parallel to bis-chelate complexes.

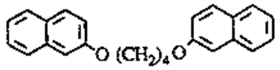
Structural data related to complexes with $n > 6$ are very limited. Two Ni(II) complexes of type **156a** [381] and **156b** [382] containing long bridging chains have a trans planar structure characteristic of MN_2O_2 Schiff base metal-chelates with non-bulky R substituents at the imino nitrogen. In this case, the metal centre adopts its preferred configuration allowed by a highly flexible bridging group. Likely a cis planar configuration for MN_2S_2 is retained in complexes containing an extended bridging group even though the corresponding X-ray studies have not yet been performed.



156

a R = $-(CH_2)_2NHP(Ph)_2Mo(CO)_4P(Ph)_2NH(CH_2)_2-$

b



G. SUMMARY

Taking proper account of structural and reaction conditions, interaction of *ortho*-hydroxy(amino-, thio-) Schiff bases **1** and **4** with Lewis acids may be steered to formation of molecular adducts **3** and **6**, avoiding the thermodynamically more stable metal-chelate complexes **2** and **5**. The peculiar structural features of **3** and **6** that were defined mostly via X-ray studies are coordination to metal through the X (O, S, NR) centres and the inclusion of relatively strong intermolecular bonds in the **3** adducts.

Analysis of structural regularities displayed by a wide variety of tetracoordinate metal-chelate complexes of Schiff base ligands bearing hydroxy, amino, thio and seleno substituents in the ortho position reveals a number of stereochemical effects exerted by the ligand environment at the metal centre. These are most clearly traced in the case of stereochemically labile complexes of transition metals, particularly Ni(II):

(1) An increase in the steric bulkiness of the substituent attached to nitrogen atoms coordinated to the metal centre favours a tetrahedral configuration. The steric

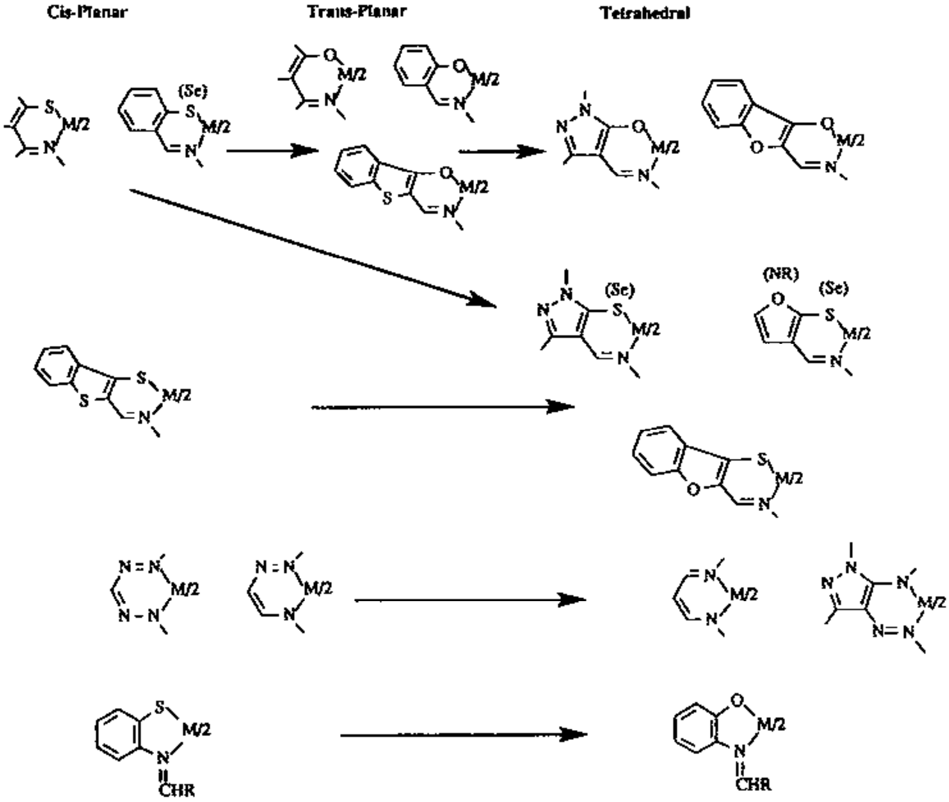


Fig. 8. The general scheme of stereoeffects in tetracoordinated Schiff base complexes **2**.

interference may also be decreased by conformational changes consisting of out of plane distortion of metallocycles occurring by bending along the N ··· X axis. There is some evidence to consider them intrinsic properties of the ligating atoms and ligand environment.

(2) In contrast to the trans square planar configuration of metal-chelate complexes with an MN_2O_2 coordination sphere **2** (X = O), their chalcogen analogues with MN_2S_2 or MN_2Se_2 coordination sphere **2** (X = S, Se) adopt cis planar configuration at the metal centre. This feature may also be noticed in complexes **5** containing 5-membered metallocycles which also display enhanced stability of a tetrahedral configuration relative to the planar one for MN_2O_2 complexes compared with those of the MN_2S_2 type.

(3) Five-membered heterocyclic rings annelated to the six-membered metallocycle in **2** stabilize the tetrahedral configuration at the metal centre in complexes of all structural types with an MN_2O_2, MN_2S_2, MN_2Se_2 and MN_4 coordination site. This trend also operates in the case of the more rigid *N*,*N*′-bridged complexes derived from tetradentate ligands.

Figure 8 serves to summarize most of the above effects pictorially.

ACKNOWLEDGEMENTS

We are grateful to Dr. H. Toftlund, Dr. J. Becher and Dr. K.S. Murray for reading the manuscript and for helpful discussions.

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