The work of Werner may be taken as a landmark between the conscious and unconscious application of complexes. He advanced the idea that valence can be divided into units of varying strength depending on the species combining with an atom or ion. Some of the valence may be left unexpended (secondary valence). Werner(1) set forth the foundations of co-ordination theory. His proposals, however, did not lead to immediate analytical consequences.

The work of Werner in the field of co-ordination chemistry which was expanded and extended during the last three decades, has been exploited to the maximum by analytical chemists. The aid of improved instruments and a deeper insight enlightened by valence bond and crystal field theories have made the analytical methods, to determine the metallic ions in moderate concentration and minute amounts, a routine procedure which otherwise used to be a problem.

Analytical investigators employ the properties like visual examination, development of colour or solubility in the detection of given ions based on some chemical reactions. These reactions may be dissolutions, precipitation, complex formation, oxidation, reduction or the like, which are characteristic of the ion in question. The overlapping range of dissolution, colour formation or salt precipitation of different but similar ions restrict their application in
analysis. Consequently, complex formation of inorganic reagents found a place in analytical chemistry.

The quantitative analysis employs not only the same type of complex species but also many organic precipitating and complexing agents like 8-hydroxyquinoline, dimethylglyoxime and EDTA. The formation of coordinate compounds by organic reagents with metal ions has been extensively used in analytical methods, like spectrophotometry, ion-exchange separations, polarographic determinations and quantitative determinations based on the rate of formation or decomposition. This inspired analysts to design more sensitive reagents which would be extremely selective for metal ions.

When a metal ion becomes a part of a complex, it acquires properties strikingly different from those of the original ion. Such changes include those in colour, stability towards oxidation-reduction, magnitude of ionic charge and sometimes reversal of the signs, solubility and crystalline forms of the salts. Blomstrand(2) and Jorgensen(3) reported the first detailed studies of the composition and behaviour of characteristic complex compounds and attempted to explain their structure by the valency theory only, assuming nitrogen and oxygen chains in organic compounds. Although their ideas were incorrect, their findings provided important experimental data, for the further evolution of the
coordination theory. One of the earliest recorded instances of introduction of complexing in analytical chemistry is the detection of silver as a diamine complex(4) and iron as a thiocyanate complex(5). The detection of Cu$^{+2}$ as a cyanide complex(6) and Ni$^{+2}$ and Co$^{+2}$ as an amino complex(7) or a cyanide complex(8) are all well established operations in the analytical chemistry.

Attempts were made to establish the use of ammine complexes of transition metals for their quantitative determination by gravimetric methods; however, the results were not encouraging though quite a few of them are known to be better suited for instrumental analysis.

Hexammine cobaltic ion is used for the determination of vanadate(9) or a ferrocyanide ion(10). Attempts were also made by Spacu and Pop(11) to determine Sb$^{+3}$ and Bi$^{+3}$ using hexammine chromium ion. Snell and Snell(12) and Burgess and Kamm(13) employed cobaltinitrite ion to determine potassium and silver respectively. Sometimes coordinating agents are also employed to sequester an interfering ion, e.g. Fe$^{+3}$ is sequestered by fluoride ions during the iodometric determination of copper(14). The complex ions are found to give less consistent results in many quantitative analyses due to their solubilities in water and overlapping of their precipitation ranges.
Several organic compounds have been found a variety of applications in analytical chemistry. Yoe and Seaver(15) classified them as solvents, wash-liquids, indicators, primary standards, photometric acids, etc. However, those compounds, which react directly with inorganic substances, are generally considered as (i) adsorption precipitants, (ii) salt-forming reagents and (iii) complex-forming agents.

(i) Adsorption precipitants:

Several organic compounds like tannins, cinchonine, starch or anthraquinone and its derivatives are found to precipitate metallic ions like $\text{Al}^{3+}$, $\text{Sr}^{2+}$, $\text{Be}^{2+}$, $\text{Cr}^{3+}$, $\text{Sn}^{2+}$, $\text{Zn}^{2+}$ and $\text{Tl}^{3+}$. However, some of them are non-stoichiometric and in most of the cases, it is difficult to explain a chemical combination. Weiser and Porter(16) and Kethafsky and Winslow(17) reported them as adsorption precipitants.

(ii) The Salt-forming Reagents:

The salt-forming reagents may be further divided into two groups, normal salt-forming and complex salt-forming. Several organic compounds with ionisable $H^+$ are found to interact with inorganic ions forming precipitates or colouration. Some of them are not selective and specific. Prodinger(18)
surveyed the use of organic reagents like benzidine and nitron for the precipitation of anions like sulphate, phosphate, nitrate, etc.

Complex-forming Reagents:

The persual of literature shows that an organic reagent, which forms a chelate or an inner complex with a metal ion, is superior to the rest in the analytical work. When an organic molecule containing both an acidic or a basic functional groups combines with a metallic ion or if in the combination, these functional groups operate, an inner complex or a chelate results. Morgan and co-workers (19-21); Yoe and Server (15); Mellan (22) suggested that the formation of chelate ring may involve either a primary (ionic) or a secondary (co-ordinate) valence and may be formed by two primary or two secondary or one primary and one secondary valence. Quaglano and Wilkins (23) believe that the inner complex is a completely chelated nonionic structure, usually formed by the union of a metal ion with a bidentate group of a uninegative charge.

The formation of chelate will depend upon

(i) the nature of the reagent,
(ii) the nature of the metal ions and
(iii) the external conditions.
An organic compound possessing a suitable number of reactive groups can act as a chelate forming ligand depending upon the coordination number of the metal ion. Diehl’s (24) suggested that the ligand may be bidentate, tridentate or quadridentate and may form a chelate ring of various sizes.

A variety of chelates of metal ions with organic reagents having bidentate groups, have been studied by several workers (19-21, 25-30). They have reported that when a group like -COOH, -SO₃H or -OH is suitably placed with a -S, -NH₂, -OH or =NOH, the latter groups are found to be coordinating with a metal ion which is linked through a primary valence (ionic) to the former.

Jantsch’s (31), Jentsch and Grunkraut’s (32) and Forrell, Ridgion and Riley’s (33) reported that when a -OH group is on an -OOC - or a β-carbon to a -COOH group, the reagent is found to form a chelate with trivalent ions like Fe³⁺, La³⁺ and other rare earth ions. Hieber and Leutert’s (34) reported that when an oximino (=NOH) group is on an -OOC - carbon to a -COOH group the nitrogen coordination with the metal results in a five membered chelate ring. Rosenheim and Vermehren’s (35), Mark’s (36) and Klement’s (37) have reported that boron, Cu⁺² and Pb⁺² are found to form complexes with organic reagents having a -COOH and =NOH, both acidic groups.
Morgan and co-workers (21, 33-40) have investigated chelates of \( \beta \)-diketones with \( \text{Be}^{2+} \), \( \text{Cu}^{2+} \), \( \text{Zn}^{2+} \), \( \text{Cd}^{2+} \), \( \text{Zr}^{4+} \), \( \text{Hf}^{4+} \), \( \text{Al}^{3+} \), \( \text{Fe}^{3+} \), \( \text{Cr}^{3+} \), \( \text{Co}^{3+} \) etc., and found them to be stable and soluble in organic solvents.

The oxygen of the carbonyl group in vicinity of a phenolic -OH group is found to be coordinating. Aromatic o-hydroxy compounds like salicylaldehyde or o-hydroxy acetophenone are reported to form inner complexes with \( \text{Co}^{2+} \), \( \text{Ni}^{2+} \), \( \text{Cu}^{2+} \) and \( \text{Fe}^{2+} \). Such compounds form a six-membered heterocyclic ring(41-45).

8-Hydroxyquinoline, 8-hydroxyquinazoline or 1-hydroxy acridine is a ligand possessing a system capable of giving rise of a five-membered heterocyclic ring and hence it is found to give chelates with transition metal ions and even nontransition metallic ions like \( \text{Al}^{3+} \) and \( \text{Mg}^{2+} \). Several workers (15, 46-52) have reported that nitrogen being quaternary will be in \( sp^3 \) hybridisation state like carbon and hence chelates are stable to the least strain in a five-membered ring.

![](image.png)
Alkyl or aryl diamines are reported to form numerous metal complexes. In many complexes, ethylenediamine is found to form a bridge between two metal atoms (53-56). It was investigated that aromatic heterocyclic bases like 1:10 phenanthroline (IV) and 2:2'-bipyridyl (V) having a \(-\text{N}=\text{C} - \text{C}=\text{N}\)-system form complexes with metal ions like Fe\(^{3+}\), Mn\(^{2+}\), Co\(^{3+}\), Cu\(^{2+}\) and Ni\(^{2+}\) (57-61).

![IV](image)

Harkins and Freiser (62) investigated the metal chelates of imidazole derivatives and 2-(2-pyridyl) imidazoline and concluded that their effectiveness is due to the \(-\text{N}=\text{C} - \text{C}=\text{N}\)-grouping.

A representative of this group, dimethylglyoxime behaves as a weak monobasic acid and forms chelates with Ni\(^{2+}\), Pt\(^{2+}\) and Pd\(^{2+}\) in which the metal is square co-ordinated to four nitrogen atoms out of which two are co-valent and two are co-ordinated bonds. Suggen (63) investigated the nickel complex of this ligand and assigned the following structure.
These complexes and their structures have also been investigated by several workers who have in general, assigned a trans configuration having a five-membered heterocyclic metal chelate ring. Cu^{+2} complex is dimeric and five-co-ordinated. On the other hand Ni^{+2} and Pd^{+2} complexes are square co-ordinated and a metal-metal interaction is proposed from the spectral analyses and magnetic properties by Miller and Sharpe(64); Miller(65); Harris and Livingstone(66); Dwyer and Nellor(67).

Salts of amino acids were the first recognised as inner complexes. Ley(68,69); Ray and Ray(70) have investigated that in such compounds a metal links with the acidic group by a primary valence and with the co-ordinating group by a secondary valence.
Chelates (VII) of copper with α-amino acids like glycine are found to be more stable and belong to a five-membered ring system. Carboxylic acids with an adjacent cyclic nitrogen atom similarly form a ring with the metals. α-Picolinic acid and quinaldinic acid of this category have been investigated and found to be specific for Fe$^{+2}$ (71-73).

The field exerted by a ligand is a major decisive factor in the formation of chelates. Probably, due to an intensive ligand field, ethylenediamine tetraacetic acid (EDTA) is able to encompass most of the transition and many of the pre- and pro-transition elements like alkaline earths and zinc family elements.

Printzinger and Nesse (74) and Bennett and Schmidt (75) prepared Cu$^{+2}$ chelate of EDTA and proved it to have a square planar arrangement. Dwyer and Garson (75) prepared the complexes formulated as $\text{H}_{2}\text{CuH}_{2}O(\text{H}_{2}\text{EDTA})^{-}$ and

(VII)
BaCu_{2}O(EDTA)\cdot4H_{2}O and showed them to be isomorphous with the corresponding nickel complexes by x-ray powder photographs. Infrared spectra, magnetic moments, and dehydration studies showed that the nickel chelates contain quinquedentate EDTA with a water molecule coordinated in the sixth octahedral position. Hence the copper chelates must also contain quinquedentate EDTA. Smith and Hoard(77) proved this by crystal structure study. Brunisholz(78) investigated that EDTA forms acid salts H_{2}^{k}EDTA\cdot7\cdotH_{2}O (M = Ba^{2+}, Sr^{2+}, Hg^{2+}) which are insoluble in water. Brintzinger and Besse (74) and Sidgwick(79) reported that elements of zinc group also form compounds: ZnZn(EDTA)\cdot7, CdCd(EDTA)\cdot7\cdotH_{2}O and H_{2}^{k}Hg(EDTA)\cdot7\cdotH_{2}O.

Vickery(80); Holleck and Hartinger(81) used lanthanum chelates of EDTA for the separation of lanthanons by ion exchange method. Saito and Terry(82) isolated alkali salts of Al^{3+}, Ga^{3+} and In^{3+} EDTA complex. Blumer and Kolthoff (83) reported that Ti^{4+} forms a complex with EDTA at a pK below 2.0. Morgan and Justus(84) found that Zr^{4+} and Hf^{4+} form 1:1 chelates with EDTA at a pH 6.0. Schwarzenbach and Sandera(85) investigated that vanadium forms several acid chelates with EDTA in different oxidation states. Brintzinger and Hunkelt(86) reported that Hg^{2+} chelates of EDTA is water soluble and it gives precipitates with hydrogen sulphide, sodium hydroxide and sodium stannite, but not
with ammonia. These reactions point to the formation of weak complex. Hoard, Smith and Lind(87) found that Cr\(^{3+}\) and Mn\(^{2+}\) chelates contain \(\eta^6\)oxadentate EDTA.

Co\(^{2+}\) chelates have been isolated as the pink solids, \(\mathrm{Ni}^2\left(\text{H}.	ext{EDTA}\right)_{2}2\mathrm{H}_2\mathrm{O}\), \(\mathrm{Na}_2\mathrm{CoH}_2\mathrm{O}(	ext{EDTA})_{2}3\mathrm{H}_2\mathrm{O}\) and \(\mathrm{Co}_2\mathrm{CoH}_2\mathrm{O}(	ext{EDTA})_{2}2\mathrm{H}_2\mathrm{O}(38-93)\). Schwarzenbach(91) found that Co\(^{3+}\) chelates are intense violet and stable in the pH range of 1.0 to 11.0.

Brinzing, Thiele and Muller(92) isolated Ni\(^{2+}\) chelates of EDTA as acid, Na\(^+\), Ba\(^{2+}\) and Ni\(^{2+}\) salts. Busch and Baiker(93) isolated several acid EDTA complexes of Pd\(^{2+}\) and Pt\(^{4+}\).

The bidentate ligands having the system (VII) are found to be selective and specific for quite a few transition metal ions.

\[
\text{(VIII)}
\]
Smith(94) and Morgan and Main-Smith(95) described that complexes formed from the adducts derived from ethylenediamine and acetylacetone(IX) as well as those from salicylaldehyde and an aromatic or aliphatic diamine possess the system(VIII).

![Diagram of complex](image)

(IX)

Joshi, Patel and Thakor(96-98) have reported the complexes derived from hydroxy ketomines and proved that the substituents in the aromatic amines have practically no effect on the effectiveness of the system.

Dubsky and Sokol(99), Pfeiffer, Breith, Lubbe and Tsuzuki(100), Calvin and Barkelev(42), Chatterjee, Parrier and Douglas(101), Singh and Kumar(102) illustrated the effectiveness of the above system with Cu$^{+2}$ and Ni$^{+2}$. Feigl and Bondi(103), Ephraim(104), Flagg and Furman(105), Biefield and Howe(106), Astin and Riley(107), Riley(108)
reported that the oximes of ortho-hydroxy aryl aldehydes possess the above systems; hence they form complexes with divalent metal ions like $\text{Pd}^{2+}$, $\text{Cu}^{2+}$, $\text{Hg}^{2+}$, or $\text{Co}^{2+}$.

It is interesting to note that salicylaldoxime behaves as a dibasic acid in an alkaline solution resulting in a salt-like chelate of the type (XI)\(^{(103)}\).

The substituents in benzene nucleus of salicylaldoxime produce reasonable changes in the characteristics of the ligand as illustrated by the investigation of salicylaldoxime acid (XII)\(^{(109)}\), salicylaldoxime (XIII)\(^{(110)}\), 3-oximinomethyl salicylic acid (XIV)\(^{(111)}\) and 5-nitro, 3:5-dibromo and 6-methoxy salicylaldoxime (XV)\(^{(105)}\).
Orthohydroxy aromatic ketoximes also possess the same reactive system having an alkyl or aryl group on the carbon atom of the \(-\hat{C} = N-\) part. Oximes 2-hydroxy-4-methoxy, 2-hydroxy-5-methoxy, 2:4-dihydroxy, 2-hydroxy-acetophenones and 2-hydroxy-1-acetophenone have been investigated by Ephraim(104) for their specificity for Cu\(^{+2}\). Poddar(45) has reported the use of orthohydroxy acetophenone oxime for quantitative determination of Cu\(^{+2}\) and Ni\(^{+2}\) and also reported this oxime for the quantitative determination of Ti\(^{+4}\) and proposed its composition TiO(OH)C\(_6\)H\(_5\)O\(_2\)N (112).
Neelkanta and Sitaraman(113); Bhatki and Kabadi(114) used resacetophenone oxime for the said ions. Sharma, Bhusa, Rastogi and Singh(115) reported 5-chloro-2,4-dihydroxypropiophenone oxime as an analytical reagent for gravimetric determination of Cu$^{+2}$, Ni$^{+2}$ and Pd$^{+2}$. Singh and Sharma(116) have used 5-methyl-2-hydroxyacetophenone oxime for gravimetric determination of Cu$^{+2}$, Ni$^{+2}$ and Co$^{+2}$ successfully. Patyal, Prakash and Singh(117) reported the use of 2-hydroxy-5-methylpropiophenone oxime as an analytical reagent for the determination of V$^{+5}$. Prakash, Dutt and Singh(118) used this oxime for the quantitative determination of Cu$^{+2}$, Ni$^{+2}$, Co$^{+3}$ and Ti$^{+4}$. Naik, Patel and Thakor(119) have used 2-hydroxy-3-chloro-5-methyl acetophenone and propiophenone oximes as analytical reagents for the quantitative determination of Cu$^{+2}$, Ni$^{+2}$ and Co$^{+2}$. Jhaveri, Patel and Thakor(120); Jhaveri, Naik, Patel and Thakor(121); Jhaveri and Naik (122) reported 2-hydroxy-3-methylketoximes as an analytical reagents for the determination of Cu$^{+2}$, Ni$^{+2}$, Co$^{+2}$, Ti$^{+4}$, V$^{+5}$, Pd$^{+2}$ and Fe$^{+2}$. Patel and Naik(123); Patel, Patel and Naik (124) reported 2-hydroxy-5-n-propoxyketoximes as an analytical reagents for Cu$^{+2}$ and Ni$^{+2}$. Desai, Naik and Naik (125) reported the use of 2-hydroxy-4-ethoxyacetophenone oxime as an analytical reagent for Cu$^{+2}$ and Pd$^{+2}$. Singh, Gupta and Malik (126 a,b) have reported the use of 2,4-dihydroxyvalerophenone oxime for electrometric studies of Cu$^{+2}$, Ni$^{+2}$ and Co$^{+2}$ as well for the
quantitative determination of Cu$^{+2}$ and Ni$^{+2}$. Trivedi and Haldar (127) studied the complexes of Ni$^{+2}$ and Co$^{+2}$ with 5-nitroresacetophenone oxime. Naik, Naik and Desai (128 a,b) have introduced 5-ethylresacetophenone oxime as an analytical reagent for Cu$^{+2}$ and Ni$^{+2}$.

Size of Chelate Rings:

Ley (68) concluded that five and six-membered chelate rings are more stable. Boeseken and co-workers (129, 130) reported stable boron complexes of $\infty \beta - d$ihydroxy compounds having five-membered chelate rings. Many ligands like ethylenediamine, diethylenetriamine, orthohydroxy acids like salicylic acid; $\beta$-diketones like acetylacetone, 2-hydroxy-azo compounds, 3-hydroxy quinoline, 1-hydroxy acridine and 1-hydroxy anthraquinone are found to form five- or six-membered chelate rings. Pfeiffer (131) reported that five-membered ring is more stable if it is entirely saturated but a six-membered chelate ring is more stable when one or more double bonds are present. Mann and Pope (132, 133); Mann (134) confirmed this by the preparation and resolution of the tetrachloro 1,2,3-triamino-propane platinate (XVI) in which though six-membered ring is possible, it should be five-membered as it is asymmetric.

![Diagram](XVI)
Calvin and Wilson (135) pointed out the similarity in bonding of enolate type of ligand with $H^+$ and $Cu^{+2}$ and further proposed two possible resonating structures for $Cu^{+2}$ chelates with enolate type of ligands:

![Structure A](image1)

![Structure B](image2)

(XVII A) and (XVII B)

(XVIII A) and (XVIII B)

(XVIII A) and (XVIII B) structures are expected to have more aromatic nature but it involves double bond formation with $Cu^{+2}$ of which availability of orbitals are questionable with respect to $Cu^{+2}$. Kimball (136), Pauling (137) and Chatt (138) supported the double bond formation between the donor and the metal atom in chelates. Chatt (138) suggested
the bonding in Zeis's salt by coordination of two Ti electrons of ethylene double bond with the formation of coordinate bond of \( \psi^g \) symmetry. The strength of the bond is reinforced by back coordination of nonbonding d electrons of platinum atom to the vacant \( \psi^g \) orbitals of the ligand.

**Nature of the donor atom:**

The nature of the donor atom has a marked effect on the stability of chelates because of a change in the basic strength, steric factor, resonance and size of the ring. Sidgwick (139, 140) considered oxygen and nitrogen nearly similar in their affinity for a metal ion and also noted that the tendency of coordination diminishes with an increase in substitution. He classified metals into three categories depending upon their relative tendency for combination with oxygen or nitrogen.

\[
\text{O} > \text{N} \quad \text{Mg}^{2+}, \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}, \text{La}^{3+}, \text{Ga}^{3+}, \text{In}^{3+}, \text{Ti}^{4+}, \text{Ti}^{4+}, \text{Zr}^{4+}, \text{Hf}^{4+}, \text{Si}^{4+}, \text{Ge}^{4+}, \text{Sn}^{4+}, \text{V}^{4+}, \text{V}^{5+}, \text{Nb}^{5+}, \text{Ta}^{5+}, \text{Mo}^{5+}, \text{W}^{5+}, \text{U}^{6+}, \text{Fe}^{3+}, \text{Co}^{2+}.
\]

\[
\text{C} \geq \text{N} \quad \text{Be}^{2+}, \text{Cr}^{3+}, \text{Fe}^{2+}, \text{Pt} \quad \text{metals}^{+2}.
\]

\[
\text{N} \geq \text{O} \quad \text{Cu}^{+}, \text{Ag}^{+}, \text{Au}^{+}, \text{Cu}^{2+}, \text{Cd}^{2+}, \text{Hg}^{2+}, \text{V}^{3+}, \text{Co}^{3+}, \text{Ni}^{2+}.
\]

It can be stated with a broad marginal limit that light metals of IA, IIIA and IVB groups form complexes with a ligand.
in which mainly oxygen acts as a donor. On the other hand, transition metals are strong nitrogen coordinators.

Bouknight and Smith (143) reported that metals, like Pt⁺², Pd⁺², Au⁺, Ag⁺ and Cu⁺² form coordinate compounds with sulphur containing ligands like dithiane C₄H₆S₂. Comin and co-workers (143) have reported chelates of Cu⁺², Ni⁺², Co⁺², Ag⁺ and Zn⁺² with sulphur and nitrogen containing ligands.

Nitrogen (1s², 2s², 2p³) is a better suited donor atom than atoms of sulphur and oxygen. Ammonia and its derivatives—primary, secondary and tertiary amines, have been employed as ligands by many workers (144-151). In many cases ligands having nitrogen donors are found to form more stable complexes than those having others.

**Effects of substitution:**

The substitution of a group on the chelating agent may influence the polarisability of the ligand, enhances the resonance of the chelating agent or produces a steric effect. Ewens (152), from the study of the dissociation constant of para-substituted benzoic acids, proposed that if a substituted group draws electrons away from the donor, the activity is decreased. Walden, Hammett and Chapman (153) studied the chelates of phenanthroline derivatives with Fe⁺² and noted that if the substituent increases Lewis basicity.
of ligand, the stability of chelate is increased and if the substituent increases the Lewis acidity of ligand, the stability of chelate is decreased. Albert and Gledhill\(^{154}\) and Albert and Magrath\(^{155}\) made a similar observation with substituted oximes.

**Steric Effect:**

Calvin and Wilson\(^{135}\) attributed the lower stability of \(\text{C}_6\text{-methyl benzoyl acetone Cu}^{+2}\) chelate to the steric effect due to the benzoyl group. Morgan and Thomason\(^{39,156}\) observed that 3-substituted \(\text{Cu}^{+2}\) acetylacetone chelates did not exhibit the usual colour. This may be due to an interference with the planar configuration and hence with the benzenoid resonance of the chelate ring. Herritt and Walker\(^{50}\) and Irving, Butler and Ring\(^{51}\) reported that 2-substituted-8-hydroxy quinolines failed to give an inner complex salt with aluminium; however, a 2-substituent does not hinder in case of \(\text{Cr}^{+3}\), \(\text{Fe}^{+3}\) and \(\text{Zn}^{+2}\).

**Effect of Metal Ion:**

Pfeiffer, Golther and Angerm\(^{41}\); Werner\(^{25}\); Diehl\(^{24}\) and others concluded that the elements of transition series including lanthanides and actinides, \(\text{Be, Mg}\), elements of groups \(\text{IIA, IIB}\) and \(\text{VIB}\) form chelates with different chelating agents. Sidgwick\(^{139,140}\) has classified them according to their
coordination tendency with nitrogen, oxygen and sulphur (page 19). Mellor and Maley (157) arranged the bivalent metals in order of decreasing stability of their complexes as under:

\[
\text{p}d^{2+}, \text{Cu}^{2+}, \text{Ni}^{2+}, \text{Pb}^{2+}, \text{Co}^{2+}, \text{Zn}^{2+}, \text{Cd}^{2+}, \text{Fe}^{2+}, \text{Mn}^{2+}, \text{Mg}^{2+}
\]

decreasing stability

This is based on the formation of their chelates with salicylaldehyde, glycine and 8-hydroxyquinoline. They proposed that \( \text{Pd}^{2+} \) and \( \text{Cu}^{2+} \) are capable of forming strong \( \text{d}sp^2 \) (square planar structures) and hence give the strongest chelates. Magnesium, a more basic metal, forms the weakest chelates. They conclude that the strength of the bonding in these chelates depends upon the ability of a metal to form homopolar bonds. Irving and Williams (58, 158) correlated the above conclusion by plotting the stability constants against the atomic numbers using chelating agents like oxime, dithizone, quinaldinic acid, ethylenediamine, salicyl aldehyde etc. Conductance measurements (68, 69) and exchange studies (159) of copper, nickel, zinc and cobalt chelates indicate nearly the same stability order.

Calvin and Melchior (160) derived a correlation of the stability constant of chelates with the second ionisation
potential of metals. This data also agrees with the former order. Calvin and Wilson (135) indicate that the d-orbitals of the metal are involved in the formation of homopolar bonds in chelates. The number of the 3d electrons increases from manganese to copper and probably because of this, the d-orbitals form homopolar bonds of increasing strength. However, in the case of zinc there is a sudden fall.

Schwarzenbach and Sandera (35) pointed out that the difference in the stability of analogous alkaline earth chelates is directly proportional to the sum of the first and the second ionisation potentials. Ackermann, Prue and Schwarzenbach (161) derived similar conclusion using the sum of the first two ionisation potentials in correlating the stability constants of chelates of Mn$^{+2}$, Fe$^{+2}$, Co$^{+2}$, Ni$^{+2}$ and Zn$^{+2}$.

Hartell and Calvin (162) reported that the strength of chelation varies directly with the value of $\frac{e^2}{r}$, where 'e' is the charge and 'r' is the ionic radius. Chaberek and Martell (163) concluded that the stability increases with the atomic number from manganese to copper and then falls in the case of zinc for reagents like EDTA, HEDTA and ethylenediamine. Van Jitert, Fernelius and Douglas (164) correlated the stability constants with electronegativity of metals which was found to have a linear relation. Calvin
demonstrated the equivalence of ionisation potential and
the product of electronegativity and hybrid bond strength
as a measure of chelating tendency while Powell and Latimer
laid stress on the entropy changes in chelation as a measure
of the stability (165).

Stevenson and Verdieck (166) have reported the asymmetric
transformation by thermal and photochemical change, the
latter is effected by circularly polarised light in case
of trioxalatochromate III.

Mozaki, Takaya, Moriuti and Noyori (167); Jean, Claude and
Evangelose (168); Abley and McQuillin (169) have used several
chiral chelates of copper, nickel, and rhodium as catalysts
for asymmetric transformation.

DETECTION OF CHELATES AND THEIR COMPOSITION:

Ley (68) used the following properties as an indication
of the cyclic structure of chelates: (i) the absence of
normal chemical reactions, (ii) the difference in chemical
properties of chelating agents, (iii) the low electrical
conductance, (iv) the characteristic colour and (v) the
ionisation of certain inner complex salts. The spade work
of Werner, Ley and Tschugaeff pointed out the existence of
chelate rings but a direct evidence was first furnished by
Pfeiffer (131) and Pfeiffer, Golther and Angern (170) by
resolving Co\textsuperscript{3+} chelate with o-hydroxy-p-methoxyacetophenone and ethylenediamine into two optically active isomers. Dwyer(171); Dubsky and Spritzmann(172) used a change in the chemical properties of Ag\textsuperscript{+} and Cu\textsuperscript{+2} as an evidence of chelation. Rosenheim and Lehman(173) reported the presence of a chelating ring in Be\textsuperscript{+2} complex with salicylic acid, based on the change in chemical properties.

**Colorimetric:**

The formation of metal chelates is often accompanied by a change in the wavelength and/or magnitude of light absorption relative to that of the free metal ions or ligand. Job(174) introduced the method of continuous variation based on these properties to determine the composition. This method uses the additive property of the two species in solution. Purkayastha and Sen-Sarma (175) and Purkayastha(176) used the molar conductance in the application of the Job's method.

**Spectrophotometry:**

The metal complexes give an absorption in the ultraviolet and visible region due to the electronic transition, in the infrared region due to the molecular vibrations, and the shifting of the frequencies due to the Raman effect. Bailer (177) reported that the interpretation of the absorption spectra and the Raman spectra leads to the
conclusion regarding their formation, configuration, stability and formulas.

Werner and co-workers (178) and Shibata (179) pointed out that the colour of complexes are due to the bonding and the structural arrangements. Experimental investigations of many workers showed that complexes give three important bands in the visible and the ultraviolet regions, the first in the range of 450 and 550 nm, the second between 320 to 400 nm and the third between 200 and 250 nm. Pauling (180) and Head (181) attributed the first band to a contribution of transition energy of the bonding electron and the vibrational energy of the central ion and the coordinating groups. However, Kiss and Czegledy (182) proposed that the assignment of the absorption bands to a particular electron is an approximation. The first band is due to the general nature of the complex rather than any specific group of electrons. Cookan and Nyiri (183) pointed out more than three absorption bands and attributed then to a hydrogen bonding, aromatic character, polarization of the molecule and an electronic shift in the case of salicylaldehyde and ethylenediamine chelates. In many cases, absorption bands of the ligand and its metal chelates are qualitatively quite similar as found in copper with ethylacetoacetate (184) and magnesium, copper and calcium with murexide (185). Ball, Dorough and Calvin (186) investigated in some cases a change in the metal
ion produces a very small shift in the position of the absorption band as illustrated by Ni$^{+2}$ and Co$^{+2}$ chelates with tetrphenylporphyrins. Haendler and Smith (137) and Geyer and Smith (138) observed that a chelate gives different absorption spectra than those of the ligand or the metal ions alone.

Sen, Mizushima, Curran and Quagliano (189) studied the infrared absorption spectra of copper, nickel and cobalt glycine chelates and observed that the metal-nitrogen bonds in these chelates are primary covalent. Duval, Freymann and Lecompte (190) investigated acetylacetone chelates of several metals and found that the $\mathrm{C} = 0$ group is modified through chelation so that a large degree of a single bond character results and a shift of the electron density towards the metal strengthens the coordinate bond.

Other methods:

Werner (191) found that the resolution of the chelates into optically active forms provides a powerful evidence for a ring structure. Morgan and Smith (95) proved the presence of a chelate structure by resolution of the diamino bis-acetylacetone ethylenediamine cobaltic ions. Spoo and Popper (192, 193) used the refractive index as an additive property in the study of complex compound. However, Haldar (194) objected to this application for certain functional groups.
Several electrometric methods are employed in the study of chelates. Copper chelates of quinoline-8-carboxylic acid were investigated polarographically by Stock (195). Kolthoff and Auerbach (196, 197) used polarographic methods to establish the composition of metal chelates.

Schwarzenbach and co-workers (185) employed potentiometric titration in the study of metal chelates of Ba\(^{+2}\) and Ni\(^{+2}\) with EDTA. Chaberek and Martell (163) used the same to prove the stepwise formation of metal chelates of Cu\(^{+2}\), Ni\(^{+2}\) and Co\(^{+2}\) with iminodiacetic acid and of Cu\(^{+2}\) with N-N(dihydroxyethyl)glycine.

Ley and co-workers (71) used conductometric titration to support the chelate formation of Cu\(^{+2}\) with amino acids. Martell (198) studied conductometric titration of EDTA with NaOH and Ca(OH)\(_2\) and proved that the chelation with calcium does not take place in an acid solution but proceeds above pH 7.0.

Sidgwick and Powell (199) and Hollor (200) reviewed enough evidence for the existence of chelate rings by x-ray crystal analyses of several chelates of acetylacetonate, salicylaldoxime, phenanthroline and salicylaldimine with different metals.

**STABILITY OF METAL CHELATE COMPOUNDS:**

The chelate formation constant is the equilibrium constant for the reaction in which the metal chelate is formed from the
hydrated metal ion and the most basic form of the chelating agent at a constant temperature.

\[ K_{HA} = \frac{[MA]^{n-m}}{[M]^{n} [A]^{-m}} \]

The determination of 'K' is based on the determination of the combination ratio of the metal and the chelating agent by suitable physical methods. The stability of complexes of Cu\(^{+2}\) with ethylenediamine, monoethanolamine and hydroxide ion, has been investigated by means of both conductometric and potentiometric titrations (201). Foley and Anderson (202) developed a method to determine the stability constant based on the application of Beer's law. Babko (203) used a colorimetric method in the above investigation. Various workers (204-207) have used potentiometric and colorimetric methods to determine the stability constants of chelates of Cu\(^{+2}\), Co\(^{+2}\), Ni\(^{+2}\) etc. with o-hydroxyketoximes.

Structure of chelates:

The combination of a bidentate ligand with a metal ion results in a tetrahedral or square-planar structure when the coordination number is four, and an octahedral structure.
when the coordination number is six. Martell and Calvin(162) observed that tetrahedral structure results when the bonds are predominantly ionic and a square-planar structure when the bonds are covalent. Pd$^{2+}$ chelates are reported to be square-planar from the chemical evidence and x-ray analyses (178,208-210). The square-planar structures of Ni$^{2+}$ and Pd$^{2+}$ chelates are supported by quantum mechanical treatment of bond orbitals(137), x-ray analyses and magnetic evidences(142,211). Cox, Pinkard, Wardlaw and Webster(212); Cox, Sharrat, Wardlaw and Webster (213) proposed trans-planar structures for Ni$^{2+}$ and Pd$^{2+}$ bis salicylaldoxime chelates. Stackelberg (214) reported that copper chelates of several bidentate ligands have square-planar structures.

In many chelates, having oxygen atom as a donor, evidences are found in favour of a tetrahedral structure. Dwyer and Mellor(215) found that oxygen coordinated nickel chelates are paramagnetic and assigned tetrahedral structures to them. On the other hand Suggen(63), Cavell and Sugden(216) and Calvin and Barkelew(42) supported a square planar structure for the chelates in which nickel is bonded to nitrogen.

Magnetic susceptibility measurements have been of great value in determining the bond type and structures of complexes. From the measurements of magnetic susceptibility,
the number of unpaired electrons, the question concerning orbital hybridisation and the degree of covalent character can be determined and hence the probable structure of complex can be assigned (217).

Tyson and Adams (211) and Calvin and co-workers (42, 213) used this method to postulate the structure of salicylaldehyde and salicylaldimine chelates of Cu^{2+}, Ni^{2+} and Co^{2+}. Russell, Copper and Vosburgh (219) reported a relation between the magnetic moment and the stability of complexes of Ni^{2+} and Cu^{2+} ions with different ligands.

Application:

Chelating agents are found to have a variety of applications. Several chelating agents like polyphosphates and polydentate amino acids soften water by deactivating Ca^{2+} and Mg^{2+}. These chelating agents are responsible for the nonprecipitation of soap with hard water which has been effectively softened. Several ion-exchange resins have been developed, are capable to remove both cations and anions from aqueous solution and hence water results in a high degree of purity. Many organic acids are used as sequestering agents at a pH above 10.0. Saccaric acid is found to be specific for Fe^{3+}. Amino acids are employed in chrome tanning of leather. Chelate complexes like alizarin lakes and chrome lakes are some of the new developments in colour technology.
Several chelating agents being used for preserving fruits, fruit juices and food stuffs. A chelating agent like EDTA in presence of iron is found to be important in rubber technology. It is also used to speed the elimination of harmful radioactive metals from the body. The chelate complexes, acetylacetonates of metals are used in the purification of metals. Several chelates are useful in many catalysed reactions (165). Fe$^{+2}$ dithioglycolate chelate is found to act as a catalyst in the oxidation of ascorbic acid.

Chaberek and Martell (165) have described metal chelates in several biological systems. Chlorophyll is an important magnesium chelate in the plant system. Hemin is a porphyrin chelate of iron which is an active constituent of the blood. Several organic acids like citric, tartaric, lactic, malic acids etc. are chelating agents which keep the metal ions away from precipitation in body fluids. Several medicines which we take, are given in the form of chelate complexes. Reid and others (220) have reported salicylic acid and its 6-hydroxy isomers as chelating agents and hence found to be effective drugs.

Certain chelating agents also find numerous applications as reagents, masking agents or indicators in various titrimetric, spectrophotometric, polarographic, chromatographic and conductometric methods of evaluation. Chelating agents
are valuable in separating metal ions by solvent extractions. Chelates are also used as bacteriacides, enzyme deactivators, or artificial oxygen carriers. The separation of two similar metals like Zr and Hf could be effected by chelate formation. The chelates of these two metals formed with theonyl trifluoroacetone possess different solubilities in benzene.
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