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Stereochemistry of Four-coordinate Chelate Compounds of Schiff Bases and Their Analogues

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The problem of the configuration of the chelate group and the metal ring in chelates of transition metals with Schiff bases and their analogues is discussed, and the influence of various factors analysed, in particular the nature of the central metal atom and the steric and electronic effects of the ligands. Various types of conformational changes in conjugated metal rings in bicyclic and tricyclic chelates are surveyed, and factors influencing these changes are noted. The conformation of the non-conjugated metal rings in tricyclic chelates is discussed. A list of 188 references is included.

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I. INTRODUCTION

A fundamental aspect of the chemistry of chelate compounds is their spatial and electronic structure, not only of theoretical interest but also very important for the practical application of chelates. The geometrical structure is related to the arrangement of energy levels in the molecule, which in turn determines the luminescent and phosphorescent properties. Stereochemical and electronic factors largely govern the reactivity and the stability of chelate compounds[1-3], as well as the possibility of using the ligands as analytical reagents[4].

Undervaluation of the structure of reagents and chelates has been a serious defect in theoretical and practical work on the extraction of chelate compounds[5]. The sterochemistry and the electronic structure of chelates determine also their redox properties[4], reactivity[6], and ability to form adducts[7-10], which is quite important for an understanding of many catalytic processes[11] and phenomena occurring in living organisms[12].

Chelate compounds containing a bis(oxa,aza)-chelate group form one of the most common and important classes of chelates. They are model analogues of certain metal enzymes and group-B vitamins[13,14]. Furthermore, these chelates develop considerable fungicidal and antimicrobial activity[15,16]. Therefore many investigations have been published on chelates of this type.

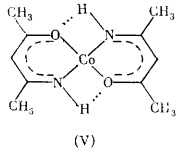
Chelate compounds obtained from Schiff bases and enaminoketones are convenient for the study of chelate structure, since varying the substituents in the metal rings permits variation in the three-dimensional structure of the molecule within wide limits. Some of the sterochemical results for such chelates have been summarised in reviews[17-22]. In the present Review, therefore, attention is directed mainly at work done during recent years, with the chief aim not of describing sterochemical features of individual chelates[18,21] but of examining the factors influencing their spatial structure.

II. CONFIGURATION OF CHELATE GROUP IN FOUR-COORDINATE COMPOUNDS

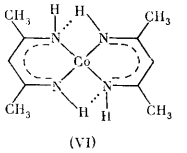
1. Effect of Nature of Metal Atom on Configuration of Chelate Group

The configuration of the chelate group in four-coordinate compounds may be square planar (with *cis* or *trans* arrangement of donor atoms around the central metal atom), tetrahedral, distorted tetrahedral, or distorted pyramidal with the metal atom at the apex. The configuration depends primarily on the nature of the metal atom, but also on the magnitude and symmetry of the ligand field. It is affected significantly also by steric hindrance in the molecule resulting from the interaction of non-bonded atoms and functional groups. Crystal packing effects must also be taken into account when the stereochemistry of a chelate in the solid state is being considered.

We can usefully consider each of these factors in greater detail on the basis of published information on the configuration of the chelate group formed by Schiff bases and enaminoketones, as summarised in Tables 1–4. These show that almost all cobalt(II) chelates, independently of the structure of the ligands, contain a chelate group of tetrahedral configuration, the most advantageous for such compounds[123]. Exceptions are bicyclic chelates of acetylacetone-mono- and di-imines[124,96] and tricyclic chelates in which 1,2-diamines serve as amino-components in the ligands[14,125-127]. However, in the first case the structure of the chelate is probably stabilised by intramolecular hydrogen bonding



(V)



(VI)

and in the second case the structure is rigidly fixed by the shortness of the ethylene bridge.

In almost all chelates of bivalent zinc, mercury, and beryllium, like those of cobalt, a tetrahedral structure is energetically most advantageous independently of the structure of the ligand. The energy of stabilisation of tetrahedral chelates by the crystal field is greatest in the case of beryllium. As a consequence, this metal differs from cobalt and zinc in not forming a planar tricyclic chelate with ethylenebis-*N*-salicylideneimine, but gives the tetrahedral bicyclic chelate[81]

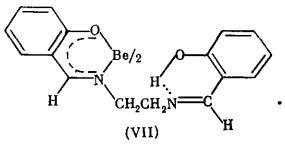
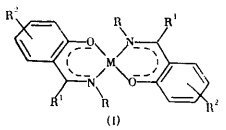

(VII)

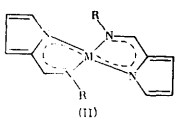
Table 1. Configuration of the chelate group in the chelates.


(I)

M	R^2	R^1	R	Configuration of chelate group* in solid**	Configuration of chelate group* in non-donor solvents	Ref.
Cu	H	H	H	sqpl	sqpl	23,24
Cu	H	H	CH_3	sqpl	sqpl	24,25,26
Cu	H	H	C_2H_5	distetr (35.6°)	sqpl	26,27,28
Cu	H	H	n-C_3H_7	sqpl	sqpl	29—31
Cu	H	H	n-C_4H_9	sqpl	sqpl	28,32,33
Cu	H	H	n-C_5H_{11}	sqpl	sqpl	34
Cu	H	H	iso-C_3H_7	distetr (59.7°)	distetr	28,30,33,35
Cu	H	H	t-C_4H_9	distetr (53.6°)	distetr	30,31,36
Cu	5,6-benzo	H	CH_3	sqpl	distetr	37
Cu	H	H	C_6H_5	sqpl	sqpl	38,39,40
Cu	5-Me, 3-CHO	H	C_6H_5	sqpl	–	41
Cu	H	H	C_6H_4OH	sqpl	sqpl	42,43
Cu	H	CH_3	H	sqpl	sqpl	44,45
Cu	H	CH_3	CH_3	sqpl	–	46
Cu	H	CH_3	iso-C_4H_9	sqpl	–	46
Cu	H	CH_3	n-C_6H_{13}	sqpl	–	47
Cu	H	CH_3	n-C_8H_{17}	sqpl	–	46
Cu	H	CH_3	n-$C_{10}H_{19}$	sqpl	–	48
Cu	H	CH_3	$C_6H_5CH_2$	distetr (29°)	–	46
Cu	H	CH_3	$C_6H_5CH(CH_3)$	distetr (26°)	–	49
Cu	H	H	$C_6H_5CH(CH_3)$	distetr (36°)	–	49
Cu	H	H	*p*-C_6H_4—CH_3	sqpl	–	50
Ni	H	H	H	sqpl	sqpl	26,51,52
Ni	H	H	CH_3	sqpl	octass	53,54
Ni	H	H	C_2H_5	sqpl	octass	54,55
Ni	H	H	n-C_4H_9	sqpl	octass	54,56
Ni	H	H	n-C_6H_{13}	sqpl	–	57
Ni	H	H	n-C_3H_7	sqpl	sqpl	58
Ni	H	H	C_6H_5	sqpl	–	59
Ni	H	H	iso-C_3H_7	distetr	eqmixt (49%)	60—62
Ni	3-CH_3	H	iso-C_3H_7	sqpl	eqmixt	62,63
Ni	3-C_2H_5	H	iso-C_3H_7	distetr (85°)	eqmixt	62,63
Ni	H	H	t-C_4H_9	–	eqmixt (95%)	64,65
Ni	3-OCH_3	H	*p*-C_6H_4-OCH_3	–	tetr	66
Ni	5,6-benzo	H	s-C_4H_9	–	eqmixt (57%)	67
Ni	3,4-benzo	H	s-C_4H_9	–	eqmixt (75%)	67
Ni	3-OCH_3	H	iso-C_3H_7	distetr (79°)	–	68
Co	H	H	n-C_4H_9	tetr	tetr	69,70
Co	H	H	s-C_4H_9	–	tetr	64
Co	H	H	iso-C_3H_7	tetr	tetr	71,72
Co	3-OCH_3	H	iso-C_3H_7	tetr	–	68
Co	H	H	C_6H_5	tetr	tetr	73—75
Co	H	H	*m*-C_6H_4-OCH_3	tetr	–	76
Zn	H	H	n-C_4H_9	tetr	tetr	69,77,78
Zn	H	H	iso-C_4H_9	–	tetr	77,79
Zn	H	H	s-C_4H_9	–	tetr	77,79
Zn	H	H	t-C_4H_9	–	tetr	77—79
Zn	H	H	iso-C_3H_7	tetr	tetr	71,79,80
Be	H	H	CH_3	–	tetr	81
Be	H	H	n-C_3H_7	–	tetr	81
Be	H	H	iso-C_3H_7	–	tetr	81
Pd	H	H	CH_3	sqpl	sqpl	82,83
Pd	H	H	C_2H_5	sqpl	sqpl	83,84
Pd	H	H	n-C_4H_9	sqpl	sqpl	83,85
Pd	H	H	iso-C_3H_7	sqpl	sqpl	83,86
Pd	3-CH_3	H	iso-C_3H_7	sqpl	sqpl	87
Pd	3-C_2H_5	H	iso-C_3H_7	sqpl	–	87
Pd	H	H	t-C_4H_9	sqpl	sqpl	83,88
Pd	H	H	C_6H_4OH	sqpl	sqpl	43

* Abbreviations: sqpl = square[sic]planar; distetr = distorted tetrahedral (relative angle of two metal rings); tetr = tetrahedral; eqmixt = equilibrium mixture of planar and tetrahedral forms of chelates (content of tetrahedral form);; octass = octahedral association complexes.
** From results of X-ray structural analysis.

Table 2. Configuration of chelate group in the chelates.


(II)

M	R	Configuration of chelate group* in solid**	Configuration of chelate group* in solution	Ref.
Cu	H	sqpl	sqpl	89,90
Cu	s-C_4H_9	–	sqpl	91
Cu	n-C_4H_9	–	sqpl	90
Cu	iso-C_3H_7	–	sqpl	90
Cu	t-C_4H_9	distetr (61°)	distetr	90,92
Cu	C_6H_5	–	sqpl	90
Ni	C_2H_5	–	sqpl	93
Ni	n-C_3H_7	–	sqpl	93
Ni	iso-C_3H_7	–	eqmixt	93
Ni	s-C_4H_9	–	eqmixt	93
Ni	t-C_4H_9	distetr (84°)	tetr	92,93
Co	t-C_4H_9	tetr	tetr	93,94
Zn	t-C_4H_9	tetr	tetr	92,93
Zn	iso-C_3H_7	–	tetr	93,95
Hg	CH_3	–	tetr	95
Hg	t-C_4H_9	–	tetr	95
Pd	CH_3	–	sqpl	93,95
Pd	iso-C_3H_7	–	sqpl	93,95

* Abbreviations as in Table 1.
** Results of X-ray structural analysis.

Chelates of bivalent palladium and platinum are mostly characterised by a square planar configuration[123]. The tendency of these metals to form such chelates is so great that this configuration appears even under exceptionally unfavourable steric conditions. Thus the chelate of palladium(II) with *N*-t-butylsalicylideneimine retains a planar structure[88] despite strong steric interactions of the t-butyl group with the azomethine hydrogen atom and with the oxygen atom of the adjacent ligand molecule.

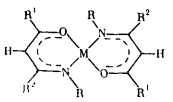
Besides the above extreme cases there exist many chelate compounds for which planar and tetrahedral structures differ little in energy of stabilisation by the crystal field. This applies especially to chelates of bivalent nickel and copper, whose stereochemistry is determined mainly by three-dimensional and electronic structural features of the ligands.

2. Effect of Structure of Ligands on Configuration of Chelate Group

(a) Steric effect of ligands

We must first consider briefly the structure of nickel and copper chelates. X-Ray results show (Tables 1 and 2) that in the solid state the chelate groups possess either a planar or a variously distorted tetrahedral configuration depending on the structure of the ligands. In solution the situation is more complicated: measurements of magnetic and dipole moments, proton magnetic resonance spectra, and electronic absorption spectra suggested[21] that an equilibrium is established between planar and tetrahedral forms of nickel(II) chelates of Schiff bases and enamino-ketones, whose position depends on the structure of the ligand and the temperature. However, other workers[128–130] are very doubtful about the establishment of such an equilibrium. Nevertheless, such studies are few and, in spite of some ambiguity in the treatment of several experimental facts, the hypothesis that an equilibrium is established between planar square and tetrahedron is generally accepted in discussion of the configuration of nickel(II) chelates in solution[131].

Table 3. Configuration of chelate group in the chelates.



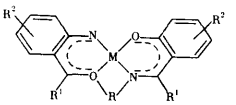
(III)

M	R¹	R²	R	Configuration of chelate group in non-donor solvents*	Ref.
Co	CH_3	CH_3	H	eqmixt (76%)	96, 97
Co	t-C_4H_9	CH_3	H	eqmixt (29%)	96, 97
Co	CH_3	CH_3	CH_3	tetr	96
Co	CH_3	CH_3	iso-C_3H_7	tetr	96
Co	CH_3	CH_3	C_6H_5	tetr	96
Ni	CH_3	CH_3	iso-C_4H_9	eqmixt (3%)	98
Ni	C_6H_5	H	s-C_4H_9	eqmixt (86%)	98
Ni	C_6H_5	CH_3	n-C_3H_7	eqmixt (23%)	98
Ni	CH_3	CH_3	iso-C_3H_7	tetr	98
Ni	C_6H_5	H	C_6H_5	eqmixt (6%)	98
Cr	C_6H_5	CH_3	H	sqpl	99
Cr	C_6H_5	CH_3	iso-C_3H_7	sqpl	99
Fe	C_6H_5	CH_3	H	tetr	99
Fe	C_6H_5	CH_3	CH_3	tetr	99
Fe	C_6H_5	CH_3	iso-C_3H_7	tetr	99
Cu	CH_3	CH_3	H	sqpl	100
Cu	C_6H_5	CH_3	iso-C_3H_7	distetr	99
Cu	C_6H_5	H	$CH(CH_3)C_6H_5$	distetr	101
Cu	p-CH_3-C_6H_4	H	$CH(CH_3)C_6H_5$	distetr	101
Cu	p-OCH_3-C_6H_4	H	$CH(CH_3)C_6H_5$	distetr	101
Cu	p-Br-C_6H_4	H	$CH(CH_3)C_6H_5$	distret	101
Pd	C_6H_5	H	CH_3	sqpl	102
Pd	C_6H_5	H	iso-C_3H_7	sqpl	102

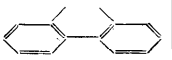
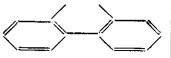
* Abbreviations as in Table 1.

There is no generally accepted view on the structure of copper(II) chelates in solution. From measurements of dipole moments Soviet workers[39,132–134] suggested that an equilibrium between planar and tetrahedral forms was established in solutions of certain such chelates. However, this hypothesis is inconsistent with the electronic absorption spectra of copper(II) chelates, which differ from those of nickel(II) chelates in being almost identical for solid specimens and for solutions[30,31,135,136] and furthermore hardly change with temperature. This indicates that only one form of the chelate is present in solution, with either a planar or a distorted tetrahedral configuration of the chelate group depending on the structure of the ligand.

Table 4. Configuration of chelate group in the chelates.



(IV)

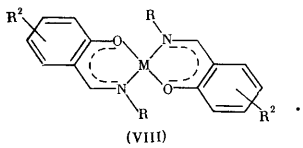
M	R²	R¹	R	Configuration of chelate group in solid and in solution*	Ref.
Mg	H	H	$(CH_2)_2$	sqpl	103
Pd	H	H	$(CH_2)_3$	sqpl	104
Cd	H	H	$(CH_2)_2$	sqpl	104
Co	H	H	$(CH_2)_2$	sqpl	14, 105
Ni	5-Cl	C_6H_5	$(CH_2)_2$	sqpl	106
Cu	H	CH_3	$(CH_2)_3$	distetr (34.4°)	107
Zn	H	H	$(CH_2)_5$	distetr	108
Ni	5-Cl	C_6H_5	$(CH_2)_3$	sqpl	106
Co	3-iso-C_3H_7	H	$(CH_2)_3$	distetr	109
Cu	H	H	$(CH_2)_4$	distetr	110—112
Zn	H	H	$(CH_2)_4$	tetr	106
Be	H	H	$(CH_2)_4$	tetr	106
Co	H	H	$(CH_2)_{4-10}$	tetr	113—115
Co	3-iso-C_3H_7	H	$(CH_2)_{4-7}$	tetr	109
Co	3-t-C_4H_9	H	$(CH_3)CHCH(CH_3)$	distetr	116
Ni	H	H	$(CH_2)_{2-5}$	sqpl	111, 117
Cu	H	H		sqpl	118
Cu	H	H		distetr (41°)	118, 119
Co	H	H		distetr (67°)	120
Co	H	H		sqpl	121
Pd	H	H		sqpl	122

* Abbrevations as in Table 1.

A similar conclusion has been reached[33] from a structural study by electron spin resonance of bicyclic copper(II) chelates of salicylideneimines *N*-substituted by n-butyl, isopropyl, or t-butyl. It was demonstrated unambiguously that these chelates exist in only one form either in the solid state or in solution, with the *g*-factor varying in parallel with the angle between the two metal rings. This view is probably more soundly based, and we shall adhere to it in describing the stereochemistry of copper(II) chelates in solutions.

It can be concluded from Tables 1–4 that all copper(II) chelates and most of the nickel chelates obtained from sterically inactive ligands have a planar chelate group. If to the nitrogen atom of the ligand are attached bulky radicals capable of interacting sterically with a radical on a neighbouring carbon atom and with the oxygen atom of the second ligand, the chelate group becomes tetrahedrally distorted in the case of copper(II) complexes, but either a tetrahedral form appears or its content increases siginificantly in the case of nickel(II) chelates. The degree of distortion and the percentage of the tetrahedral form increase with the volume of the radical attached to the nitrogen atom.

Steric stresses may increase not only with change in the *N*-substituent but also on the introduction of various substituents R^2 into the salicylaldehyde ring:



(VIII)

The greatest effect will obviously be exerted by radicals present at position 3 in the aromatic ring. Indeed, Japanese workers have found[138] that the chelate group in copper(II) complexes from 3-t-butyl- and 3-cyclohexylsalicylaldehydes is more distorted than in chelates of the unsubstituted aldehyde. Similarly, the content of the tetrahedral form in the nickel(II) chelate of *N*-isopropyl-3,4-benzosalicylideneimine ($R = iso\text{-}C_3H_7$, $R^2 = 3,4$-benzo) has increased to 68% from the 50% in *N*-isopropylsalicylideneimine ($R = iso\text{-}C_3H_7$, $R^2 = H$),[65] which is due to the steric effect of the bulky 3,4-benzo-group. The tetrahedral structure of the nickel chelate of 3-methoxy-*N*-*p*-methoxyphenylsalicylideneimine ($R = p\text{-}CH_3O.C_6H_4$, $R^2 = 3\text{-}CH_3O$)[66] is probably also a consequence of steric effects of the 3-methoxy-group.

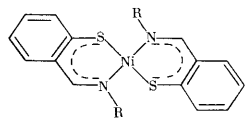
(b) Electronic effect of ligands

Ring substituents in salicylaldehyde are able to exert not only a steric but also an electronic effect on the configuration of the chelate group, with the latter effect quite often opposing the former. Such an electronic influence is most clearly evident when the steric demands made by the nature of the *N*-substituent require a minimal difference in energies of stabilisation of planar and tetrahedral forms by the crystal field.

This principle is illustrated by the stereochemical investigation[30,31,61,64,65,139] of chelates (I: M = Cu, Ni; $R = n\text{-}C_3H_7$, $iso\text{-}C_3H_7$, $t\text{-}C_4H_9$; and $R^2 = 3,4$- or 5,6-benzo, 3- or 5-Cl, 3- or 5-NO_2), showing that, independently of the nature of R^2, all the chelates with $R = n\text{-}C_3H_7$ have a planar chelate group, but those with $R = t\text{-}C_4H_9$ have a tetrahedral or distorted tetrahedral structure. Yet the configuration of the chelate group when $R = iso\text{-}C_3H_7$ depends significantly on R^2. In the solid state the structure is distorted tetrahedrally when $R^2 = H$, 3,4-benzo, and planar when $R^2 = 5,6$-benzo, 3- or 5-Cl, 3- or 5-NO_2. The nickel(II) chelate containing 5,6-benzo retains a planar structure even in solution, whereas the corresponding chelate with $R^2 = H$ contains 50% of the tetrahedral form in solution. The electronic influence of chlorine atoms, which tends to flatten the chelate group as with a 5,6-benzo-substituent, can be traced in nickel(II) chelates by comparing the square–tetrahedron equilibrium free energies: for chelates with $R^2 = H$, 3-Cl, 5-Cl, ΔF has the respective values −0.52, 0.35, and 0.15 kcal $mole^{-1}$ at 120 °C.

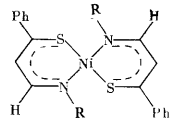
In connection with the effect of isosteric ligands on the configuration of nickel(II) chelates considerable interest attaches to a comparison[140] of chelates from amino-derivatives of 3-hydroxymethylenecamphor with analogous chelates from enamino-ketones of pentane-2,4-dione (III: M = Ni and $R^1 = R^2 = CH_3$), 1-phenylbutane-1,3-dione (III: M = Ni, $R^1 = C_6H_5$, and $R^2 = CH_3$), and Schiff bases of salicylaldehyde (I) and pyrrole-2-aldehyde(II). An attempt was made[140] to assess qualitatively the tendency of different isosteric ligands, containing the same *N*-substituents, to form tetrahedral chelate groups. The results showed this tendency to be greatest for chelates from amino-derivatives of 3-hydroxymethylenecamphor, and least for chelates of Schiff bases of pyrrole-2-aldehyde. These differences are most probably a consequence of different ligand field strengths in these chelates. Schiff bases of pyrrole-2-aldehyde are ligands having a strong field, and therefore tend to form planar chelate groups. But steric features of the five-membered camphor ring lead to a weak ligand field, so that they give chelates with a maximum content of the tetrahedral form.

The ligand field strength depends not only on the substituents in the metal ring but also on the nature of the donor atoms. Such an effect is clearly demonstrated by an investigation of the nickel(II) chelates with certain sulphur analogues of Schiff bases and enamino-ketones[98,141,142]



(IX)

$R = CH_3$, C_2H_5, $iso\text{-}C_3H_7$, $s\text{-}C_4H_9$, $t\text{-}C_4H_9$



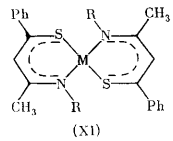
(X)

$R = (C_2H_5)_2CH$, $iso\text{-}C_4H_9$, $iso\text{-}C_5H_{11}$, C_6H_5

Almost all chelate groups formed by *N*-alkyl-*o*-mercaptobenzylideneimines have a square planar structure[141]. The only exception has $R = t\text{-}C_4H_9$, whose strong steric effect prevails over the electronic effect of the sulphur atom. Flattening of the chelate group on the replacement of oxygen by sulphur is indicated also by the fact that the content of the tetrahedral form in solutions of chelates of enamino-thiones is little more than half that for the corresponding enamino-ketones[98].

3. Competitive Effects of Nature of Metal and Ligand on Configuration of Chelates

When considering the effect of various factors on the configuration of a chelate group, we must bear in mind that in many cases one such factor is dominant, while the remainder operate only on the background of this main effect. For example, the electronic effect of the sulphur atom in zinc and cadmium chelates of enamino-thiones is insufficient to balance the tendency of these metals to form tetrahedral chelates, so that the compounds



(XI)

M = Zn, Cd;
R = $iso\text{-}C_3H_7$, $C_6H_5{-}CH_2$, $C_6H_5{-}CH(CH_3)$

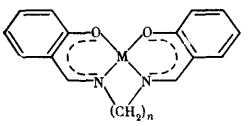
have a tetrahedral structure[143]. The absolute configuration of the chelate group in them may be either Δ or Λ: because of the absence of factors stabilising either absolute configuration, the proton magnetic resonance spectra for these chelates indicate rapid inversion $\Delta \rightleftharpoons \Lambda$, with intermediate formation of a planar chelate. This inversion occurs far more rapidly in chelates from enamino-thiones than in corresponding chelates from enamino-ketones. The difference is attributed[143] to the "flattening effect" of the sulphur atom discussed above.

Another example is provided by the stereochemistry[144] of nickel(II) and zinc(II) chelates with (−)-propylenebis-*N*-salicylideneimine. The steric demands of the ligand are

such that the chelate group in these compounds should be planar. However, this configuration is realised only in the nickel chelate, whereas the zinc chelate is non-planar owing to the tendency of this metal ion to form a tetrahedral configuration.

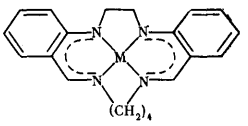
It is generally difficult to predict which of the factors will predominate, and hence the structure of the resulting chelate. The only exceptions are found when the factors act in the same direction, as e.g. in cobalt(II) and zinc(II) chelates in which bulky branched amines have been used in the ligand. The tetrahedral structure of these chelates is due both to steric features of the ligands and to the energy requirements of the metal ion. If, however, the different factors do not act in parallel, the structure of the chelate group will be determined by competition between them. Thus comparison of results for the three-dimensional structure of bivalent palladium, copper, and nickel chelates with ligands containing isopropylamine[86,35,60] shows that the tendency of the palladium ion to form planar complexes prevails over the steric requirements of the ligands, and the chelate has a square planar structure. In the nickel and copper chelates, however, the steric effect of the ligand predominates over the tendency of these metal ions to form planar chelates, so that the resulting compounds have a distorted configuration.

Another example is provided by investigations[145–153] on the tricyclic chelates



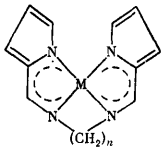
(XII)

M = Co, Ni, Cu; n = 2–4



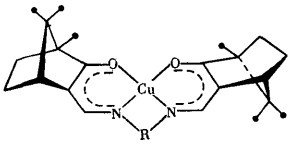
(XIII)

M = Co, Ni, Cu



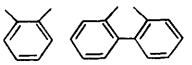
(XIV)

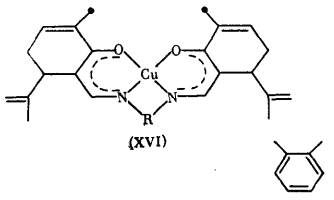
M = Cu, Ni; n = 2–5



(XV)

R = $(CH_2)_n$, where n = 2–6, 8;



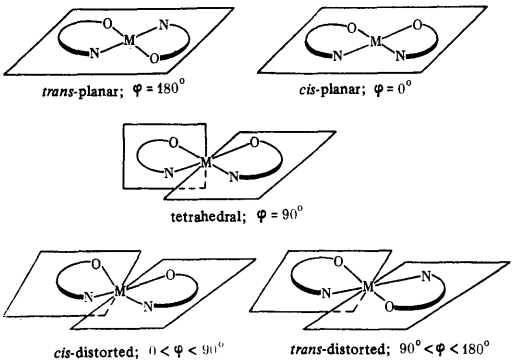


(XVI)

$R = (CH_2)_n$, where n = 2—6,8,10;

(see also Table 4). Inspection of geometric models of these chelates shows that lengthening the polymethylene bridge should cause distortion of the planar configuraiton of the chelate group owing to diminished interaction of non-bonded atoms in the distorted structures. However, this distortion is readily and completely realised only in cobalt(II) chelates, and is completely absent from nickel(II) chelates.

The structure of tricyclic copper(II) chelates is most interesting. Various structures can be realised when the planes of the metal rings undergo mutual rotation through an angle ϕ:



trans-planar; $\varphi = 180^\circ$

cis-planar; $\varphi = 0^\circ$

tetrahedral; $\varphi = 90^\circ$

cis-distorted; $0 < \varphi < 90^\circ$

trans-distorted; $90^\circ < \varphi < 180^\circ$

Electron spin resonance and spectropolarimetric studies[150–153] on such chelates obtained from enamino-ketones of oxymethylene-camphor and -carvone have shown that chelates containing a polymethylene bridge with $n = 2$ have a planar *cis* structure, whereas those with $n = 8$, 10 have a *trans* structure with a planar arrangement of the chelate group. The *trans*-planar configuration of the latter is probably a consequence of the considerable length of the octa- and decamethylene bridges, which enables the chelate molecule to assume the energetically most favourable *trans*-planar configuration. Owing to the greater length of the trimethylene bridge, chelates with $n = 3$ are somewhat distorted relative to a planar structure.

The e.s.r. spectra of solid chelates with $n = 4–6$ indicate that they are individual compounds existing in the same form with distortion of the chelate group to ensure denser packing. Yet the e.s.r. spectra of these chelates in low-temperature toluene glasses indicated[150–152] that solutions of each of the chelates contain three isomeric complexes, α, β, and γ with chelate groups differing in stereochemistry and distinguished by the angle of rotation ϕ of the planes of the two metal rings.

The current absence of the exact dependence of the g-factor on the angle ϕ prevented these workers from estimating the latter for each isomer. However, comparison of the e.s.r. parameters of these chelates with those of related compounds of known stereochemical structure indicated that all the γ-isomers were *trans*, with the chelate group most distorted tetrahedral in the presence of a tetramethylene bridge ($n = 4$). On the other hand, the α and β-isomers have a distorted tetrahedral configuration of the coordination sphere with a *cis* arrangement of the donor atoms; the latter isomers are considerably more distorted than the former. In the β-isomers, as in the γ-isomers, the degree of distortion of the chelate group diminishes as the polymethylene bridge becomes longer. The initial proportions of rotational isomers appearing after dissolution do not remain constant[150–152], but change with time, with a gradual increase in the concentration of the α-isomer, whose chelate group is least distorted relative to a planar *cis* structure.

To summarise, it can be concluded that the tendency of the planar configuration of the chelate group to be distorted increases as the chelating metal changes in the sequence

$$Pd<Cr<Cu\approx Ni<Co<Fe<Zn<Cd<Be.$$

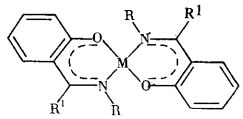
The tendency of the metal ion to form chelates having a tetrahedral configuration varies in the same sequence, provided that the ligand favours such a configuration. The chelate group in compounds of the same metal with isosteric ligands will be more "flattened" the more intense the ligand field in the chelate.

III. CONFORMATION OF CHELATES OF SCHIFF BASES AND THEIR ANALOGUES

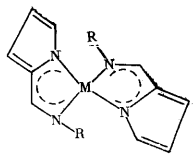
Comparatively few papers have appeared on the conformations of chelates, although this problem is of no less interest than the configuration of the chelate group. This is probably due to the complexity involved in investigating the structure of chelate molecules, since the great majority of physicochemical methods used to study chelate compounds are incapable of registering conformational changes. X-Ray structural analysis is the most accurate method for determining the conformation of a metal ring in the solid state. Proton magnetic resonance and spectropolarimetry are used to study the conformational structure of chelates in solution.

1. Conformation of Conjugated Metal Rings

X-Ray examination of four-coordinate chelates has shown that flat molecules with a completely coplanar arrangement of all the atoms are atypical. The only examples[51,89] of planar chelates are



(XVII)



(XVIII)

with M = Ni and R = R¹ = H in (XVII), and M = Cu and R = H in (XVIII), in both of which no atom departs significantly from the plane. Far more often chelates are met in which the general coplanarity of the molecule is disturbed by folding of the conjugated metal rings along the O....N line, so that the molecule as a whole has the form of a step:

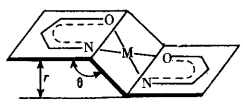
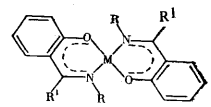


Table 5 summarises published data on the step distortion of metal rings in chelate compounds of several metals with Schiff bases.

The cause of step distortion in chelates obtained from Schiff bases is steric interaction of substituents in the metal ring, the distance between which is significantly less[46] than the sum of the van der Waals radii. Such distortion disturbs the coplanarity of the system and hence diminishes the degree of delocalisation of electron density in the quasi-aromatic metal ring, which is disadvantageous energetically. However, this is balanced by the increased distance between non-bonded atoms resulting in all cases from step distortion along the O...N lines, which lessens steric stresses in the molecule and also lowers its total energy.

Table 5. Data on the conformational structure of the chelates.



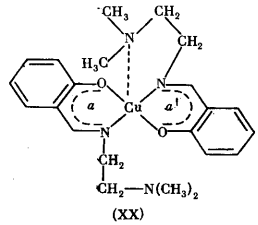
(XIX)

M	R¹	R	r, Å	Ref.
Cu	H	H	0.29	23
Cu	H	C_6H_5	0.24	27
Cu	H	n-C_3H_7	0.32	29
Cu	H	iso-C_3H_7	0.34	35
Cu	H	n-C_4H_9	0.74	32
Cu	H	t-C_4H_8	0.67	36
Cu	H	C_6H_5	0.89	38
Cu	H	p-CH_3-C_6H_4	0.90	50
Cu	H	OH	0.13	154
Cu	CH_3	H	0.48	44
Cu	CH_3	CH_3	1.91	46
Cu	CH_3	iso-C_3H_9	2.24	155
Cu	CH_3	n-C_9H_{17}	2.66	46
Cu	CH_3	n-$C_{10}H_{21}$	2.34	48
Cu	CH_3	C_6H_5—CH_2	1.68	46
Cu	CH_3	$C_6H_5CH(CH_3)$	1.22	46
Ni	H	C_6H_5	1.78	55
Ni	H	C_6H_{13}	0.65	57
Pd	H	iso-C_3H_7	0.42	86
Pd	H	t-C_4H_9	1.72	89

It must therefore be expected that the magnitude of the distortion will depend on the volumes of the substituents R and R¹ in the metal ring and on the related steric stresses within the molecule. Indeed, it is readily seen from Table 5 that r is significantly greater for chelates of Schiff bases obtained from *o*-hydroxyacetophenone ($R^1 = CH_3$) than for corresponding chelates based on salicylaldehyde ($R^1 = H$). In the former case attachement of methyl to the azomethine carbon atom enhances significantly the steric stresses within the molecule, with a consequent increase in step distortion of the metal rings.

Simple relations between the volume of the radical R and the distance r have not yet been found. The probable reason is that variation in R leads to change not only in the relative arrangement of the metal rings but also in the configuration of the chelate group and the length of the carbon–nitrogen bonds.

Steric stresses in a chelate molecule and the associated step distortion of the metal rings can be caused not only by interaction of juxtaposed atoms and groups but also by certain other structural features of the ligands. An example is provided by X-ray results[156] for the chelate



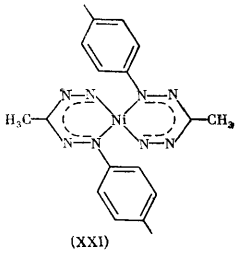
(XX)

in which one molecule of the Schiff base is terdentate, whereas the other is bidentate. Coordination of the ligand through three donor atoms increases the stress in this moiety, leading to conformational non-equivalence of the metal rings *a* and *a'*, with *a* almost planar and *a'* having $r = 0.13$ Å.

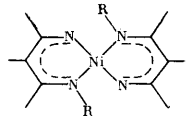
Analogous conformational non-equivalence of the two metal rings has been found in the zinc(II) chelate of *N*-*o*-methoxyphenylsalicylideneimine[157], which has a *cis*-octahedral structure owing to coordination of the zinc atom with the methoxyl-oxygen atom. One of the metal rings is planar, whereas for the other $\theta = 31.5°$. Such non-equivalence of the metal rings is attributed[157] to the difference in the angles of rotation of the anisidino-rings about the two conjugated metal rings.

Steric stresses in a molecule can be eliminated not only by a stepped conformation of the metal rings but also by distortion of the planar configuration of the chelate group to a tetrahedral or distorted tetrahedral configuration. Which path is followed depends primarily on the tendency of a given metal atom to form the energetically most stable configurations Since, as already mentioned, a tetrahedral configuration is the most stable for four-coordinate cobalt(II) chelates, steric stresses are removed from such chelates mostly by the formation of compounds having a tetrahedral chelate group and almost planar metal rings[65,71,73]. However, a stepped structure is formed with all sterically hindered chelates of metal ions that cannot give a tetrahedral configuration. Thus in the palladium(II) chelate of *N*-t-butylsalicylideneimine[88] the chelate remains planar, but the metal rings are strongly deflected from the plane at an angle $\theta = 36°$.

The situation is far more complicated with chelates of metals for whose ions planar and tetrahedral configurations do not differ greatly in energy, as with the nickel(II) chelates



(XXI)



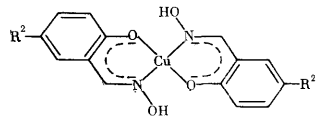
(XXII)

R = Alk, Ar.

Thus the diamagnetic chelate (XXI) has a planar chelate group and a strongly step-distorted metal ring ($\theta = 37°$, $r = 1.6$ Å),[158] but in paramagnetic chelates (XXII) steric stresses are removed mainly by distortion of the planar geometry of the chelate group[159].

The magnitude of the step distortion of metal rings depends not only on steric factors but also on electronic structural features of the ligand. The ligand field intensity affects not only the conformation of the chelate group (Section II, 2*b*) but probably also the conformational structure of the metal rings. Thus comparison of X-ray structural data for copper(II) chelates of *N*-t-butylsalicylideneimine[36] (XVII: M = Cu, R = t-C_4H_9, and R^1 = H) and *N*-t-butylpyrrolideneimine[92] (XVIII) M = Cu and R = t-C_4H_9) shows that the latter chelate, in contrast to the former, has an almost planar metal ring. This is probably due to intensification of the ligand field when the donor oxygen atom in (XVII) is replaced by a donor nitrogen in (XVIII).

The effect of the ligand field intensity on the step distortion of the metal ring is confirmed also by X-ray results for the copper chelates of the oximes of salicylaldehyde and its 5-chloro-derivative[154,160]

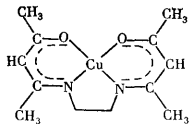


(XXIII)

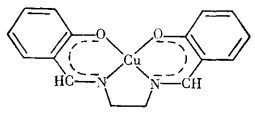
R^2 = H, Cl

Introduction of the chlorine atom weakens the ligand field, which in turn increases considerably the distortion of the metal rings: values of *r* for the chelates obtained from unsubstituted and substituted salicylaldehyde oximes are respectively 0.13 and 0.76 Å.

Interesting information on the effect of ligand field intensity on the general planarity of the molecule has resulted from a structural investigation[161–165] of outer-sphere adducts of *NN'*-ethylenebis(acetylacetoneiminato)copper(II) and *NN'*-ethylenebis(salicylideneiminato)copper(II)



(XXIV)

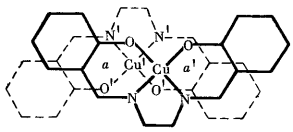


(XXV)

having the compositions (XXIV).$\frac{1}{2}H_2O$, (XXIV).$[CH_3NH_3]^+[ClO_4]^-$, (XXV).$CHCl_3$, and (XXV).*p*-HO.C_6H_4.NO_2. The water, chloroform, and *p*-nitrophenol molecules and the methylammonium ion form hydrogen bonds with the oxygen atom of the metal ring, which tend to increase the π back-bonding of the oxygen atom to the d_π orbitals of the copper atom, i.e. to strengthen the field of the ligands in the chelates. Since water is less capable than methylammonium of forming hydrogen bonds, and chloroform less than *p*-nitrophenol, the ligand field strength will gradually increase on passing from (XXIV) to the hemihydrate and then to the methylammonium adduct, and also on passing from the very weak adduct of (XXV) with chloroform to that with *p*-nitrophenol. X-Ray results for these chelates show that the degree of distortion of the metal rings decreases in the same sequence. Thus, whereas the angle of fold of the metal ring $\theta = 15.5°$ in the chelate (XXIV),[161] it is only 3.5° in the hemihydrate[162], and the metal rings are completely planar in the methylammonium adduct[163]. Similarly, the step distortion of the metal rings $r = 0.55$ and 0.2 Å in the adducts of (XXV) with chloroform and with *p*-nitrophenol respectively. It was concluded[161–165] from these results that the planarity of the molecule can even serve as a criterion for assessing the ligand field strength in a chelate: the greater the general planarity of a molecule the stronger the ligand field in it.

Furthermore, step distortion of metal rings is sometimes a consequence not of the structure of the ligand but of specific intermolecular interactions or lattice effects. Thus a stepped conformation of metal rings has been found in copper(II) chelates of acetylacetone[166], benzoylacetone[167], and salicylaldehyde[168,169], in which there are no steric interactions between the two metal rings and their substituents.

The conformational difference between the two metal rings in the chelate

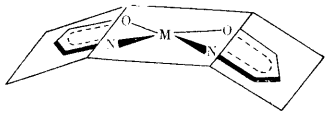


(XXVI)

has also been attributed[165] to intermolecular interactions. The angle of fold of the metal ring *a* is almost double that of *a'*. The greater "flattening" of the latter metal ring is a consequence of intermolecular interaction of the oxygen atom in ring *a* with the copper atom of a second chelate molecule.

Another example is provided by X-ray structural data[170] for the copper chelate of the Schiff base of salicylaldehyde and aminoethanol (XVII: M = Cu, R^1 = H, and R = CH_2CH_2OH). The unit cell contains two independent molecules, the angle of fold of the metal rings in one of which is almost double that in the other. The differences observed in the conformational structure of the metal rings in the two molecules are attributed[170] to effects of their crystalline packing.

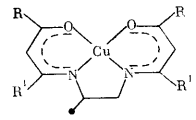
In the above systems distortion of the metal rings yields a stepped molecular structure, with the two metal rings bent in opposite directions relative to the plane of the chelate group CuO_2N_2. Recent work has shown that chelates of Schiff bases may have not only a stepped but also an "umbrella-shaped" structure



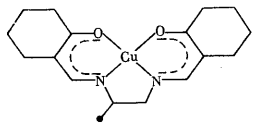
in which the two metal rings are bent in the same direction. Such an "umbrella" structure has been found in particular in the monohydrate of *NN'*-ethylenebis(acetylacetoneiminato) copper (XXIV).H_2O,[171] in which the copper atom is coordinated with the oxygen atom of the water molecule ($\theta = 11.8°$), in *NN'*-ethylenebis(salicylideneiminato)iron(III) chloride[172], in the copper(II) chelate of the Schiff base of *o*-aminobenzaldehyde and propylenediamine[173] (5°), in the dimer of *NN'*-ethylenebis(thiosalicylideneiminato)cobalt(II) (21.4°),[174] and in *NN'*-*o*-phenylenebis(salicylideneiminato)palladium(II).[122] However, the reasons for the appearance of an "umbrella" and not a stepped structure in these cases are not yet clear.

Study of the conformations of conjugated metal rings is quite complicated, since the description of the conformational structure depends on the method of choosing the median plane. Work by Porai-Koshits et al.[175] on the conformations of the metal rings in certain copper(II) and nickel(II) bis-salicylideneiminates suggests that these rings are labile, but the number of possible ways in which they can be distorted is limited. Besides a planar arrangement of all the atoms in a metal ring and folding of the ring along the O....N line, cases have also been examined[175] in which metal and nitrogen atoms are expelled from the plane of the metal ring, or metal and oxygen atoms lie on one side of the median plane, while the nitrogen and attached carbon atom lie on the opposite side.

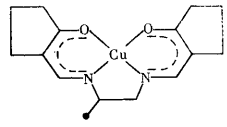
It must again be emphasised that all the structural results for conjugated metal rings considered hitherto have been obtained by X-ray structural analysis and are valid for the conformations of solid chelates. An attempt to assess the conformation of conjugated metal rings in solution involved[176,177] spectropolarimetric examination of the chelates



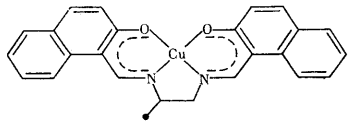
(XXVII)



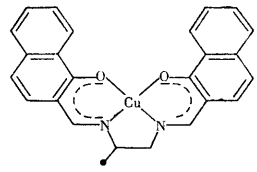
(XXVIII)



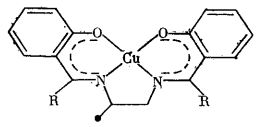
(XXIX)



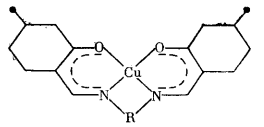
(XXX)



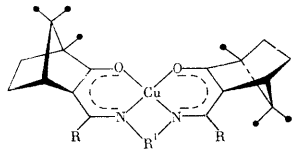
(XXXI)



(XXXII), R = H, CH_3



(XXXIII), R = $(CH_2)_2$,



(XXXIV)

R = H, R^1 = $(CH_2)_2$;

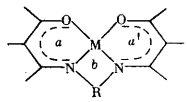
R = CH_3, R^1 = $(CH_2)_2$

The circular dichroism spectra showed a change in sign of the Cotton effect of the $d_{xy} \rightarrow d_{x^2-y^2}$ transition band and a hypsochromic shift in the intraligand $\pi-\pi^*$ transition band on replacement of the azomethine hydrogen atom by a methyl group and on passing from ethylenediamine to *o*-phenylenediamine chelates. Detailed analysis of these spectra indicated that the observed change in sign was due neither to change in conformation of the central non-conjugated metal ring nor to change in configuration of the chelate group but to change in conformation of the conjugated metal rings accompanying change in azomethine *N*- and *C*-substituents capable of steric interaction. It is emphasised[176,177] that, if the change in substituents does not affect the steric stresses in the chelate molecule (as with changes in R), the conformation of the conjugated metal rings remains unchanged.

2. Conformation of Non-conjugated Metal Rings

Besides the chelate compounds having conjugated metal rings already considered there exist a large number of chelates containing also non-conjugated metal rings. They

include primarily tricyclic chelate compounds of the type



(XXXV)

R = $(CH_2)_n$, n = 2-12

formed by quadridentate Schiff bases, in which the non-conjugated polymethylene ring *b* is fused with two conjugated rings. Chelates of this type having $n = 2$, i.e. obtained from 1,2-diamines, have been the most thoroughly studied. Thus in the work already cited[161-165,171,173] investigation of the structure of the conjugated metal rings was accompanied by detailed study of the conformation of the ethylene- and propylene-diamine rings in (XXIV), (XXV), and their adducts, and also in the copper(II) chelate of *NN'*-propylenebis-(*o*-aminobenzylideneimine). X-Ray structural data on the conformations of the non-conjugated metal rings in these chelates (Table 6) show that the most stable form of the five-membered non-conjugated metal ring is the skew conformation

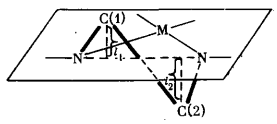


Table 6. Distances l_1 and l_2 of carbon atoms $C_{(1)}$ and $C_{(2)}$ in ethylene bridge from plane of chelate group CuO_2N_2.

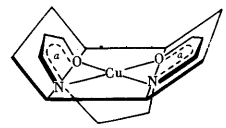
Compound	l_1, Å	l_2, Å	Ref.
(XXIV)	0.44	—0.12	161
(XXIV)·1/2H_2O	0.18	—0.11	162
(XXIV) $[CH_3NH_3]^+$ $(ClO_4)^-$	0.05	0.05	163
(XXIV)·H_2O	—0.11	—0.15	171
(XXV)	0.49	—0.24	178
(XXV)·$CHCl_3$	0.44	—0.12	164
(XXV)·p-HO—C_6H_4—NO_2	0.28	—0.20	165
(XXXVI) *	0.16	—0.14	173
(XXXVII) **	0.44	—0.22	172

* *NN'*-Propylenebis (*o*-aminobenzylideneiminato)copper(II).
** *NN'*-Ethylenebis(salicylideneiminato)iron(III) chloride.

Comparison of Table 6 with the angles of fold of the conjugated metal rings in the same compounds shows that the conformation of the non-conjugated metal ring depends significantly on the structure of the conjugated rings fused with it. It can be concluded firstly that a stepped structure of the chelate molecule as a whole favours a skew conformation of the ethylenediamine ring and secondly that the distance of the carbon atoms $C_{(1)}$ and $C_{(2)}$ of the ethylene bridge from the CuO_2N_2 plane is determined mainly by the magnitude of the step distortion.

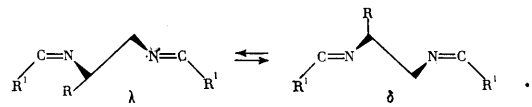
Table 6 shows that these two carbon atoms of the diamine bridge do not usually form an ideally skew conformation, but are situated unsymmetrically with respect to the plane of the chelate group CuO_2N_2. Such lack of symmetry is a consequence of the non-equivalence of the angles of fold of the two conjugated metal rings. From a comparison of the distances l_1 and l_2 of these atoms with the step distortions of the conjugated metal rings it was concluded that the departures of the bridge carbon atoms from the plane of the chelate group diminish with decrease in the angle of fold of the conjugated metal rings. Thus values of l_1 for the chelates (XXIV), (XXIV).$\frac{1}{2}H_2O$, and (XXIV).$[CH_3NH_3]^+[ClO_4]^-$, for which this angle is 13.5°, 3.5°, and 0°, are respectively 0.44, 0.18, and 0.05 Å. Among these compounds the greatest interest attaches to the chelate (XXIV).$[CH_3NH_3]^+[ClO_4]^-$, in which complete coplanarity of the conjugated metal rings leads to formation of the sterically unfavourable completely eclipsed conformation of the ethylene bridge.

The partly eclipsed *cis* conformation of the ethylene bridge (with the two bridge carbon atoms on the same side of the CuO_2N_2 plane) is found in the chelates (XXIV).H_2O and *NN'*-ethylenebis(trifluoroacetylacetoneiminato)nickel(II)[179] with an umbrella structure of the molecule

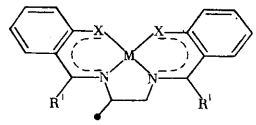


The reason for such an uncharacteristic *cis*-eclipsed conformation of the ethylene bridge is that steric interaction of the bridge carbon atoms with the metal rings *a* is less than for a skew conformation. Yet in *NN'*-propylenebis-(*o*-aminobenzylideneiminato)copper(II) (XXXVI) and in *NN'*-ethylenebis(salicylideneiminato)iron(III) chloride (XXXVII), which like the preceding compounds possess an umbrella structure, the ethylene bridge has an eclipsed conformation. Such a conformation of the non-conjugated metal ring in these chelates is determined mainly not by the way in which the metal rings are folded but by the configuration of the chelate group, which has a distorted tetrahedral structure with a relative angle of rotation of the two metal rings of 9° and 10° respectively.

With a skew conformation the ethylene bridge can have either a λ- or δ-conformation, which are enantiomeric:

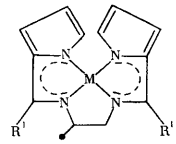


If the substituent R = H, the λ- and δ-conformations of the metal rings are equivalent. With substituted ethylenediamines (e.g. in chelates based on propylenediamine—R = CH_3), however, steric interactions of the radicals R and R^1 should lead to non-equivalence of λ- and δ-conformations, so that one of them will be formed preferentially. Indeed, X-ray results for copper(II) chelates of *NN'*-propylenebis-(*o*-aminobenzylideneimine)[173] and *NN'*-propylenebis(salicylideneimine)[180] show that the propylene bridge has the δ-conformation with an axial methyl group. 1,3-Interaction of R and R^1 is far weaker with an axial than with an equatorial methyl group.



(XXXVIII)

X = O, R^1 = H, CH_3, M = Cu, Ni;
X = N, R^1 = H, M = Cu

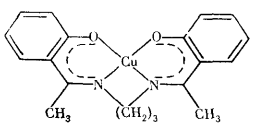


(XXXIX)

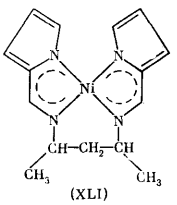
R^1 = H, CH_3

A δ-conformation of the propylene ring in solution was indicated also by a spectropolarimetric investigation[181,182] of the chelates (XXXVIII). The same conclusion has been reached[183,184] for analogous titanium(IV) monoxide and iron(III) chelates, and also in a study[176] of conformational aspects of the chelates (XXVII: $R = CH_3$, C_6H_5 and $R^1 = H$, CH_3).

The chelates (XXXIX: $R^1 = H$) have the propylene ring in the λ-conformation[185], which was explained by weakening the 1,3-equatorial interactions between the methyl group and the azomethine hydrogen atom in chelates (XXXIX) from Schiff bases of pyrrole-2-aldehyde in comparison with chelates (XXXVIII) from Schiff bases of salicylaldehyde. Such weakening is due to the smaller size of the five-membered metal ring in the former case relative to the six-membered ring in the latter. In chelates (XXXIX) of 2-acetylpyrrole ($R^1 = CH_3$), however, the steric stresses in the molecule due to interaction of the two methyl groups are already quite strong, and the central metal ring has the δ-conformation. A 1,2-diaxial conformation of a five-membered metal ring has been found also in the cobalt(II) chelate of the Schiff base of salicylaldehyde and butane-1,2-diamine[186].



(XL)



(XLI)

Very little information has been obtained on the conformation of non-conjugated central metal rings containing more than two carbon atoms. The central metal ring in the chelate (XL), formed by a trimethylene bridge, has a twisted boat conformation[187], but the analogous metal ring in (XLI) possesses a half-chair conformation with both methyl groups in equatorial positions[188]. X-Ray examination of the chelate (XIII) has established[149] that the tetramethylene bridge has a half-boat conformation. It was suggested[149] that the conformation of the central metal rings in chelates obtained from polymethylenediamines as amino-components will probably be determined by the configuration of the chelate group: a planar or slightly distorted planar chelate group should give a boat conformation, but a tetrahedral or nearly tetrahedral group should yield a chair conformation. However, the literature is devoid of results supporting this hypothesis.

* * *

Thus inspection of the literature shows that the conformation of metal rings, like the configuration of the chelate group, depends on the nature of the central metal atom, the spatial and electronic structure of the ligands, and also the character of the intermolecular interactions. Full information on the stereochemistry of chelate compounds can be obtained only by using a combination of diverse physicochemical methods, enabling the structure of chelates to be characterised not only in the solid state but also in solutions.

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