CHAPTER I
INTRODUCTION
The beginning of the chemistry of the complex compounds was marked by a chance observation made by Tassaert (1) who got orange crystals having a composition of CoCl₂·6NH₃ in an attempt to precipitate cobalt hydroxide by the addition of ammonia to cobalt chloride solution. The valence theories, that existed then, were found to be quite inadequate to account for the formation of this and such other compounds soon discovered and hence they came to be known as "Complex Compounds". The first logical attempt to explain metal ammonia compounds was made by Berzilius (2). This was further developed by Graham (3), Claus (4), Olding (5), Blomstrand (6) and Jorgensen (7) but their theories are only of historical importance.

Complete credit must be given to Werner not only for advancing a correct explanation for the characteristics of these compounds but also for producing a theory which anticipated later developments in structural chemistry and was sufficiently flexible to accommodate them without essential alteration. In this immortal and revolutionary paper "Contribution to the Theory of Affinity and Valence" (6) published in 1891 Werner suggested the existence of two types of valencies, the principal or "primary" and "auxiliary" or secondary. The fundamental postulates of his coordination theory may be best stated in his own words (6): "Even when, to judge by the valence number, the combining power of certain atoms is exhausted, they still possess in most cases the power of participating further in the construction of complex molecules with the formation of very definite atomic linkages. The possibility of this action is to be
traced back to the fact that, besides the affinity bonds designated as principal valencies, still other bonds on the atoms, called auxiliary valencies, may be called into action.

The auxiliary valencies were originally considered to be different from the principal valencies; since they did not allow ionisation while the principal valencies did. But, according to Werner, there is a connection between them, for if an atom forms strong primary bonds with certain other atoms, it usually forms strong secondary bonds with them too. It is also possible for a primary valency to be converted into a secondary one. Werner also observed that the secondary valencies of an atom must always be satisfied. If a molecule from the secondary valency is driven out, its place is taken either by positive or negative ions or neutral groups.

The number of groups, neutral molecules or oppositely charged ions, held around a central atom in the "first sphere of attraction" or coordinated by auxiliary valencies is characteristic of the central atom, and is referred to as coordination number. The coordination number is usually six, sometimes four and rarely two or even eight depending on the central atom. The number of groups thus held by the auxiliary valencies are in a characteristic spatial arrangement. The compounds formed in this way are called complex or coordination compounds and may be non-ionic, a cation or an anion depending on the charges carried by the central atom and the coordinated groups. Thus, in the case of hexammine-platinic chloride, six ammonium molecules are coordinated about
the platinic ion, forming a new complex cation \( \text{Pt(NH}_3\text{)}_6^{4+} \), the chlorine being in the "second sphere of attraction". The coordination of negative ion is exemplified by the ferrocyanide anion \( \text{Fe(CN)}_6^{4-} \) in which six \( \text{CN}^- \) ions are coordinated about a central ferrous ion, forming thereby, a complex anion with a nett negative charge of four units.

These views were further supported by Werner and Nolati's (10) conductivity studies. This was possibly the first use of a physico-chemical method in the study of complexes. Evidence for the spatial arrangements became available later by the resolution of optical isomers (11), X-ray crystal analysis (12), measurements of dipole (13) etc.

The development of electronic theory of valency by Lewis (14) and Kossel (15) resulted in the final acceptance of the Werner's concepts of primary and secondary valencies. The primary or principal valency became identified with electrovalency or covalency and the auxiliary or secondary valency with coordinate covalency.

Sidgwick (16) was the first to explain the coordination in terms of electronic theory of valency. He postulated that all ions or molecules capable of being coordinated to the metallic atoms must possess at least one "lone pair" of electrons. A study of the polynuclear complex compounds showed that the number of coordinate links which may be formed by any one coordinating group is never greater than the number of "lone pairs" available. Coordinate
link is a special case of semipolar bond, the coordinating group acting as a donor, and the central atom as acceptor. It appears that the formation of most stable complex compounds corresponds, in certain cases, to the acquisition by the central atom of the effective atomic number of the next higher inert gas. This concept has been very successful in explaining the molecular formulae of the carboxylics and the nitrosyls. To explain many exceptions, it has been suggested that an additional important tendency is towards the production of symmetrical structures (planar, tetrahedral, octahedral or cubic) irrespective of the actual number of electrons involved.

The above ideas have been supported in the modern times by the following three theories:

(1) **Electrostatic Theory (or Crystal Field Theory)**:

The electrostatic theory was first put forward by Kossel (17). Works of Cartledge (18), Fajans (19), Van Arkel and de Boer (20) and Carrick (21) further developed this theory. The present modified form of the theory is due to further improvements made by the contributions of Schlapp and Penny (22) and van Vleck (23).

In this theory an attempt has been made to treat the complex, in a semiquantitative way as electrostatic attraction between the metal ion and oppositely charged ions, or dipolar molecules like water and ammonia. But a more reasonable agreement with the facts has been obtained by taking into account polarisation
or deformation of the ions due to the electrostatic field.

This concept has been extensively applied to explain the remarkable colour and magnetic changes associated with complex formation. In the transition metal ions, the inner d-orbital is more or less incompletely filled up with the electrons; the ground state of the d-shell is described by the Hund's rule of maximum multiplicity which states that all the unfilled d-levels must be first filled singly before spin-pairing will take place. These are referred to as the degenerate d-electrons. During coordination, the anions or cations set up a strong electrostatic or crystalline field and the normally degenerate d-levels are split up into sub-levels of lower or higher energy. The sub-levels of lower energy are now first filled by the electrons. Thus the unpaired electrons may get paired and a paramagnetic cation may be converted into a strikingly diamagnetic one. The charges in the electron cloud may also affect the colour.

This theory takes no cognizance of directed covalent or electron-pair bonds between the ligands and central atom, and hence fails to account for (i) the formation of the complexes involving π-bonds, and (ii) the resolution of asymmetric complexes into their optically active modifications.

As the splitting of the d-orbitals may also result by covalent bond formation, the crystal field theory has been
combined with the molecular orbital theory by some workers under the name of "ligand field theory" (24) for better interpretation of facts.

(2) **Atomic Orbital or Valency Bond Theory**

In principle this theory pictures the electron pair bond as arising when two atoms are brought together in a manner such that their approximate atomic orbitals interact. Such interpretation will lead to bonding if (a) the electrons in the two orbitals have opposite spin so that electron pairing may result, and (b) the orbitals of the two bonding electrons overlap. The extent of overlap frequently determines the covalent bond strength. Since the electron cloud is in space, the concept of directed valence follows. A modification of this theory is met with in Pauling's (25) concept of hybridisation of bond orbitals. He postulated that the resonance between the outer orbital differing but little in energy from one another, now equivalent "hybridised orbitals" are forced directed symmetrically in space. For the elements of short periods, except in some forcing circumstances, it will mostly $sp^3$ hybridisation. But, in transition elements, the lower $d$-electrons differ little in energy from the higher $s$ and $p$ electrons, and hexacoordinate octahedral structure becomes possible by $d^2sp^3$ hybridisation.

These concepts can be illustrated by taking cobaltic ion. Cobalt is $3d^7 4s^2$ and cobaltic ion is $3d^6$. By Hund's rule of maximum multiplicity, only the lowest orbit is doubly filled
while the remaining 4d orbitals are singly filled by unpaired electron, so that cobaltic ion is paramagnetic. In hexammine cobaltic ion six ammonia molecules supply six pairs of electrons, and to get six equivalent orbitals for these electrons, a rearrangement of electrons and level occurs. The electrons occupying orbitals singly are paired up, thus freeing two of the 3d levels for the hybridisation process. The combination of two d, one s and three p orbitals give six equivalent hybrid bonds resulting in d^2sp^3 hybridisation. Since all the electrons are paired the complex is diamagnetic.

Kimball (26) has carried out a comprehensive treatment of coordination involving different codes of hybridisation and has shown relationship between coordination number and configuration.

This theory, thus, accounts for spatial arrangement in complexes and can account qualitatively for magnetic and other properties. It suffers from a lack of precision in quantitative interpretation, and, hence it has received certain criticisms (27).

(3) Molecular Orbital Theory:

The atomic orbital theory assumes that a new set of directed orbitals is obtained through the hybridisation of atomic orbitals and the bond between the group arises from the overlap of one of the orbitals of the set and the bonding orbital of the coordinating ligand. In short, a highly localised bond is formed.
involving only a bonding function from each of the two groups which are joined. In the molecular orbital method (28) suitable localised orbitals for the molecule as a whole can be obtained by a combination of approximate atomic functions. Addition of two \( \sigma \)-orbitals functions gives a molecular orbital which concentrates the electronic charge between the two nuclei and is symmetrical around the internuclear axis. Such an orbital is known as \( \sigma \)-bonding orbital. Subtraction of two \( \sigma \)-functions give an orbital which is also symmetrical around the internuclear axis, but concentrates the charge away from the space between the two nuclei. This is known as \( \sigma \)-antibonding orbital. In contrast too-\( \sigma \)-bonds, the combination of two \( p \) orbitals gives a molecular bonding orbital which results in concentration of charge in ribbon shaped streamer above and below the internuclear axis. This type of orbital is not symmetrical around a bond axis and represents a component of angular momentum. It is known as a \( \pi \)-orbital. Finally, if the electron in an atom is not disturbed seriously by the presence of the second nucleus, the orbital is termed non-bonding.

This theory has been applied to coordination compounds by Van Vleck (29). According to him the ligand supplies the bonding electrons, and the \( d \) electrons originally present in the metal ion are accommodated in the non-bonding \( d \)-orbitals and the antibonding molecular orbitals. This corresponds to the splitting of \( d \)-orbitals of the crystal field theory. The energy separation of the nonbonding
d-orbitals as well as the energy required for the pairing of the originally unpaired electrons, determines the formation of electron pairs in the complex.

The molecular orbital theory, though complicated, is the most successful approach towards the experimental facts and is capable of offering satisfactory explanations for the various properties of the complexes, such as, chemical, stereochemical, optical and magnetic, even those of the usual complexes like metal carbonyls and metal nitrosyls.

Classification of Complex Compounds:-

The complex compounds can roughly be classified as follows:-

(1) **Complex Salts** - These are composed of complex ions and belong to the typical ionic compounds. The linkages between the particles comprising the complex ion are electron pair bonds in many cases. The complex salts may further be classified as follows:-

(a) **Ion-ion Complexes** - These are produced from ions. The bonding can be either ionic, as in (SiF₆)²⁻ or atomic as in [Fe(CN)₆]⁴⁻.

(b) **Ion-dipole Complexes** - These are formed by the union of ion and dipole molecules (eg. water, ammonia). Bonding can either be electrostatic as in metallic hydrates eg. [Mg(OH₂)₆]²⁺ or electron pair as in the ammoniates of trivalent cobalt, [Co(NH₃)₆]³⁺.

(c) **Ion-polarolar Complexes** - The polyhalides, such as KI₃ belong to this group, at least formally. The bonding can be based on electrostatic polarisation and on atomic bonding.
(2) Atomic (or element) complexes—They can be regarded as consisting of atom around which molecules are coordinated. It is mainly the atomic bonds, in addition to Vander Waal's forces, which produce the coherence. Metal carbonyls and nitrosyls belong to this group.

(3) Molecular compounds—These are complexes of molecules. The molecular compounds formed by Van der Waal's forces which dissociate readily and also stable aggregates which can form unsaturated molecules belong to this class. "Clathrate" or cage compounds exemplified by hydroquinone compounds of type \((\text{C}_6\text{H}_4\text{O}_2)_3\cdot\text{X}\) \((\text{X}=\text{HCl, HBr, H}_2\text{O, CH}_3\text{OH, }\text{SO}_2\text{H, }\text{CN etc.})\) can be included in this class.

Two limiting types of molecular compounds, which exist in solution, have been recognised: (i) Those compounds which are reversibly dissociated into their components in the solid phase or in solution and, therefore, have the constituents loosely linked. These are termed "normal complexes" by Biltz (30). Potassium cadmium cyanide which dissociates in the following manner belongs to this class.

\[
\text{K}_2\text{Cd(CN)}_4 \rightleftharpoons 2\text{KCN} + \text{Cd(CN)}_2
\]

\[
2\text{K}^+ + [\text{Cd(CN)}_4]^2- \rightleftharpoons 2\text{K}^+ + 2\text{CN}^- \quad \text{Cd}^{2+} + 2\text{CN}^-
\]

(2) And those which afford no reversible dissociation and in which the coordinate linkage is indistinguishable in the strength and directional properties from a normal covalency. This is exemplified
by hexamine cobaltic ion \([\text{Co(NH}_3\text{)}_6]^{3+}\) and the ferrocyanide anion \([\text{Fe(CN)}_6]^{4-}\). Ray and Dhar (31) observed that the paramagnetic central ion suffers profound alteration in magnetic properties during the formation of such complex compounds. This type of alteration is possible only when there is a coupling of unpaired electrons in the atom. Such complexes which involve the coupling of electrons in the inner level are termed "Penetration Complexes," whereas those of the former type in which the bonding occurs outside the inner d-level are known as "Associated Complexes".

(4) **Auto complexes**—The heavy metals have a pronounced tendency to coordinate with the halogens to form complex halogen-anions in the simple halides themselves. This is indicated by the anomalous colours of the substances, which may be due to auto complex formation, e.g., \(\text{Cu(CuBr}_3\) or \(\text{Cu(CuBr}_2\) which show black colour. Another case of auto complex formation involves cobalt chloride, \(\text{CoCl}_2\). The anhydrous salt and its concentrated solutions are blue due to the presence of \((\text{CoCl}_4)^{2-}\) anion. The hydrate and its solutions are, however, cherry red or pink in colour because of the cation \([\text{Co(Hg)}_6]^{2+}\).

(5) **Complexes formed by hydrogen bonding**—Under certain conditions a hydrogen atom is attracted by rather strong forces to two atoms, instead of only one, so that it may be considered as a bond between them. This is known as "hydrogen bond". Only the most electronegative atoms like F, O, N, Cl should form hydrogen bonds and the strength of the bond should increase with
the increase in electronegativity of the two bond atoms. The 
nature of the forces responsible for the hydrogen bond are still 
not completely understood. Davies (32) has suggested that the 
forces are largely Vander Waal's forces on which valency forces 
are superimposed, thereby strengthening the bond. Thus, the 
bonding of water molecules to anions in the formation of 
hydrated cations may occur by means of hydrogen bonds as in the 
sulphate ions.

(6) **Super complexes**— From the studies in dialysis of complex 
ions in presence of various other ions, Brintzinger (33) reached 
to general conclusion that the species generally regarded as 
complex, such as \( [\text{Co(NH}_3\text{)}_6]^{3+} \) and \( [\text{Co(NH}_3\text{)}_5\text{Cl}]^{2+} \) are in the 
presence of other ions further complexed to form two shelled 
complexes as \( ([\text{Co(NH}_3\text{)}_6]^{3+}[\text{W}_4]^\text{2-}) \) and \( ([\text{Co(NH}_3\text{)}_5\text{Cl}]^{2+}[\text{SO}_4]^\text{2-}) \). 
Such complex compounds are termed "Super Complexes". Their 
existence can best be considered as an electrostatic phenomenon, 
probably more comparable to the Debye-Hückel ionic atmosphere 
than the true coordination compounds.

(7) **Polynuclear complexes**— Complexes containing more than 
one central atom are known as "Polynuclear Complexes". The 
anions of pyro-acids, \( \text{S}_2\text{O}_7^\text{2-} \), \( \text{Cr}_2\text{O}_7^\text{2-} \), \( \text{P}_2\text{O}_7^\text{3-} \) furnish 
simplest examples of this type.

(8) **Chelate and inner complexes**— Cyclic structure resulting from 
the union of central atom with two or more donor groups of a sin-
gle molecule or ion is termed "Chelate Compound" or "metal chelate"
and the donor is known as "chelating agent". The term "chelate" was first proposed by Morgan and Drew (31). Chelates have exceptionally high stability and, in many cases, have remarkable and valuable properties. The electron pair bonds formed between the electron-accepting metal and the electron donating complexing or chelating agent may be "essentially ionic" or "essentially covalent" depending on the metal donor atoms involved. Since many organic molecules have more than two positions through which covalent and coordinate covalent bonds with the metal may be formed, the terms unidentate, bidentate, tridentate, quadridentate etc., were proposed by Morgan to denote complexes formed with molecules or ions containing one, two, three, four etc. donor groups respectively. Obviously, complexes with unidentate substances would not involve chelation.

The coordination number of the metal may be taken as a guide for the determination of the number of molecules or ions of the complexing agent that will be bound to a single metal ion. A metal of coordination number four, for example, will bind two bidentate molecules or residues, while a hexacovalent metal would be capable of holding three bidentate groups or two tridentate groups.

It is worth mentioning that a given chelating agent would not always form the same polydentate structure. Thus according to Hartell and Calvin (35), a chelating agent capable of functioning as semidentate with metals of coordination number six would necessarily be quadridentate with a tetracoordinate metal.
A number of amino acid cyclic complexes (cooper glycinate) were reported by Ley (26) in 1924. He called these as inner complex salts. The term "inner" indicated ring formation, "complex" indicated secondary or coordinate bonds and "salt" was used to denote the primary bond formed between the metal and the negative carboxyl group. The inner complexes have characterised themselves as a special case of chelate formation because of certain properties i.e., they (i) produce colours unlike the normal salts of the metal, (ii) are insoluble in water but soluble in organic solvents and (iii) have very low dissociation. The most common inner complexes are formed with bidentate chelating agents having one replaceable hydrogen and metals, the coordination numbers of which are exactly twice the principal valencies. Common examples are the amino acid salts, the acetyl acetonate and β-dioxime salts. Ley restricted the inner complexes to non-ionic substances only and found support from Diehl (37) and others. Liebhafsky (38) questioned this restriction. It is now possible to interpret that electrolytic dissociation caused by groups not involved in complex formation would not disqualify the complex formed being classified as an inner complex. Thus, it is possible to have inner complex salts, inner complex anions, and inner complex cations. The inner complex anions and cations are sometimes called "inner complex salts of the second order".
Factors affecting the formation and stability of complex compounds

The important factors governing the formation and stability of complex ion and complex compounds may be summarised as follows.

1) Nature of the Metal Ion: This is of primary importance. The most stable complexes result from the cations derived from the transition metals and the metals immediately following the transition elements. The stability of the complex compound is largely related to electronic configuration and depends upon the type of bonding involved. If the bonding is essentially of an ion-dipole character, then we must expect that strongest bonds will be formed by the smallest ions with greater ionic charges since they produce electrostatic fields of greatest intensity.

Mellor and Maley (40) observed that the stability seemed to decrease with increasing basicity of the metal. This suggests that the strength of the binding in the chelates depends on the ability of the metal to form homopolar bonds. The most stable chelates will be formed by the metals forming strongest homopolar bonds.

Very strong donor-acceptor bonds, as in the transitional metals, can be formed when the suitable orbitals are available to receive the electrons. According to Irving and Williams (41) strongest bonds would be formed when the donated electrons are accepted most readily. Thus the second ionisation potential is the quantitative measure of the "willingness" of the bivalent ions to accept electrons.
(2) **Nature of the Coordinating Group:** Almost any group (ion or molecule) having an atom with an unshared electron pair may act as a coordinating agent, although there is a marked difference in the ease with which such groups attach and in the stabilities of the resulting products. In general, a more strongly coordinating group will replace a more weakly coordinating one to produce a product of greater stability. The characteristics of the ligand which are generally recognised as influencing the stability of the complexes are (i) proton affinity of the ligand, (ii) the number of metal chelate rings per ligand, (iii) the size of the chelate ring, (iv) the steric effects, (v) the possibility of the metal ligand bond participating in the resonating structures of the chelate molecule and (vi) the ligand atom.

The ligand behaves as a base and this is because the role played by the hydrogen ion and the metal ions is essentially the same; so that a ligand, with a larger affinity for proton or in other words, strongly basic may well show the same behaviour towards the metal ions. Riley (42) suggested that any factor which increases localisation of the negative charge in the coordinating ligand makes the electron more readily available and thus increases the ability of the base to coordinate. Larson (43) attempted to establish a linear relationship between the basic strength of a ligand and its complex forming ability. The validity of this relationship was questioned by later workers (44, 45) but now it seems well established that when systems
of sufficient structural similarity are compared, a linear relationship between \( pK_{\text{complex}} \) and \( pK_{\text{base}} \) is obtained. This relationship is supported by the work of Bruehlman and Verhoek (46) on silver-amine complexes. Further work on amines (47), amino-carboxylates (48) and diketones (49) also suggest the same relationship.

Chelation or ring formation is also one of the very important factor affecting the stability. Thus ethylene diamine complex of nickel is stable in solution at high dilution, but the analogous methylamine complex dissociates completely to precipitate nickel hydroxide under the same conditions (50).

The stability of chelate is also affected by the number of rings within a particular chelate. The greater the number of the rings in the chelate, the greater is the stability. As a result of quantitative studies on stability constants Calvin and Bailes (51) proved this.

The size of the chelate ring has also a marked effect on the stability of chelates. No examples of three membered chelate rings are known and four membered rings are known only for some carbonate- and polynuclear hydroxo- and halogeno-complexes. Classical work of Ley (36) on amino acid complexes has shown that chelates with five and six membered rings are most stable. Mann (52) resolved tetrachloro-1:2:3-triamino platinate (IV) chelates and established that saturated five membered rings are most stable. Schwarzenbach et. al. (53), have extensively studied the stability
constants of complexes of EDTA and of polymethylene diamines and related ligands and observed that five membered rings are most stable. Silver (I) appears to be an exception. The presence of two or more double bonds in a six membered ring make it most stable. Rings of seven or more members are comparatively uncommon, but are well established.

The substitution of a group in a ligand also has a pronounced effect on its complexing properties. This may affect the tendency for chelation in one of the two ways - (i) it may influence the acidity of the ligand or may interfere with or enhance the resonance of the chelate ring, or (ii) the addition of groups on the ligand may, by purely steric effects, prevent the ligand ions or molecules from acquiring the orientation about the central metal ion most favourable for chelations.

Recent determinations (54) of the formation constants of various metal complexes with chelating ligands including those with sexidentate character established that the formation of heterocyclic rings in complexes with polydentate rings enhance the stability of the complexes. The stability, as a rule, goes on increasing with the number of functioning groups available for coordination. This is known as "chelate effect" (55). The unusual stability of EDTA complexes of even weakly coordinating metals like those of the alkaline earth is a typical illustration of this effect. This increased stability of chelates is
attributed, by Irving and Williams (56), to the reduction of the repulsive forces between the neighbouring ligands as compared to those in complexes with monodentate groups.

(3) **Nature of the ion outside the coordinating group:** The external ions have a tendency to enter the coordination sphere and thus affect the thermal stabilities of the coordination compounds. $\text{CN}^-$, $\text{SCN}^-$, $\text{Cl}^-$, $\text{Br}^-$, $\text{NO}_3^-$ and $\text{C}_2\text{O}_4^-$ have a pronounced tendency to do this and sometimes do so at the expense of materials already coordinated with the metal. Ions such as $\text{NO}_3^-$, $\text{ClO}_4^-$ show little or no such tendency. Complete absence of coordination reactions is generally assured in perchlorate solution, which are commonly used when no complexing is desired.

(4) **Steric effects:** Steric factors also play an important role in the formation of numerous complexes. The most common type of the steric hindrance is the one in which the clashing of the groups on two coordinated ligands results in a distortion of bond angles and a decrease in stability. This has been described as "$E$-strain" by Brown. The representative example of this kind of steric hindrance can be seen in the complexes of copper with substituted 8-hydroxy quinolines and 8-hydroxy quinazolines (67). Substitution in all positions except 2 results in the formation of stable complexes; 2-substituted compounds form least stable complexes.

Another kind of steric hindrance is determined by the
metal ion. Most stable structures arise when the bonds of the metal are so directed in space that they overlap the orbitals of the ligand without serious distortion of either set of orbitals. Stability is observed to decrease when the bonds of the metal and those of the coordinating group do not have the same basic geometry.
LITERATURE SURVEY OF NICKEL COMPLEXES

Nearly all the metal ions are capable of forming complex compounds. The tendency for complex formation is more strong in transitional elements since they have incompletely filled d-shell. Nickel, being one of the members of the first transition series, has a strong complexing tendency. A large number of nickel complexes have been reported in the literature but only relevant references of nickel complexes have been given here.

Nickel is known to form complexes with halogens. Klemm and coworkers (58, 59) prepared fluoro complexes of nickel. Fluoroborate (60, 61) and fluoroberylate (62, 63) complexes of nickel are also known.

Nickel forms large number of complexes containing nitrogen since it has a great affinity for nitrogen. Some of the important nickel complexes containing nitrogen are with amino acids (64-68), pyridine and quinoline derivatives (69-76), amines (77-80), cyano (81-83), amonia (64), urea and thiourea (85-89), thiocyanate and cyanate (90) and semicarbazide (91).

Numerous complexes of nickel with β-diketones and β-ketoesters are reported. Some of them are with benzoyl acetone (92), acetyl acetone, dipivaloylmethane, diisobutyryl methane (93-95), dibenzoyl methane (96,97), ethyl acetoacetate, ethylbenzoacetate and 2-furoyl benzoxy methane.
Tyson and Adams (98) synthesised nickel disalicylaldehyde and disalicyladimine and assigned probable configuration on the basis of magnetic measurements. Nickel complexes of salicylaldehyde and derivatives have also been studied by a number of workers (98-101).

Nickel complexes with phenols, nitroso-phenols, amino-phenols, (102-105), and thiosulphates (106) are also reported.

Delsil (107) studied the formation of malate and tartarate complexes of nickel by polarimetric and electrometric methods. He showed that the metal replaced one acid hydrogen and one hydroxy hydrogen in malic acid and one or both hydroxyl hydrogen in tartaric acid.

Bobtelsky and Jordan (106) investigated the tartaric and citrate complexes of nickel in dilute aqueous and 50% alcoholic solution by conductometry, and photometry, potentiometric and pH methods. The formation of 1:1 complex in both the cases have been reported by them. Bobtelsky and Heitner (109) carried out spectrophotometric study of citrate and tartarate complexes of nickel. Migal and Sychev (110) also investigated the citrate complex of nickel by conductometric, photometric and potentiometric methods and reported the formation of 1:1 and 1:2 complexes in acid or neutral solution. They observed that increase in temperature and concentration favours the formation of 1:2 complex. Patnaik and Pani (111) studied the citrate complex by pH titration method
in pH range 3.5-7. Carla Heitner and coworkers (112) determined the stoichiometry at all pH and reported the existence of 
\[ \text{[NiH}_2\text{Cit]}^0, \text{[NiHcit]}^- \text{ and [NiCit]}^- (\text{H}_4\text{Cit} \text{ is citric acid}). \]
Pyatnitskii (113) studied in addition to tartarate complex, the succinate, and dimethoxysuccinate complexes of nickel in alkaline and ammoniacal solutions. A chromatographic study of the tartarate and citrate complexes have been carried out by Singh and Dey (114, 115).

Bobtelsky and Bar-Gadda (116) determined the stoichiometry and stability of phthalate, succinate, malonate, salicylate and lactate complexes of nickel.

Siddhanta and Banerjee (117) studied the acetate complexes of nickel and determined its stabilities. Tanaka and Kato (118) determined the formation constants of the acetatonicel complex by polarographic method. Logan and Costa (119) prepared complexes of nickel oxalates and phthalates with \( \beta^- \) and \( \gamma^- \)-picolines and pyridine and determined their heats of formation. Singh and Dey (120) carried out a chromatographic study of the oxalate complex of nickel.

Kiss and Faredin (121) studied the light absorption of the nickel complexes of orthoanilic and sulphanilic acids. Laster and Anderson (122) investigated by spectrophotometric method the reaction between nickel and salicylate ions and observed that 1:1 complex is formed between pH 5 and 9. They said that there is some indication of formation of one or more different complexes at about pH 7. Stoichiometry and stability of the sulphosalicylate
complex has been studied spectrophotometrically by Banks and Singh (123). Nair and Talanta studied the stability of the sulphanilic acid complex by pH method.

Absorption studies of the trihydroxyglutarate complex was made by Grigoreva (124).

Harris and Sweet determined the stability of 5-sulphoanthranilic acid complex (125).

The above paragraphs give more or less an up-to-date idea of the work done on nickel complexes. It is obvious that earlier workers were mainly interested in the preparation of the nickel complexes. Some workers have determined the stabilities of the nickel complexes but most of them have confined themselves to amino acids, tartaric acid and citric acid complexes. A few examples of hydroxy acids and dibasic acids are also reported in the literature but it appears that no systematic approach to these have been made. Therefore, the author thought it worthwhile to study the complexes of nickel with organic acids systematically and to determine their composition, stability and structure. The sodium salts of the following organic acids have been used:

(1) Dibasic acids:-(a) Malonic, succinic, glutaric, adipic, cyclohexane-dicarboxylic and phthalic acids.
(b) Dibromosuccinic, aspartic and glutamic acids.

(2) Unsaturated acids:- Maleic, fumaric, citraconic, itaconic, aconitic, acrylic, crotonic and cinnamic acids.

(3) Hydroxy acids:- Malic, lactic, glycollic, gluconic, tartaric, citric and mandelic acids.
REFERENCES


11. Werner, Ber., 1911, 41, 1887.


19 Fajans, Z. Krist., 1928, 166, 321.


21 Garrick, Phil. Mag., 1930, 12, 134; 1931, 11, 741; 1932, 14, 914.


24 Griffith & Orgel, Quart. Rev., 1957, 11, 381.


26 Kimball, J. Chem. Phys., 1940, 8, 188.

Orgel & Sutton,


31 Ray, ibid., 1927, 174, 188;
J. Ind. Chem. Soc., 1928, 5, 73.


33 Britzinger, Z. Anorg. allgem. Chem., 1934, 222, 172;
1935, 223, 253; 1936, 224, 221; 1936, 227, 341; 1937, 228, 416; 1948, 256, 98.
36 Ley, Z. Electrochem., 1904, 12, 954.
49 Van Uitert, Fernelius, J. Amer. Chem. Soc., 1953, 75, 457,
& Douglas, 2732, 2739, 3677.
Van Uitert, Hass, ibid, 1953, 75, 455.
Fernelius & Douglas,
50 Diehl, Chem. Revs., 1937, 21, 94.
1967, 42, 1886.
Martell et al., ibid., 1952, 74, 5052, 5057, 6021 & 6296.


56 Irving & Williams, J. Phys. Chem., 1951, 55, 121.


59 Klemm, Benda & Hoppe, ibid., 1961, 308, 179.

60 Spacu & Dima, ibid., 1935, 222, 185.


64 Lang, Biochem. Z., 1939, 221, 366.


67 Li, Doody & White, J. Amer. Chem. Soc., 1958, 80, 5901.

68 Sarcine, Hakagawa & others, ibid., 1958, 80, 5018.


70 Davis & Logan, ibid., 1940, 62, 1276.


75 Lumme, Suomen Kemistilehti, 1958, 318, 294.
86 Braibanti
88 & Coghi
93 Jensen & Haneske-Hadsen,
96 Ferneilus & Douglas,
98 Ferneilus & Douglas,
101 Porai-Koshits,
115 Singh & Dey, ibid., 1960, 165, 179.
120 Singh & Dey, J. Chromatog., 1959, 2, 96.