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RECENT ASPECTS OF THE STEREOCHEMISTRY OF SCHIFF-BASE–METAL COMPLEXES

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CONTENTS

ABBREVIATIONS

aca · R,	*N*-substituted acetylacetoneaminato
acaen,	bis(acetylacetone)ethylenediaminato
acal · R,	*N*-substituted β-acetoaldiminato
acalen,	*N*,*N'*-ethylenebis(β-acetaldiminato)
acatn,	bis(acetylacetone)trimethylenediaminato
bzaen,	bis(benzoylacetone)ethylenediaminato
bza · R,	*N*-substituted benzoylacetoneaminato
bzalen,	*N*,*N'*-ethylenebis(benzoylacetaldiminato)
bzalpbam,	*N*,*N'*-*o*-phenylenediaminebis(benzoylacetaldiminato)
bzatn,	bis(benzoylacetone)trimethylenediaminato
M,	metal
naphal,	5:6-benzosalicylideneiminato
Ph,	phenyl
py,	pyridine
sal,	salicylaldehyde
salen,	bis(salicylaldehyde)ethylenediiminato
salteten,	bis(salicylaldehyde)tetramethylenediaminato
saltn,	bis(salicylaldehyde)trimethylenediiminato
Y,	CH_3, C_2H_5

A. INTRODUCTION

Compounds called "Schiff bases" include various types, but in this article, we are concerned mainly with (a) Schiff bases formed from salicylaldehyde and

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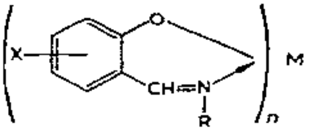
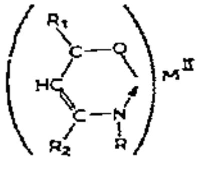
substituted salicylaldehydes and (b) the condensation products from β-diketones and amines ((I) and (II)). Metal complexes of these organic ligands have been studied for a long time. One of the better known examples is the bis(salicylaldehyde)-ethylenediiminato-complex of cobalt(II), which is able to absorb oxygen reversibly in the solid state. The solution paramagnetism, which is shown by some nickel(II)



(I)



II

complexes of Schiff bases, has also been known for many years. The rapid development related mainly with these compounds aroused much interest and research activity in this field of coordination chemistry, with the result that numerous interesting conclusions have been reached in recent years. An exhaustive survey of these studies will not be attempted, but some of the main achievements, which are of significance in the stereochemistry of coordination compounds, will be the principal concern in this review.

B. SYNTHESIS, STRUCTURE AND BONDING

Metal complexes of *N*-alkyl- and *N*-aryl-salicylideneimines are prepared by one of the following general methods.

Method (1): metal salt+salicylaldehyde+amine (in solution)
Method (2): $M(sal)_2$+amine (in solution)
Method (3): metal salt+Schiff base
Method (4): $M(X \cdot sal \cdot R)_2 + H(X \cdot sal \cdot R) + H_2O_2$
Method (5): $M'(sal \cdot R)_2$+metal salt (exchange of the metal ion)

The corresponding metal complexes of β-ketoamines are prepared in a similar way.

For some reactions, the addition of alkali is necessary; $NaHCO_3$ or Na_2CO_3 is often used, but in those cases where water must be avoided, potassium-, sodium- or lithium alcoholate is employed. The preparative procedures, including the reaction period, temperature, and the amount and the kind of solvent, vary both with the ligands and the central metal ion. In general, the preparation, of β-ketoaminato-complexes is more difficult than that of the corresponding salicylideneiminato-complexes, and it is often necessary to carry out all procedures in an inert atmosphere.

One must be careful not to say that a compound cannot be synthesized, even if many unsuccesful attempts have been made. There have been many examples in the past of the successful synthesis of compounds which on theoretical and empirical grounds, were believed at one time to be incapable of isolation.

Various methods are employed for determining the structure of the complexes. Those often used include determination of magnetic moment, electronic spectrum and nuclear magnetic resonance, in addition to elemental analysis and molecular weight determination.

(i) Cobalt(III) complexes

Many complexes of the $Co(sal \cdot R)_3$ type are known[1-4], where $R = CH_3$, C_2H_5, n-C_3H_7, n-C_4H_9, CH_2Ph, Ph, 4-CH_3Ph, 4-CH_3OPh and 4-ClPh. They are all diamagnetic.

By refluxing cobalt acetate, salicylaldehyde and an *n*-alkylamine in ethanol (Method (1)), cobalt(III) complexes of the $Co(sal \cdot R)_3$ type are readily obtained as dark-green crystals. Complexes of the $Co(sal \cdot aryl)_3$ type, however, show some tendency to be reduced to the tetra-coordinate cobalt(II) complex when their solutions are warmed for some time. Method (4), therefore, is better utilized for the preparation of $Co(sal \cdot aryl)_3$. The difference in this respect between sal · n-alkyl and sal · aryl is readily explained in terms of the ligand-field strength, since it is known that with strongly coordinating ligands the hexa-coordinate cobalt(III) complex is more stable than the tetra-coordinate cobalt(II) complex. The difference might also be due in part to steric strain[2], but this effect is probably not very important.

So far, the synthesis of $Co(sal \cdot iso\text{-}C_3H_7)_3$ or $Co(sal \cdot tert\text{-}C_4H_9)_3$ has not been successful, and this is ascribed to the steric condition.

For the octahedral complexes of the $Co(sal \cdot R)_3$ types, structural isomers of *cis*- and *trans*-forms are possible. However, only one form has ever been isolated in the crystalline state. Dipole-moment measurements show that all cobalt(III) compounds so far isolated have a *trans*-octahedral configuration[5]. This conclusion is in agreement with the assumption made previously on the basis of the steric condition[2].

It is well known that bis(salicylaldehyde)ethylenediiminatocobalt(II) in the solid state absorbs oxygen reversibly[6,7]. The nature of the $Co–O_2$ bond has been studied by a number of investigators, but it seems that the final answer has not been reached at the moment[8]. Moreover, many of the compounds derived from Co(salen), for example, those formulated as Co(salen)OH, Co(salen)py, Co(salen)-Cl and so on[6-9], are not well characterized. In this connection, it is significant to examine and explore the possibility of isolating typical hexa-coordinate complexes of cobalt(III), starting from Co(salen), since these complexes might provide a clue to the solution of the problem of the bond nature in the above-mentioned complexes.

Cobalt(III) complexes of the $[Co(salen)X_2]Y$ type, where X denotes OH_2,

NH_3, py, CH_3NH_2, $C_2H_5NH_2$, n-$C_3H_7NH_2$, n-$C_4H_9NH_2$, NO_2^- or CN^-, have been synthesized as yellow or orange crystals by oxidizing Co(salen) with hydrogen peroxide[10]:

$$Co(sal \cdot R)_2 + amine + H_2O_2 \rightarrow [Co(sal \cdot R)_2(amine)_2]^+$$
$$Co(salen) + R \cdot NH_2 + H_2O_2 \rightarrow [Co(salen)(R \cdot NH_2)_2]^+$$
$$Co(salen) + MNO_2 + H_2O_2 \rightarrow [Co(salen)(NO_2)_2]^-$$

These cobalt(III) complexes are stable in the atmosphere, and diamagnetic. They show no "sharp absorption band" at about 8.2×10^3 cm^{-1}, which is characteristic of square-planar complexes of cobalt(II), (see Section (ii)). They show a band due to to C=N stretching vibration at about 1540 cm^{-1}, regardless of the nature of the substituent X, but Co(salen) and its oxygen adduct show the corresponding band at about 1530 cm^{-1}. These findings indicate that the cobalt ion in the oxygen adduct is in a state, which is not exactly the same as either Co^{II} or Co^{III}, but intermediate between the two. It is thus considered that the linkage of the oxygen molecule with the cobalt ion is very weak.

In the light of the results, it is worthwhile to reconsider the bonding in the so-called Co(salen) · py, Co(salen)· $\frac{1}{2}O_2$, and Co(salen)X complexes, and their relation with octahedral cobalt(III) complexes.

Several compounds, formulated as Co(X · salen)(NO) were prepared as green crystals[11], having magnetic moments of about 0.5 B.M. From an examination of the infrared-absorption bands due to the NO group, it was concluded that the compounds may be regarded as containing either NO^- coordinated to Co^{III} or NO^+ coordinated to Co^{I}.

(ii) Cobalt(II) complexes

a. Tetra-coordinate complexes of N-substituted salicylideneimines

Many complexes of the Co(sal · R)$_2$-type have been synthesized as orange-red crystals, with R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, n-C_5H_{11}, iso-C_3H_7, 1-ethylpropyl, cyclohexyl, tert-C_4H_9, Ph, ClPh, CH_3Ph, CH_3OPh, 2,6-$(C_2H_5)_2$Ph, α-naphthyl and β-naphthyl[1-3, 12-17].

When R is methyl or ethyl, the cobalt(II) complex is so readily oxidized that special caution must be paid in the preparation to prevent undesirable oxidation[14]. Preparation of complexes of the Co(sal · R)$_2$-type with R = 2-substituted aryl groups, also required considerable effort and care [15].

For tetra-coordinate cobalt(II) complexes, either a square-planar or a tetrahedral configuration is possible. On the basis of electronic spectra, in particular ligand-field bands, together with the magnetic moments, it was concluded that the complexes of the Co(sal · R)$_2$ type have a tetrahedral configuration of a high-spin type[2, 3, 12-17]. The electronic spectra of cobalt(II) complexes depend upon the configuration of the complexes. The difference in the ligand-field bands between different configurations is so apparent that the electronic spectrum may be regarded as diagnostic of the stereochemistry of the cobalt(II) complexes[3, 12–14]. In fact, it is rather straightforward, in many cases, to determine the configuration of a cobalt(II) complex using its ligand-field bands as a criterion. Typical electronic spectra for the different configurations of cobalt(II) complexes are shown in Fig. 1, where assignment for the main peaks is also given.

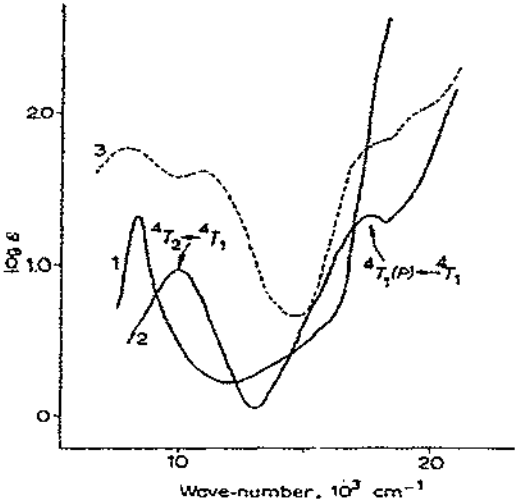
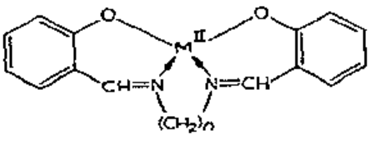


Fig. 1. Electronic spectra of cobalt(II) complexes in solution. (1) Co(salen) in $CHCl_3$ (planar); (2) Co(sal · n-C_4H_9)$_2$ in pyridine (octahedral); (3) Co(sal · n-C_4H_9)$_2$ in C_2H_5OH (tetrahedral).

Compounds of type III, which have a square-planar configuration because of steric requirements, exhibit a sharp band at about 8 × 10^3 cm^{-1}. This band is found to be characteristic of the square-planar cobalt(II) complex[13]. A precise



(III)

assignment for this peak cannot be made at present, but it is certain that the band arises from an orbitally-forbidden *d–d* transition, judging from its small oscillator strength. It is interesting to note that Co(sal · H)$_2$ and Co(sal · OH)$_2$ in non-donor solvents, which show a sharp peak at about 8.3 × 10^3 cm^{-1}, are assumed to have a square-planar configuration[13]. These square-planar cobalt(II) complexes are all of a low-spin type. As described below, this square-planar configuration of Co(sal · H)$_2$ differs from complexes of the Co(sal · alkyl)$_2$ type, the latter having a tetrahedral configuration. This difference may possibly show that the stronger is the ligand field, the more the square-planar configuration is favoured for cobalt(II) complexes of this type. The ligands, sal · H and sal · OH, produce a stronger ligand field than sal · alkyl. The steric factor may also play a part in this case, since a hydrogen bond of an N–H–O type would be formed in *trans*-Co(sal · H)$_2$, stabilizing the square-planar configuration. In this connection, it is interesting to point out that hydrogen bonding of an O–H–O type was reported to exist in bis-(salicylaldoximato)nickel(II)[18].

Tetrahedral cobalt(II) complexes of Schiff bases exhibit characteristic electronic spectra (curve 3, Fig. 1). The electronic spectra reveal that complexes of the Co(sal · alkyl)$_2$-type, which have magnetic moments of about 4.3 to 4.5 B.M., are tetrahedral (except for the complex with R = CH_3). In a similar way, it was concluded that complexes of the Co(sal · aryl)$_2$ type have a high-spin tetrahedral configuration[15].

Complexes of the Co(3-CH_3O · sal · R)$_2$ type, where R denotes n-C_3H_7, n-C_4H_9, iso-C_3H_7, tert-C_4H_9, cyclohexyl, Ph, CH_3Ph, CH_3OPh, 2,6-(CH_3)$_2$Ph, and 2,6-(C_2H_5)$_2$Ph, have also been prepared[19]. It was concluded, in a similar way, that they also have a tetrahedral high-spin configuration in the solid state and in non-donor solvents.

In such a coordinating solvent as pyridine, the configuration around the cobalt(II) may be different from one compound to another, and an examination in this respect often conveys important information about the stereochemistry of cobalt(II).

For R = n-alkyl, complexes of the Co(sal · R)$_2$ type in pyridine take up two pyridine molecule to give hexa-coordinate complexes[14–17]. On the other hand, the tetrahedral configuration of Co(sal · tert-C_4H_9)$_2$ persists in pyridine[14]. This is obviously due to the steric condition. For R = iso-C_3H_7, sec-C_4H_9, 1-ethylpropyl or cyclohexyl, the steric hindrance is not as great as in Co(sal · tert-C_4H_9)$_2$, but much greater than in Co(sal · n-alkyl)$_2$. The electronic spectra of these complexes in pyridine are only slightly different from the spectra of the same complexes in non-donor solvents. It is presumed that in pyridine there is an equilibrium consisting of the tetrahedral Co(sal · R)$_2$ and the octahedral Co(sal · R)$_2$(py)$_2$, possibly together with the penta-coordinate Co(sal · R)$_2$py. The percentage of the tetrahedral species in the pyridine solution, as approximately estimated from the electronic spectra, was about 90% for Co(sal · iso-C_3H_7)$_2$ and about 55% for Co(sal · cyclohexyl)$_2$ at room temperature, if the possible existence of the penta-coordinate solvate was discarded.

When R denotes Ph, ClPh, CH_3Ph, naphthyl or CH_3OPh, Co(sal · R)$_2$ takes up two pyridine molecules to form a hexa-coordinate complex, Co(sal · R)(py)$_2$. This is not, however, the case with the complexes for R = 2,6-(CH_3)$_2$Ph and 2,6-(C_2H_5)$_2$Ph, where the steric hindrance is significant. The electronic spectrum of Co(sal · 2,6-(CH_3)$_2$Ph)$_2$ in pyridine is different from either of the typical spectra for the tetrahedral and the octahedral complexes of cobalt(II). It was concluded, from the electronic spectrum and the steric condition, that in pyridine there is formed a penta-coordinate complex as a predominant species, Co[sal · 2,6-$(CH_3)_2$Ph$]_2$py, although it is also possible that in pyridine there is an equilibrium between the penta-coordinate solvate and the tetrahedral parent complex. A hexa-coordinate species, Co(sal · R$)_2$(py$)_2$, might be present in pyridine, but the amount of this species would be insignificantly small. As discussed later, the spectrum of Co[sal · 2,6-$(CH_3)_2$Ph$]_2$ in pyridine is quite similar to the solid spectrum of Co[sal · 2,6-$(CH_3)_2$Ph$]_2$py. The electronic spectrum of Co[sal · 2,6-$(C_2H_5)_2$Ph$]_2$ in pyridine is similar to the spectrum of Co[sal · 2,6-$(CH_3)_2$Ph$]_2$ in pyridine, and it is concluded that the penta-coordinate pyridine solvate is also a predominant species in the pyridine solution of this complex[19]. The existence of the penta-coordinate solvate, Co(sal · 2,6-Y_2 · Ph$)_2$py, in solution was also confirmed by the equilibrium studies. The occurrence of penta-coordination in these complexes may be due to steric hindrance.

The equilibrium in the pyridine solution depends upon the nature of the substituent X. This is shown by comparing Co(sal · R$)_2$ with Co(3-CH_3O · sal · R$)_2$. For R = n-alkyl, Ph or monosubstituted phenyl groups, the complexes of the Co(3-CH_3O · sal · R$)_2$-type in pyridine exist as hexa-coordinate complexes Co(3-CH_3O · sal · R$)_2$(py$)_2$. The tetrahedral configuration of Co(3-CH_3O · sal · tert-$C_4H_9)_2$, however, persists in pyridine solution. This behaviour of Co(3-CH_3O · sal · R$)_2$ is quite similar to that of the corresponding complexes of the Co(sal · R$)_2$-type.

The difference between the two series have been observed for complexes with R = iso-C_3H_7, cyclohexyl, 2,6-$(CH_3)_2$Ph and 2,6-$(C_2H_5)_2$Ph, where more or less significant steric hindrance is expected. In a pyridine solution of these complexes at room temperature only about 15% exists as the tetrahedral form for R = cyclohexyl, and about 20% for R = iso-C_3H_7 as estimated from electronic spectra. Comparison seems to show, qualitatively, that Co(3-CH_3O · sal · R$)_2$ has a higher tendency to take the fifth or the sixth ligand than has Co(sal · R$)_2$.

With R = 2,6-$(CH_3)_2$Ph or 2,6-$(C_2H_5)_2$Ph, Co(3-CH_3O · sal · R$)_2$ binds two pyridine molecules to form a hexa-coordinate complex, Co(3-CH_3O · sal · R$)_2$(py$)_2$. Judging from the steric condition, this pyridine solvate is considered to be considerably distorted from the regular octahedron, a fact which is also inferred from the low frequency of the band maximum (8.8×10^3 cm^{-1})[19]. This also differs from results with corresponding complexes of the Co(sal · R$)_2$ type.

It is thus found that the substitution of CH_3O for H in the benzene ring enhances the ability of the cobalt(II) in the complex to take a coordination number exceeding four. This is due not to the steric factor, but to the inductive effect of the OCH_3 group.

A similar substituent effect was observed earlier in connection with the oxygen-absorbing ability of cobalt(II) complexes of the Co(X · salen) type.

In a similar way, it was concluded that bis(2,6-dimethylphenyl-3 : 4-benzosalicylindeneiminato)cobalt(II), which is tetrahedral in non-donor solvents and in the solid state, exists predominantly as the penta-coordinate solvate, Co(X · sal)$_2$py in pyridine[21]. The occurrence of the penta-coordination in this compound is also due to the steric condition.

Some of the pyridine solvates have been isolated as fine crystals. For R = n-alkyl, phenyl, or monosubstituted phenyl, the compounds of the Co(sal · R)$_2$(py)$_2$ type have been obtained as orange crystals, and concluded to be hexa-coordinate, from electronic spectra and magnetic moments. They have magnetic moments of about 4.9 to 5.1 B.M.

No pyridine solvate of Co(sal · tert-C_4H_9)$_2$ and Co(sal · iso-C_3H_7)$_2$ has been obtained so far, even when the parent complexes are recrystallized from pyridine. On the other hand, a pyridine solvate, formulated as Co(sal · cyclohexyl)$_2$py, is readily isolated as red crystals from the parent complex. Since the electronic spectrum and magnetic moment of Co(sal · cyclohexyl)$_2$py in the solid state do not differ greatly from those of the parent complex, it is concluded that the pyridine solvate in the solid state contains the tetrahedral cobalt(II) complex[20]. The pyridine molecules in the solvate are not bound with the cobalt(II) ion, but occupy interstices in the crystal lattice[20].

No pyridine solvate has been obtained either from Co(3-CH_3O · sal · tert-C_4H_9)$_2$ or from Co(3-CH_3O · sal · iso-C_3H_7)$_2$[19]. However, a pyridine solvate, Co(3-CH_3O · sal · cyclohexyl)$_2$(py)$_2$, was isolated as orange crystals, and concluded, from the electronic spectrum and magnetic moment, to be a hexa-coordinate complex of cobalt(II)[22]. This is obviously different from the corresponding salicylideneiminato-complex.

b. Penta-coordinate complexes of N-substituted salicylideneimines

With R = 2,6-$(CH_3)_2$Ph, the compound formulated as Co(sal · R)$_2$py was isolated as green crystals. The electronic spectrum of this solvate is quite similar to the spectrum of the parent complex in pyridine. As discussed in the earlier part of the present review, it is certain that this pyridine solvate in the solid state is neither the tetra-coordinate nor the hexa-coordinate complex, but the penta-coordinate complex[20]. This compound, which has a magnetic moment of about 4.5 B.M., is one of the first examples of a penta-coordinate cobalt(II) complex of a high-spin type, and differs from the previously-reported penta-coordinate complexes, which are of a low-spin type[23]. Other examples of high-spin penta-coordinate cobalt(II) complexes have been described quite recently[24].

Compounds of the type Co(3-CH_3O · sal · R)$_2$(py)$_2$, where R denotes 2,6-sCH_3)$_2$Ph or 2,6-$(C_2H_5)_2$Ph, have been obtained as green crystals[21,22]. Since the (pectral of these solvates in the solid state are quite similar to the pyridine-solution spectra, the species with the same configuration is present both in the solid state and in pyridine. As discussed already in this review, these pyridine solvates in the solid state, consist of octahedral complexes, $Co(3\text{-}CH_3O \cdot sal \cdot R)_2(py)_2$, which are, however, considerably distorted from the regular octahedron, and display a *d–d* band at very low frequency (about 8.3×10^3 cm^{-1}).

With 5:6-benzo-salicylideneimine, a pyridine solvate, formulated as $Co(naphal \cdot R)_2py$, was obtained as green crystals (R denotes $2,6\text{-}(CH_3)_2Ph$). The solid spectrum of the compound is similar to the spectrum of the pyridine solution, and the compound in the solid state contains the high-spin penta-coordinate cobalt(II) species[21].

The magnetic moments of the penta-coordinate cobalt(II) complexes described above are slightly higher than those for the tetrahedral parent-complex, and lie between about 4.5 and 4.7 B.M.

The compound, $Co(sal \cdot CH_3)_2$, is peculiar when compared with the other members of this series. Thus the colour of the *N*-methyl-substituted complex (olive-brown) is different from that of the other members of $Co(sal \cdot alkyl)_2$, and possible peculiarity in the structure of $Co(sal \cdot CH_3)_2$ in the solid state was pointed out[14]. It has been shown by an X-ray crystal-structure analysis that $Co(sal \cdot CH_3)_2$ in the solid state is a binuclear molecule, in which the cobalt(II) ions are penta-coordinated[25] as shown in Fig. 2.

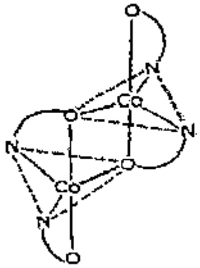
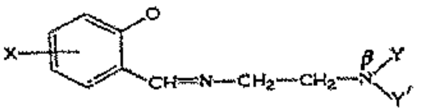


Fig. 2. Molecular configuration of $Co(sal \cdot CH_3)_2$ in the crystalline state.

Another penta-coordinate cobalt(II) complex was discovered in the course of studying complexes with ligands of type (IV)[26]. When both R and R′ are aryl groups, the complexes have a tetrahedral configuration. The cobalt(II) complex with X = 5-Cl and R = R′ = C_2H_5 has a square-pyramidal configuration,



(IV)

established by an X-ray study to be isomorphous with the corresponding nickel(II) compound having a penta-coordinate configuration (V)[27]. The following cobalt(II) complexes also show similar electronic spectra in the solid state, and may be considered to have a penta-coordinate configuration of the type (V): (X = H, 3-Cl;

$R = R' = C_2H_5$), ($X = 3\text{-Cl}$; $R = R' = -(CH_2)_4-$) and ($X = 3\text{-}CH_3$, $5\text{-}CH_3$, 3-Cl; R, $R' = -(CH_2)_5-$). It was concluded that the stereochemistry of these complexes seems to be related with the donor ability of the *β-nitrogen*, and the steric requirements.

In many cases, the compound isolated from the pyridine is the predominant species in solution. There are, however, some other cases where the species, which is present as a very minor component in pyridine, separates out as crystalline solid from the solution. With $R = 2,6\text{-}(C_2H_5)_2Ph$, $Co(sal \cdot R)_2py$ is obtained as brown crystals from the pyridine solution of the parent complex[21]. The electronic spectrum of the solid is quite different from the solution spectrum; in the pyridine solution, the predominant species was concluded to be a penta-coordinate molecule of $Co(sal \cdot R)_2py$. The main features of the *d–d* bands of the brown crystals with the composition of $Co(sal \cdot R)_2py$ correspond to those of the hexa-coordinate cobalt(II) complex, although the band maxima lie at considerably lower frequencies. It is most likely that the brown solid, $Co[sal \cdot 2,6\text{-}(C_2H_5)_2Ph]_2py$, consists of a hexa-coordinate cobalt(II) complex, distorted considerably from a regular octahedron. It is likely that this pyridine solvate is a binuclear complex, in which the cobalt(II) ions are hexa-coordinate, the oxygen atom acting as a bridge.

c. Cobalt(II) complexes of β-ketoamines

It is interesting to compare bis(β-ketoaminato)metal complexes with the corresponding complexes of the *N*-substituted salicylideneimines, and to examine the effect of the ligand-field strength on the structure of the metal complexes.

Complexes of the $Co(aca \cdot R)_2$ and $Co(bza \cdot R)_2$ type have been synthesized, and their configurations examined on the basis of their electronic spectra and magnetic moments[28]. These complexes show no absorption in the region near $8 \cdot 10^3\ cm^{-1}$, where a square-planar complex of cobalt(II) is expected to absorb[13]. The electronic spectra of these complexes in the solid state and in non-donor solvents show the main features characteristic of a typical cobalt(II) complex with a tetrahedral configuration[28]. Therefore, complexes of the $Co(aca \cdot R)_2$ and $Co(bza \cdot R)_2$ type, R being aryl groups, have a high-spin tetrahedral configuration.

The synthesis of complexes of the $Co(aca \cdot R)_2$ and $Co(bza)_2$ type have also been reported[29], with $R = H$, CH_3, n-C_3H_7 and iso-C_3H_7. From the electronic spectra and magnetic moments, it was concluded that these complexes in the solid state and in non-donor solvents have a high-spin tetrahedral configuration, except for the complexes with $R = H$. In the solid state, $Co(aca \cdot H)_2$ and $Co(bza \cdot H)_2$ are square-planar and low-spin, since they show a sharp band characteristic of the square-planar complex of cobalt(II) at about $8.0 \times 10^3\ cm^{-1}$. In non-donor solvents, however, the equilibrium (1) is exhibited by the latter two complexes.

$$\text{planar (low-spin)} \rightleftharpoons \text{tetrahedral (high-spin)} \qquad (1)$$

The occurrence of the square-planar form for these complexes was regarded by Everett and Holm as due to the steric condition. However, the electronic factor seems to be more important, as discussed in the succeeding section. The ligands aca · H and bza · H produce stronger ligand field than aca · alkyl and bza · alkyl, and this may give rise to the difference in the structure of the cobalt(II)complexes.

The behaviour of these cobalt(II) complexes in pyridine is very interesting. The conclusions, which were based upon electronic spectra, are summarized as follows[28]:

(1) With R = 2-ClPh, 3-ClPh or 4-ClPh, Co(aca · R)$_2$ exists exclusively in pyridine as an octahedral complex of the form, Co(aca · R)$_2$(py)$_2$. With R = CH$_3$Ph, α-naphthyl or 2,6-(CH$_3$)$_2$Ph, Co(aca · R)$_2$ does not react with pyridine, a tetrahedral configuration being retained. It is to be noted that for R = CH$_3$Ph or α-naphthyl, where no serious steric hindrance is expected to be present, complexes of the Co(aca · R)$_2$ type maintain the tetrahedral configuration even when dissolved in pyridine. Even isopropylamine, which has a stronger power for coordination, shows no tendency to be bound with the cobalt(II) ion in Co(aca · · R)$_2$. This fact indicates that there are some cases where penta- or hexa-coordination is not allowed, even if it is favoured from steric considerations. The stability of the tetrahedral form vis-à-vis the octahedral form is found to be remarkably high for these complexes. The drastic difference, observed between Co(aca · ClPh)$_2$ and Co(aca · CH$_3$Ph)$_2$ may be due not to the steric factor, but to the difference in the inductive effect between CH$_3$ and Cl.

(2) When R = CH$_3$Ph, ClPh or α-napththyl, Co(bza · R)$_2$ exists exclusively in pyridine as a hexa-coordinate solvate, Co(bza · R)$_2$(py)$_2$. The remarkable difference in this behaviour between Co(aca · R)$_2$ and Co(bza · R)$_2$ is regarded as due not to the steric factor, but to the difference in the ligand field produced.

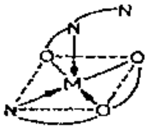
All these results seem to indicate that the stronger is the ligand field, the higher the stability of the tetrahedral form vis-à-vis the penta-coordinate or the hexa-coordinate form.

(3) When R = 2,6-(CH$_3$)$_2$Ph or 2,6-(C$_2$H$_5$)$_2$Ph, Co(bza · R)$_2$ exists predominantly in pyridine as a penta-coordinate complex, Co(bza · R)$_2$(py).

d. Five-coordination in cobalt(II) complexes

There are two types of penta-coordinate cobalt(II) complexes, one being of a low-spin type and the other of a high-spin type. The complexes of the former type, which were reported many years ago[23, 30], are formed with ligands producing a very strong ligand field, necessary for the spin-pairing to occur. For this type, the destabilization of the highest d_{z^2} orbital seems to take place, and the trigonal-bipyramidal configuration, on the basis of $4s4p^24d^2$ hybridization, may be more probable.

The penta-coordinate cobalt(II) complexes of a high-spin type have only recently been synthesized for the first time with Schiff bases as ligands. The most probable configurations for these complexes are *(1)* a square-pyramidal and *(2)* a trigonal-bipyramidal configuration. Although the square-pyramidal configuration seems to be favoured from the crystal-field stabilisation energy, the energy difference between the two configurations is so small, because of the weaker ligand field, that a small change in the steric condition, bond nature or even the crystal packing influences the final configuration of the compound. According to the X-ray structure analysis, Co[sal · 5-$CH_2CH_2N(C_2H_5)_2$]$_2$ has a square-pyramidal configuration[27], and Co(sal · CH_3)$_2$ is a binuclear compound, in which the cobalt(II) ions take a trigonal-bipyramidal coordination[25]. Steric considerations indicate that Co(sal · 2,6-(CH_3)Ph)$_2$py may possess a configuration obtained by adding one pyridine molecule to the distorted tetrahedral unit of Co(sal · 2,6-(CH_3)$_2$Ph)$_2$. The magnetic moments of these complexes (about 4.5 to 4.8 B.M.) are found to lie between the values for the octahedral form (4.8 to 5.2 B.M.) and those for the tetrahedral form (4.3 to 4.5 B.M.). There are some exceptions to this, and no precise classification of magnetic moments seems to be feasible, until more data on the molecular configuration are available.



(V)

The electronic spectra (ligand-field bands) of penta-coordinate high-spin cobalt(II) complexes are neither simple, nor well-defined. Several different types of spectra are observed for the penta-coordinate high-spin cobalt(II) complexes, as shown in Fig. 3, while only one type, of a characteristic pattern, is known for octahedral or tetrahedral cobalt(II) complexes (Fig. 1). This fact underlines the complexity of the nature of the penta-coordination in cobalt(II) complexes.

The following may be cited as the factors that may influence the occurrence of penta-coordinate cobalt(II) complexes of a high-spin type.

(1) steric factor (shape of ligands, crystal-packing effect)

(2) electronic factor (nature of M–L bond, CFSE, ligand field).

It seems to be necessary that steric hindrance against hexa-coordination should be large, though this need not definitely exclude hexa-coordination. There are few examples of penta-coordination in Schiff-base complexes, in which steric hindrance against hexa-coordination is not very significant. It also seems to be necessary that hexa-coordination should be allowed from the orbital energy alone, if there were no steric hindrance. If the ligand field is stronger than a threshold value, the tetrahedral form may be much more stable than the penta- or the hexa-coordinate form, as is evident from comparison of Co(aca · R)$_2$ with Co(sal · R)$_2$ and Co(bza · R)$_2$. It should be remembered, however, that when the ligand field is extremely strong, the cobalt(II) complex would assume the square-planar configuration. In many cases, the difference in stability between the tetrahedral, the penta-coordinate and the hexa-coordinate form is not very large. Therefore, a slight change in the steric condition may sometimes give rise to an enormous change in the structure of the complexes.

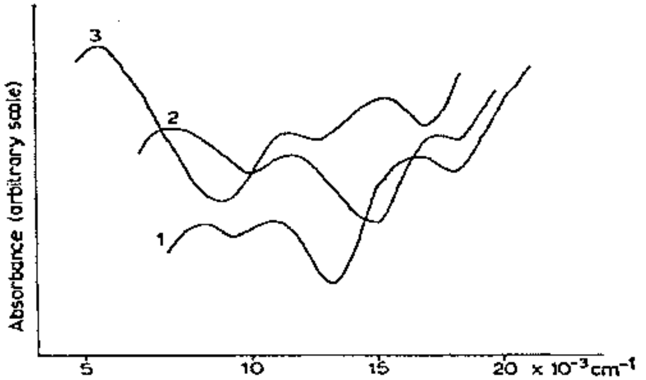


Fig. 3. Reflectance spectra of penta-coordinate cobalt(II) complexes. (1) $Co(sal \cdot 2,6\text{-}(CH_3)_2Ph)_2 \cdot py$; (2) $Co(5\text{-}Cl \cdot sal \cdot CH_2CH_2N(C_2H_5)_2)_2$[26]; (3) $Co_2(sal \cdot CH_3)_4$[49].

(iii) *Nickel(II) complexes*

a. Nickel(II) complexes of N-substituted salicylideneimines

Since the discovery of the "solution paramagnetism" in $Ni(sal \cdot R)_2$, various studies have been carried out concerning the synthesis and structure of the compounds of this series. It is getting more and more evident, as the studies go on, that various interesting problems, which are important to coordination chemistry, are involved in the chemistry of nickel(II) complexes of Schiff bases. The complete elucidation of the phenomenon of "solution paramagnetism", which was a difficult and painstaking task, has been settled only recently. The story is very instructive and interesting to coordination chemists, but we will not be concerned with the details, because of the limitation of space and scope of this review.

The investigation of these nickel(II) complexes originated from the discovery of the paramagnetism of the diamagnetic solid, $Ni(sal \cdot CH_3)_2$, in inert solvents[31]. Phenomena of a similar nature were subsequently observed for related complexes of this series. In order to interpret these phenomena, different assumptions were proposed at an earlier stage. Some of them included the equilibrium (2) in non-donor solvents, and bond formation between the nickel(II) ion and such solvent molecules as benzene and chloroform. None of these assumptions were fully substantiated by firm and reliable evidence at the time of presentation.

$$\text{planar (diamagnetic)} \rightleftharpoons \text{tetrahedral (paramagnetic)} \qquad (2)$$

It became evident, after many years, that the paramagnetism shown by these nickel(II) complexes of salicylideneimines in solution or in the solid state is due to association of the originally square-planar diamagnetic complexes to yield hexa-coordinate paramagnetic nickel(II) species[32, 33b]. For nickel(II) complexes with a d^8 configuration, the electronic spectrum depends critically upon the configuration of the complex. The difference in the spectrum from one stereochemistry to another is so clear that the spectrum may be regarded as diagnostic of the configuration. Typical spectra for different configurations are shown in Fig. 4.

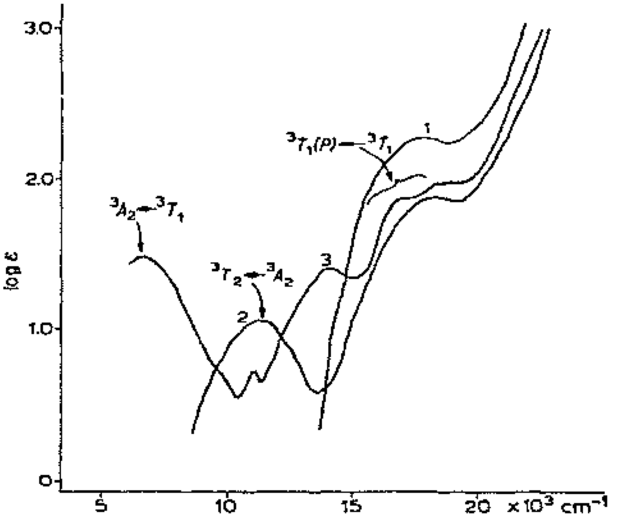


Fig. 4. Electronic spectra of nickel(II) complexes in solution. (1) Ni(saltn) in $CHCl_3$ (planar); (2) Ni(saltn) in pyridine (octahedral); (3) Ni(sal · tert-C_4H_9)$_2$ in $CHCl_3$ (tetrahedral).

The tetra- and the hexa-coordinate nickel(II) complexes, in general, take a square-planar and an octahedral configuration, respectively. In fact, for Ni(sal · · CH_3)$_2$, two types of the pure substance were isolated in the solid state, one being brown, diamagnetic and the other green, paramagnetic[32]. The former consists of the square-planar molecules, and the latter forms an associated polymer, in which the nickel(II) ion takes an octahedral coordination. For R = tert-C_4H_9, iso-C_3H_7 and cyclohexyl, complexes of the Ni(sal · R)$_2$ type may be expected to have a configuration distorted from the square-plane, because of the steric condition. It was concluded from the electronic spectrum that Ni(sal · tert-C_4H_9)$_2$, Ni(sal · iso-C_3H_7)$_2$ and Ni(sal · C_6H_{11})$_2$ are distorted from the square-planar configuration[33]. This conclusion was later confirmed by X-ray studies[34]. From the extent of the spectral shift toward a lower frequency, it was concluded that the distortion from the planarity in Ni(sal · R)$_2$ becomes smaller in the order[33a]: tert-C_4H_9 > iso-C_3H_7 > C_6H_{11}. It was also pointed out and confirmed experimentally that, in this case, the paramagnetism of Ni(sal · sec-alkyl)$_2$ in solution may not be due to the association of the complex molecules[33]. Then it was found out that at a higher temperature another type of equilibrium, namely (2), exists for these complexes. This equilibrium (2) also appears for Ni(sal · n-alkyl)$_2$ at a higher temperature, the concentration of the tetrahedral species in solution increasing with temperature[35]. This was confirmed by extensive studies of proton magnetic resonance[36], following the method of analysis, which was first applied in the study of the nickel(II) complexes of troponeimines[37]. The configuration of Ni(X · sal · R)$_2$, R being sec-alkyl, depends upon the nature of X. This was thoroughly studied by Sacconi and his co-workers[33b], who found that the energy difference between the tetrahedral and the square-planar form in this case is so small that a slight change produced by exchanging X may cause a remarkable configurational change.

In summary, the following equilibria are generally assumed to be present in solution:

$$\text{associated octahedral (paramag.)} \underset{\text{A}}{\rightleftharpoons} \text{planar (diamag.)} \underset{\text{B}}{\rightleftharpoons} \text{tetrahedral (paramag.)} \quad (3)$$

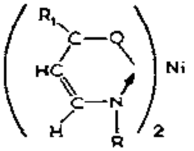
The equilibrium is shifted to the right with increasing temperature or with dilution. The equilibrium B becomes important only at a higher temperature above about 80°. The state of the equilibrium also depends upon the nature of R.

One might, however, question whether this conclusion does apply to most nickel(II) complexes, as seems to be currently believed. The experimental data might be interpreted without the assumption of the equilibrium B, but on the assumption that there is one species at a given high temperature, the configuration and the chemical bonding undergoing change with temperature. Before the idea of the universal applicability of the equilibrium (3) is finally accepted, the experimental data must be examined carefully and precisely.

b. Nickel(II) complexes of N-substituted β-ketoamines

The complexes of the Ni(aca · R)$_2$ and the Ni(bza · R)$_2$ type have been synthesized, where R denotes Ph, CH$_3$Ph, ClPh, 2,6-(CH$_3$)$_2$Ph, 2,6-(C$_2$H$_5$)$_2$Ph and naphthyl[38]. These complexes are all square-planar and diamagnetic in the solid state. It is interesting to note that even the complexes with R = 2,6-(CH$_3$)$_2$Ph and 2,6-(C$_2$H$_5$)$_2$Ph, where steric hindrance may be significant, are square-planar. In contrast to the corresponding complexes of *N*-substituted salicylideneimines, these complexes of the Ni(aca · R)$_2$ and the Ni(bza · R)$_2$ type exist predominantly in non-donor solvents as the diamagnetic, square-planar molecules, and at room temperature there is practically no contribution from the associated or tetrahedral species[38]. It was pointed out that the tendency toward association in the aca series is much lower than in the sal · R series. This difference between the β-ketoamine and the salicylideneimine complexes may be due to the stronger ligand field produced by the β-ketoamines, since the stronger ligand field will increase the energy difference between the $d_{x^2-y^2}$ orbital and the next-highest orbital of the nickel(II) ion, making the highest $d_{x^2-y^2}$ orbital less readily inclined towards bond formation as would be necessary in a hexa-coordinate nickel(II) complex.

With R = n-C_3H_7 and n-C_4H_9, complexes of the Ni(bza · R)$_2$ type were concluded, from studies of the spectra, magnetic moments and proton magnetic-resonance spectra, to be square-planar in the solid state and in non-donor solvents[39]. Similarly, Ni(bza · iso-C_3H_7)$_2$, Ni(bza · sec-C_4H_9)$_2$ and Ni(bza · cyclohexyl)$_2$ are tetrahedral. It was also concluded that the stability of the tetrahedral form was much higher for Ni(aca · R)$_2$ than for Ni(sal · R)$_2$. For example in solution at 25°, about 51% of the molecules take the tetrahedral form for Ni(sal · · iso-C_3H_7)$_2$, and nearly 100% of the molecules are tetrahedral for Ni(aca · iso-C_3H_7)$_2$.



(VII)

Numerous complexes of *N*-substituted derivatives of bis-(β-acetaldiminato)- and bis(benzoylacetaldiminato)-nickel(II) have been synthesized, and their configurations compared with those of the corresponding salicylideneimines (VI)[40]. The main results are summarized as follows.

(1) Square-planar Ni(acalen), Ni(bzalen) and Ni(bzalpham) are red and diamagnetic in the solid state and do not react with pyridine.

(2) Complexes of the Ni(acal · R)$_2$ and Ni(bzal · R)$_2$ type, where R denotes CH_3 and CH_3Ph, are green and diamagnetic in the solid state. They show slight paramagnetism in non-donor solvents, but their paramagnetism is smaller than that for the corresponding complexes of salicylideneimines. In pyridine, they combine with two molecules of pyridine to form hexa-coordinate complexes. It seems that Ni(bzal · H)$_2$ does not combine with a pyridine molecule.

c. Nickel(II) complexes with coordination number exceeding four

It is interesting to examine the configuration of the nickel(II) complexes of Schiff bases in pyridine, and to discuss and compare the ability of the nickel(II) ion to exceed coordination number four. The conclusions are based mainly upon electronic spectra and magnetic moments. It was concluded that the complexes of the Ni(sal · R)$_2$ type bind two molecules of pyridine to form hexa-coordinate complexes, when R denotes n-alkyl, Ph and XPh. For R = tert-C_4H_9, iso-C_3H_7 and cyclohexyl, however, steric hindrance is expected to be much larger than for R = n-alkyl and monosubstituted phenyl groups. For R = tert-C_4H_9, Ni(sal · R)$_2$ does not combine with pyridine and retains the tetrahedral configuration, when dissolved in pyridine. For R = iso-C_3H_7 or cyclohexyl, Ni(sal · R)$_2$ combines with two molecules of pyridine to form a hexa-coordinate complex, Ni(sal · R)$_2$-

$(py)_2$. It is to be noted that the behaviour of the nickel(II) complexes in pyridine is different from the behaviour of the cobalt(II) complexes.

For R = 2,6-$(CH_3)_2$Ph and 2,6-$(C_2H_5)_2$Ph, the steric hindrance due to the two alkyl groups at the 2- and the 6-position is expected to be considerable. Since the electronic spectra of Ni(sal · 2,6-Y_2 · $Ph)_2$, Ni(bza · 2,6-Y_2 · $Ph)_2$ and Ni(aca · · 2,6-Y_2 · $Ph)_2$ in pyridine are almost identical with the spectra of the compounds in non-donor solvents, it is concluded that these nickel(II) complexes do not combine with pyridine in the pyridine solution[38]. This result is considered to be mainly due to the steric condition.

As will be discussed in the section concerning copper(II) complexes, complexes of the Cu(sal · $R)_2$, Cu(bza · $R)_2$ and Cu(aca · $R)_2$ type when R denotes 2,6-$(CH_3)_2$Ph or 2,6-$(C_2H_5)_2$Ph, combine with one molecule of pyridine. This difference between copper(II) and nickel(II) may be interpreted in terms of the bonding nature of the metal ions and in terms of the steric condition. In the complexes of copper(II) with a d^9 configuration, the copper–ligand bond distance along the z-direction is generally found to be appreciably longer, due to the Jahn–Teller effect, than the copper–ligand distance in the xy-plane. On the other hand, the six bonds between the nickel(II) ion and ligands are essentially equivalent in octahedral complexes of nickel(II) with a d^8 configuration. It is, therefore, reasonable to expect that the two substituents in the 2- and 6-position may prevent the pyridine molecule from combining with the nickel(II) ion, whereas in the corresponding copper(II) complex, the pyridine molecule may be bound at a little farther distance despite possible steric hindrance.

In some cases, the electronic factor may become more important. There are some nickel(II) complexes, which show little or no tendency to exceed coordination number four, in spite of a favourable steric condition allowing hexa-coordination. It was concluded from the electronic spectra that Ni(sal · $H)_2$ in pyridine is octahedral, forming Ni(sal · $H)_2(py)_2$, while Ni(bza · $H)_2$ and Ni(aca · $H)_2$ are square-planar in pyridine. This difference may be considered to be due not to the steric factor, but to the difference in the ligand field produced. It is quite reasonable to assume that, for sal · H, the ligand field is not strong enough to give rise to spin-pairing in the nickel(II) ion, but that, for bza · R and aca · R, the ligand field is strong enough to cause spin-pairing. The strength of the ligand field produced is estimated, from a consideration of these observations, to increase in the following order: sal · aryl < sal · alkyl < sal · H < bzal · H < acal · H < bza · H < aca · H. It is also well-established that the strength of the ligand field increases when R changes in the following order: aryl < alkyl < H.

It is interesting, in this connection, to compare the nickel(II) complexes of Schiff bases formed from polymethylenediamines, (III). These nickel(II) complexes are known to be square-planar, but the strain in this configuration varies with the chain length n. Many of these complexes have been known for a long time[41]. Some new complexes of this series have also been prepared recently[42].

The electronic spectra clearly indicate that Ni(salen) does not combine with pyridine, while Ni(saltn) or Ni(salteten) do combine with two molecules of pyridine to form a hexa-coordinate pyridine solvate[38]. This result is different from what one expect on the basis of the steric factor; the ligand-field strength seems to play a more important part in this phenomenon. From the steric factor alone, the hindrance against hexa-coordination would be expected to be larger for saltn than for salen. It is considered that spin-pairing occurs more readily in Ni(salen) than in Ni(saltn) or in Ni(salteten), since salen produces a stronger ligand field than saltn or salteten. In a similar way, the fact that the association of the complexes is more difficult for Ni(aca · R)$_2$ than for Ni(sal · R)$_2$ may be readily understandable, since aca · R as a ligand produces a stronger ligand field than sal · R.

In a similar way, Ni(bzaen) and Ni(acaen) do not combine with pyridine, while Ni(bzatn) and Ni(acatn) combine with two pyridine molecules to form hexa-coordinate complexes[38]. It is always found that the ethylenediiminato-complex of nickel(II) displays absorption maxima at much higher frequencies than the corresponding trimethylenediiminato-complex. From a comparison of the experimental results, the following order is obtained for the strength of the ligand field:

sal · aryl < sal · alkyl < sal · H < salteten < saltn < bza · R < aca · R <
< bza · H < aca · H < salen < acaen

Sacconi and his co-workers studied a series of complexes of the Ni(X · sal · · R)$_2$ type, R being $CH_2CH_2N(Y)Y'$, to examine the availability of the fifth and the sixth coordination position of nickel(II) and the bonding power of the terminal nitrogen atom[43]. From the electronic spectra and the magnetic moments, it was concluded that the nickel(II) complexes are monomeric and hexa-coordinate for $Y = H, Y' =$ n-alkyl; $Y = H, Y' =$ benzyl; and $Y = Y' = CH_3$. The complexes are planar for $Y = H$, $Y' =$ 2-substituted phenyl; $Y = Ph$, $Y' = CH_3$; and $Y = Y' = Ph$.

The nickel(II) complex with $Y = Y' = C_2H_5$ has a square-planar or an octahedral configuration depending upon the group X, which includes 3-CH_3, 5-CH_3, 5-C_2H_5, 5-NO_2, and 5 : 6-benzo. The exceptions are those complexes with X = 3-Cl, 5-Cl and 3 : 4-benzo, which are penta-coordinate with magnetic moments of about 3.3 B.M.[44]. This has been confirmed by an X-ray analysis of the 5-Cl derivative whose structure is shown diagrammatically in (V)[45]. The complexes are the first reported examples of high-spin penta-coordinate derivatives of nickel(II). Low-spin penta-coordinate complexes of nickel(II) have been reported previously[23, 46]. A crystal-field model of high-spin penta-coordinate nickel(II) complexes has been presented on the basis of both the trigonal-bipyramidal and square-pyramidal configurations. The results of the calculation were reported to be in agreement with the observed spectra[47].

Equilibria exist between planar diamagnetic species and paramagnetic species in solution. The equilibrium depends upon the nature of the solvent as well as upon the temperature. The percentage of the planar, diamagnetic, species depends upon the substituent X and increases along the series X = 3 : 4-benzo < < 5-Cl < H < 5-CH_3 < 3-CH_3 < 5-C_2H_5 < 5 : 6-benzo. This order is in agreement with the order for the equilibrium between the planar and the tetrahedral forms of the bis(*N*-sec-alkyl-salicylideneiminato)nickel(II) complexes[47].

The factors influencing the occurrence of penta-coordinate cobalt(II) complexes of a high-spin type were discussed in Section B(ii)d. A similar discussion applies to the occurrence of penta-coordination in the nickel(II) complexes. Comparison reveals that, considering the electronic factor, the borderline ligand field between the tetra-coordinate and the penta-coordinate complex for nickel(II) is different from that for cobalt(II). It is interesting to note that for some ligands the tetra-coordinate cobalt(II) complex alone takes up an additional group, while the corresponding tetra-coordinate nickel(II) complex does not. When the ligand-field strength is larger than a threshold value, the fifth or the sixth coordination position may not be avilable for the additional ligand. The borderline ligand field for cobalt(II) seems to be lower than for nickel(II). For some ligand-field strengths, the energy difference between the penta-coordinate and the other configurations may be very small. Thus, when a small amount of Ni(sal · CH_3)$_2$ is introduced into the host lattice of Zn(sal · CH_3)$_2$, in which the zinc(II) ion takes a penta-coordinate configuration[48], the nickel(II) ion is forced to take the same configuration[49].

Holm and his co-workers[50] synthesized nickel(II) complexes of the Ni(X · · sal · R)$_2$-type, where R denotes ligands bearing a terminal OCH_3 group. It was concluded that only for R = $CH(CH_3)CH_2OCH_3$, an α-branched group, are the nickel(II) complexes hexa-coordinate with the two oxygen atoms of the methoxy groups bound to the nickel(II) ion. For R = $CH_2CH_2OCH_3$ or $CH_2CH_2CH_2$-OCH_3, the nickel(II) complexes are diamagnetic and square-planar.

It was also found[51] that, with R = CH_2CH_2OH or $CH_2CH(CH_3)OH$, the nickel(II) complexes are octahedral in the solid state and in non-donor solvents, in which they are monomeric. The bonding ability of the hydroxy group is higher than for the methoxy group, and thus this result is quite reasonable. For R = = $C(CH_3)_2CH_2OH$, steric hindrance is expected to prevent hexa-coordination of the nickel(II) ion. In fact, for R = tert-C_4H_9, the nickel(II) complex is tetrahedral in the solid state and in solution. However, the electronic spectrum and the magnetic moment indicate that Ni(sal · $C(CH_3)_2CH_2OH$)$_2$ is hexa-coordinate in the solid state. This is different from Ni(sal · tert-C_4H_9)$_2$. Moreover, Ni(sal · $C(CH_3)_2$-CH_2OH)$_2$ in pyridine is neither hexa-coordinate nor tetra-coordinate. It is most likely that the complex in pyridine is penta-coordinate, one molecule of pyridine being bound to the nickel(II) ion and the two Ni–OH bonds being thereby broken. In non-donor solvents, the configuration is different, depending upon the solvent used. Detailed examinations are now under investigation.

(iv). Copper(II) complexes

Many complexes of the Cu(sal · R)$_2$ type have been prepared. Most of them are considered to be square-planar[52, 53]. Some of them, however, consist of a binuclear unit, in which there is very weak copper-to-copper bond[54]. For Cu(sal · R)$_2$, R being alkyl or aryl groups, the square-planar configuration is stable, but when there is considerable steric hindrance, the distortion from the planarity may occur. Thus for R = tert-C_4H_9, iso-C_3H_7 and cyclohexyl, it was concluded from the electronic spectra that the complexes of the Cu(sal · R)$_2$ type are distorted from the square plane[33]. It was also concluded that the distortion decreases in the following order tert-C_4H_9 > iso-C_3H_7 > C_6H_{11}. This was confirmed by X-ray studies, which showed that the angles between the two N–Cu–O planes is 80° for the complex with[55] R = tert-C_4H_9 and 60° for the complex with[56] R = iso-C_3H_7.

Whether the complexes of the Cu(X · sal · R)$_2$-type take a tetrahedral or a planar configuration depends upon the nature of X. This was thoroughly studied by Sacconi on the basis of electronic spectra[33b]. It was concluded that the complex is tetrahedral for X = H, 3-CH_3, 5-CH_3, and 3 : 4-benzo, and square-planar for R = 3-Cl, 5-Cl, 3-Br, 3-NO_2, 5-NO_2 and 5 : 6-benzo. It is interesting to note that the copper(II) complexes with R = iso-C_3H_7 and X = 3-CH_3 or 5-CH_3 are tetrahedral, while the corresponding nickel(II) complexes are planar. Magnetic properties of some nickel(II) and copper(II) complexes of this series were also investigated[57].

The behaviour of these copper(II) complexes is interesting. It seems that the energy difference between the penta-coordination and the hexa-coordination is quite small and it is often difficult to differentiate between the two. The electronic spectrum of the copper(II) complex changes considerably when the tetra-coordinare, square-planar, complex takes up the fifth ligand to form the penta-coordinate complex. The change in the spectrum observed on going from the penta-coordinate to the hexa-coordinate complex is not very apparent. In general, when a tetra-coordinate, planar, complex of copper(II) combines additional ligands[58] there is a shift to a lower frequency and a broadening of the absorption band.

It was found, from the electronic spectra, that the complexes of the Cu(sal · · R)$_2$ type combine with one or two molecules of pyridine when dissolved in pyridine; R denotes n-alkyl, phenyl and monosubstituted phenyl groups. For R = tert-C_4H_9 and iso-C_3H_7, there is practically no change in the spectrum so that it is concluded that little or no configurational change occurs when the complexes are dissolved in pyridine[38]. This is obviously due to the steric factor. It was also concluded that Cu(sal · 2,6-Y_2Ph)$_2$, Cu(bza · 2,6-Y_2Ph)$_2$ and Cu(aca · 2,6-Y_2Ph)$_2$ in pyridine are penta-coordinate with one molecule of pyridine bound to the copper(II) ion. This result is different from the corresponding nickel(II) complexes, as indicated earlier.

Comparison clearly reveals that the tendency of the tetra-coordinate complex to take up another ligand is higher for Cu^{II} than for Ni^{II}. Thus Cu(salen), Cu(acaen) and $Cu(aca \cdot H)_2$ in pyridine combine with pyridine molecules to form penta- or hexa-coordinate complexes, while the corresponding nickel(II) complexes retain the original, square-planar configuration[38].

(v). Palladium(II) and platinum(II) complexes

Palladium(II) and platinum(II) greatly favour a tetra-coordinate, square-planar, configuration, and complexes of the $Pd(sal \cdot n\text{-}alkyl)_2$[59], $Pd(sal \cdot aryl)_2$[60], $Pt(sal \cdot n\text{-}alkyl)_2$[60], $Pt(sal \cdot aryl)_2$[61], $Pd(aca \cdot n\text{-}alkyl)_2$[62] and $Pd(aca \cdot aryl)_2$[62] type are considered to have a square-planar configuration. Since, however, the square-planar configuration for $Pd(sal \cdot tert\text{-}C_4H_9)_2$ and $Pt(sal \cdot tert\text{-}C_4H_9)_2$ is sterically difficult, these complexes might be expected to have a configuration distorted from the square-planar configuration. In fact, these complexes have electronic spectra which seem to be in agreement with a distorted configuration[60]. A final conclusion must await an X-ray crystal-structure analysis.

For R = iso-C_3H_7, cyclohexyl or 2,6-$(CH_3)_2$Ph, the palladium(II) and the platinum(II) complexes are considered to be square-planar[60–62]. All the complexes prepared so far fail to combine with pyridine, when dissolved in it[60,62], in agreement with the current theory. In palladium(II) and platinum(II) compounds with a d^8 configuration, the $d_{x^2-y^2}$ orbital is highly destabilized, making the spin-paired singlet much more stable than the spin-free triplet state. Penta- or hexa-coordination in these metal ions occurs much less frequently than is the case with the nickel(II) ion.

(vi). Other metal complexes

Schiff-base complexes of other metals have also been studied. Vanadyl(IV) complexes of the $(X \cdot sal \cdot R)_2VO$ type were prepared by Sacconi and Campigli[63], R being $CH_2CH_3N(Y)Y'$. The compounds with $Y = Y' = CH_3$ and $Y = H$, $Y' = C_2H_5$ take a penta-coordinate, square-pyramidal configuration. Complexes of a different formula were also reported.

In addition to $Mn(sal \cdot CH_3)_2$, which is isomorphous with the corresponding cobalt(II) and zinc(II) complexes[48], complexes of the $Mn(sal \cdot n\text{-}alkyl)_3$-type have also been prepared; they are expected to be octahedral but distorted due to the Jahn–Teller effect[64].

Complexes of the $Zn(sal \cdot R)_2$-type, R being alkyl or aryl groups, are considered to have a tetrahedral configuration, except for $Zn(sal \cdot CH_3)_2$, which is a binuclear molecule with penta-coordinate zinc(II) ions[49]. Complexes of the $Mg(sal \cdot R)_2$ type are also considered to have a tetrahedral configuration[65].

The chemistry of Schiff-base–metal complexes is now developing rapidly, but there are still many problems of fundamental importance left for extensive studies in the future. An attempt has been made here to stress the stereochemical aspects of the chemistry of Schiff-base complexes, and to grasp the present status of our knowledge in this field. It is hoped that this review may play some part in stimulating interest in this area. The advances achieved will certainly fertilize other related fields in coordination chemistry.

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