The work of Werner may be taken as a landmark between the conscious and unconscious applications 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 foundation of coordination theory. His proposals, however, did not lend to immediate analytical consequences.

- The work of Werner in the field of coordination chemistry which was expanded and extended during the last three decades, has been exploited to the maximum by analytical chemists. The aid of improved instrumentation 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 use 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 dissolution, 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 EDTA, 8-hydroxyquinoline and dimethylglyoxime. 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. Holmström(2) and Jørgensen(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 evaluation 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(II) as a cyanide complex(6) and Ni(II) and Co(II) as an amino complex(7) and a cyanide complex(8) are all well-established operations in the analytical chemistry.

Attempts were made to establish the use of amine 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.

Hexamine 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(III) and Bi(III) using hexamine chromium ion. Snell and Snell(12) and Burgess and Kamm(13) employed cobaltinitrite ion to determine potassium and silver respectively. Sometimes coordinating agents(14) are also employed to sequester an interfering ion. 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.

ORGANIC COMPOUNDS IN ANALYTICAL CHEMISTRY

Several organic compounds have been found to have variety of applications in analytical chemistry. Yoe and Sarver(15)
classified them as solvents, wash-liquids, indicators, primary standards, photometric aids 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 anthraquinons and its derivatives are found to precipitate metallic ions like Al(III), Hf(IV), Be(II), Ti(III), Sn(II) and Zr(IV). 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 Liebhafsky 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.

(iii) 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 Sarver (15); Mellan (22) suggested that the formation of chelate ring may involve either a primary (ionic) or a secondary (coordinate) valence and may be formed by two primary or two secondary or one primary and one secondary valence. Quagliano and Wilkins (23) believe that the inner complex is a completely chelated nonionic structure, usually formed by the union of a metallic 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 (24) suggested that the ligand may be bidentate, tridentate or quadridentate and may form a chelating ring of various size.

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, -SO$_3$H or -OH is suitably placed with a =S, -NH$_2$, -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(31), Jantsch and Grunkraut(32) and Ferrell, Ridgion and Riley(33) reported that when a -OH group is on a $\alpha$- or $\beta$- carbon to a -COOH group, the reagent is found to form a chelate with trivalent ions like Fe(III), La(III) and other rare earth ions. Hieber and Leutert(34) reported that when oximino (=NOH) group is on a $\alpha$-carbon to a -COOH group and the nitrogen coordination with the metal results in a five membered chelate ring. Rosenheim and Vermehren(35), Wark(36) and Klement(37) have reported that boron, Cu(II) and Pb(II) are found to form complexes with organic reagents having a -COOH and a -OH, both acidic groups.

Morgan and coworkers(21, 38-40) have investigated the chelates of $\beta$-diketones with Be(II), Cu(II), Zn(II), Cd(II), Zr(IV), Hf(IV), Al(III), Fe(III), Cr(III), Co(III), 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-hydroxyacetophenone are reported to form inner complexes with Co(II), Ni(II), Cu(II), Fe(II), Ti(IV), etc. 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 to a five-membered heterocyclic ring and hence it is found to give chelates with transition metal ions and even with nontransition metallic ions like Al(III) and Mg(II). 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.

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 -N=C-C=N- system form complexes with metal ions like Fe(II), Mn(II), Co(II), Cu(II) and Ni(II) (57-61).
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 \(-N = C - C = N-\) grouping.

A representative of this group, dimethylglyoxime behaves as a weak monobasic acid and forms chelates with Ni(II), Pt(IV) and Pd(II) in which the metal is square coordinated to four nitrogen atoms out of which two are covalent and two are coordinated bonds. Sugden (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(II) complex is dimeric and five coordinated. On the other hand Ni(II) and Pd(II) complexes are square coordinated 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 Mellor (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 coordinating group by a secondary valence.

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{H}_2\text{N} \\
\text{O} & \quad \text{Cu} \\
\text{O} & \quad \text{C} = \text{O} \\
\text{NH}_2 & \quad \text{CH}_2
\end{align*}
\]

(VII)

Chelates (VII) of Cu(II) with $\alpha$-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. $\alpha$-Picolinic acid and quinaldic acid of this category have been investigated and found to be specific for Fe(II) (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.

From the polarographic evidence, the complexes \( \text{Ti(IV)}(\text{EDTA})^- \), \( \text{Ti(IV)}(\text{EDTA})^2- \), and \( \text{Ti(III)}(\text{EDTA})^- \) have been identified (74, 75). Below pH 2.0, \( \text{Ti(IV)}(\text{EDTA})^- \) is stable for
at least 17 days. At higher pH, a yellow colour develops after 60 hours. Above pH 2.5, \( \text{Ti(IV)O(EDTA)} \) is the predominant species which can be polarographically reduced to \( \text{Ti(III)(EDTA)} \). Likewise, below pH 2.0, \( \text{Ti(IV)(EDTA)} \) can be reduced to \( \text{Ti(III)(EDTA)} \) but solutions of the latter reduce water with evolution of hydrogen. The absorption spectrum of \( \text{Ti(III)(EDTA)} \) has been examined with reference to the crystal field theory but its stereochemistry has not been discussed(76).

Schwarzenbach and Sandera(77) have isolated the complexes \( \text{Na}_{2}\text{V(III)(EDTA)} \cdot \text{H}_2\text{O} \) (yellow), \( \text{Na}_{2}\text{V(VI)O(HgO)(EDTA)} \cdot \text{2H}_2\text{O} \) (deep blue) and \( \text{Ba}_{2}\text{V(IV)O(HgO)(EDTA)} \cdot \text{5H}_2\text{O} \) (blue). \( \text{Na}_{2}\text{V(III)(EDTA)} \cdot \text{4H}_2\text{O} \) can be completely dehydrated forming a red brown powder which dissolves in water to give the original colour of the hydrated complex. The V(III) and Fe(III) chelates have similar acidic properties. The yellow colour of \( \text{V(III)(EDTA)} \) changes to red with alkali due to the formation of \( \text{V(III)(EDTA)OH} \). Above pH 12, a brown precipitate forms. Below pH 2.0, \( \text{V(III)(EDTA)} \) does not take up protons, indicating that EDTA is sexadentate. It seems probably that the V(III) chelates has the same structure as the Fe(III) chelate.

Ringbom and co-workers(78,79) have found evidence for the formation of an EDTA complex of the vanadyl ion, \( \text{VO}_2(EDTA) \) (greenish yellow). Below pH 3.0, a proton is taken up to form
$[	ext{VO}_2(\text{H.EDTA})]^-$, accompanied by a slight colour change. The
pK value (3.60) for the dissociation of this proton suggests
that carboxyl group of EDTA is not coordinated as the formula
indicates. It is difficult to understand how EDTA could be
quiquedentate, as two of the octahedral positions must be
occupied by the two oxide ions of $\text{VO}_2^+$. It is possible that
the complex is seven-co-ordinate like the structure proposed
for the Fe(III) chelate. The weak complex $[\text{V(V)(EDTA)}]^+$ has
been detected in solution by Sajo(30). In the pH range 1.0 -
3.5, the stability constant ($7.07$) remains constant but above
pH 3.5, it varies indicating the formation of different species.

Acetylacetone undergoes keto-enol tautomerism,

\[
\begin{align*}
\text{H}_3\text{C} - \text{C} - \text{CH}_2 - \text{C} - \text{CH}_3 & \overset{\text{H}_3\text{C} - \text{C} = \text{CH} - \text{C} - \text{CH}_3}{\sim} \\
\text{OH} & \text{O}
\end{align*}
\]

By loss of a proton, it can form six membered rings with
a large number of metal ions. Most of the metal chelates are

neutral complexes of the types $[\text{M(II)(acac)}_2]^-$ for $\text{M(II)}=\text{Be, Cu,}$
Zn, etc. $\gamma \overset{\text{M(III)(acac)}}{\text{M(III)}} = \text{Al, V, Cr, etc.}$ and $\gamma \overset{\text{M(IV)(acac)}}{\text{M(IV)}} = \text{Zr, Ce, U, etc.}$ (acac = acetylacetonate).

The chelates of Si(IV), Ti(IV) and B(III) are of interest, since they are rare complexes of these elements in cationic complexes. The first two elements have a maximum coordination number of six and cannot form neutral chelates $\gamma \text{M(acac)}$ as can the heavier quadrivalent elements Zr, Ce and Th, which can display a coordination number of eight. Consequently Si(IV) and Ti(IV) form the complexes $\gamma \text{M(acac)}_\text{X}$ (X = a complex ion such as $\text{FeCl}_4^-$(81).

Uranium complexes of $\beta$-diketones of the types $\gamma \text{U(O.CO.CR.CO.CO.CH.CO.R')}$ and $\gamma \text{UO}_2(\text{R.CO.CH.CO.R'})_2$ have been described (82) and the infrared spectra of uranyl $\beta$-diketonates have been examined (83, 84). Salicylic acid forms anionic complexes like $\gamma \text{VO(C}_6\text{H}_4\text{CO}_2)$.

Both phenolic groups in catechol can lose a proton to give a doubly negatively charged chelate group which will form complexes with elements having a high affinity for oxygen (e.g. Ti, Zr, Hf, V... etc). The following complexes are known.

\[ \overset{\text{H}_2(\text{I}) \gamma \text{M(IV)}(\text{cat.})_3 \overset{n \cdot \text{H}_2\text{O}}{\text{M(IV)}} = \text{K, NH}_4; \overset{\text{M(IV)}}{\text{M(IV)}} = \text{Ti, Zr, Th, etc.}, \text{cat.} = \text{catechol} \] (85). \( \overset{(\text{NH}_4)_3 \overset{\text{V}}{\text{V}}(\text{cat.})_3 \overset{2\cdot \text{H}_2\text{O}}{\text{V}} \)

The chelate forming reaction between some o-diphenols and
anions of Mo(VI), V(V) and Sn(IV) has been studied(87).

V(III) forms normal oxinate (H₂Q = oxime) of the type M(III)₂Q₃ and uranium forms more complicated oxinate of the type UO₂·Q₂·QH with 8-quinolinol(83).

Titanium tetrachloride adds on chloride ion forming the complex chlorotitanate ion\(\text{[TiCl}_6\text{]}^{2-}\). Of the chlorotitanates, the ammonium salt \((\text{NH}_4)_2\text{[TiCl}_6\text{]}·2\text{H}_2\text{O}\) and several other salts of organic bases are known. Titanium tetrafluoride has a strong tendency to form fluorotitanates of the type \(\text{M}_2\text{(Ti.F}_6\text{)}\) (89). 5,7-Dibromo-8-hydroxyquinoline forms a sparingly soluble complex \(\text{TiO(C}_9\text{H}_4\text{Br}_2\text{ON)}_2\) with titanium salts in hot dilute acid solution containing 25% to 30% acetone(90). Cupferron forms insoluble complexes with a number of metal ions like Fe(III), V(V), Ti(IV), W(VI), etc. in both weakly acid and strongly acid solutions(90). 8-Hydroxyquinoline (oxime) forms sparingly soluble complexes with Ti(IV) and U(VI) which have the composition \(\text{TiO(C}_9\text{H}_6\text{ON)}_2\) and \(\text{UO}_2\text{(C}_9\text{H}_6\text{ON)}_2\)(90).

Uranyl acetate has a tendency to add on an additional acetate group to form complex anion \(\text{[UO}_2\text{(CH}_3\text{COO)}_3\text{]}^{2-}\). It therefore, readily forms complex salts with other acetates. Of these, the salts of the type \(\text{M}[\text{UO}_2\text{(CH}_3\text{COO)}_3\text{]}\) and \(\text{M}_2\text{[UO}_2\text{(CH}_3\text{COO)}_3\text{]}\) are specific due to their crystallising power. The latter is a double salt when a saturated solution of uranyl acetate mixed with an equivalent proportion of magnesium salt, a yellow crystalline complex of sodium uranyl
acetate precipitate out having the composition, 
Na₂Mg₃UO₂(CH₃COO)₇·7H₂O (89).

Orthohydroxy aromatic ketoximes possess the reactive 
system having an alkyl or aryl group on the carbon atom of 
the -C=N- part. Oximes; 2-hydroxy-4-methoxy, 2-hydroxy-5-
methoxy, 2:4-dihydroxy, 2-hydroxy aceto phenones and 2-hydroxy-
1-acetonaphthone have been investigated by Ephraim(91) for 
their specificity for Cu(II). Poddar(45) has reported the use 
of o-hydroxy acetophenone oxime for quantitative determination 
of Cu(II) and Ni(II) and also reported this oxime for the 
quantitative determination of Ti(IV) and proposed its 
composition TiO(OH)C₆H₆O₂N(92).

Neelkantam and Sitaraman(93), Bhatki and Kabadi(94)
used resacetophenone oxime for gravimetric determination of 
and Cu(II), Ni(II) successfully. Katyal, Prakash and 
Singh(96) reported the use of 2-hydroxy-5-methylpropiophenone 
oxime as an analytical reagent for the determination of V(V). 
Gusev, Kumov and Sokolova(97) reported 2-hydroxy-1-naphthaldoxime 
for gravimetric determination of V(V) and proposed its 
composition, VO(C₁₁H₇O₂N)₂. Tayal(98) used 2-hydroxy-5-
chloroacetophenone oxime for the quantitative determination of 
V(V). Prakash, Dutt and Singh(99) used 2-hydroxy-5-methylpropio-
phenone oxime for the quantitative determination of Cu(II), 
Ni(II), Co(II) and Ti(IV). Naik, Patel and Thakor(100) have 
used 2-hydroxy-3-chloro-5-methylaceto phenone and propiophenone
oximes as analytical reagents for the quantitative determination of Cu(II), Ni(II) and Co(II). Jhaveri, Patel and Thakor (101); Jhaveri, Naik, Patel and Thakor (102); Jhaveri and Naik (103) reported 2-hydroxy-4-methylketoximes as an analytical reagents for the determination of Cu(II), Ni(II), Co(II), Ti(IV), V(V), Pd(II) and Fe(II). Prakash, Dutt, Yog and Singh (104) reported 2-hydroxy-5-methylpropiophenone for quantitative estimation of Ti(IV) and proposed its composition, TiO(OH) \( (C_{10}H_{12}O_2) \). Singh, Kansal, Ojha and Singh (105) have reported 2-hydroxy-5-chloroacetophenone oxime for gravimetric determination of Ti(IV). Lal and Halhotra (106) used 3-bromo-2-hydroxy-5-methylacetophenone oxime as an analytical reagent for determination of Ti(IV) and V(V). Patel and Naik (107); Patel, Patel and Naik (108) reported 2-hydroxy-4-n-propoxyketoximes as an analytical reagents for Cu(II) and Ni(II). Desai, Naik and Naik (109) reported the use of 2-hydroxy-4-ethoxyacetophenone oxime as an analytical reagent for Cu(II) and Ni(II).

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, stearic factor, resonance and size of the ring. Sidgwick (113, 114) 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.

\[
\begin{align*}
\text{O} > \text{N} & \quad \text{Mg(II), Ca(II), Sr(II), Ba(II), Ga(III), In(III),} \\
& \quad \text{Ti(III), Ti(IV), Zr(IV), Th(IV), Si(IV), Ge(IV),} \\
& \quad \text{Sn(II), V(IV), V(V), Nb(V), Ta(V), Mo(V), U(IV),} \\
& \quad \text{U(VI), Fe(III), Co(II).} \\
\text{O} \sim \text{N} & \quad \text{Be(II), Cr(III), Fe(II), Pt(II) metals.} \\
\text{N} > \text{O} & \quad \text{Cu(I), Ag(I), Au(I), Cu(II), Cd(II), Hg(II), V(III),} \\
& \quad \text{Co(III), Ni(II).}
\end{align*}
\]

It can be stated with a broad marginal limit that light 
metals of 1A, 2A and 4B groups form complexes with a ligand 
in which mainly oxygen acts as a donor(115). On the other 
hand, transition metals are strong nitrogen coordinators.

Bouknight and Smith(116) reported that metals, like 
Pt(II), Pd(II), Au(I), Ag(I) and Cu(II) form coordinate 
compounds with sulphur containing ligands like dithiane, 
\( \text{C}_4\text{H}_8\text{S}_2 \). Gonic and coworkers(117) have reported chelates of 
Cu(II), Ni(II), Co(II), Ag(I) and Zn(II) with sulphur and 
nitrogen containing ligands.

Nitrogen \((\text{1S}^2, \text{2S}^2, \text{2P}^3)\) 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(118-125). In many cases ligands 
having nitrogen donors are found to form more stable complexes
than those having others.

**Effect 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. Evens (126) 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 (127) studied the chelates of phenanthroline derivatives with Fe(II) 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 the ligand, the stability of chelate is decreased. Albert and Gledhill (128) and Albert and Magrath (129) made a similar observation with substituted oximes.

**Effect of Metal Ion**

Pfeiffer, Golther and Angem (41); Werner (25); Diehl (24) and others concluded that the elements of transition series including lanthanides and actinides, beryllium, magnesium, elements of 3A, 4B and 5B groups form chelate with different chelating agents. Sidgwick (113, 114) has classified them according to their coordination tendency with nitrogen, oxygen and sulphur.
Nature of the metal-ligand bond
Ligands which have lone pairs available including the $\sigma$ ion, should form double-bond most readily with metals having vacant orbitals. The early transition metal ions e.g. Ti(IV), V(V), etc. readily form bonds with such ligands. Kimball(110), Pauling(111) and Chatt(112) supported the double bond formation between the donor and the metal atom in chelates. Infrared studies by Barraclough and Nyholm(130) and theoretical investigation by Gray and Ballhausch(131) support the conclusion that double bonds between the metal and the ligand are formed.

Effect of Ligand Basicity on the Stability of Complex
When electrophillic or nucleophillic substituents are introduced in a parent organic reagent the basicity of the donor atom of the ligand and the coordination ability of the ligand may change, provided such incoming substituents neither participate in complex formation nor do their bulks cause steric hindrances. For example, the introduction of substituents (Cl, Br, I) into a parent organic reagent 8-hydroxyquinoline increases the basicity of nitrogen or oxygen atom in it. This makes substituted hydroxyquinoline to effectively complex with Fe(III), Cu(II), Ti(IV) and V(V) (152). Such complexes are more stable in acid medium than those formed with 8-hydroxyquinoline.
DETECTION OF CHELATE AND THEIR COMPOSITION

Ley(68) used the following properties as an indication of the cyclic structure of chelates,

(i) absence of normal chemical reactions
(ii) difference in chemical properties of chelating agents
(iii) low electrical conductance
(iv) characteristic colour and
(v) 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(132) and Pfeiffer, Golther and Angern(133) by resolving Co(III) chelate with o-hydroxy-p-methoxyacetophenone and ethylenediamine into two optically active isomers. Dwyer (134), Dubsky and Spritzman(135) used a change in the chemical properties of Ag(I) and Cu(II) as an evidence of chelation. Rosenheim and Lehmann(136) reported the presence of a chelating ring in Be(II) complex with salicylic acid, based on the change in chemical properties.

1. 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(137) 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(138) and Purkayastha(139) used the molar conductance in the application of the Job's method.

2. 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. Baier (140) 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 coworkers(141) and Shibata(142) 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 (143) and Head (144) 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(145) 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. Csokan and Kyiri (146) pointed out more than three absorption bands and attributed them to a hydrogen bonding, aromatic character, polarisation 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 (147) and magnesium, copper and calcium with murexide (148).

Hoendler and Smith (149) and Geyer and Smith (150) observed that a chelate gives different absorption spectra than those of the ligand or the metal ions alone. Dural, Freyman and Lecompte (151) investigated acetylacetone chelates of several metals and found that the $>\text{C} = \text{O}$ 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. Comyns and Sacconi (83, 84) have also studied the infrared spectra of uranyl $\beta$-diketonates. The study of the infrared spectra of metal chelate by Barraclough and Nyholm (130) concluded that double bond is found between the metal and ligand in case of Ti(IV) and V(V) due to lone pair of electrons.

Nigam, Gupta and Mehrotra (153) studied the structure of Ti(IV) chelates with amidoximes and N-arylbenzamidoximes by IR spectra. They observed Ti-O absorption in the region 640 cm$^{-1}$ - 510 cm$^{-1}$ and found a new band in 370 cm$^{-1}$ - 350 cm$^{-1}$.
assignable to Ti-N.

Other Methods

Lerner (154) found that the resolution of the chelates into optically active forms provides a powerful evidence for a ring structure. Specu and Popper (155, 156) used the refractive index as an additive property in the study of complex compound. However, Halder (157) objected to this application for certain functional groups.

Several electromagnetic methods are employed in the study of chelates. Copper chelates of quinoline-8-carboxylic acid were investigated polarographically by Stock (158). Kolthoff and Auerbach (159, 160) used polarographic methods to establish the composition of metal chelates.

Sidgwick and Powell (161) and Mellor (162) reviewed enough evidence for the existence of chelate rings by X-ray crystal analysis of several chelates of acetylacetone, salicylaldoxime, phenanthroline and salicylaldimine with different metals.

As a result of development of newer techniques, studies on thermal dissociation of transition metal complexes have gained tremendous impactus and have attained a new light. Most of the older reports (163-165) are concerned with precipitation of Ti(IV) and V(V) with oxine and 2-methyloxine from the standpoint of gravimetric estimations only. During
the last twenty years, the study of thermal dissociation of coordination complexes of transition metals have certainly elucidated and characterised many of the transition states which are otherwise untractable. Besides thermogravimetric analysis, many other techniques like DTA, DSC, mass spectra, etc. are being increasingly applied in order to have better understanding. Dutta and Lahiri (166), Dutt, Ghosh and Lahiri (167), Dutta and Ghosh (168, 169) and Dutta, Shymal and Ghosh (170) have studied thermal decomposition of oxovanadium complexes. Duval, Wandlandt and many other scientists (171-183) have studied the thermal decomposition of many transition metal complexes.

Malhotra, Mahagen and Chaudhury (184) have carried out thermogravimetric analysis of naphthoxides of Ti(IV). They found different intermediates on the basis of weight changes noted from the TGA curve and concluded that the final product is TiO₂. Mani and Sitakara Rao (185) studied the catalytic activity of ferric OH⁻-O²⁻ system by TGA and suggested the formation of FeO-OH at 200°C and the conversion of FeO·OH to Fe₂O₃ above 250°C.

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.
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(II) with ethylenediamine, monoethanolamine and hydroxide ion, has been investigated by means of both conductometric and potentiometric titrations (186). Foley and Anderson (187) developed a method to determine the stability constant based on the application of Beer's law. Babko (188) used a colourimetric method in the above investigation. Various workers (189-193) have used potentiometric and colourimetric methods to determine the stability constants of chelates of Cu(II), Co(II), Ni(II), V(V), 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. Hartell and Calvin observed that tetrahedral structure results when the bonds are predominantly ionic and a square-planar structure when the bonds are covalent.
In many chelates, having oxygen atom as a donor, evidences are found in favour of a tetrahedral structure. Dwyer and Mellor (195) found that oxygen-coordinated nickel chelates are paramagnetic and assigned tetrahedral structure to them. On the other hand, Sugden (63) and Calvin and Barkelew (42) supported a square planar structure for the chelates in which nickel is bonded to nitrogen.

Jhaveri (101) proposed square planar structure for Ti(IV) complexes with 2-hydroxy-4-methylacetophenone oxime and 2-hydroxy-4-methylpropiophenone oxime on the basis of absorption spectra and magnetic property of these Ti(IV) complexes.

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 (99,101,196).

Tyson and Adams (197) and Calvin and coworkers (42,198) used this method to postulate the structure of salicylaldehyde and salicylaldimine chelates of Cu(II), Ni(II) and Co(II). Russell, Cooper and Vosburgh (199) reported a relation between the magnetic moment and the stability of complexes of Ni(II) and Cu(II) ions with different ligands.
Chelating agents are found to have a variety of applications. Several chelating agents like polyphosphates and polydentate amino acids soften water by deactivating Ca(II) and Mg(II). These chelating agents are responsible for the non-precipitation 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. Sarcemic acid is found to be specific for Fe(III). 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 (200). Fe(II) dithioglycolate chelate is found to act as a catalyst in the oxidation of ascorbic acid.

Chaberek and Hartell (200) 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 (201) 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 extraction. Chelates are also used as bactericides, 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. Lipinska and others (202) studied the complexes of rare earth elements with certain oximes which are useful in hydrometallurgy.
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