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SCHIFF BASE NICKEL(II) COMPLEXES WITH COORDINATION NUMBER EXCEEDING FOUR

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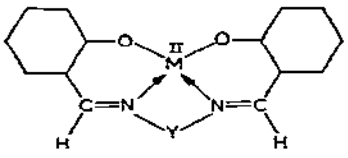
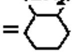
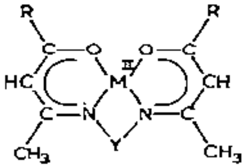
It is well known that the coordination number of nickel(II) varies from one compound to another, depending upon the ligands. Theoretical studies dealing with the factors determining the stereochemistry of nickel(II) complexes have often been presented, but detailed experimental observations have not been quite sufficient.

In the present work, we have used Schiff bases and related compounds as ligands and synthesized nickel(II) complexes of types I, II and III. The ability of these complexes to have coordination numbers exceeding four has been examined, and the possibility of finding five-coordinated complexes has been explored. In particular, the following questions have been raised. (A) What type of configuration does the four-coordinated complex assume when surrounded by a sufficiently large number of ligand molecules like pyridine? (B) When another coordinating



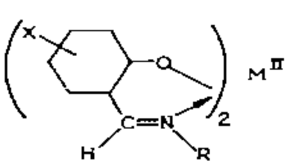
I

M(salen): $Y=(CH_2)_2$
M(salpn): $Y=CH(CH_3)CH_2$
M(saltn): $Y=(CH_2)_3$
M(salph): Y = 



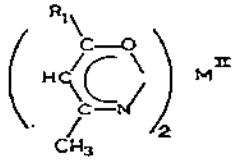
II

M(acean) $R=CH_3$, $Y=(CH_2$
M(acapn) $R=CH_3$, $Y=CH(CH_3)CH_2$
M(acatn) $R=CH_3$, $Y=(CH_2)_3$
M(bzaen) $R=Ph$, $Y=(CH_2)_2$
M(bzatn) $R=Ph$, $Y=(CH_2)_3$
M(eaaen) $R=OC_2H_5$, $Y=(CH_2)_2$



IIIa

M(X-sal·R)$_2$



IIIb

M(aca·R)$_2$: $R_1=CH_3$
M(bza·R)$_2$: $R_1=Ph$

atom is present at the other end of R, how does it behave toward the metal ion? The data obtained with the nickel(II) complexes are compared with those obtained with the corresponding complexes of cobalt(II) and copper(II)[1-3].

The ability of the nickel(II) ion to take a coordination number exceeding four is governed mainly by the following factors:

(1) electronic factor (nature of M–L bond, electronegativity of M and L, ligand field strength, CFSE),

(2) steric factor (shape of ligands, crystal-packing effect). Depending upon these factors for example, the four-coordinated nickel(II) complex, when dissolved in pyridine, may or may not take up pyridine.

There are square-planar nickel(II) complexes, which show little or no tendency to combine with a pyridine molecule in spite of the absence of steric hindrance. When there is no steric hindrance, a strong ligand field will favour a four coordinate square-planar configuration over five- and six-coordination, 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 toward bond formation. The nature of the M–L bond, such as its π-bonding character, also plays a part in this phenomenon. Even if the ligand field produced is not so strong, the nickel(II) complex may favour a square-planar configuration over the six-coordinated one, if extensive π-bonding is involved in the M–L bond, as in the complexes of biuret, succinimide, phthalimide and related compounds. Throughout the series of ligands employed in the present work, the extent of π-bonding character does not differ greatly, so that this effect is assumed to be equal for the complexes under discussion.

Nickel(II) complexes of types I and II are square-planar and diamagnetic in non-donor solvents. The configuration of these complexes, when dissolved in pyridine, was determined on the basis of their electronic spectrum and is shown in Table 1. The electronic spectrum is known to be diagnostic of the stereochemistry of nickel complexes[1,3], some typical examples being shown in Fig. 1. When dissolved in pyridine, all the analogues for $n = 3$ bind two pyridine molecules to form six-coordinated complexes. The drastic change on going from $n = 2$ to $n = 3$ is considered to be due not to the steric factor but to the electronic factor. The trimethylene derivatives are considered to produce a weaker ligand field than the dimethylene derivatives, since strain is caused by the trimethylene chain on complex formation[5]. In fact, the dimethylene analogues of this series show d–d absorption bands at much higher frequencies than the corresponding trimethylene analogues. It is interesting to note that the d–d band maxima of Ni(salen) and Ni(salpn) (18.7 kK) lie at considerably higher frequencies than the other complexes, such as Ni(saltn) (16.9 kK, log ε 1.85), Ni(bzaen) (17.7 kK, log ε 2.21), Ni(bzatn) (17,4 kK, log ε 2.26), Ni(acaen) (17.7 kK, log ε 1.90), Ni(acatn) (17.3 kK, log ε 1.70)[6] and Ni(eaaen) (16.7 kK, log ε 2.0). It is also worth noting that Ni(eaaen) retains the original square-planar configuration in pyridine. In general, eaa.R is

TABLE I

CONFIGURATION OF SCHIFF BASE NICKEL(II) COMPLEXES IN PYRIDINE[1,7,9,11,13]

Six-coord. solvates with two pyridine molecules	*unsolvated (original four-coord.)*
Ni(saltn), Ni(bzatn)	Ni(salen), Ni(bzaen)
Ni(acatn), Ni(salph)	Ni(acaen), Ni(eaaen)
Ni(X–sal.H)$_2$	Ni(bza.H)$_2$, Ni(aca.H)$_2$
Ni(X–sal.n–alkyl)$_2$	Ni(X–sal. t–C_4H_9)$_2$
Ni(X–sal. i–C_3H_7)$_2$	
Ni(X–sal.Ph)$_2$	Ni(sal.2,6–Y_2Ph)$_2$
Ni(X–sal.monosubst. Ph)$_2$	Ni(5–Cl–sal.2,6–Y_2Ph)$_2$
Ni(3–CH_3O–sal.2,6–Y_2Ph)$_2$*	Ni(5–Br–sal.2,6–Y_2Ph)$_2$
Ni(5–NO_2–sal.2,6–Y_2Ph)$_2$	Ni(5,6–benzo–sal.2,6–Y_2Ph)$_2$
	Ni(bza.2,6–Y_2Ph)$_2$
	Ni(aca.2,6–Y_2Ph)$_2$
Ni(X–sal.CH_2CH_2OH)$_2$	
Ni(X–sal.$CH_2CH(CH_3)OH$)$_2$	

*Y = CH_3 and C_2H_5

considered to produce a much weaker ligand field than bza.R and aca.R, but the five-membered ring involving the nickel(II) ion in Ni(eaaen) also seems to be particularly suited for stable complex formation, due to a favourable steric condition. In order to yield a six-coordinated pyridine solvate, the ligand field is required to be weaker than that of eaaen. This is found to be the case with Ni(salph).

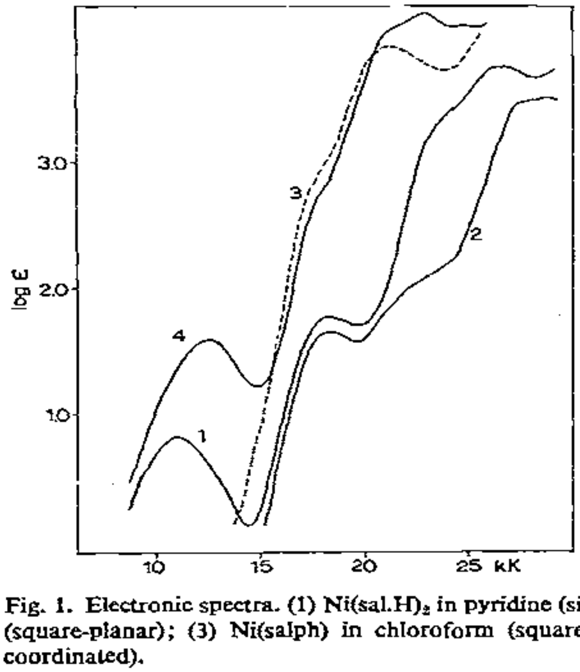


Fig. 1. Electronic spectra. (1) Ni(sal.H)$_2$ in pyridine (six-coordinated); (2) Ni(aca.H)$_2$ in pyridine (square-planar); (3) Ni(salph) in chloroform (square-planar); (4) Ni(salph) in pyridine (six-coordinated).

Many of the results for the nickel(II) complexes are similar to those of the corresponding copper(II) complexes, but some are different. Thus Cu(salen) and Cu(salpn) in pyridine take up pyridine molecules to form pyridine solvates with a coordination number exceeding four. This affords an example indicating that five-coordination in copper(II) complexes occurs at a slightly weaker ligand field than in nickel(II) complexes.

When R denotes n-alkyl, phenyl and monosubstituted phenyl, complexes of the Ni(sal.R)$_2$ type form six-coordinated pyridine solvates, Ni(sal.R)$_2$(py)$_2$, in pyridine (py denotes a molecule of pyridine). It is significant that Ni(sal.H)$_2$ forms a six-coordinated solvate in pyridine, while Ni(aca.H)$_2$ and Ni(bza.H)$_2$ do not, as shown in Fig. 1. This difference is due not to the steric factor, but to the electronic factor.

When steric hindrance is considerable, a complication may take place. For $R = t-C_4H_9$, where steric hindrance is most remarkable, these complexes take a distorted square-planar configuration in the solid state and in non-donor solvents[7,8], and retain this distorted configuration even in pyridine[9]. Other cases, where the steric hindrance is considerable include the complexes Ni(X-sal.i-C_3H_7)$_2$, which take a tetrahedral or a square-planar configuration depending upon the nature of X[7,8], and which bind two pyridine molecules to give six-coordinated pyridine solvates of the Ni(X-sal.i-C_3H_7)$_2$(py)$_2$ type, when dissolved in pyridine[9].

As examples representing a similar case, where steric hindrance is large, nickel(II) complexes with R = 2,6-(CH_3)$_2$Ph and 2,6-(C_2H_5)$_2$Ph have been examined in the present work, where Ph denotes a phenyl nucleus. In these complexes, steric hindrance arising from the two alkyl groups at the 2- and the 6-position is expected to be significantly large. For these R groups, Ni(aca.R)$_2$, Ni(bza.R)$_2$ and Ni(X-sal.R)$_2$ have been prepared as pure crystals by methods similar to those reported previously[1], (X denotes H, 5–Cl, 5–Br, 3–CH_3O, 5–NO_2 and 5,6-benzo). These nickel(II) complexes, which are diamagnetic in the solid state, are concluded from their electronic spectrum to be square-planar in non-donor solvents and in the solid state. It was reported previously[8,10] that, for R = Ph and X = Ph, the nickel(II) complex in non-donor solvents consists of an equilibrium mixture, the equilibrium depending upon temperature, concentration and the nature of solvent. No such equilibrium, however, is present for R = 2,6-disubstituted phenyl, where the square-planar complex is the only species present in non-donor solvents[11].

For R = 2,6-(CH_3)$_2$Ph and 2,6-(C_2H_5)$_2$Ph, Ni(aca.R)$_2$, Ni(bza.R)$_2$ and Ni(sal.R)$_2$ in pyridine retain the original square-planar configuration, the fifth and the sixth coordination site being left vacant. This result is considered to be due to a steric effect, since Ni(aca.Ph)$_2$, Ni(bza.Ph)$_2$ and Ni(sal.Ph)$_2$ in pyridine are present solely as Ni(aca.Ph)$_2$(py)$_2$, Ni(bza.Ph)$_2$(py)$_2$ and Ni(sal.R)$_2$(py)$_2$, respectively. It is interesting to note that the corresponding complexes of copper(II) bind an additional pyridine molecule at the fifth coordination site[2,11]. This difference between the nickel(II) and the copper(II) complexes was previously discussed in terms of the bonding nature of the metal ions and the steric condition arising from the two alkyl groups[11]. Another point to note in this connection is that five-coordination occurs more readily in copper(II) complexes than in nickel(II) complexes. For the pyridine solvates of the above complexes, the five-coordinated configuration seems to be more favourable than the six-coordinated one owing to the steric condition.

The electronic states of the oxygen and the nitrogen atom of these ligands are expected to change in a delicate way on changing X. This change is likely to be slight, but some cases are known, where this slight change causes a remarkable effect on the stereochemistry of the metal complex. For X = 5,6-benzo, 5–Cl and 5–Br, and R = 2,6–$(CH_3)_2$Ph and 2,6–$(C_2H_5)_2$Ph, the complexes of the Ni(X-sal.R)$_2$ type bind no additional pyridine molecule, the original square-planar configuration being retained in pyridine[12]. This result is the same as that for X = H[11]. On the other hand, for X = 3–CH_3O and 5–NO_2, the corresponding nickel(II) complexes, when dissolved in pyridine, exist as the six-coordinated pyridine solvates of the Ni(X-sal. 2,6–Y_2Ph)$_2$(py)$_2$ type, Y being CH_3 or C_2H_5. This difference, which is not considered to be due to the steric factor, indicates that although steric hindrance in these complexes seems to be more or less effective, it does not absolutely exclude six-coordination; the electronic tendency to attain a coordination number of six may be more important than the steric hindrance in some complexes of this type. This result may be interpreted in terms of the difference in the electronic factor between various X groups. It is known that the effect of OCH_3 and NO_2 is generally stronger than that of Cl, Br and 5,6-benzo.

In the case of the corresponding cobalt(II) complexes, five-coordinated pyridine solvates are often formed[3], but this is not the case with the nickel(II) complexes, showing that the stability of the five-coordinated species vis-à-vis the four- and the six-coordinated one is lower for the nickel(II) complexes than for the cobalt(II) complexes.

When another coordinating atom is present at the other end of R, this would affect the stereochemistry of complexes of the Ni(X-sal.R)$_2$ type. In order to examine this effect, we have prepared compounds of the Ni(X-sal.R)$_2$ type, where R=CH_2CH_2OH, $CH_2CH(CH_3)OH$ and $C(CH_3)_2CH_2OH$, and X=H[9], 3–CH_3O[9] and 5,6–benzo[13]. The electronic spectra indicate that for R=CH_2CH_2OH and $CH_2CH(CH_3)OH$ the nickel(II) complexes are octahedral in the solid state and in non-donor solvents, in which they are also monomeric. Previous studies[9,14] show that, for R=$CH_2CH_2OCH_3$ or $CH_2CH_2CH_2OCH_3$, the nickel(II) complexes are diamagnetic and square-planar. The nickel(II) complexes are six-coordinated with the two oxygen atoms of the methoxy groups bound to the nickel(II) ion, only when R is $CH(CH_3)CH_2OCH_3$. This result seems to be reasonable, since the bonding ability of the hydroxyl group is higher than that of the methoxy group.

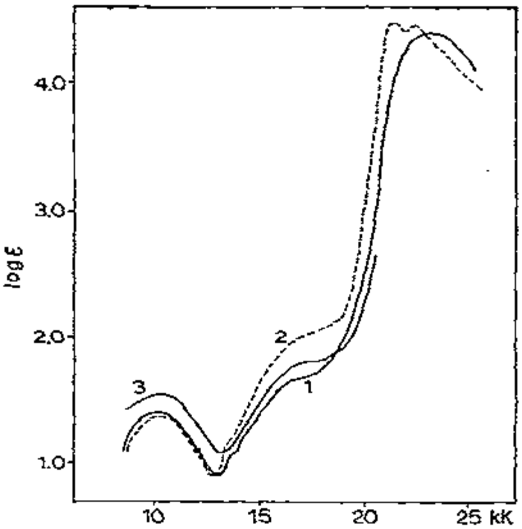
For R=$C(CH_3)_2CH_2OH$, the steric condition around the nickel(II) ion is much congested and complexes of the Ni(X-sal.R)$_2$ type take various configurations depending upon X. In the solid state, Ni(sal.R)$_2$ and Ni(3–CH$_3$O.sal.R)$_2$ are paramagnetic and distorted octahedral, but Ni(5,6-benzo.sal.R)$_2$ is diamagnetic and square-planar.In solution,the configuration of the complexes depends remarkably upon the solvent. The details will be discussed elsewhere[15].

The corresponding complexes of copper(II) were also examined, and it was concluded that these copper(II) complexes took a square-planar configuration, the hydroxyl group not being bound with the copper(II) ion[2]. This result, which is different from that of the corresponding nickel(II) complexes, might appear to be in contradiction to the conclusion in the preceeding section that a coordination number greater than four occurs in copper(II) complexes at a slightly weaker ligand field than in nickel(II) complexes. This difference, however, may be explained as due to the steric condition; the geometry of the ligand restricts the region which the hydroxyl group can reach for coordination. For the binding of the hydroxyl group with the copper(II) ion, it is required that this region must include the fifth and/or the sixth coordination site of the copper(II) ion, where the Jahn-Teller distortion is expected to be operative. On the other hand, the six M–L bonds in the nickel(II) complexes are essentially equivalent.

It is worth mentioning that, in addition to the complexes of the Cu(X-sal.R)$_2$ type, we have synthesized complexes of Cu(X-sal.CH$_2$CH$_2$CH$_2$O) and Cu (X-sal.C(CH$_3$)$_2$CH$_2$O) type, which are binuclear and have a subnormal magnetic moment at room temperature, (X denotes H and 5,6-benzo for the first type and H, 5,6-benzo and 3–CH$_3$O for the second type[2,16]).

Complexes of the Ni(X-sal.R)$_2$ type have also been synthesized and examined, where X denotes H, 3–CH$_3$O and 5,6-benzo for R = 2–CH$_3$O.Ph and 3–CH$_3$O for R = 2–C$_2$H$_5$O.Ph[17]. These complexes are paramagnetic with a magnetic moment corresponding to two unpaired electrons. The electronic spectrum, which obeys Beer's law over a wide concentration range, clearly indicates that they are octahedral and monomeric in non-donor solvents. Some of the spectra are shown in Fig. 2. It is concluded that the oxygen atoms of the methoxy group are bound to the nickel(II) ion. The difference between CH$_2$CH$_2$OCH$_3$ and 2–CH$_3$O.Ph, as observed in the present work, may be explained, at least partly, in terms of the difference in the electronic state of the oxygen atoms and also in terms of the strength of the ligand field produced by the Schiff bases, since the stronger ligand field is expected to enhance the stability of the four-coordinated configuration vis-à-vis the six-coordinated one.

It is interesting to compare these nickel(II) complexes with the corresponding cobalt(II) complexes[18,19]. The complexes of the Co(X-sal.R)$_2$ type have heen prepared for the following X and R: R = 2–CH$_3$O.Ph and 2–C$_2$H$_5$O.Ph for X = H and R = 2–CH$_3$O.Ph and 2,5–(C$_2$H$_5$O)$_2$.Ph for X = 3–CH$_3$O. All of the above cobalt(II) complexes in the solid state show electronic spectra which are similar to the spectra of the same complexes in non-donor solvents, so that it appears that they



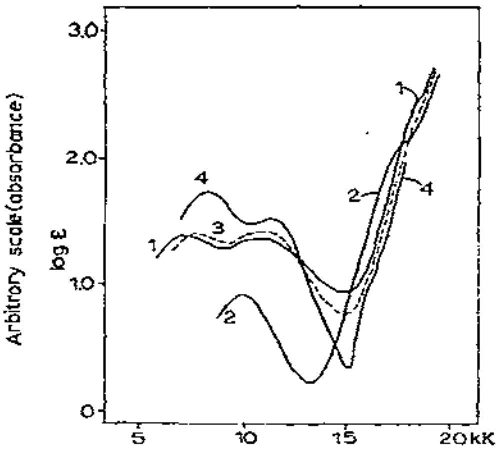


Fig. 2. Electronic spectra. (1) Ni(sal.2–CH$_3$O.Ph)$_2$ in chloroform; (2) Ni(5,6–benzo–sal.2–CH$_3$O.Ph)$_2$ in benzene; (3) Ni(5,6–benzo–sal.2–CH$_3$O.Ph)$_2$ in the solid state (by reflectance).

Fig. 3. Electronic spectra in solution. (1) Co(sal.2–CH$_3$O.Ph)$_2$ in chloroform, (2) Co(sal.2–CH$_3$O.Ph)$_2$ in pyridine; (3) Co(sal.2–C$_2$H$_5$O.Ph)$_2$ in chloroform; (4) Co(sal.4–CH$_3$O.Ph)$_2$ in benzene.

take a similar configuration in the solid state and in non-donor solvents. As shown in Fig. 3, a significant difference is observed in the ligand field bands between Co(sal.2–CH$_3$O.Ph)$_2$ and Co(sal.4–CH$_3$O.Ph)$_2$, the spectrum of the latter being typical of a tetrahedral cobalt(II) complex[16]. This fact indicates that the configuration of Co(sal.2–CH$_3$O.Ph)$_2$ is different from the tetrahedral configuration taken by other cobalt(II) complexes of these Schiff bases. The spectra of those complexes with a 2–CH$_3$O or 2–C$_2$H$_5$O group was similarly different from that of a typical tetrahedral complex of cobalt(II). It is most likely that the CH$_3$O or the C$_2$H$_5$O group at the 2-carbon position may be weakly bound with the cobalt(II) ion.

The absorption spectra of these complexes are different from those of typical six-coordinated cobalt(II) complexes; the d–d band at about 8–11 kK of the former complexes is considerably broader than the band for the latter. Magnetic moments of all these complexes (4.3 to 4.5 BM) greatly deviate from the moment (about 5 BM) expected for the octahedral complex, but lie within the range for a tetrahedral configuration. An octahedral configuration for these complexes may therefore be excluded. A five coordinate configuration seems most probable on the basis of the experimental data so far available.

All of these cobalt(II) complexes show electronic spectra in pyridine typical of octahedral cobalt(II) complexes as indicated in fig. 3. It is concluded that they take up two pyridine molecules to form six coordinated molecules, the weak bond between the cobalt(II) ion and the OCH_3 or OC_2H_5 group thereby being broken.

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