CHAPTER - I

INTRODUCTION

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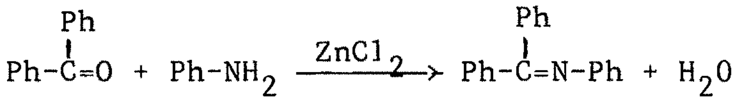
Schiff base is formed by the reaction of primary Amine with carbonyl compounds[1]. i.e. Aldehydes or Ketones. The condensation of primary Amine[2-9] with an aldehyde or ketone is carried out by heating the reaction mixture. The reaction is reversible and tends to attain an equilibrium. Hence reaction remains incomplete[10-13].

Schiff[14] may be regarded as the first to have defined the composition of a metal complex with such a ligand by establishing the 1:2 metal-ligand ratio in copper complexes derived from N-arylsalicylaldimines.

Subsequently studies have utilized Schiff bases derived from salicylaldehyde or related phenolic aldehydes to a very large extent owing to the ease with which they can be prepared. The pioneer work of Pfeiffer must be referred to in this regard. In a classic series of papers reviewed in 1940 he and his collaborators studied problems of synthesis, metal exchange, ligand replacement, transmination, stereochemistry and esterification, utilizing particularly salicylaldimine derivatives of Copper(II).

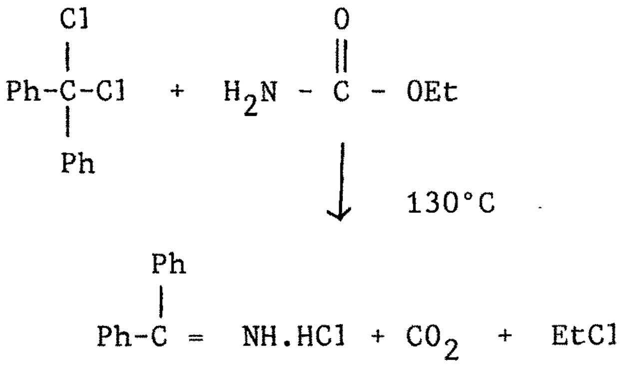
Most reactive aldehyde like Benzaldehyde give N-Benzalaniline on reaction with Aniline at room temperature in absence of any solvent[15]. Ethanol is often used as a solvent for the synthesis of Schiff base in good yield[16-19] by this method. Acid catalysts like zinc chloride and p-toluene sulfonic acid are used for the synthesis of an imine. The reaction of benzophenone with aniline is relatively slow,



$$\mathrm{Ph-\overset{Ph}{C}=O + Ph-NH_2 \xrightarrow{ZnCl_2} Ph-\overset{Ph}{C}=N-Ph + H_2O}$$

It is best carried out in presence of $ZnCl_2$ and aqueous 40 % hydrobromic acid, certain dry salts of amine are used for the synthesis of imines with ketones or aldehydes give good yield[20].

From Dichloro derivatives of a ketone :

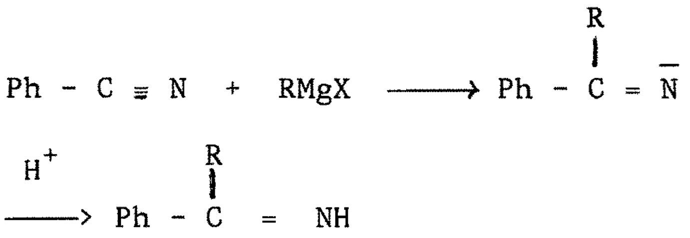


$$\mathrm{Ph-\underset{Ph}{\overset{Cl}{C}}-Cl + H_2N-\overset{O}{\overset{\|}{C}}-OEt \xrightarrow{130^\circ C} Ph-\overset{Ph}{C}=NH.HCl + CO_2 + EtCl}$$

In place of less reactive ketones their more reactive derivatives viz. dichloro derivatives were often used in the synthesis of imines[21-23]. Benzophenone imine is prepared by heating benzohydrylidene dichloride with urethane[24,25].

By addition of a nitrile :

Addition reaction of nitrile is a useful preparative method for an imine.



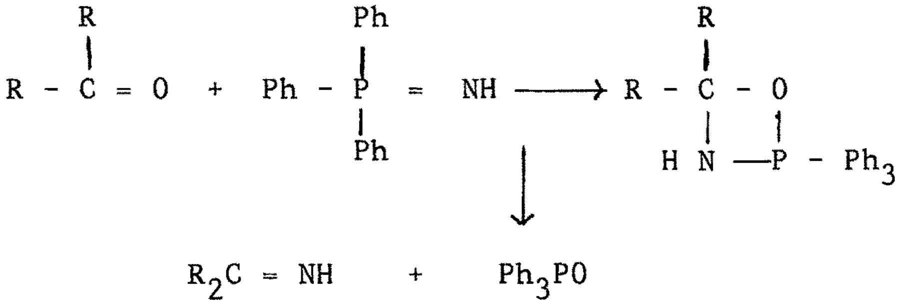
$$Ph - C \equiv N + RMgX \longrightarrow Ph - \overset{R}{\overset{|}{C}} = \bar{N}$$

$$\xrightarrow{H^+} Ph - \overset{R}{\overset{|}{C}} = NH$$

Addition of Grignard reagent to R - CN yields a ketimine salt which is converted into imines on careful acidification[26,27].

From Iminophosphorus derivatives :

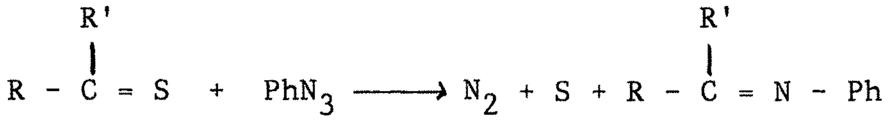
In this synthesis, two steps are supposed to involve. First step is the formation of a cycloaddition compound which easily breaks into an imine.



$$R-\overset{R}{\overset{|}{C}}=O + Ph-\underset{\underset{Ph}{|}}{\overset{\overset{Ph}{|}}{P}}=NH \longrightarrow R-\overset{\overset{R}{|}}{\underset{\underset{HN}{|}}{C}}-\underset{\underset{P-Ph_3}{\uparrow}}{O} \qquad \downarrow \quad R_2C=NH + Ph_3PO$$

From Thioketone and an azide :

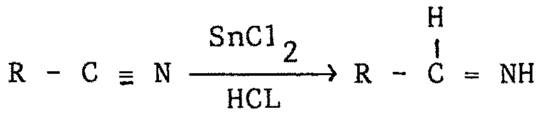
A thioketone condenses with an azide giving an imine. The reaction is accomplished by boiling a solution of thioketone and phenylazide in cyclohexanone[28].



$$R-\overset{\overset{R'}{|}}{C}=S + PhN_3 \longrightarrow N_2 + S + R-\overset{\overset{R'}{|}}{C}=N-Ph$$

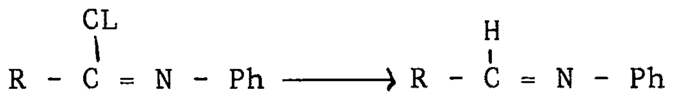
By Reduction of an Appropriate Substance :

There are several reductive reactions that lead to an imine. It has been reported that reduction of nitrile by Stephen reduction yields an imine[29].



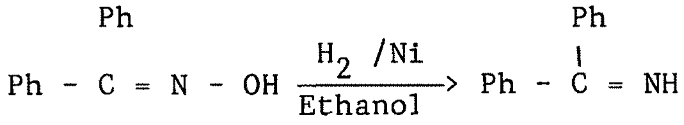
$$R-C\equiv N \xrightarrow[HCL]{SnCl_2} R-\overset{\overset{H}{|}}{C}=NH$$

Reduction of an imidylchloride is also reported to yield an imine.



$$R - \overset{CL}{\overset{|}{C}} = N - Ph \longrightarrow R - \overset{H}{\overset{|}{C}} = N - Ph$$

Reduction of oxime and of a hydroazone[30] also yield an imine.



$$Ph - \overset{Ph}{C} = N - OH \xrightarrow[\text{Ethanol}]{H_2\ /Ni} Ph - \overset{Ph}{\overset{|}{C}} = NH$$

The reduction of oxime is not a good method for the synthesis of imine because of reduction of imine is also accomplished in same step[31].

Synthesis of Complexes :

Metal complexes of these ligands have been synthesized by one of the following reactions :-

(1) The direct reaction of a primary amine with a preformed salicylaldehyde - metal complex

$$Cu(OC_6H_4CHO)_2 \ + \ 2\ NH_2C_6H_5$$

$$\longrightarrow Cu(OC_6H_4CH = NC_6H_5)_2 + 2H_2O$$

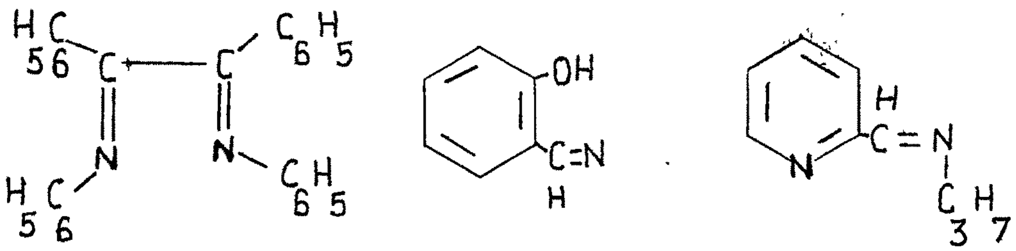
This method[31] was developed by Pfeiffer and is probably the most general method available. The two reactants are usually heated in a solvent such as an alcohol in which water is soluble and the product allowed to crystallize. Alternatively a solvent such as chloroform or benzene can be used and water distilled off during the course of reaction.

(2) The reaction of a metal salt, usually an acetate, with a preformed Schiff base in aqueous ethanol and similar solvent. A base is often added to aid in the removal of an acidic proton from the ligand if required. The method is not convenient if the Schiff base is readily hydrolysed. A variation of this procedure is to prepare strong alkoxide base e.g. potassium t-butoxide in t-butanol, dissolve the Schiff base in this solution and then add an appropriate anhydrous salt of the metal. The later method is particularly useful if hydrolysis of the base and complex can occur. Other procedures involving the use of an anhydrous metal salt, the Schiff base and a proton acceptor [illegible] suitable solvents may be devised for particular circumstances.

(3) The reverse reaction to (1) namely reacting the primary amine complex of a metal with a ketone or aldehyde has been termed "the templete synthesis".

The preparation, chemical and physical properties and chemical reactions of Schiff base have been reviewed by Layer[32]. Two excellent reviews of Schiff base complex which appeared in 1960 and 1968 first stressed the chemistry of inner complexes where as the later dealt in detail with the chemistry of salicylidene, ketoamines and closely related ligands. Transition metal complexes with Schiff base as ligand have been among the most widely studied coordination compounds.

In general, the azomethine group $>C=N$ which is the functional group of a Schiff base is aided in -forming a stable complexes by either a second group (A), an acidic group like a phenolic OH (B) or another donor group (C)



(A) (B) (C)

Fig.-1.0

Several complexes containing two or more metal ions linked to each other within the complex through one or more shared entities referred to as "bridging groups" have been studied[33-43].

The Mechanism of the Formation of Schiff base Complexes :

An attempt has been made by Nunez and Eichhorn to study the formation of a metal Schiff base complex by measuring the kinetics of the reaction between salicylaldehyde , glycine and Nickel(II) or Copper(II) ions[43]. They concluded that the order of mixing the reactants materially affected the rate of formation of the final complex. If either nickel - glycine, or nickel salicylaldehyde complexes are formed before the third component is added (salicylaldehyde or glycine respectively) the reaction is much slower than when nickel reacts directly with the preformed Schiff base. The kinetic analysis suggests that the intermediate (Fig.1.1)can form which further reacts to give the final complex. (Fig.1.2).

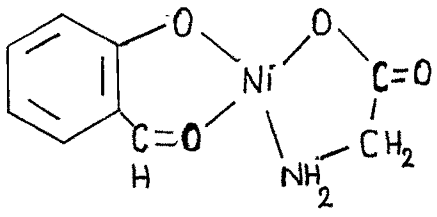


Fig. 1.1

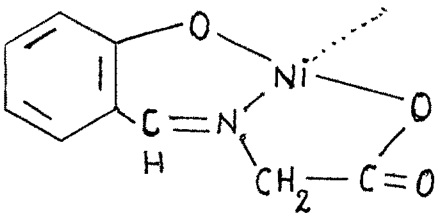


Fig.1.2

A further study of the reaction of bis (salicylaldehydato) - copper(II) with cyclohexylamine has established the first order rate dependence on both copper complex and Amine. The rate is much faster between salicylaldehyde and the amine which suggests strongly that the reaction involving a direct attack by the amine on the carbon atom of a coordinated carbonyl group rather than requiring complete dissociation of a salicylaldehyde anion from the copper as a first step (Fig.1.3). The polarizing power of the attached copper ion or the carbon atom would encourage nucleophilic attack at that point.

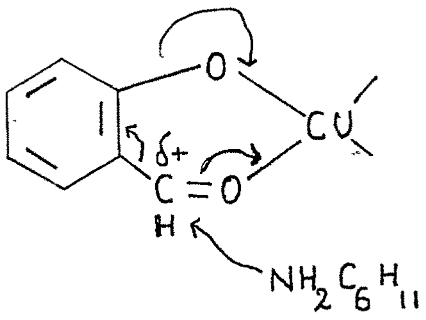


Fig. 1.3

The metal ions help to bring the ligands closer in the mixed ligand complexes. In a system containing one metal ion (M^{+n}) and two bidentate ligands, A and L with significant difference in complexing tendencies, simple complex (MA_2) is formed by the combination of the more complexing ligand (A) and metal ion. The other ligand remains unbound in solution. However, if the complexing tendencies of the two ligands are similar, the formation of the mixed ligand complex could be seen as[44]

$$M + A + L \rightleftharpoons MAL \qquad \text{.........([illegible])}$$

The charges on the ligands have been omitted for convience. The coordination number of the metal ions has been presented to be four. However the above equation is an over simplification of the equilibrium which may proceed in two ways :

$$M + A_2 \rightleftharpoons MA_2; \quad MA_2 + L \rightleftharpoons MAL + A$$

$$M + L_2 \rightleftharpoons ML_2; \quad ML_2 + A \rightleftharpoons MLA + L$$

It was suggested by Watter[45] and later by Kids[46] that the tendency of mixed ligand complex formation is determined by the reproportionation constants and from statical conversion. It should have a value 4. Under purely statistical consideration when there is no interaction between MAL, MA_2 and ML_2 are formed 25 % each.

Sharma and Schubert[49] have given a general treatment of statistical factors in the formtion and stability of ternary complexes rather than complexes containing one type of ligand.

However, the values of formation constants for mixed ligand complexes are observed to be higher or lower than expected from statistical considerations. As proposed by Bjerrum[50] in case of binary complexes, this may be because of electrostatic effect or reset effect, the latter constituting all contribution to the formation constant which can not be explained statistically or electrostatically.

Another way of showing that the formation of mixed ligand complexes is favoured to compare the difference in the formation constants :

K^{MA}_{MAL} and $K^{MA}_{MA_2}$ and also

K^{MA}_{MAL} and $K^{ML}_{ML_2}$ with greater

Contribution from-nonstatistical factors

$$\log (K_1) = \log K^{MA}_{MA_2} - \log K^{MA}_{MAL}$$

is less and

$$\log (K_2) = \log K^{MA}_{MAL} - \log K^{ML}_{ML_2}$$

$$K_{reprop} = \frac{(MAL)^2}{(MA_2) \quad (ML_2)}$$

$$= \frac{(\frac{1}{2})^2}{(\frac{1}{4}) \times (\frac{1}{4})}$$

$$= 4$$

$$\text{Log } K_{reprop} = 0.6$$

This equation has been further rearranged byBunnett and Peris[47] to show that

$$\log K_{reprop} = 2 \log K^{M}_{MAL} - \log (K^{M}_{MA_2} + K^{M}_{ML_2})$$

$$= (\log K^{M}_{MAL} - \log K^{M}_{MA_2}) + (\log K^{M}_{MAL} - \log K^{M}_{ML_2})$$

Thus, in a mixed system the probability of formation of mixed ligand complex is more than the binary complexes. According to W. B. Schaap and D.L. McMasters[48] from statistical considerations formation of mixed ligand complex MAL should be preferred over simple complexes MA_2 and ML_2, whenever the concentrations of the ligand involved are such that the products of the formation constants for the simple complexes and the concentrations of the ligands raised to the appropriate power approximately equal.

It can be seen that out of the two ways the consideration of $\log K_{reprop}$ has statistical basis while log K calculation implies that the corresponding binary (1:1) complexes contribute to the formation of MLA.

i.e. $MA + L \rightleftharpoons MAL$ and $ML + A \rightleftharpoons MLA$

In the cases of systems, containing same or lesser amounts of ligands than the total ions, consideration of log K may be preferred. However in the systems containing excess of L and A, $\log K_{reprop}$ should be preferably used.

It was observed by Watters and co-workers[51,52] that the value of $\log K_{reprop}$ is more than the expected value of 4. The formation of the mixed ligand complex is dependent on the factors other than the statistical.

Absorption Spectra of Metal Complexes :

Crystal field theory extended a satisfactory explanation for the spectra of complexes. For d^1 case ground state is ^2D. Due to octahedral crystal field it gets split into T_{2g} (lower) and E_g (higher) states. The transition of electron from T_{2g} to E_g absorbs energy in the visible range and a peak is observed in the absorption spectrum as in the case of $[Ti(H_2O)_6]^{+3}$.

When we deal with ionic systems having more than one but less than nine "d" electrons, the number of terms which arise in the free ions are, for d^2 or d^8, ^3F, ^1D, ^3P, ^1S and ^1G, for d^3 or d^7 ^4F, ^4P, ^2P, ^2G, ^2H, ...for d^4 and d^6 ^5D, ^3H, ^3G, ^3P, ^3D and for d^5, ^6S, ^4G, ^4P, ^4D, ^4F. The Orgel diagram[53] shows how the ground spectral terms are split up by weak crystal fields of different intensity. The diagram is simplest for the splitting of a D term. This is shown in figures (1.4)and (1.5)for the ground state terms in d^1, d^4, d^6 and d^9 systems.

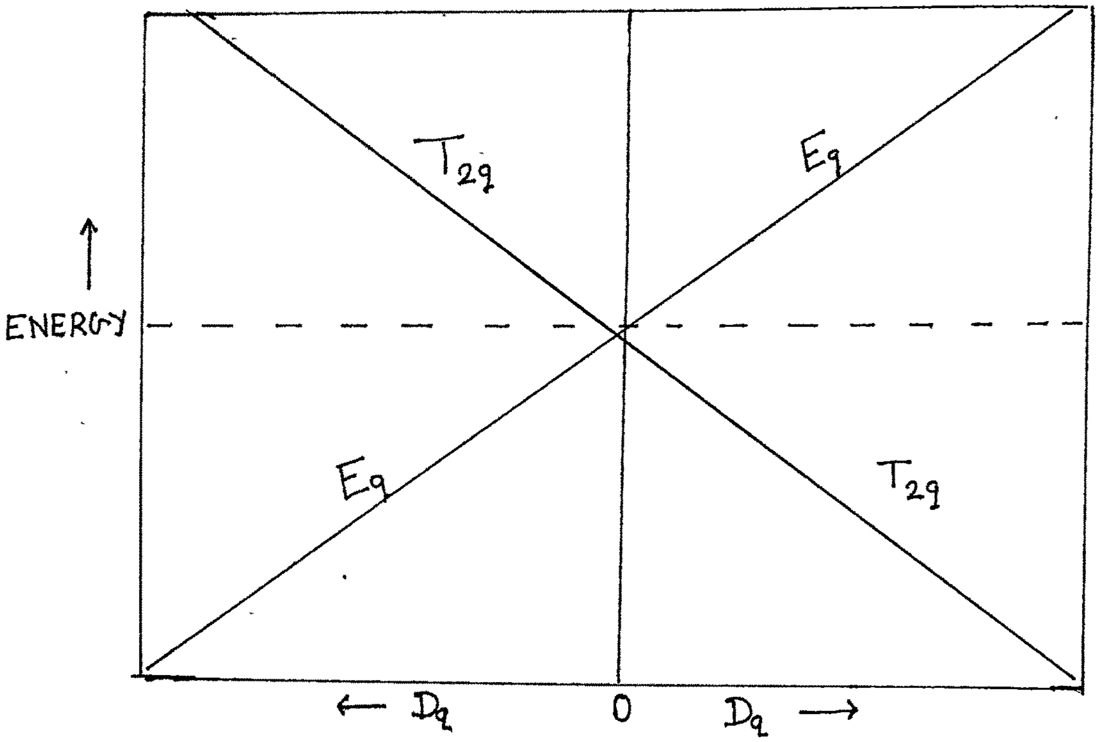


Figure - 1.4

d^9, d^4 octahedral d^1, d^6 octahedral

d^1, d^6 tetrahedral d^9, d^4 tetrahedral

(orgel diagram for d^1, d^4, d^6 and d^9 complexes)

In d^2, d^3, d^7 and d^8 systems the splitting of F and P terms, with maximum spin have been shown in Figure - 1.5

The orgel diagram for octahedral Vanadium(III) as seen in Figure (1.5) predicts three spin allowed transitions. These are

1 $^3T_{1g}(F) \longrightarrow {}^3T_{2g}(F)$

2 $^3T_{1g}(F) \longrightarrow {}^3T_{1g}(P)$

3 $^3T_{1g}(F) \longrightarrow {}^3A_{2g}$

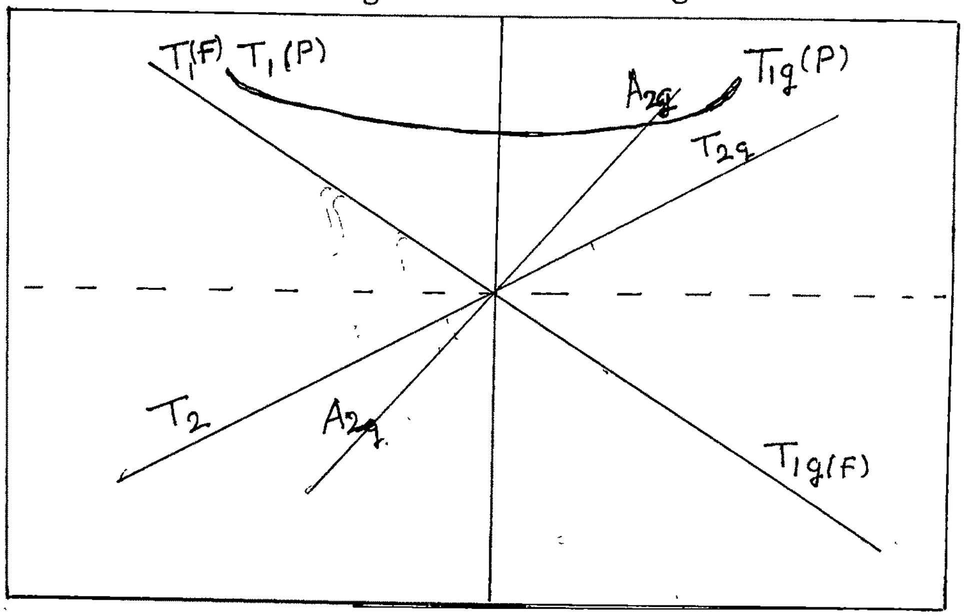


Fig.-1.5 (Orgel diagram for d^2, d^3, d^7 and d^8 complexes)

Further more it predicts that ν_1 will be lowest in energy Dq may be determined from the orgel diagram. Thus, by using the absorption spectra, it is possible to calculate the D_q values in case of the same complexes of metal ion with various ligands and the ligands can be arranged in a sequence of their field strengths. Such a series is known as spectrochemical series.

In Tarabe and sugano[54] diagrams, however, splitting of all possible states in both weak and strong field is shown.

Cu^{+2} (d^9) and Ni^{+2} (d^8) have respectively, ^2E_g and $^3A_{2g}$ ground states in octahedral field and $^2T_{2g}$ and $^3T_{1g}$ ground states in the tetrahedral field. On absorption of energy the transition to higher states is possible. Since the absorption in the ultraviolet or visible range requires a change in dipole moment, the following selection rules govern the absorption spectral of the complexes.

(1) Transitions between the states of different multiplicity are multiplicity forbidden.

(2) In a molecule, which has a centre of symmetry $g \longrightarrow g^*$ and $u \longrightarrow u^*$ transitions are Laporte forbidden.

(3) Simultaneous excitation of more than one electron is not allowed.

Thus in accordance with the second condition, no d-d transition should be allowed in octahedral complexes. However, due to vibronic coupling, the Laporte forbidden transitions are allowed in the octahedral complexes. They result in absorptions of low intensity.

In accordance with the above rules, the following transitions should occur in Ni^{+2} octahedral complexes.

$$^{3}A_{2g} \longrightarrow {}^{3}T_{2g} \quad (F)$$

$$^{3}A_{2g} \longrightarrow {}^{3}T_{1g} \quad (F)$$

$$^{3}A_{2g} \longrightarrow {}^{3}T_{1g} \quad (P)$$

These are all Laporte forbidden and hence extinction coefficients are low. The first one, is a low energy transition and is observed in the near I. R. region. The second one occurs in the visible range and the third is a high energy transition appearing in the ultraviolet region. This is true for a symmetrical octahedral field. In case of octahedral Ni^{2+} complexes with nonequivalents ligands, the Oh symmetry gets reduced to D_{4h} (distorted octahedral and square planar). This involve further splitting of the spectral state and hence the nature of the spectrum undergoes a change.

In the tetrahedral field the transitions possible are

$^{3}T_{1g}(F) \longrightarrow {}^{3}T_{2g}(F)$

$^{3}T_{1g}(F) \longrightarrow {}^{3}T_{1g}(P)$

$^{3}T_{1g}(F) \longrightarrow {}^{3}A_{2g}(F)$

Since the tetrahedral complexes have no centre of symmetry, the d-d transitions are allowed and hence the extinction coefficients of the peaks in the spectra of tetrahedral Ni^{2+} complexes are expected to be high[55].

In case of Cu^{+2} complexes (d^9) there should be expected one transition in both octahedral ($E_g \longrightarrow T_{2g}$) and tetrahedral ($T_{2g} \longrightarrow E_g$) complexes.

However, in accordance with Jahn - Tellor theorm[56] the octahedral Cu^{+2} complexes undergo distortion. As a result of it, there is further splitting of the T_{2g} and E_g orbitals and the redistribution of electrons results in the liberation of extra amount of energy and this stabilises the complex. Consequently both the spectral states $^{2}E_g$ and $^{2}T_{2g}$ undergo further splitting into two components each as shown in the following Figure (1·6).

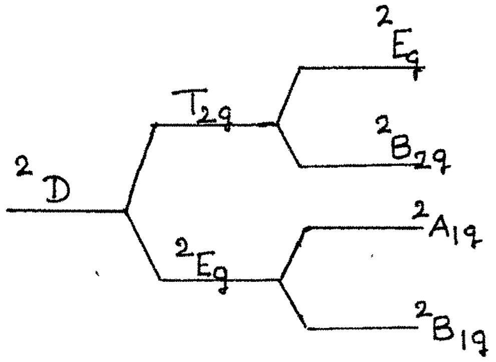


Fig. 1.6

Three transitions should, therefore, be possible corresponding to $^2B_{1g} \longrightarrow {}^2A_{1g}$, $^2B_{1g} \longrightarrow {}^2B_{2g}$ and $^2B_{1g} \longrightarrow {}^2E_g$. These bands are closely spaced and in some cases may overlap each other.

The crystal field theory can thus provide an explanation for the spectra produced due to d-d transition in the transition metal ions. It can also explain the magnetic , stereochemical, thermodynamic and kinetic properties of the complexes. But most serious limitations of the theory is that it does not consider any interaction between metal and ligand orbitals. It cannot, therefore, explain charge transfer bands produced due to transitions of electrons from ligand to metal ion. It does not also account for bonding which is of significant importance in several transition metal complexes.

It also fails in the cases of complexes wherein the occurrance of forbidden d-d transition bands is explained by the consideration of mixing of metal "d" orbitals with the ligand orbitals. Further the energy of ground ^3P states of Ni^{+2} ion in complexes obtained from absorption spectral data is found to be less than the free Ni^{+2} ion value, as obtained from emission spectral studies[57]. This decrease has been attributed to the increase in the distance between metal "d" electrons in the complex due to the expansion of d electron clouds of the metal ions on the ligand atom orbitals. Widening of the d electron cloud is termed Nephalauxetic effect[58]. The common ligands can be arranged according to their ability to cause cloud expansion. The presence of M-L covalent interaction has also been substantiated by magnetic, NMR, ESR and Mossbauer studies[59].

An alternative theory was therefore suggested by the joint attempt of number of chemists. It is termed ligand field theory.

It is a hybrid approach in which the computational advantages of the crystal field theory are preserved, but it considers that certain parameters should be changed in order to account for some amount of covalent interaction between metal and ligand orbitals. Unlike the crystal field theory it considers that inter electronic parameter in complexes are not same as in the free metal ion, but it undergoes variation depending on the extent of the metal ligand orbital overlap. The recah parameter which is a measure of the inter electronic repulsion in the free metal ion, undergoes a lowering in complexes. The extent of lowering is a measure of the amount of covalent interaction. Therefore, the ligand field theory has been termed as adjusted crystal field theory by cotton[60-61] and can be considered as a compromise between the crystal field and molecular orbital theories.

Magnetic Moment Study :

Magnetic susceptibilities of the complexes isolated were determined by Guoy method[62-65] using Mettler balance and electromagnet of constant current strength (3 amps) in all cases. the following equation was used

$$X_g = \frac{a + \beta\ dw}{m} \qquad \text{-------} (1.0)$$

where β = tubes constant,

$$a = X_2\ \varrho_2\ V = 0.029 \times V \times 10^{-6}$$

80 cms and known weights and volumes and uniform bore size, were calibrated at room temperature by using Hg $Co(CNS)_4$ of known magnetic susceptibility (X_g = 16.44 x 10^{-6}). The substance was filled up to 4.0 cms in the tube; and they were tapped equal number of times to peack the substance in the tube closely. The tube constant β was found by weighing the tube inside and outside the field and using the equation :

$$\beta = \frac{16.44\ W \ - \ 0.029V}{dw} \times 10^{-6} \quad ..... \ 1.1$$

where W = weight of the substance, V = volume of the tube, dw = difference of weights in the field and without the field + tube magnetism (i.e. diamagnetic correction of the glass tube).

$$g\ dw = 1/2\ (K_1 - K_2)\ H^2\ A \quad ....(1.2)$$

where

g = gravitational constant,

dw = difference in weight by keeping specimen in the field and out of field,

K_1 = volume susceptibility of the material,

K_2 = Volume susceptibility of the media i.e.Air,

H = field, strength,

A = Area of cross section.

$$2g\, dw/H^2A = X_1 \rho_1 - X_2 \rho_2 \quad \ldots\ldots \quad (1\cdot3)$$

where

ρ_1 = density of specimen, ρ_2 = density of Air.

X_1 = mass susceptibility of specimen

X_2 = mass susceptibility of Air

or

$$X_1\, M/V = 2g\, dw/H^2A + X_2 \rho_2 \quad \ldots\ldots. \quad (1\cdot4)$$

M = mass, V = volume

where

$$X_1 = 2g\, dw\, V/H^2A + X_2 \rho_2 V \quad \ldots\ldots. \quad (1\cdot5)$$

since g, X_2 and ρ_2 are constants, H is maintained constant, A and V are constants for a particular tube.

Determination of Magnetic Susceptibility :

The complex was first finely powderd and was filled in the tube (whose β constant is known) upto the calibration mark with equal number of tapping. The tube was suspended in the balance and weighed. A current of 3 amps was passed through electromagnet with the help of rheostate connected with the instrument in the series. Thus the tube was weighed with the field and without the field. The magnetic susceptibilities of the complexes were calculated using equation (5) and magnetic moments were obtained using the following equation :

$$\mu_{eff} \text{ in B. M.} = 2.84\sqrt{Xm.T} \quad \ldots\ldots\ldots \quad (1{\cdot}6)$$

Xm = molecular susceptibility of the specimen

T = absolute temperature at which the readings have been taken.

For getting correct values of μ, diamagnetic susceptibility is added to X^m and X^M corrected is obtained which is used for calculation of μ_{eff}.

Biological Activity :

The Bactericidal Activity of Schiff's bases has been studied in the early days of Chemotherapy[66]. Condensation products of salicylaldehyde with sulphonamide are not only complexing agents but are also bacteristatic agents. These compounds are screened against B - subtilis, s.typhi, S.aureos, S.dysentrious, B-anthracis, p-micrabilis. A-hydrophila, p-aerugenosa, K.pneumoniae, C.oris and E.Coli for their antibacterial activity[67]. Schiff bases have general promine as pharmacologically important substances. The potential anticancer Schiff's bases have been reported[68,69].

Schiff base complexes of Mn(II), Co(II), Ni(II) Cu(II) metal ions derived from O-amino benzoic acid, ethylenediamine, [illegible] aniline, [illegible] O-sulfonic acid, 2-chloro-4-nitroaniline, 2-aminopyridine, O-phenylenediamine, p-amino benzoic acid and p-toluidine with heterocyclic aldehydes and ketones like 2-Acetyl furan, 2-furyl glyoxal, 2-acetyl thiophen show antifungal and antibacterial activity[70-75].

8-Hydroxyquinoline and its metal chelates are long back recognised as potential bactericides and fungicides[76]. Esposito and Electcher[77] observed the activity of 1:1 complex of Copper(II) 8-hydroxyquinoline in the biosynthesis of peteridines. Presumably, it is believed that the inhibitory effect of complex on the enzyme site is responsible to govern the process.

Sahai[78] have prepared and characterized metal complexes of Fe(III), Co(III), Ni(II), Cu(II), Zn(II), La(III) and Th(IV) ions with salicylanilide and studied their fungicidal and bactericidal activity. The potential of metal chelates as drug is now well established[79]. EPR and thermal studies on the reaction of copper acetate with 8-hydroxyquinoline in the solid phase has been carried out by Kaur[80]. Synthesis and fungitoxicity of complexes of the schiff bases derived from 2-hydroxy-1-naphthaldehyde and 2-amino thiazole was carried out by A. Nayak and coworkers[81].

Metal complexes[82,83] play a vital role in metabolic and toxicological functions in the biological systems. The schiff bases derived from sulpha drugs and salicylaldehyde have been successfully used as chelating agents[84-87].

S.B. as Pigments :

Reaction of 2-hydroxy-1-naphthaldehyde with O-aminophenol and alkyl 3-amino-4-hydroxy benzoates followed by treatment with Cu salt gives yellow to greenish yellow pigments[88-92]. Heterocyclic isomethine metal complexes dyes give yellow to reddish shades to synthetic fiber[93]. Metal hydroxy schiff base complexes are used in textile dyeing[94]. Unsymmetrical 1:2 azo-azomethine chromium complexes prepared from 2-hydroxy benzaldehyde and 1-(2-aminoethyl) pyrrolidine gives light and wet fast blue color for polyamide fibres[95-96].

The formation of a diazodye of 8-hydroxyquinoline by coupling with benzidine is well known[97]. A pyridine solution of 8-hydroxyquinoline has been used for preparing diazo dyes with p-phenylenediamine and O-dianisidine. Pyridine medium is very suitable for coupling reaction[97,98].

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