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# **CHAPTER - I**

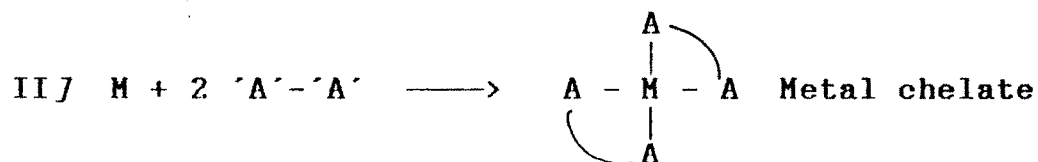
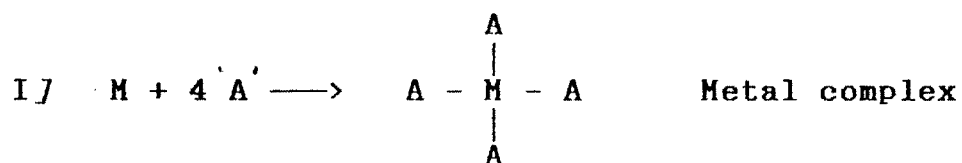
## **INTRODUCTION**

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CHAPTER - IINTRODUCTIONI) COMPLEX AND CHELATES :

When a metal ion combines with an electron donor, the resulting substance is said to be a complex or co-ordination compound.

The substance which combines with the metals contains two or more donor groups so that one or more rings are formed in the resulting structure, then it is called as a chelating agent. The bond is formed between the electron accepting metal and the electron donating complexing or chelating agent. The bond may be ionic or covalent depending on the metals and donor atoms involved.



where, M = Metal ion

A = Complexing agent.

The molecular or addition compounds which retain their identity even in solution and the properties of which are different from those of their constituents are called complex salts or co-ordination compounds.

The highest occupied orbitals and the lowest unoccupied orbitals on a metal ion overlap with the orbitals on a ligand having appropriate symmetry and energy. The strength of such a bond depends on the extent of mutual polarisation of the metal ion and the ligand.

Any molecule or ion attached to a metal ion is referred as a ligand. Depending on number of co-ordinating sites possessed by the chelating agent, it is classified as bi-, tri-, quadri-, sexidentate reagent [1.1].

Co-ordination compounds occur in plants as well as in animals. Chlorophyll, an important constituent of plant life, is a co-ordination compound containing Mg(II). The colour of blood is due to haemoglobin which is a co-ordination compound of Fe(II).

Conditions required for the formation of complex :

A molecule may react with metal ion to form complex under the following conditions :

- 1) The appropriate grouping of acidic and basic nature present on the molecule.

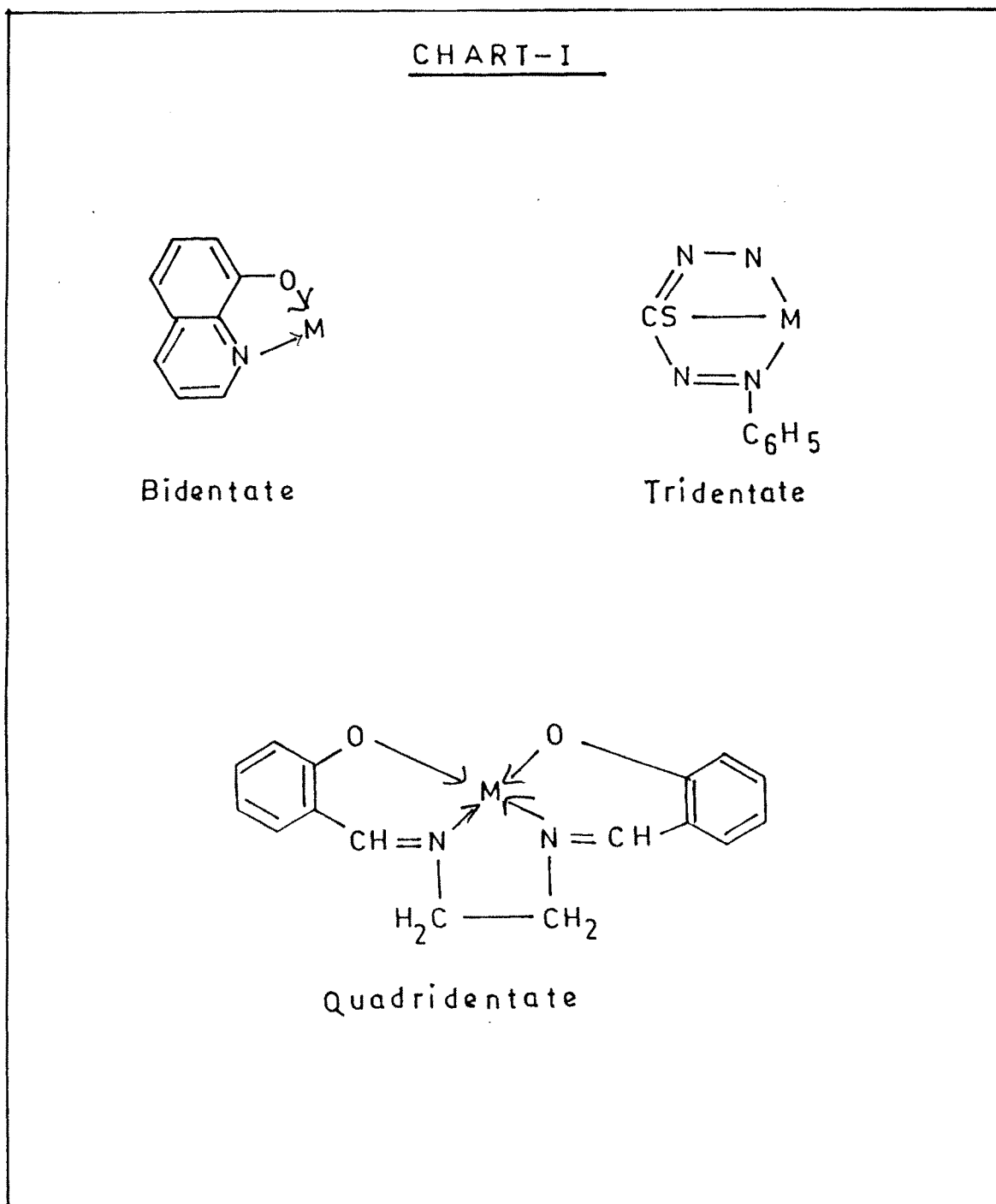


FIG. 1-1

- 2) The stereochemical arrangement of the grouping relative to each other allows a stable chelate ring to be formed.
- 3) There should be minimum steric hinderance due to other substituents on the ligand preventing the close approach of the metal ion to the coordinating groups.

#### Theories for the formation of Metal Complexes :

Present day knowledge about 'complex compounds' has been developed from Pioneer work of A.Werner<sup>1</sup> in 1893. The work of Werner was elaborated by Lewis<sup>2</sup>, Kossel, Sidgwick<sup>3</sup>, Pauling<sup>4</sup> and others. The theory is yet not complete and does not give satisfactory account for the formation of complexes and also for the properties of complexes.

The various other theories such as, (1) Crystal field theory<sup>5-7</sup> (2) Molecular orbital theory<sup>(8)</sup> (3) Ligand field theory are developed to explain kinetic, magnetic, spectral properties of complexes.

According to Werner<sup>1</sup> the complex may be either charged or neutral. Development of co-ordination chemistry from its initial stages is mainly due to pioneer worker. Werner's concept of two valencies was the first approach in the attempt to study the nature of complexing ligand molecule.

The electronic concept of co-ordination compounds indicates that complexes are formed as a result of Lewis-acid base reactions. The covalent bond is formed between metal ion

which acts as a Lewis acid and the ligand which is Lewis base. Thus, the covalent bond consists of a pair of electrons shared by two atoms. That means all metal ions are capable of forming co-ordination compounds. The tendency of metal ion towards formation of co-ordination compounds increases with increasing electronic affinity of metal ion. Almost all molecules and ions with at least one free pair of electrons will tend to form complexes with metal ions.

A modification of Werner's theory was made by Sidgwick<sup>3</sup> who suggested the term co-ordinate bond for a linkage that was formed when a donor atom supplied an electron pair to be shared with a metal atom or ion. Metals loosing electrons and accepting a share of many electron pairs would cause the metal ion to have a normal negative charge. This led to valence bond theory which was developed by Pauling<sup>4</sup>, Heitler, London and others.

Pauling<sup>4</sup> put forth the valence bond theory based on the hybridisation of orbitals. However, it could not interpret the absorption spectra and the magnetic properties of the metal complexes. Van Vleck<sup>5-8</sup> applied molecular orbital theory to study of 'complex compounds'.

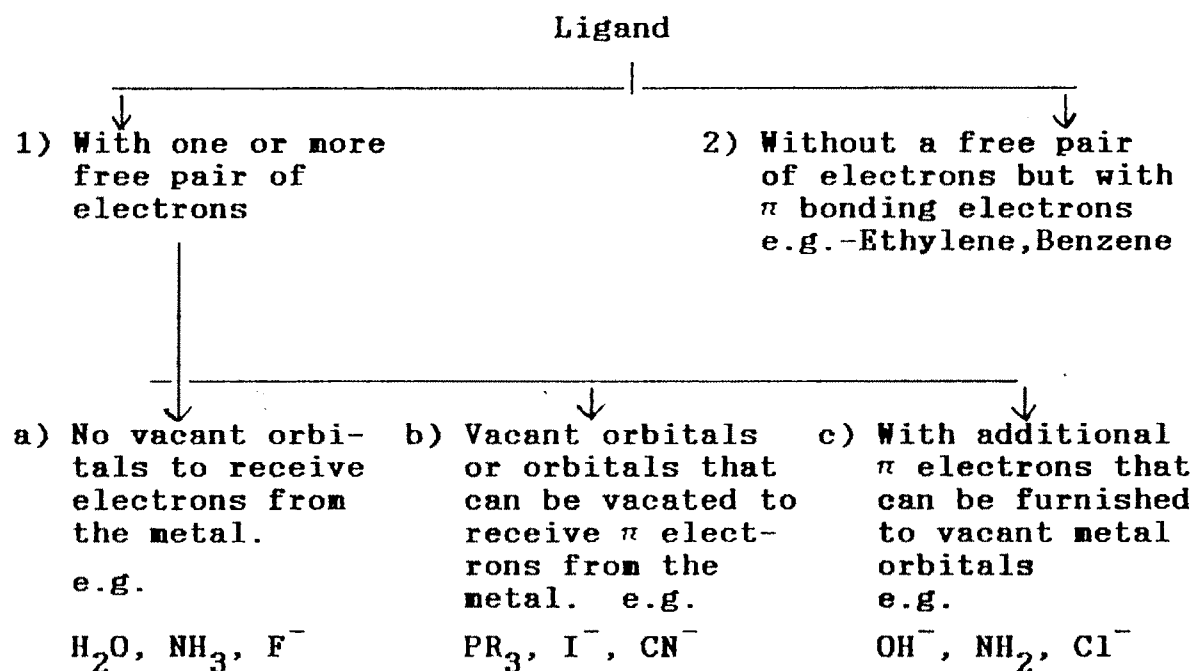
Ilse, Hartmann and Orgel<sup>9</sup> successfully applied the crystal field theory to explain the variations in the stabilities of the transition metal complexes. Both C.F.T. and M.O.T. in combination gave rise to ligand field theory. This theory is useful in interpreting various properties of

co-ordination compounds such as spectra, stabilities, and magnetic character.

The transition metals have the strongest tendency for combining with electron donors. Chelating agents show a stronger affinity for metal ions than do the simple complexing agents. Transition metals usually form covalent bonds with electron donors. Certain transition metals such as Pd, Pt exist in aqueous solution only in the form of covalent compounds. On the other hand, the chelate binding of alkaline earth and alkali metal ions must be predominantly ionic.

Different types of ligands :

Ligands are classified on the bases of electrons present on ion.



## II) COMPLEXES OF DIFFERENT METAL IONS :

### Nickel Complexes of Some Quadridentate Schiff Base Ligands :

A series of Ni(II) complexes can be synthesised<sup>10</sup> by condensation of Ni(II) and Schiff base derived by condensation of 5-chloro-2-hydroxy benzophenone with a series of alkane diamines i.e.  $\text{NH}_2(\text{CH}_2)_n\text{NH}_2$  (where  $n=2-12$ ). These complexes are highly soluble in non donor solvents. In non-donor solvents these complexes are low spin planer monomers with the Schiff base acting as quadridentate ligands, although in some cases there is a small degree of molecular association some complexes having  $n=5-12$ , show octahedral and square planer structure in solid state.

### Co-ordination complexes of Cu, Ni, Fe with Schiff bases derived from hydroxynaphthaldehydes and salicylaldehyde<sup>11</sup>

#### 1) Nickel(II) Complexes :

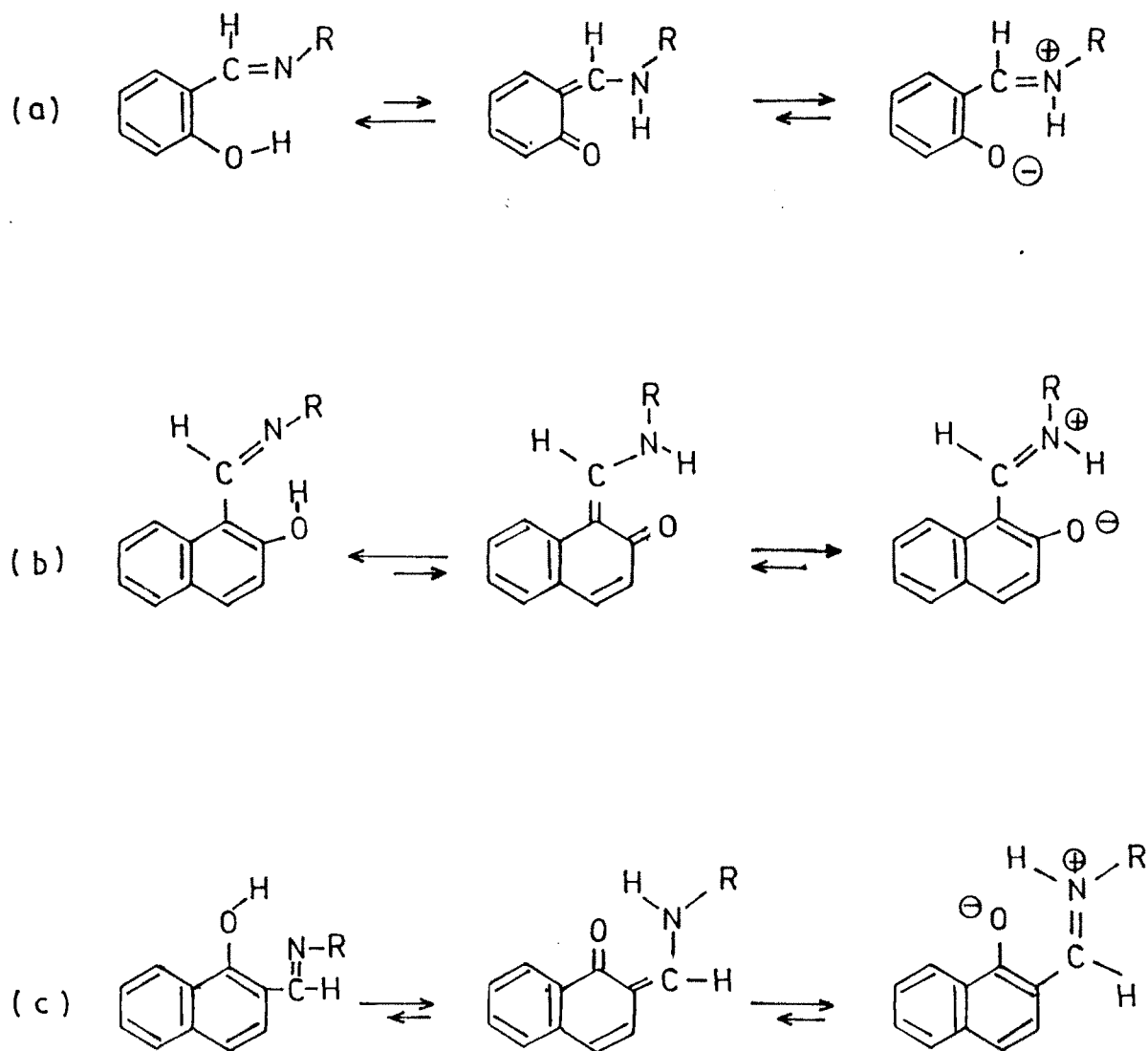
In tetradentate nickel complexes obtained from Schiff bases no solvent effect was observed in their electronic spectra while copper shows the changes. This difference in the two complexes is due to the molecular orbitals which are involved in the transitions. The substituents showed marked change in the stereochemistry of the complexes (2.1 and 3.1).

#### Electrochemistry of nickel complexes :

It is observed that, for nickel complexes with tetradentate Schiff bases that the stabilization of Ni(I) and



## CHART - II



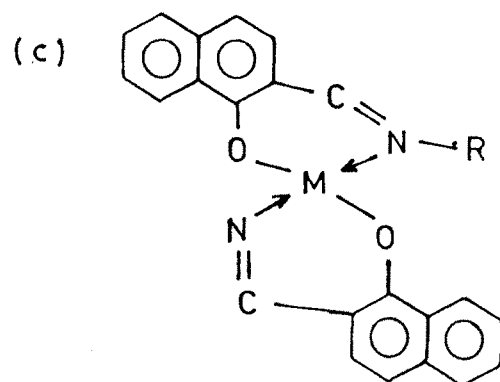
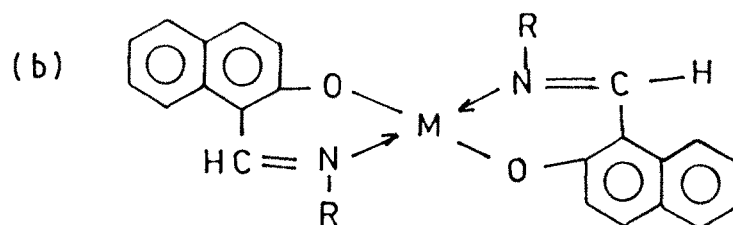
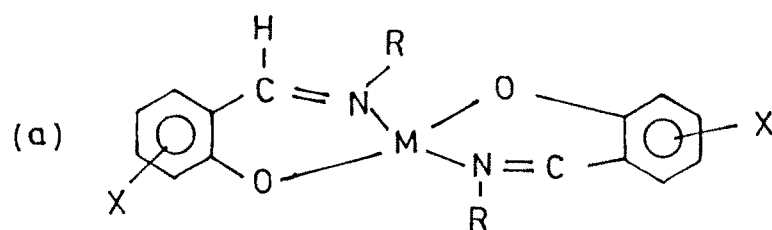
Keto-amine or Enol-imine tautomeric equilibria for

(a) Salicylaldimines

(b) 2-hydroxy-1-naphthaldimines

(c) 1-hydroxy-2-naphthaldimines

CHART-III



Where R = Alkyl or aryl group

M = Divalent metal ion

X = Halogen

Metal complexes derived from ligands a, b, c .

Ni(II) oxidation states depends upon structure of the complex in solution.

In pseudotetrahedral species only the Ni(III) oxidation state stabilized, while in planer species Ni(I) and Ni(II) is stabilized. Some stabilization of Ni(I) has been observed by nitro substitution.

## 2) Copper Complexes :

In solution monomeric planer or tetrahedral structure was observed. Tetrahedral geometry was observed for ligands with bulky substituents in solid state.

In solution, the structure of complex depends on polarity and donor capacity of the solvent.

### Electrochemistry of Cu-complexes :

For Cu(II) complexes with tetradentate Schiff base, only Cu(I) was stabilized. Due to the size Cu(II) is stabilized with five membered fused ring.

### Tetradentate Schiff base complexes of Co(II)<sup>12</sup> :

The metal complexes, containing tetradentate ligands exist in square planer or tetrahedral geometry depending upon the number of methylene groups in the central chelate ring.

The Ni and Cu derivatives of tetradentate Schiff base shows decrease in ligand field strength as number of methylenes increased from 2 to 4 in above complex. However Ni complex maintain a spin pair square planer

geometry even when four bridging carbon atoms are present.

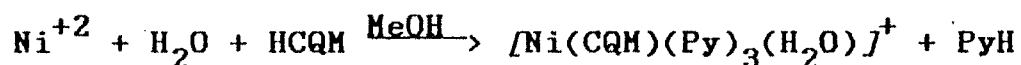
In Cu(II) complexes (4.1), there is decrease in ligand field strength with small but significant increase in magnetic moments as bridge length increases. There is an increase in the distortion from planarity towards a tetrahedral geometry with increase in the bridge length. Co(II) shows more tendency for the formation of tetrahedral complexes than Ni or Cu.

Preparation of Co(II) Complexes :

Schiff base is obtained by refluxing salicylaldehyde and molecule of aliphatic diamine in methanol for 15 min. To this warm solution of Schiff base an excess of triethyl amine in methanol was added. To this solution cobalt chloride hexahydrate in methanol was added. The complex formed readily.

Preparation of  $[\text{Ni}(\text{CQM})(\text{Py})_3(\text{H}_2\text{O})]\text{PF}_6\text{H}_2\text{O}$  <sup>13</sup> :

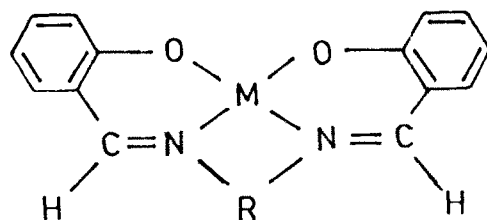
This complex was prepared by reacting  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  with isonitrosocamphor [HCQM] in presence of excess of pyridine.



In the absence of pyridine no identifiable compound could be isolated. When precipitated as the  $\text{PF}_6^-$  salt, the dark brown paramagnetic crystalline product was obtained.

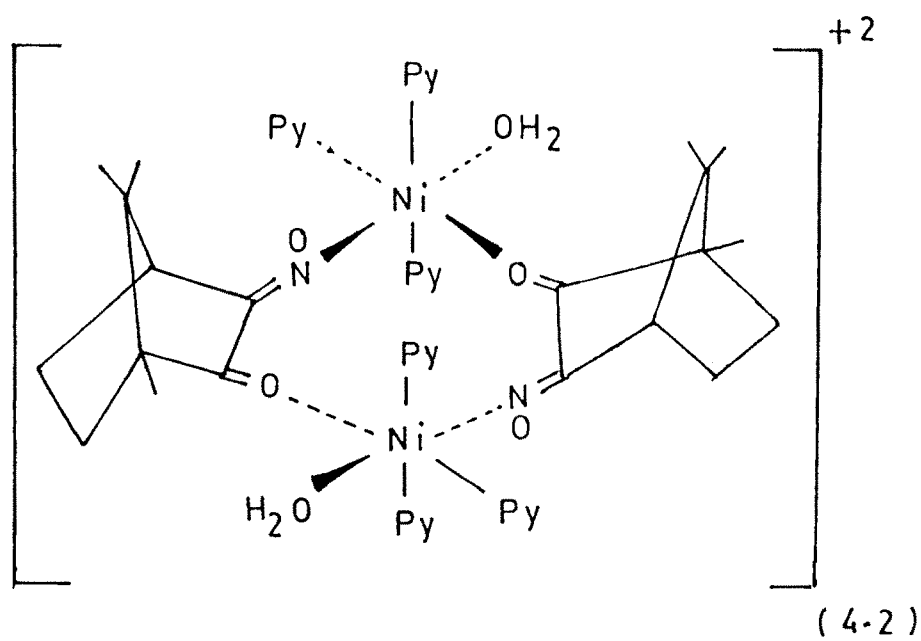
The I.R. spectrum of the complex with that of HCQM shows

CHART-IV



Where  $R = (CH_2)_n$   
(4.1)

Tetradentate schiff base metal complex .



Dimeric structure of  $[Ni(CQM)(Py)_3(H_2O)]$  complex .

FIG. 4.1

$\nu(\text{C}=\text{N})$  and  $\nu(\text{C}=\text{O})$  frequencies at 1653 and 1751  $\text{cm}^{-1}$  respectively. A new band of strong intensity at 1540  $\text{cm}^{-1}$  can be assigned to the  $\nu(\text{C}=\text{N})$  mode of the co-ordinated oxime. Another band is found at 1670  $\text{cm}^{-1}$  with strong intensity.

The anion  $\text{PF}_6^-$  gives a characteristic broad, intense absorption between 820 and 860  $\text{cm}^{-1}$ . The co-ordination of pyridine to Ni(II) is evidenced by the vibrational frequencies of pyridine at 626  $\text{cm}^{-1}$  and 426  $\text{cm}^{-1}$ . Absorption at 236  $\text{cm}^{-1}$  is due to  $\nu(\text{M}-\text{Py})$ .

A possible dimeric structure for

$[\text{Ni}(\text{CQM})(\text{Py})_3(\text{H}_2\text{O})]\text{PF}_6\text{H}_2\text{O}$  is shown in the structure [4.2] in which  $\text{CQM}^-$  bridges two Ni atoms through nitrogen and oxygen. The pyridine molecule occupies positions above and below the  $\text{CQM}^-$  plane of co-ordination and away from the bridge head methyl of  $\text{CQM}^-$  ligand and  $\text{H}_2\text{O}$  molecule occupies the remaining sites to complete the octahedral co-ordination of Ni(II).

Ni(II) complexes with N-Isopropylidene ethylene diamine Schiff base<sup>14</sup> :

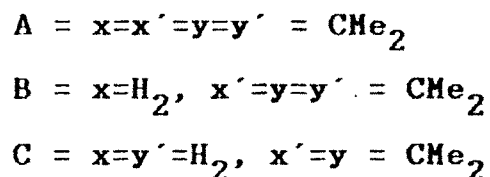
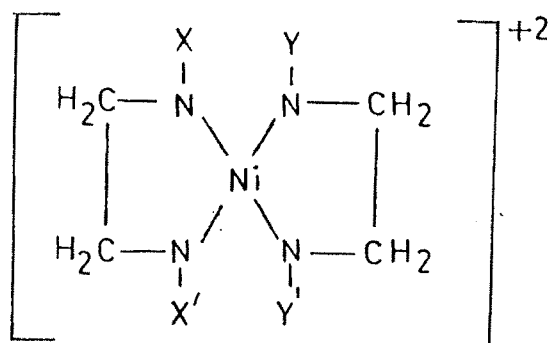
The reaction between the pre-formed di-imine and appropriate metal salt under anhydrous conditions gives co-ordination complexes of  $\alpha$ -di-imine. As aliphatic imines are very unstable and difficult to isolate, most of the complexes obtained are from aromatic di-amines.

## Preparation :

When trisethylene diamine nickel(II) perchlorate is dissolved in anhydrous acetone. From this we can isolate bis (NN' di-isopropylidene ethylene diamine) nickel(II) perchlorate (A). The reaction is fast in the presence of bases such as pyridine or ethylenediamine on heating or on exposure to ultraviolet light. The presence of traces of water retards the reaction.

The perchlorates (A) and (B) form bright yellow crystals which are sparingly soluble in cold water, alcohols, acetone. The perchlorates (C) form large orange crystals which are more soluble than other two perchlorates. All three perchlorates are diamagnetic in solid and in aqueous solution.

Perchlorate (A) is chemically very stable, it was unattacked by concentrated acids or alkalis and they are decomposed by powerful oxidising agents.

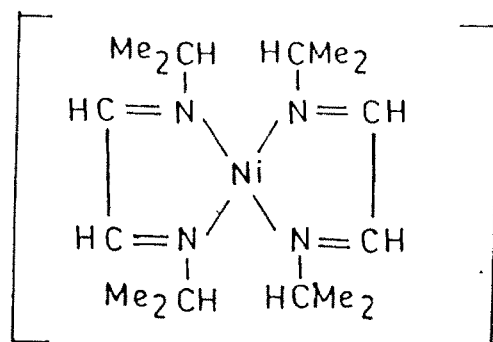


Diamagnetic four coordinate nickel(II) complexes are normally square planar<sup>15</sup>. The azomethine group C:N is also

planar in structure. The molecule (A) is required by these conditions to be co-planar, but a planar model, with standard co-valent radii, indicates that there would be considerable interference between the methyl groups of adjacent isopropylidene groups, which must be removed by the skewing of the molecule. The strain resulting from such distortions would be expected to decrease the stability of the molecule. This effect is probably responsible for the fact that (B) with three isopropylidene groups, is less stable than (C), which has only two, and consequently no strain.

Schiff bases are usually readily hydrolysed by water or by dilute acids and hence the resistance of these compounds is unusual.

The strain inherent in structure (A) would be removed by the tautomeric change to structure (D) in which the interference between the methyl groups is eliminated and the C:N groups are conjugated and endocyclic.



Similarly, Ni(II) and Cu(II) complexes are prepared by using 1,3-propane diamine, triethylenetetraamine isopropylene diamine, 1,2 diamine and acetone.



#### Visible and Ultra-Violet Absorption Spectra :

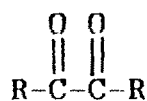
The visible spectra of (A), (B), (C), (D) are very similar, with a peak at 436 nm. The ultraviolet spectra of (B) and (C) are also similar, showing two peaks which are attributed to the imine groups conjugated through  $\pi$  bonding by the nickel. The conjugation is more efficient in the case of (A) which has four symmetrically arranged isopropylidene groups and in (A) the two peaks in the U.V.

#### Infrared Spectra :

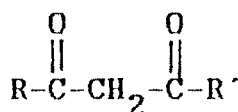
The I.R. spectra support the suggested structures for the Schiff bases of these compounds. All the three have absorption in the C:N stretching region and the relative intensity increases in the order (C)<(B)<(A) as the number of C:N group in the molecule increases. (B) and (C) show absorption in the  $\text{NH}_2$  stretching and deformation regions. In (B), with one  $-\text{NH}_2$  and three C:N groups the height of the  $\text{NH}_2$  deformation peak is less than that of the C:N stretching peak, with the relative heights reversed in (C) with two  $-\text{NH}_2$  and two C:N groups.

#### Diketones :

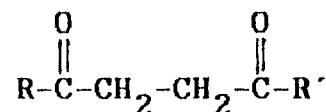
Diketones comprise a class of compounds characterised by the presence of two oxo groups. They are classified as 1,2 or  $\alpha$  (I), 1,3 or  $\beta$  (II), 1,4 or  $\gamma$  (III) diketones according to the position of the oxo groups.



(I)

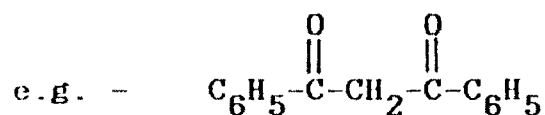


(II)



(III)

R and R' may be alkyl or aryl or acyclic group. 1,3 or  $\beta$  diketones are generally referred as diacyl methane derivatives.



If both the carbonyl groups are present in the ring system then such compounds are called cyclic diketones.

$\beta$ -Diketones :

$\beta$ -Diketones are 1,3 dicarbonyl compounds of the type

$$\begin{array}{c} \text{O} \quad \quad \text{O} \\ \parallel \quad \quad \parallel \\ \text{R}'-\text{C}-\text{CH}_2-\text{C}-\text{R} \end{array}$$
 . The methylene group is reactive methylene group. The methylene group is flanked by two carbonyl groups which are endowed with considerable reactivity, the hydrogen atom at C<sub>2</sub> becomes very reactive and take part in many reactions.

$\beta$ -diketones form cyanohydrins with HCN, oxime with NH<sub>2</sub>OH, hydrazones with hydrazine, with methyl iodide give methyl derivatives where both the hydrogen atoms at the methylene group are replaced by methyl group. These reactions proved saturated ketoester structure. However, reactions with

bromine and colouration with ferric chloride solution show unsaturation and enolic nature.



$\alpha$ -Diketones :

$\alpha$  Diketones are 1,2 dicarbonyl compounds of the type

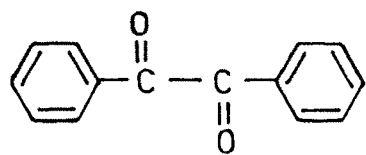
$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{R}-\text{C}-\text{C}-\text{R}' \end{array}$ . In aliphatic 1,2 diketones such as glyoxal, diacetyl there is appreciable interaction between the two keto groups because of trans coplaner configuration of the molecules.

In aromatic 1,2 diketones such as benzil there is little or no interaction between the keto groups of benzil owing to skew configuration. There is measurable conjugative interaction between the keto groups from benzil even in skew configuration.

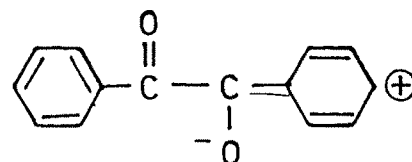
Benzil is reported to have skew configuration in which two benzoyl groups are not in the same plane but lie in the planes at right angles to each other. The absorbing units must act as individual benzoyl groups as shown in [5.1]. Absorption spectra of substituted benzils are very close to that of acetophenone.

Benzil shows absorption at 216  $m\mu$  which suggests that there is strong interaction between the two  $>\text{C}=\text{O}$  in benzil.

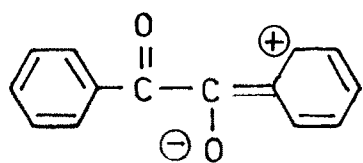
CHART-V



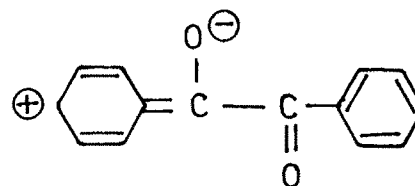
[I]



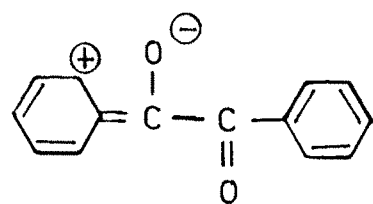
[II]



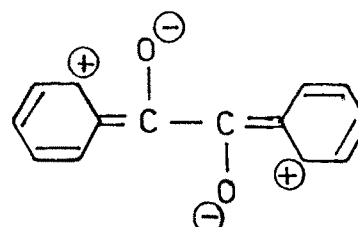
[III]



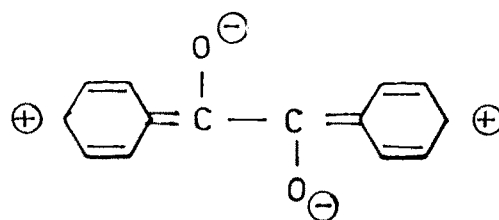
[IV]



[V]



[VI]



[5.1] Canonical forms of Benzil

FIG. 5.1

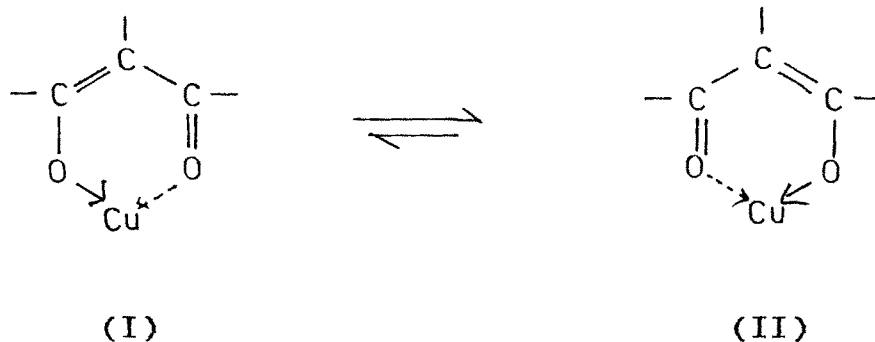
Benzoin absorbs at shorter wavelength 248  $m\mu$  with considerable reduction in the intensity as compared to benzil. This shows that there is conjugative interaction of the carbonyls in benzil.

If the dominant forces setting the shape of the molecule were superimposed then skew structure for benzil is arised.

Cu chelate compounds with various  $\beta$ -diketone ligands<sup>18</sup> :

Acetyl acetone complex :

The complete resonance between forms(I) and (II) leads to the modification of the character of both  $>C=O$  and  $-C-O$  links



As a result both take an intermediate double bond character. The two bands are of approximately equal intensity.

In hydrogen bonded chelate compounds of  $\beta$ -diketones, the ketone frequency is determined by the character of the adjacent double bond. In the metal chelate complexes, in which the metal is not co-linear with oxygen atoms other factors will operate.

### III) COMPLEXES OF DIKETONE :

#### Chelates of $\beta$ -diketone<sup>19</sup> :

Dipivaloyl methane was prepared by condensation of phenyl pivalate or methyl pivalate with pinacolone using NaCl or lithium amide. The crude product is converted to its Cu chelate by using cupric acetate in hot aqueous EtOH.

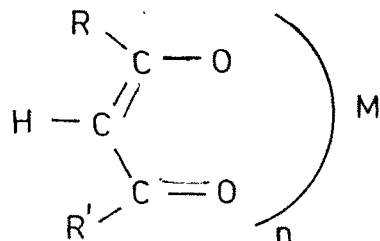
#### General methods for preparation :

1) An ethanol solution of the  $\beta$ -diketone was added to an aqueous solution containing metal chloride or metal sulphate and excess of sodium acetate. The metal chelate formed is removed by filtration.

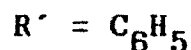
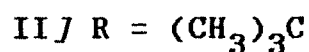
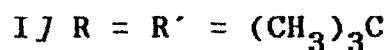
2) Toluene solution of  $\beta$ -diketone was heated under reflux with the metal for several days and residual metal was removed by filtration.

I/ Dipivaloyl methanato chelates are remarkably soluble in organic solvents such as benzene, pet. ether.

II/ Benzoyl pivaloylmethide are less soluble in hydrocarbon solvents.



Where,  $n$  = charge on metal ion



Bis (dipivaloyl methanato) cobalt(II) was prepared without difficulty but hydrocarbon solution of the compound is oxidised rapidly on exposure to air. The analogs of Fe(II) and Mn(II) are not obtained in pure form as they undergo oxidation.

Carbonyl complexes of rhodium(I) with  $\beta$ -diketones<sup>20</sup> :

Dicarbonyl  $\beta$ -diketonato rhodium complexes of the type  $[\text{Rh}(\text{CO})_2(\text{LL})]$  have been prepared [where LL=diketone].  $[\text{Rh}(\text{CO})_2(\text{LL})]$  reacts with  $\text{PPh}_3$  to give complexes of the type  $[\text{Rh}(\text{CO})(\text{LL})\text{L}']$  [where  $\text{L}' = \text{PPh}_3$ ] by the replacement of one of the CO groups by  $\text{PPh}_3$ .

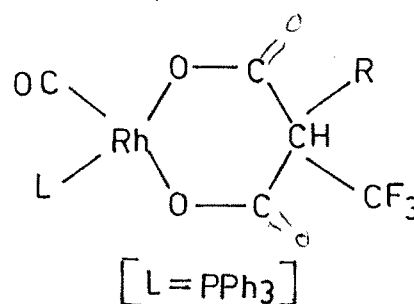
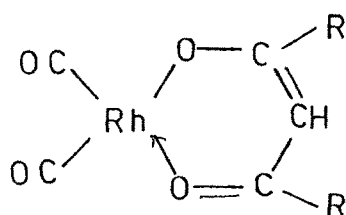


Preparation of  $[\text{Rh}(\text{CO})_2(\text{LL})]$  :

A solution of  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  (0.05 gm, 0.19 n mole) in dimethyl formamide 30 ml was refluxed with stirring for 30 minutes. The solution obtained is further treated with  $\beta$ -diketone (0.25 n mole). The mixture stirred for 15 min and cooled. On adding  $\text{H}_2\text{O}$  to the reaction mixture, solid complex separates out. It is filtered, washed, dried and recrystallised from  $\text{CH}_2\text{Cl}_2$  or pet.ether.

Preparation of  $[\text{Rh}(\text{CO})_2(\text{LL})\text{L}']$  :

To a solution of  $[\text{Rh}(\text{CO})_2\text{LL}]$  in dichloromethane  $\text{PPh}_3$  was added. On addition there is rapid evolution of CO occurred. The reaction mixture was stirred for 1 hr, concentrated and pet. ether added when solid was separated out.



Addition complexes of benzil with metal halides<sup>21</sup> :

Benzil forms complex with different metal halides such as tin chloride, titanium chloride and bromide in 1:1 and with antimony(V) chloride in 1:2 proportion. There is no effect of change in the concentration of the reactant, reaction time, reaction temperature, solvent on the stoichiometry of the complexes. There is no evolution of HCl or HBr during the formation of complexes.

The presence of two benzene rings adjacent to carbonyl groups acts as electron sinks, thereby reducing their donor power. Furthermore 1:1 adducts may be 5 membered ring compounds and therefore not expected to be very stable complexes.



Metal ion control in the synthesis of octahedral nickel(II) complexes of  $\alpha$ -Diketo bis (3 aminopropylimines)<sup>22</sup> :

The reaction of  $\alpha$ -diketones with 1,3 diamino propane in the presence of nickel(II) salts yields a new family of chelate compounds. The new ligands 2,3 butane dione bis (3 aminopropyl imine), 2,3 pentanedione bis (3 aminopropyl imine) and 1,2 cyclohexanedione bis (3 aminopropyl imine) could not be prepared in the absence of the metal ion.

More obvious route of chelate formation is the reaction of a diamine with an  $\alpha$ -diketone in the presence of a metal ion.

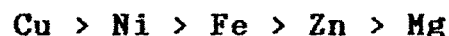
#### IV] PROPERTIES AND STABILITY OF METAL IONS<sup>23</sup> :

Following conditions must be fulfilled for the formation of complex, only then the given molecule may react with metal ion to form complex.

- 1) An appropriate acidic and basic grouping must be present in the molecule.
- 2) There should be minimum steric hinderance due to other substituents on the metal ion to the co-ordinating groups.
- 3) Ionic forces which are related to both charge and radius of metal ion.
- 4) The relative tendencies of various metals to form homo-polar bonds with electron donors.

Many attempts are made to list the metal cations on the

basis of their ability to co-ordinate with one or two specific ligands. Pfeiffer, Thielert and Glaser<sup>23</sup> obtained the following order of stability of the complexes of the following metals



1) Stability on the basis of presence of 3-d electrons :

Irving and Williams have correlated their data by plotting the stability constants Vs atomic number of the metals. The order  $\text{Mn} < \text{Fe} < \text{Co} < \text{Ni} < \text{Cu} < \text{Zn}$  obtained indicates the correlation between stability and number of 3d electrons in these transition metals and also their ability to form homopolar bonds.

2) Stability on the basis of formation constant of metal chelates and second ionisation potential :

Martell and Calvin<sup>23</sup> proposed a general relationship between formation constant of metal chelates and second ionization potential of metal ions. Since the ionization of Cu, Ni and Co involves the removal of an electron from a 'd' orbital. The energy released in the replacement of that electron would vary in the order  $\text{Cu} > \text{Ni} > \text{Co}$  which is the order of stability constants observed. Calvin and Melchior suggested that a 'd' orbital is involved in the binding of chelates of this type by these metals.

### 3) Localisation of negative charge :

Ives and Riley<sup>24</sup> have suggested that the factor which increases the localisation of the negative charge increases the stability of the complex. This is due to the fact that increase in the localisation of negative charge in the coordinating ligands makes the electrons more readily available and thus increases the ability of a base to coordinate. The first attempt in this direction was made by Lorrsson.

### 4) Basicity of the metal :

Mellor and Maley<sup>25,26</sup> have pointed out that the stability of the complexes of bivalent metal ions follows the order, Pd > Cu > Ni > Pb > Co > Zn > Cd > Fe > Mn > Mg irrespective of the nature of the ligands involved.

Mellor and Maley concluded that Pd, Cu which are capable of forming strong  $dsp^2$  bonds (square planer) formed the strongest chelates. The stability of metal complexes seemed to be decreased with increasing basicity of metal ion involved.

The weakly basic Cu and Pd forming the strongest metal complex and the most strongly basic Mg metal forming the weakest metal complex.

This clearly indicates the strength of the bonding in these metal chelates depends on the ability of the metal to

form homopolar bonds. The metals which form the strongest homopolar bonds form the most stable chelates.

The homopolar component of the metal donor bond is greater for nitrogen because of the greater basicity of its unshared pair of electrons and hence the greater tendency for this pair of electrons to enter into homopolar bonding.

Thus, the dependence of nitrogen bonding on the second ionization potential is greater than is the bonding of oxygen. The polar component of these bonds is greater for oxygen than for nitrogen.

#### V) FACTORS GOVERNING STABILITY OF COMPLEXES :

The important factors which affect stability are summarised below :

##### 1) Resonance in the chelate :

Calvin and Wilson<sup>28</sup> showed that resonance might affect the formation and stability of a chelate. They considered the formation of Cu complexes of acetyl acetone and other  $\beta$ -diketones of substituted salicylaldehydes and 2-hydroxy 1-naphthaldehyde. All gave the same chelated stable rings.

##### 2) Nature of the donor atom :

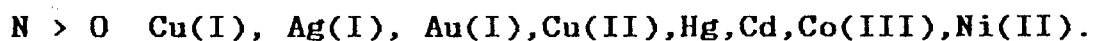
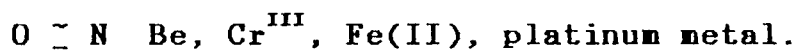
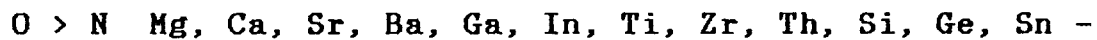
Sidgwick<sup>27</sup> has given an interesting discussion of the tendencies of various donor groups to form complexes with metals. Halogens, which act as donor only in the form of

their negative ions cannot form chelates. Similarly  $H_2O$ ,  $H_2S$ ,  $NH_3$  are important complex formers but cannot contribute to the formation of a chelate ring. The most important chelating donors are primary amine, secondary amine, tertiary amine, oxime and imine groups.

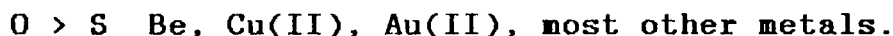
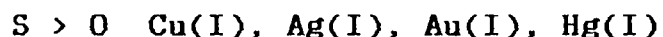
According to Sidgwick, oxygen and nitrogen may be considered quite similar in their affinities for metal ions, both form very strong chelates or complexes with a wide variety of metals. Tendency for co-ordination diminishes for both elements with increasing substitution :



Sidgwick divided the metals into three categories depending on their relative tendencies for combination with oxygen or nitrogen as follows,



Although S & O bear a formal resemblance to each other in many ways. The tendencies for chelate formation are not same. Sidgwick has given following comparison.



Effect of substitution is opposite to that observed for oxygen and nitrogen.



The greater the substitution the greater donor power of sulfur atom.

### 3) Substitution effect :

Substitution of a group in the chelating agent may affect the stability of metal chelate in one of the following ways.

1) It may influence the basicity of the donor atom or may interfere with or enhance the resonance of the chelating ring.

2) Substituted group, due to its steric effect<sup>28-31</sup> prevent the ligand ion or molecule from acquiring the orientation about the central metal ion most favourable for chelation.

### 4) Steric hindrance :

Steric effect plays an important role in deciding the stability of complex. If the steric interference is greater, greater will be the size of the ligand molecule and smaller the radius of the cation. Among the transition metals the radii of bivalent ions are much the same and hence the varying geometry of the ligand is of predominant importance. This will however, no longer be true, when ions of very different sizes are considered. Steric effects affect the

mode of packing of ligands round a central ion due to the following factors.

- 1) The size of the central ion
- 2) Structural modifications in the ligand
- 3) The orbitals available (since these will impose a particular geometric arrangement of ligands).

5) The basicity of the ligand :

The stability of complex increases with increase in the basicity of the ligand. In case of transition metal ions tending to form covalent bonds with the donor atoms, the ligands with higher basicity, form stronger bonds with metal ion than oxygen. The ligands with low pK values are not good co-ordinating agents and are less stable. Ligands with high pK values like 8-hydroxy quinoline do form chelate rings with metal ions.

6) The size of the chelate ring :

Formation of five and six membered rings is the most favoured because such rings are free from strain. According to Bayer strain theory, the most stable rings are six membered rings with two double bonds and five membered ring with no double bond. A six membered ring with one double bond will be more stable than a five membered ring with one double bond and considerably stronger than six membered ring with no double bond.

## 7) Temperature :

Variation in temperatures influences the formation constants of metal complexes. The thermodynamic parameters predict that whether the reaction is endothermic or exothermic. Enthalpies give information about the strength of the metal ligand bonds while entropies give information about the structural aspects like chelate effect and steric effect.

Thus in general, the stabilities of metal complexes increase with high charge on the central ion, small radius of the central ion, and a large electron affinity of metal ion.

VI) RESUME OF TRANSITION METAL  $\alpha$ -DIONE COMPLEXES :

The highest occupied orbitals and lowest unoccupied orbitals on a metal ion overlap with the group orbitals on a ligand having the appropriate symmetry and energy. The strength of such a bond depends on the extent of mutual polarisation of the metal ion and the ligand. When more than one group on the same ligand i.e. multidentate ligand participates in metal-ligand bonding, a metal containing heterocyclic ring is formed. The complexes containing a metalloheterocyclic ring have in general higher thermodynamic stability than the complexes containing the corresponding monodentate ligand. An enormous interest has, therefore, been created in the multidentate ligands. Among the bidentate ligands the chemistry of  $\beta$ -diones<sup>32-37</sup>, salicylaldimines<sup>38-42</sup> diimines<sup>43-45</sup> is well developed. The chemistry of  $\alpha$ -diones,



however not fully recognised.

Nature of metal  $\alpha$ -dione bond :

The enolisation constant of acyclic  $\alpha$ -diones is generally lower as compared to that of acyclic  $\beta$ -diones.<sup>46</sup> Therefore, one envisages that  $\alpha$  dione will prefer to act as a neutral ligand. Each carbonyl group will act as a two electron donor.

The non bonding orbitals on oxygen in cis- $\alpha$ -diones will participate in the formation of metallocycloheterocyclic five membered ring, the C=O groups in trans  $\alpha$  diones will behave as separate monodentate ligands. The bonding ability of C=O group will allow  $\alpha$ -diones to substitute other ligands. There will be no change in the oxidation state of metal ion during this type of substitution reaction.

When the softness of ligands originally present in a complex is higher than that of  $\alpha$ -dione, there is a possibility of an increase in the oxidation state of metal ion during a reaction with  $\alpha$ -dione. In this type of oxidative addition reaction the C=O group will be reduced to C-O. Thus, 1,2 dione will be converted to 1-ene-1,2 diolate ion.

$\alpha$ -dione as a four electron donor :

In the complex,  $\alpha$ -dione behaves as a four electron donor. In the reactions trans  $\alpha$ -dione isomerises to Cis- $\alpha$ -dione. The participation of C=O groups of  $\alpha$ -dione in metal-ligand bonding<sup>47</sup> is reflected in the I.R. spectra. A large

negative shift ( $C-O-70\text{ cm}^{-1}$ ) in  $\nu C=O$  group has been observed in the I.R. spectra of the complexes.

The ligands containing one  $>C=O$  group behave as the two electron donors. When each  $C=O$  group of  $\alpha$ -dione acts as a separate monodentate group, it also behaves as a two electron donor. The I.R. spectra of these complexes display a strong band in the region  $1645-1590\text{ cm}^{-1}$  associated with the coordinated  $C=O$  group<sup>48</sup>.

Ligation of  $\alpha$ -dione as  $\alpha$  diolate :

When metal (o) complexes contain mainly  $\sigma$  donor ligands such as substituted phosphine and isocyanides the metal atom acts as a sink for electrons.<sup>49</sup> These complexes react with other ligands in such a way that the electron density on the metal atom releases to the incoming ligand. In case, the incoming ligand is not good  $\pi$  acceptor, there is a possibility of the reduction of the ligand with a simultaneous oxidation of the metal ion. Since the  $C=O$  group is not a good  $\pi$  acceptor, the  $\alpha$ -diones are expected to be reduced to the  $\alpha$  diolates under these conditions.

The bonding of  $C=O$  group as a  $\pi$  ligand :

The overlap of filled ligand  $\pi$  orbitals on  $C=O$  group with the empty metal orbitals is theoretically possible. The complexes containing this type of overlap with  $\pi$  orbitals on  $C=N$  group are known<sup>50-55</sup>.

It has been shown that, in hydrogen bonded chelate compounds of  $\beta$ -diketones the C=O frequency is determined almost wholly by the character of the adjacent double bond. In the case of metal chelate compounds, however, in which the metal cannot be colinear with the oxygen atoms, other factors will operate. Thus the O-O distance might change with alterations in the covalent or ionic radii of the metal atoms and they should also depend to some extent on the configuration of the metal atom.<sup>53</sup>

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