CHAPTER III

GENERAL SURVEY OF TRANSITION METAL COMPLEXES
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(a) Brief outline on coordination complexes:

The real advancement in the field of coordination chemistry began after the discovery of hexamine cobalt(III) chloride, CoCl$_3$·6NH$_3$ by Tassaert in 1798. The isolation of orange crystals of CoCl$_3$·6NH$_3$ from two fully stable compounds, CoCl$_2$ and NH$_3$ posed a puzzling question: by what mechanism could two stable compounds combine to form yet another very stable compound? Increasing number of compounds of this type were prepared in the following century. Several theories were proposed by such workers as Graham (1837), Claus (1854), Blomstrand (1869) and Jorgensen (1878) to explain the structure of these complex compounds but they were inadequate to explain subsequent experimental data.

It was Alfred Werner who solved the problem in 1893 by giving his well known theory of 'primary' and 'secondary' valencies, which has remained the basis of coordination chemistry ever since. According to Werner, primary valencies can bind ionizable atoms or radicals while the secondary valencies bind ions or neutral molecules. Werner further introduced a new measure for the binding power of the atom, which was also expressed in integral units and to which the name coordination
number was given. This represents the total number of anions, groups or molecules which may be directly associated with a cation giving rise to a closely associated complex in the form of a distinct entity, to which the name coordination compound was given. The groups, molecules or ions, thus held around the central atom, are said to be co-ordinated with it. The coordinated units known as ligands are arranged symmetrically around the central atom, viz. tetrahedrally, octahedrally, cubically or in square planar form as the case may be, though they may be otherwise ionizable. To each kind of central ion is thus assigned a definite coordination number. The transition metal ions are found to be active in forming these coordination complexes.

Werner's theory made little impact upon chemists until 1911 when he resolved certain coordination compounds into their optical isomers. The electronic theory of valency enunciated by Lewis in 1916 and interpreted and extended for many systems by Langmuir in 1919 and others in the succeeding decade, enabled chemists to express Werner's valency concepts in terms of electrons. Much credit for this particular application of the new theory of valency must go to Sidgwick and to Lowry. The primary valencies of Werner were interpreted as arising from electro valency or electron transfer and the secondary valencies were
regarded as consisting of covalency or electron-pair sharing. Sidgwick accepted the Lewis concept of the two-electron covalent bond between two atoms in a molecule and introduced the coordinate bond for the case in which both the electrons in the shared pair originate on the same atom. Noting that all molecules and ions which can attach to metal ions have at least one unshared pair of electrons, he suggested that this free electron pair is partially donated to the metal ion in the formation of a dative or semipolar bond and it is sometimes represented with an arrow, $M \leftarrow L$, to indicate that the donor group, $L$ has supplied both the electrons to the acceptor, $M$.

In 1939 the stage was set for renewed activity in this field promoted by the availability of physico-chemical methods and instruments and by the valence bond theory developed by Linus Pauling. The results of work done in the last few years have been substantial advances in the areas of kinetic and thermodynamic stability, mechanisms of reaction, stereochemistry, oxidation-reduction, synthesis and theories of bonding.

According to Lewis\(^7\) acid-base concept, the complex compounds are formed between the metal ion (an acid or acceptor) and the ligand (a base or donor).
Regardless of the nature of the coordinating group, the stability of the first transition series is given by \[ Mn^{+2} < Fe^{+2} < Co^{+2} < Ni^{+2} < Cu^{+2} < Zn^{+2}, \] which is known as natural order, or Irving and Williams order. So far two schemes have been proposed to systematise the stability of the complexes.

The electron acceptors are divided broadly into three classes, namely class(a), class(b) and intermediate, by Ahrland, Chatt and Davis which is somewhat connected with the electronegativities. Class(a) [alkaline earths, rare earths, Th(IV), Mn(II), Cr(III), U(IV)] acceptors can form most stable complexes with the first ligand atom of each family (N, O and F), whereas class(b) [Pt(II), Au(II), & (III), Cu(I), Ag(I), Hg(II)] acceptors can form most stable complexes with the second or subsequent ligand atom of each family. Each oxidation state of a metal is regarded as a different acceptor and for this reason many metals are placed in the third group of intermediate which includes Mo, W, Mn, Ta, Re, Fe, Co, Ni, Ru, Rh, Os, Ir, Cu, Zn, Cd, Tl, Pb, Bi, Po etc.

Pearson and Schwarzenbach proposed the second approach in the form of hard and soft acids and bases (HSAB concept). 'Hard' metal ions behave like proton in their ability to coordinate with the ligands, possess small size and high positive oxidation states and have no
valence shell electrons to be easily removed or distorted. 'Soft' metal ions are comparatively large with low or zero oxidation state, and have valence electrons to be easily removed or distorted. The ligand in which the coordinating atom has low polarizability and high electronegativity is called 'hard' base and others with high polarizability and low electronegativity are called 'soft' bases. Hard acids prefer to coordinate with hard bases and soft acids prefer to coordinate with soft bases. A cation which is a relatively hard acid or border line can be made softer by coordination with soft ligand and thus achieves greater ability to coordinate more number of soft ligands. The reverse phenomena is also true. It is important to note that complexes formed between hard acids and soft bases do exist and are thermodynamically stable to hydrolysis.

Factors influencing complex stability.

A stable complex is one which retains its identity for considerable length of time and fails to give in solution the normal analytical reactions of its constituents. It can also be defined in terms of the equilibrium constant for the formation of the complex. The equilibrium constant of a reaction is a measure of the heat released in the reaction and the entropy change during the reaction. The greater the amount of heat evolved in a reaction the more stable are the reaction products.
Since complex formation is essentially a reaction between a cation and anion or dipole, the stability of a complex obviously depends on the nature of the metal and of the ligand.

(a) Effect of metal ion on the stability of complexes.
   (i) Size and charge: Because of the significant influence of electro-static forces in these systems, the smaller the size and the larger the charge of a metal ion the more stable are the metal complexes. Thus stability is favoured by a large charge to radius ratio of the metal ion.
   (ii) Crystal field effects: The crystal field stabilization energy (C.F.S.E) plays an important role in the stability of transition metal complexes and appears to be responsible for the natural order of stability of complexes of the first row transition metals.
   (iii) Electronegativity: The bonding between a ligand and the central ions is, to some extent, due to the donation of electrons by the ligand to the central ion. It might be expected then, that a strongly electron attracting central ion i.e. one with a high electronegativity would form the stabllest complexes.

(b) Effect of ligand on stability of complexes:
   (i) Base strength

   The greater the base strength of a ligand, the greater is the tendency of the ligand to form stable complexes with class(a) metals.
(ii) Chelate effect

The stability of a metal chelate is greater than that of an analogous nonchelated metal complex, for example, $\left[\text{Ni(en)}_3\right]^{2+} > \left[\text{Ni(NH}_3)_6\right]^{2+}$. The more extensive the chelation, the more stable the system.

(iii) Chelate ring size

The most stable metal chelates contain saturated ligands that form five-membered chelate rings or unsaturated ligands that form six-membered rings.

(iv) Steric strain

Because of steric factors, large bulky ligands form less stable metal complexes than do analogous smaller ligands, for example, $\text{H}_2\text{N.CH}_2\text{.CH}_2\text{.NH}_2$ forms more stable complexes than $(\text{CH}_3)_2\text{N.CH}_2\text{.CH}_2\text{.NH}(\text{CH}_3)_2$. The strain is some times due to the geometry of the ligand coupled with the stereochemistry of the metal complex. For example $\text{H}_2\text{N.CH}_2\text{.CH}_2\text{.NH.CH}_2\text{.CH}_2\text{.NH}_2$ can coordinate its four nitrogens at the corners of a square, but $(\text{N(CH}_2\text{.CH}_2\text{.NH}_2)_3$ can not, thus the straight chain tetramine forms more stable complexes with $\text{Cu}^{2+}$ than does the branched chain amine, which is unable to assume the preferred square planar geometry.
Broadly extensive studies of coordination compounds have been made on the following two aspects, (i) synthesis, characterisation and determination of structure and bonding using different physico-chemical methods. (ii) Study of the kinetic reactivity and thermodynamic stability of coordination compounds in solution.

The present investigation deals with the synthetic, bonding and structural aspects of coordination compounds and hence, for the sake of relevance to the present work, only this aspect will be reviewed briefly in the following pages.

Preparation of complex compounds:

An important problem for a coordination chemist has always been the preparation of compounds in pure state. Factors like the nature of the reactants, products and especially the medium generally control the purity and the yield. Since the time of Werner, efforts have been made to improve the synthetic methods of coordination chemistry. Several methods are available for isolating the compound in solid state. It is difficult to make mention of all the methods used at present, however few generalised methods used for preparation of the complex compounds are described below.
(A) Substitution reactions

The majority of complexes may be prepared by substitution reactions. These substitution reactions can be carried out either in aqueous or non-aqueous medium or a mixed solvent medium. The intention is to provide the desired dielectric constant for the medium.

(i) Reaction in aqueous medium

The action of excess of ammonia on aqueous solutions of copper(II) salts.

\[ \text{Cu(H}_2\text{O)}_4^{2+} + 4 \text{NH}_3 \rightarrow \text{Cu(NH}_3)_4^{2+} + 4\text{H}_2\text{O} \]

(ii) Reaction in non-aqueous medium

In the preparation of some complexes the presence of water must be avoided. For example, the action of ammonia on hydrated chromium(III) salts leads to the precipitation of insoluble hydroxy complexes and not to the formation of \( \text{Cr(NH}_3)_6^{3+} \). This complex is readily prepared, however, by reaction between liquid ammonia and anhydrous chromium(III) chloride.

Preparations requiring the use of non-aqueous solvents are those in which the ligand is insoluble in water or the metal ion has a great affinity for water. In the present investigation, most of the complexes have been prepared in non-aqueous medium.
Some times metal complexes are prepared in a mixture of water and water miscible solvent. (Aqueous and non-aqueous) Metal complexes of pipyridine and phenanthroline are generally prepared in this way. Thus addition of an alcoholic solution of bipyridine to an aqueous solution of FeCl$_2$ readily yields the complex $\text{Fe(bipy)}_3^2+$. Fe(H

\[ \text{Fe(H}_2\text{O})_6^{2+} + 3 \text{bipy} \xrightarrow{\text{H}_2\text{O} - \text{C}_2\text{H}_5\text{OH}} \text{[Fe(bipy)}_3^2+] + 2 + 6\text{H}_2\text{O}. \]

(iii) Reactions in the absence of solvent

The direct reaction between an anhydrous salt and a liquid ligand can be used to prepare metal complexes. In many cases the liquid ligand present in very large excess also serves as a solvent for the reaction mixture.

Potassium thiocyanate melts at 173°C and may be used as a solvent at a temperature above this. For example in this medium water is readily displaced from the $[\text{Cr(H}_2\text{O})_6]^{3+}$ ion.

\[ [\text{Cr(H}_2\text{O})_6]^{3+} + 6 \text{NCS}^- \xrightarrow{180^\circ \text{molten KNCS}} [\text{Cr(NCS)}_6]^{3-} + 6\text{H}_2\text{O}. \]

(B) Simple addition reactions

Examples of simple addition reactions of transition metal complexes are confined to those ions which readily change their coordination number. Copper(II) provides many examples.

$\text{Cu(acac)}_2 + \text{py} \rightarrow [\text{Cu(acac)}_2\text{py}]$
(C) **Oxidation-reduction reaction**

The preparation of many metal complexes often involves an accompanying oxidation reduction reaction. This technique is used extensively in the preparation of cobalt(III) complexes. Cobalt(II) salts being always the starting material and either air or hydrogen peroxide is the usual oxidising agent.

The preparation of hexammino cobalt(III) chloride by oxidation of an aqueous solution of cobalt(II) chloride made alkaline with ammonia in the presence ammonium chloride

\[
2\text{CoCl}_2 + 2\text{NH}_4\text{Cl} + 10\text{NH}_3\text{H}_2\text{O}_2 \xrightarrow{\text{charcoal}} 2\left[\text{Co}\left(\text{NH}_3\right)_6\right]\text{Cl}_3 + 2\text{H}_2\text{O}.
\]

This reaction is catalysed by the presence of charcoal.

Many chromium(III) complexes are prepared from chromium(VI) (i.e. chromates or dichromates). A wide variety of reducing agents may be used, but where suitable, the ligand itself functions as a reducing agent. Other chromium(III) complexes are prepared by the oxidation of chromium(II) salts.

An aqueous solution of oxalic acid and potassium oxalate reduces potassium dichromate to the trisoxalatochromium(III) anion.

\[
\text{K}_2\text{Cr}_2\text{O}_7 + 7\text{H}_2\text{C}_2\text{O}_4 + 2\text{K}_2\text{C}_2\text{O}_4 \rightarrow 2\text{K}_3 \left[\text{Cr}(\text{C}_2\text{O}_4)_3\right] + 6\text{CO}_2 + 7\text{H}_2\text{O}.
\]
(D) **Thermal dissociation reactions**

By controlled heating some complexes can be degraded to others, a volatile compound being expelled. For example, on heating blue copper(II) sulphate loses water in a stepwise manner until above ca 220° the anhydrous sulphate is left.

\[
\begin{align*}
\text{CuSO}_4 \cdot 5\text{H}_2\text{O} & \xrightarrow{96.5°} \text{CuSO}_4 \cdot 4\text{H}_2\text{O} \xrightarrow{102°} \text{CuSO}_4 \cdot 3\text{H}_2\text{O} \\
\text{(blue)} & \xrightarrow{220°} \text{CuSO}_4 \xrightarrow{115°} \text{CuSO}_4 \cdot \text{H}_2\text{O} \\
\text{(colourless)}
\end{align*}
\]

Many other complexes behave similarly and heating (usually under vacuum) to a carefully controlled temperature is a useful preparative method. Examples of complexes prepared by thermal dissociation reactions are,

\[
\begin{align*}
[\text{Cr(en)}_3]^+ \text{Cl}_3 & \xrightarrow{210°} \text{cis}[\text{Cr(en)}_2\text{Cl}_2]^+ \text{Cl} + \text{en}. \\
[\text{Cr(en)}_3]^+(\text{SCN})_3 & \xrightarrow{130°} \text{trans}[\text{Cr(en)}_2(\text{SCN})_2]^+\text{SCN} + \text{en}.
\end{align*}
\]

(E) **Reactions of coordinated ligands**

New metal complexes may be prepared by substitution reaction of the coordinated ligands. One relatively simple complex which has been the subject of extensive study is trisacetylacetonato chromium(III).
The action of bromine in acetic acid leads to bromination of the acetylacetone ring.

Examples of other groups which have been used to replace the active hydrogen atoms in metal acetylacetonates are \(-\text{NO}_2, -\text{NH}_2, -\text{N}_3^+, -\text{CHO}, -\text{COCH}_3\) and \(-\text{SCl}\).

**Coordination number and stereochemistry**

Significant advances in assigning the correct coordination number and preferred stereochemistry are due to the help of various physical measurements like x-ray diffraction, magnetic moment, dipole moment, conductivity and spectral measurements.

**Coordination number two**

The relatively rare coordination number two is exhibited by the \(d^{10}\) ions, \(\text{Cu}(I), \text{Ag}(I), \text{Au}(I)\) and \(\text{Hg}(II)\), or \(d^0\) ions such as \(\text{UO}_2^{+2}\) with a linear (group \(D_h\)) or bent (group \(C_{2v}\)) geometry. The best known example of coordination number two is the complex ion formed when silver salts dissolve in aqueous ammonia, \(\text{Ag(NH}_3)_2^{+}\).
This, like all other known cases of this coordination number, is linear, $\text{H}_2\text{N} - \text{Ag} - \text{NH}_3$. Other complexes of this coordination number, which is almost entirely confined to copper(I), silver(I), gold(I), and mercury(II), are $[\text{CuCl}_2]$ and $\text{Hg(CN)}_2$. Non-linear complex compounds of coordination number two are unusual.

**Coordination number three**

The two most symmetrical arrangements are planar and pyramidal with $D_{3h}$ and $C_{3v}$ symmetry respectively. A relatively less common unsymmetrical T shape form with $C_{2v}$ symmetry is also observed in few cases. Out of the three arrangements, the most favoured planar one is suitable for $\text{SP}^2$ hybridization of bonding. The only known three-coordinate complexes of transition metals were those formed by the $d^{10}$ ions of univalent copper, silver and gold. Thus a number of $[\text{CuL}_3]^+$ ions are known, and crystal structure studies have shown the Cu$^+$ ion to have a trigonal planar environment of sulphur (or selenium) atoms when $L = \text{ethylenethiourea}$ (Weinmyer et al$^{12}$), $\text{R}_2\text{PS}$, $\text{R}_2\text{PSe}$ or $\text{R}_3\text{AsS}$ (Tielhof et al$^{13}$).

Other typical examples of trigonal planar, three coordinate complexes are, $\text{Au(P Ph}_3)_2\text{Cl}$ and $\text{Ag(P PhMe}_2)_2\text{I}$ (Baenziger et al$^{14}$), $\text{Ag(FNO)ClO}_4$, $\text{Ag(PicNO) ClO}_4$ and $\text{Ag(FNO)NO}_3$ (Pradhan and Ramana Rao$^{15}$), $\text{Cu(P Ph}_3)_2\text{Cl}$ (Davies et al$^{16}$), $\text{Cu}\left[\text{SC(NH}_2)_2\right]_3\text{Cl}$ (Amma et al$^{17}$), $\text{Cu(SP Ph}_3)_3\text{ClO}_4$ (Eller et al$^{18}$).
Steric requirements also appear to play a major role in determining the structure of compounds incorporating bulky $-N(SiMe_3)_2$ groups. Thus a number of transition metal compounds have been prepared with stoichiometry $M\left[N(SiMe_3)_2\right]_3$, and in the titanium, vanadium, chromium and iron compounds it has been shown that each transition metal has a trigonal planar arrangement of nitrogens$^{19,20}$.

Coordination number 4 four

The principal stereochemistries observed for coordination number four are tetrahedral (Td group) and square planar, ($D_{4h}$ group) although various distorted versions of these two structures may be found when all the ligands are not the same or if the d levels are filled unevenly. The tetrahedral arrangement is found for complexes of divalent beryllium, zinc, cadmium and mercury, and of trivalent boron, aluminium and gallium. The principal factors that determine whether a transition metal ion will form tetrahedral or square planar complexes are (a) the crystal field stabilization energy, and (b) mutual repulsion between the ligands - which, in turn, will depend on the 'bulk' of the ligand and on its electronegativity. When the CFSE is low, tetrahedral configuration is favoured rather than the square planar one. Thus, for all transition metals, four coordinate complexes would be square planar except the $d^0$, $d^5$(spin-free) and $d^{10}$ ones.
where CFSE is zero. However, the mutual repulsion between the ligands must also be taken into account. The steric factor will be particularly important when the field is weak and the CFSE correspondingly small. For the tetrahedral arrangement the metal ions use \( sp^3 \) or \( sd^3 \) hybrid orbitals and \( dsp^2 \) or \( sp^3d \) hybrid orbitals are used for square planar configuration. Few interesting examples of each arrangement are described below:

**Tetrahedral**

Most of the known tetrahedral complexes are either anionic, \([MX_4]^{-2}\) or \([MX_3L]^{-}\) where \( L \) is a neutral ligand or neutral \( ML_2X_2 \). Quite a number of tetrahedral nickel(II) complexes have been characterized including the anions \([NiCl_4]^{-2}\), \([NiBr_4]^{-2}\) and \([NiI_4]^{-2}\). Some complexes involving bulky tertiary phosphine ligands are also tetrahedral e.g. \( Ni(P\ Ph_3)_2Cl_2 \), \([Ni(P\ Bu_3)Br_3]^{-}\) (Alyea et al.\(^{21}\)). Another tetrahedral complex is \( Fe(SPMe_2NPMe_2S)_2 \) in which the iron has a somewhat distorted tetrahedral environment of sulphur atoms (Churchill et al.\(^{22}\)). Copper(II) forms tetrahedral complexes, and the only tetrahedral fully characterized are \([CuBr_4]^{-2}\) and \([CuCl_4]^{-2}\) anions.

**Square-planar**

This form of coordination is especially characteristic of certain elements like Ni(II) and Cu(II) but is is common for those ions having \( d^8 \) configurations—rhodium(I),
iridium(I), palladium(II), platinum(II) and gold(III) e.g. \([\text{PtCl}_4]^{-2}\), \([\text{PdCl}_4]^{-2}\) and \([\text{AuF}_4]^{-}\) anions. The best known dimethylglyoximato nickel(II) and bisacetylacetonato copper(II) complexes are square planar in nature.

**Coordination number five**

There are two basic configurations that can be adopted by compounds of coordination number five, e.g. trigonal bipyramidal (TBP) (group \(D_{3h}\)) and square pyramidal (SP) (group \(D_{4h}\)). Because of their similar energy, the two structures are interconvertible. This is an ideal example of stereochemical non-rigidity. In case of transition elements for all configurations other than \(d^0, d^{10}\) and spin-free \(d^5\), the CFSE associated with SP arrangement is greater than that for a TBP ligand distribution. Of course this difference of energy is not very high. Few typical examples of SP or distorted SP compounds are \([\text{MnCl}_3]^{-2}\), \([\text{Ni(O AsMe}_3)_2]^+\), \(\text{Cu(acac)}_2\). The TBP configuration is associated with quite a large number of compounds, although often the structure is found to be distorted. A classical example is \(\text{Zn(acac)}_2\) which has been found to possess a structure intermediate between TBP and SP. Some interesting examples of TBP configuration are \(\text{Zn(dtc)}_2\text{py}, \text{Cr(NMe}_3)_2\text{Cl}_3, \text{Zn(terpy)}\text{Cl}_2\).
Over the past ten years quite a number of five coordinate complexes have been prepared with stoichiometry $ML_5$, $ML_4L'$, $ML_3L''$, $ML_2L''$, $ML_2B$, $ML_B$, $ML_T$, $ML'T$ and $ML(Tet)$, where $L, L', L''$ = monodentate, $B$ = bidentate, $T$ = tridentate and $Tet$ = tetradentate ligand; with a large number of central metal atoms such as Ti, V, Cr, Mo, Mn, Re, Fe, Co, Ni, Ru, Pd, Os, Pt, Cu, Zn and Cd in addition to many non transition elements. Both the high and low-spin complexes with either TBP and SP structure are known. It is seen that low-spin complexes are formed when three or more donor atoms come from the second or subsequent row of the periodic table (i.e. P, As, S, Br, I) and that high-spin complexes result when the majority of the donor atoms are nitrogen. Ramana Rao and coworkers$^{23,24}$ have also reported a good number of five coordinate Zn(II) complexes. Recently Pradhan and Ramana Rao$^{25}$ have reported some interesting five coordinated divalent nickel complexes of the type $Ni(dtc)_2L$, where $L =$ substituted pyridine.

**Coordination number six**

This is the most common coordination number where the six ligands lie at the vertices of a regular octahedron (group $O_h$) or a distorted octahedron. There
are three principal forms of distortion of the octahedron, viz. tetragonal (group $D_{4h}$), rhombic (group $D_{2h}$) and trigonal (group $D_3^d$). Another comparatively less common six coordinate geometry is trigonal prism (group $D_3^h$).

**Coordination number seven**

Most of the seven coordinated complexes can be properly described in terms of one of the ideal geometries, pentagonal bipyramid (PBP) (group $D_{5h}$), capped octahedron (CO) (group $C_{3v}$) or capped trigonal prism (CTP). By now, over two hundred seven coordinate structures have been determined. Some of the simpler examples of each geometry are:

- Pentagonal bipyramid: $[ZrF_7]^{-3}$, $[V(CN)_7]^{-5}$, $ReF_7$, $[UO_2F_5]^{-2}$
- Capped octahedron: $MoX_4\cdot 3PR_3$, $[W(CO)_4\cdot Br_3]^{-}$

Generally PBP arrangement is favoured when bidentate ligands are involved, except when the complexes contain carbonyl or bulky groups, in which case the CO structure dominates. CO and CTP structures are also found for complexes involving bidentate groups, particularly those of stoichiometry $ML_5B$ in which some of the monodentate ligands are carbonyl groups.

**Coordination number eight**

Generally eight coordination is common for complexes formed between large cations and small ligands, since over crowding will be at a minimum and the steric strain
less. Eight coordination is mainly found for complexes of metal ions of the second and third transition series, the lanthanides and actinides, which have \( d^0 \), \( d^1 \) or \( d^2 \) electronic configurations and a formal charge of +3 or more. The molecular geometries for eight coordinate complexes are often found to be distorted from the ideal ones. The different possible geometrical arrangements are cubic (group \( O_h \)), square anti prism (group \( D_{4d} \)) dodecahedral (group \( D_{2d} \)) and hexagonal bipyramidal (group \( D_{6h} \)). Two other relatively less common geometries, bicapped trigonal prism (group \( D_{3h} \)) and bicapped trigonal anti prism (group \( D_{3d} \)), are also known. The hexagonal bipyramidal arrangement is found mostly with uranyl complexes of the type \( UO_2L_2B_2 \) and \( UO_2B_3 \), where \( L = \) monodentate, \( B = \) bidentate ligand. The compound \( [UO_2(dtc)_3]^− \) is also known to possess \( D_{6h} \) symmetry. \([Et_4N]_4[U(NCS)_8] \) (Countryman and McDonald)\(^{26}\) \([Bu_4N]_3[Mo(CN)_8] \), \([ZrF_8]^{-4} \), \( Ti(diars)_2Cl_4 \), \( Ti(NO_3)_4 \), \([Zr(ox)_4]^{-4} \) and \([Th(dtc)_4]^{-4} \) are few examples of dodecahedral configuration. Another interesting examples of dodecahedral configuration is \( [Ph_4As]_2[Mn(NO_3)_4] \) (Drummond and Wood)\(^{27}\). The bidentate acetylacetonate ligand gives square antiprism structure in \( M(acac)_4 \) complexes. Besides, the compounds \( [La(F_2pyO)_6]^{3+} \), \( [TaF_8]^3 \), \( [UF_8]^{-4} \), \([Mo(CN)_8]^{-3} \) and \([U(NCS)_3]^{-4} \) are also known to possess
D$_{4d}$ symmetry. In recent years, several eight coordinate complexes have been characterized for first row elements. Ramana Rao and coworkers have also reported a number of eight coordinated manganese(II) and cobalt(II) complexes with probable structures.

**Coordination number nine, ten, eleven and twelve**

Such high coordination numbers are comparatively rare and the best characterized complexes are those formed by the lanthanide and actinide elements.

For coordination number nine, the two ideal geometries are the mono capped square antiprism, e.g. [Pr(terpy)Cl(H$_2$O)$_5$]$^{+2}$, and the tricapped trigonal prism, e.g. [Yb(dmso)$_3$(NO$_3$)$_3$] (Bhandary et al$^{32}$).

Complexes of ten coordination may have a configuration of either bicapped square antiprism or bicapped dodecahedron. Of the two configurations, the bicapped square antiprism is known to possess less energy. This coordination number is found in [La(EDTA)(H$_2$O)$_4$], [La(dmso)$_4$(NO$_3$)$_3$] (Graziani et al$^{33}$).

Coordination number eleven has been observed for Th in Th(NO$_3$)$_4$·5H$_2$O (Akhtar and Smith$^{34}$).

An authentic example of coordination number twelve is [Ce(NO$_3$)$_6$]$^{-3}$, in which the six bidentate nitrate groups establish an icosahedron around cerium(III).
(b) Metal-ligand bonds in coordination complexes

The important aspect for the coordination compounds of transition metals is how to describe and characterise the bonding between the central ion and the ligand in terms of some electronic theory. Presently, coordination chemist is exposed to the frontiers of knowledge regarding the structure, stability and general properties of coordination compounds through the following theories:

1. The valence bond theory.
2. The crystal field theory.
3. The ligand field theory.
4. The molecular orbital theory.

1. The Valence Bond Theory

The application of the valence bond theory to complexes is due to Pauling\textsuperscript{35}. It deals with the electronic structure of the ground state of the central metal atom and is concerned primarily with the kind of bonding, stereochemistry and gross magnetic properties present in complexes.

According to the valence bond theory the bonding results from overlap of an orbital of the ligand containing an unshared pair of electrons with hybridized orbitals of the metal ion. This may be thought of either as a sharing of the electron pair between the metal ion and ligand or as a partial donation of the ligand electrons to the metal
ion. Pauling's theory takes into account the following assumptions: (1) The central metal atom must make available a number of orbitals equal to its coordination number for the formation of covalent bonds with suitable ligand orbitals. (2) A covalent σ bond arises from the overlap of a vacant metal orbital and a filled σ orbital of the donor group. (3) In addition to the σ bond, a π bond may be formed if the metal atom contains suitable d electron in an orbital which can overlap with the vacant orbital of the donor atoms. This bond will change the charge distribution on both the metal and the ligand in such a way as to strengthen the σ bond.

The strongest covalent bond will be formed when the charge clouds overlap one another as much as possible. In order to satisfy this criterion it has been shown that the original atomic orbitals should be hybridized to form a new set of equivalent bonding orbitals having definite directional properties. Thus one 4s, three 4p and two 3d orbitals can be combined to produce a set of six d^2sp^3 hybrid orbitals directed towards the corners of a regular octahedron. These hybrid orbitals are then available for occupancy by electron pairs from the coordinated groups. The spatial orientation of the hybrid orbitals defines the stereochemistry of the metal complex. The non bonding electrons of the metal ion are arranged in accordance with Hund's rule in the remaining orbitals. For maximum stability the d orbitals employed in the hybridization process are of the next lower principal quantum number than the s or p.
In order to account for the different magnetic properties of a given metal ion in various complexes, Pauling postulated that strong electron donating ligands such as CN\(^-\) would form covalent bond with metal ions. In order to provide vacant orbitals for hybridization it would be necessary to pair electrons in non-bonding orbitals of the metal in the complex. For weak ligands or highly electronegative ones, such as F\(^-\), ionic bonds would be formed. Thus, metal complexes were classified under 'covalent' and 'ionic' on the basis of the observed magnetic moment. The term 'ionic' has been criticized because many of the complexes supposed to be ionic on the basis of magnetic criterion have properties such as volatility and solubility in organic solvents which are associated with covalent compounds. It is suggested that in such complexes the s, p and d orbitals of the same principal quantum number are hybridized to produce \(sp^3d^2\) hybrid orbitals. Complexes formed by utilizing \(sp^3d^2\) hybrid orbitals would still be covalent and it would not be necessary to pair electrons in the lower d orbitals. However, such complexes would be less stable than the complexes formed by utilising \(d^2sp^3\) hybridized orbitals. Other terms that were introduced to distinguish the apparent two types of complexes are: outer and inner orbital (Taube), spin-free and spin-paired (Nyholm) and high-spin and low spin (Orgel). Most of these terms have lost their original value now and the only ones generally retained are the truly descriptive ones, namely, high-spin low-spin and spin-free - spin-paired.
Though the valence bond theory has been extremely useful in explaining and predicting stereochemistry of complexes, it suffers from the following defects:
(i) It is restricted to qualitative explanations.
(ii) It does not permit the interpretation or prediction of spectra.
(iii) It does not account for detailed magnetic properties.
(iv) It can not explain or predict the relative energies of different stereochemistries.
(v) It can not explain or predict the properties resulting from or dependent upon the energy splittings of the d orbitals.

2. Crystal field theory

The crystal field theory was originally proposed by Bethe as a modification of the simple electrostatic picture of complex formation. These principles were applied by Schlapp and Penny and also by Van Vleck to account for the magnetic properties of the transition metal ions and their complexes.

The five d orbitals which are degenerate in 'free' ion of the metal, split up into different energy levels. Under the influence of the electrostatic field of the ligands according to nature and extent of the field. In an octahedral or tetrahedral cubic field, two sets of orbitals are observed: a set of doubly degenerate orbitals $d_z^2$ and $d_{x^2-y^2}$ ($e_g$) and another set of triply degenerate orbitals $d_{xy}, d_{xz}$ and $d_{yz}$ ($t_{2g}$).
The energy of separation between two sets is called C.F.S.E. or $\Delta$ or 10Dq. These split orbitals always maintain the centre of gravity, e$_g$ orbitals separated by $3/5 \Delta_0$ and t$_{2g}$ orbitals by $2/5 \Delta_0$ from original position of the free-ion degenerate state.

An octahedral symmetry often distorts in the presence of a non-cubic or a strong ligand field or when the trans ligands are gradually withdrawn from an octahedral site. The e$_g$ and t$_{2g}$ orbitals get further split up and in the limiting case d$_{xy}$ orbital crosses over the d$_{2z}$ orbital ultimately setting up a square planar environment. Figure-1 shows the crystal field splittings of the d orbitals of a central ion in complexes having different geometries.

The value of the splitting parameter varies from complex to complex and depends upon the nature of the ligands and on the metal ion. The spectrochemical series of the ligands which reflects the decreasing order of the crystal field splitting and is independent of the metal ion, is represented as:

$$CN^- > \text{NH}_3 > \text{H}_2O > F^- > Cl^- > Br^- > I^-$$

According to Ballhausen$^{40}$, if the cation, the anions and the cation-anion distance are the same in both octahedral and tetrahedral cases, the ratio of $\Delta_t$ to $\Delta_o$ will be 4/9.

However, inspite of all this sort of pragmatic success, this electrostatic model suffers from some drawbacks.
Fig. 1 Crystal Field Splittings of the d Orbitals of A Central Metal Ion in Complexes of Different Symmetries.
The theory provides an explanation for tetrahedral and octahedral configurations for the four and six coordinate complexes respectively, but the existence of four coordinated square planar complexes could not be accounted for satisfactorily. Also, the formation of stable complexes by non planar ligands like carbon monoxide could not be explained. It is found that the second and third row transition elements form more stable complexes than the smaller elements of the first row. This contradicts the idea of the CFT that for a given set of ligands the smaller ions should form stronger bonds. Finally, being based on a purely electrostatic model, the CFT offers no explanation for the degree of covalency between the metal ion and the ligands. This is against the experimental evidence coming from a variety of sources all showing that the d electrons spend a part of their existence in orbitals belonging to the ligand atom.

Some consequences of inner d orbital splitting

The d orbital splitting affects the magnetic, thermodynamic, spectral and structural properties of the transition metal complexes. In order to predict the magnetic properties of a transition metal ion in its complexes, it is necessary to determine the unpaired electron spins which it has or may have. By referring to the crystal field splitting diagram of an octahedral complex it is clear that for d^1, d^2, d^3, d^8, d^9, and d^10 ions in octahedral environments, there will always be 1, 2, 3, 2, 1 and 0
unpaired electrons, respectively, which is independent of the value of $\Delta_0$. For $d^4$, $d^5$, $d^6$, $d^7$ ions, the number of unpaired electrons can be either 4, 5, 4, 3 respectively in case of high spin configuration or 2, 1, 0, 1 respectively in case of low spin configuration depending upon the magnitude of $\Delta_0$ relative to $P$ (pairing energy) for the particular ion. The value of $P$ can be evaluated fairly from the data on the spectrum of the gaseous ion. For the ligands favouring low-spin complexes $\Delta$ is greater than $P$, while for all the ligands giving high spin complexes, $P$ is greater than $\Delta$. The value of $\Delta$ can be either directly obtained or indirectly computed from the position of various absorption bands in the electronic spectrum of a given complex.

3. The ligand Field Theory

The historical origin of the ligand field theory is the crystal field theory. In a sense, the IFT is a combination of CFT and MOT and thus, can be defined as the theory of the origin and consequences of the splitting of inner d or f orbitals of ions by their chemical environments. The theory is a superior tool for dealing with complexes as it involves the best features of both CFT and MOT.

The CFT with suitable modifications to account for a certain degree of covalent bond formation of the metal ion (or atom) with polar or non-polar ligands is IFT and thus, is often referred to as adjusted crystal field
theory. In an octahedral complex, the higher \( e_g \) orbitals are utilised in covalent bond formation with the \( \sigma \) orbitals of the ligands and the lower energy \( t_{2g} \) orbitals of the metal are utilised for \( \pi \) bond formation with suitable \( \pi \) orbitals of the ligands. The LFT has been most successful in interpreting in detail the magnetic properties, stereochemistry, stability, liability and absorption spectra of the complexes.

Briefly speaking, in the LFT approximation, the nature of the ligand and its orbitals are specifically included in the energy level scheme. Symmetry orbitals are constructed from the ligand array and these are then combined with orbitals of the central metal, which have the approximate symmetry to form full molecular orbitals. There are several steps in applying this method:

(a) It is necessary to decide upon the symmetry of the complex and find out the point group to which it belongs.

(b) Using this symmetry point group, the linear combination of the available ligand orbitals are constructed such that they transform according to the irreducible representation of the group.

(c) It is essential to determine to which irreducible representation of the point group the orbitals of the metal ion belong in the presence of the field.

(d) The ligand group orbitals are then combined with the metal orbitals of the same symmetry, forming the final MO's.
4. The Molecular Orbital Theory

The application of MOT to coordination complexes is mainly due to Van Vleck. The theory assumes that, under the symmetry restriction, the overlap of the ligand group orbitals and the metal ion orbitals will occur to some extent. This model, thus includes the electrostatic situation as one extreme, maximal overlapping of orbitals as the other extreme, and all intermediate degrees of overlap in its scope. The symbols used in the MOT are of group theoretical origin which represent the symmetry class of the metal orbitals with matching symmetry of the ligand orbitals and the molecular orbitals resulting from the overlap of these two. These symbols are quite informative, for example, the symbol $a_{1g}$ stands for a single full symmetry molecular orbital, $e_g$ represents a pair of equivalent with different space orientation orbitals and $t_{1u}$ symbolizes for a set of three equivalent orbitals with varying orientations in space. The subscripts $g$ and $u$ stand for centro-symmetric ($g$ from gerade meaning even) or anticentrosymmetric ($u$ from ungerade meaning uneven), respectively. The molecular orbitals are polycentric and are obtained by linear combination of atomic orbitals. The molecular orbitals obtained by the maximum positive overlap of metal orbitals with its matching symmetry of ligand orbitals are known as bonding MO, whereas maximum negative overlap of these two results in antibonding MO. The orbitals are named by their symmetry designations, using asterisk to indicate that the molecular orbital is
antibonding. Different steps involved in the linear combination of atomic orbitals of an octahedral complex (e.g. Ti(\(H_2O\))^3+) are as follows:

(a) The orbitals of the central metal atom and the ligand orbitals combine to form molecular orbitals. The \(t_{2g}\) orbitals of the metal ion lying between the bonding and antibonding orbitals will remain as non-bonding orbitals.

(b) The resultant molecular orbitals are arranged in order of increasing energies and the electrons are fed into them.

(c) The molecular orbitals possess the greater characterization of the atomic orbitals which are closest to them in energy and lesser (but, definite) characteristics of the component orbitals which are well separated in energy.

(d) The ligand electrons are adjusted in the bonding molecular orbitals which are nearer in energy to the ligand group atomic orbitals and hence they partake more of ligand character.

(e) The electrons of the central metal ion are then adjusted in the triply degenerate non bonding \(t_{2g}\) orbitals and the doubly degenerate antibonding \(e^*\) orbitals. The difference between the \(t_{2g}\) and \(e^*\) orbitals is equal to the crystal field splitting parameter, \(\Delta\).
This parameter, $\Delta$ is dependent upon various factors such as stereochemistry of the complex, the nature of the ligand, the charge on the central metal ion and the principal quantum number of the d valence orbitals.

For considering the molecular orbital diagram for an octahedral complex like Ti(H$_2$O)$_6^{+3}$ each electron of the valence orbitals must be accounted for to construct Fig.2. The complex is considered to be composed of Ti$^{+3}$ and six water molecules. Each of the six valence orbitals of the water molecules furnishes two electrons, for a total of twelve. Along with one electron from 3d orbital of Ti$^{+3}$, the total number of electrons are thirteen which need to be placed in the MO shown in Fig.2. The ground state of Ti(H$_2$O)$_6^{+3}$ is, therefore, $a^2_1g e^4_6 t^6_1u t^1_2g$ with $s = \frac{1}{2}$. There is only one electron in the nonbonding $t^2g$ level. Consistent with this ground state, Ti(H$_2$O)$_6^{+3}$ is paramagnetic with $s = \frac{1}{2}$.

The difference in energy between $t^2g$ and $e^*_g$ is called $\Delta$ or 10D$_q$. Excitation of the electron in $t^2g$ to $e^*_g$ occurs with absorption of light in the visible region of the spectrum and Ti(H$_2$O)$_6^{+3}$ is therefore coloured reddish violet. The colours of any other transition metal complexes are also due to such d-d transitions. The MOT is no doubt the best theory so far, but it suffers from drawbacks that the theory involves a lot of complicated mathematical procedures.
Fig. 2 Molecular Orbital Diagram for an Octahedral Complex with Six Sigma-Bonding Ligands.
Molecular orbital energy level schemes have been worked out for most of the geometries encountered in coordination chemistry. These include linear, square planar, tetrahedral, octahedral and trigonal bipyramidal structures.
The structural identification of coordination compounds is made by various methods.

(i) Chemical analysis helps in determining the empirical formula.

(ii) Molecular weight determination distinguishes between the discrete and polymeric compounds.

(iii) Measurement of molar conductance helps in determining the coordination number of metal ion.

(iv) Experiments based on (a) spectroscopic methods (b) diffraction methods, (c) magnetic methods and (d) miscellaneous methods are of immense help for structural investigation of the complex compounds.

Out of these four, the fourth one, which takes into consideration the position of the central nucleus, the inter nuclear distance, the bond angle and bond length among the constituting atoms or groups, is quite an important tool in the hands of the chemists. These studies have a major say regarding the symmetry of the complexes. Out of these, the methods which have been used in the present investigation are given below:

(1) **Molecular weight determination**

Determination of molecular weight indicates whether the compound is monomer or polymer and also whether it is
ionic or non-ionic. Hence this measurement helps in the tentative assignment of the coordination number. Different methods are available for determination of molecular weight based on elevation of boiling point, depression of freezing point etc.

(2) Conductance measurement

The molar conductance method is quite helpful for determination of coordination number of the metal ion provided no association or dissociation takes place in the solution state. Conductance is an additive property of a solution depending on all the ions present. Generally, it is measured in $10^{-3} - 10^{-4}$ molar solution and the observed values are compared with the standard values of molar conductance. The values reveal the ionic or non-ionic nature including the number of ions present in the system. Some standard values of molar conductance for 1:1, 1:2 electrolytes in common solvents are given in Table 1.

Of course, one need to be careful regarding the solvolytic effect and the dissociation of the complex in the medium, which may occur as follows:

$$\left[ ML_6 \right] X_2 \rightleftharpoons \left[ ML_4 X_2 \right] + 2L$$

$$\left[ ML_4 X_2 \right] + \text{solvent} \rightleftharpoons \left[ ML_4 (\text{solvent}) \right] X_2.$$ 

In such a case, the stability of the complex, nature of the ligand and solvent molecules play important roles.
<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\Lambda M$ (mhos)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1:1</td>
</tr>
<tr>
<td>Water</td>
<td>90-130</td>
</tr>
<tr>
<td>Methanol</td>
<td>80-120</td>
</tr>
<tr>
<td>Ethanol</td>
<td>35-45</td>
</tr>
<tr>
<td>Acetone</td>
<td>100-140</td>
</tr>
<tr>
<td>Pyridine</td>
<td>60-80</td>
</tr>
<tr>
<td>Nitromethane</td>
<td>150-175</td>
</tr>
<tr>
<td>Nitroethane</td>
<td>50-70</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>25-35</td>
</tr>
<tr>
<td>1,2 dichloroethane</td>
<td>14-20</td>
</tr>
<tr>
<td>Ethylenedichloride</td>
<td>50-70</td>
</tr>
<tr>
<td>Dimethylformamide</td>
<td>20-80</td>
</tr>
<tr>
<td>Dimethylsulfoxide</td>
<td>35-45</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>120-160</td>
</tr>
</tbody>
</table>
Magnetic susceptibility measurement is one of the most useful techniques for determination of oxidation state, bond type and stereochemistry of the metal ion. When a substance is placed in a magnetic field, the latter induces a magnetic moment in the molecules resulting in the following three types of magnetic effect.

(i) **Diamagnetism**

Diamagnetism is a property possessed by all forms of matter having at least some electrons in closed shells. It arises from the interaction of the applied magnetic field with the field induced in the completed shells of electrons. This field must necessarily oppose the applied field. The effect of this interaction is to cause the diamagnetic sample to move away from the applied field in order to diminish the interaction. Hence, the diamagnetic susceptibility is a negative quantity.

Even an atom with a permanent magnetic moment will have diamagnetic behaviour working in opposition to the paramagnetism when placed in a magnetic field, provided only that the atom has one or more closed shells of electrons. Thus, the net paramagnetism measured is slightly less than the true paramagnetism because some of the latter is cancelled out by the diamagnetism.

Since the magnitude of the diamagnetic effect is usually 10 to 1000 times less than that of the paramagnetic effect, substances with unpaired electrons almost always have
a net paramagnetism. Of course, a very dilute solution of a paramagnetic ion in a diamagnetic solvent such as water may be diamagnetic because of the large ratio of diamagnetic to paramagnetic species in it. Another important feature of diamagnetism is that its magnitude does not vary with temperature. This is because the moment induced depends only on the sizes and shapes of the orbitals in the closed shells and these are not temperature dependent.

(ii) Ferromagnetism and antiferromagnetism

These two effects are the result of interactions between the dipoles on the neighbouring atoms i.e. the interionic interactions. All the paramagnetic substances are associated with some interionic interactions below certain temperature and thus exhibit ferromagnetic and antiferromagnetic behaviour, depending on the sign of the interaction. The ferro- and antiferromagnetic interactions are decreased when the magnetic species are separated from one another physically.

(iii) Paramagnetism

The magnetic properties of an atom or ion are qualitatively associated with the spin and orbital moment of the electron. The atoms, ions or molecules with unpaired electrons exhibit paramagnetism.

The magnetic moments of atoms, ions and molecules are usually expressed in Bohr Magnetons, (B.M.). The Bohr magneton is defined as:

\[ 1 \text{B.M.} = \frac{\frac{eh}{4\pi mc}} \text{.......... (1)} \]
where \( e \) is electronic charge, \( h \) is Planck's constant, \( m \) is the electron mass and \( c \) is the speed of light. This is not, however, the moment of a single electron.

The magnetic moment, \( \mu_s \), of a single electron is given, according to wave mechanics, by the equation

\[
\mu_s = g \sqrt{s(s+1)}
\]

(2)

where \( s \) is the absolute value of the spin quantum number and \( g \) is the 'gyromagnetic ratio' (g factor). For the free electron, \( g \) has the value 2.0023. So the spin magnetic moment of one electron can be calculated as

\[
\mu_s = 2 \sqrt{\frac{1}{2}(\frac{1}{2}+1)} = \sqrt{2} = 1.73 \text{ BM.}
\]

Thus any atom, ion or molecule having one unpaired electron should have a magnetic moment of 1.73 BM from the electron spin alone. This may increase or decrease by an orbital contribution.

The magnetic moments are not measured directly but can be calculated from the magnetic susceptibility. The molar susceptibility, \( \chi_M \), can be obtained as

\[
\chi_M = \chi_G \times M
\]

where \( M \) is the molecular weight of the substance and \( \chi_G \) is the gramme susceptibility. The 'effective magnetic moment', \( \mu_{\text{eff}} \), which gives directly the number of unpaired electrons present in the metal ion is given by the expression

\[
\mu_{\text{eff}} = \left[ \frac{3 \hbar T}{N \beta^2} \chi_M \right]^{\frac{1}{2}}
\]

(3)

where \( N = \text{Avogadro number} \), \( \hbar = \text{Boltzman constant} \)

\( T \) = Absolute temperature and

\( \beta = \text{Bohr magneton} \ (9.273 \times 10^{-21} \text{ erg/gauss}) \)
N, K and $\beta$ being constants the quantity $\left(\frac{3\, K}{N\, \beta^2}\right)^{\frac{1}{8}}$ reduces to 2.839 and the equation (3) is modified as

$$\mu_{\text{eff}} = 2.839 \left[ \kappa_M \cdot T \right]^{\frac{1}{8}} \quad \text{............... (4)}$$

where $T$ is a measurable quantity and $\kappa_M$ can be calculated from the magnetic pull exerted on a certain bulk of material, in a particular field strength. Thus, $\mu_{\text{eff}}$ can be easily calculated. This is most conveniently done by Gouy method.

In practice most of the transition metal compounds are 'magnetically dilute' i.e. the atom with a permanent magnetic moment is surrounded by other atoms without any permanent magnetic moment. Hence a diamagnetic correction is always applied to the molar susceptibility using Pascal's constant.

$$\kappa'_M = \kappa_M + \text{diamagnetic correction} \quad \text{............ (5)}$$

where $\kappa'_M$ is the 'corrected molar susceptibility'.

Equation (4) can now be written as

$$\mu_{\text{eff}} = 2.84 \sqrt{\kappa'_M} \cdot T \quad \text{............... (6)}$$

Curie's law gives a relationship between $\kappa'_M$ and $T$ as

$$\kappa'_M = \frac{C}{T} \quad \text{......................... (7)}$$

where $C$ is known as Curie's constant. The modified form of this equation is given by

$$\kappa'_M = \frac{C}{T - \Theta} \quad \text{............... (8)}$$

where $\Theta$ is known as the Weiss constant.
Application of paramagnetism

The determination of magnetic moment is of great value to coordination chemists for the elucidation of the following:

1) Valency of the metal ion,
2) The bond type
3) The stereochemistry of the metal ion.

1) Valency of the metal ion

Different valency states can be distinguished from the number of unpaired spins present, which is obtained directly from the magnetic susceptibility measurement. The decision is specially easy with first two transition elements because Hund's rule is obeyed for simple ions. The Cu$^{+1}$ and Cu$^{+2}$ may be distinguished because the former is diamagnetic and the latter has one unpaired electron. Similar is the case for Ag$^{+1}$ and Ag$^{+2}$. Mn$^{+2}$ contains five unpaired electrons whereas Mn$^{+3}$ has only four, corresponding to moments of 5.9 and 4.9 B M respectively. When electron pairing occurs, valency states of manganese can be distinguished since $\left[\text{Mn(CN)}_6\right]^{-4}$ has $\mu_{\text{eff}}$ value of 1.80 B M whereas $\left[\text{Mn(CN)}_6\right]^{-2}$ has $\mu_{\text{eff}}$ value of 3.18 B M.

2) Types of bonds in complexes

Magnetic moment can be used to distinguish between two types of bonding in metal complexes namely ionic and covalent which give rise to spin-free and spin-paired states respectively. A large difference is usually
noticed in the magnetic moments of the metal complexes involving different bonding. This has been very widely used in the past few years. Brustal and Nyholm have well illustrated the bonding scheme in explaining the magnetic behaviour of dipyridine and diarsine complexes of transition metals.

iii) Stereochemistry of complexes

The knowledge of the bond type and the coordination number of the metal atom helps the coordination chemists to draw inference regarding the stereochemistry of a complex.

Some common stereochemical arrangement and orbital combinations

<table>
<thead>
<tr>
<th>Coordination number</th>
<th>Shape</th>
<th>Bond orbitals</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>linear</td>
<td>sp</td>
</tr>
<tr>
<td></td>
<td>angular</td>
<td>p²</td>
</tr>
<tr>
<td>3</td>
<td>triangular plane</td>
<td>sp²</td>
</tr>
<tr>
<td></td>
<td>pyramidal</td>
<td>p³</td>
</tr>
<tr>
<td>4</td>
<td>square planar</td>
<td>dsp²</td>
</tr>
<tr>
<td></td>
<td>tetrahedral</td>
<td>sp³</td>
</tr>
<tr>
<td>5</td>
<td>bipyramid</td>
<td>sp³d</td>
</tr>
<tr>
<td></td>
<td>square pyramid</td>
<td>dsp³</td>
</tr>
<tr>
<td>6</td>
<td>octahedral</td>
<td>d²sp³</td>
</tr>
<tr>
<td></td>
<td></td>
<td>or sp³d²</td>
</tr>
</tbody>
</table>
4. Infrared spectra

Infrared spectra originate in transitions between two vibrational levels of the molecule in the electronic ground state and are usually observed as absorption spectra in the infrared region.

Infrared spectroscopy involves the twisting, bending, rotating and vibrational motions of atoms in a molecule. Upon interaction with the infrared radiation, portions of the incident radiation are absorbed at particular wave lengths. The multiplicity of vibrations occurring simultaneously produces a highly complex absorption spectrum which is unique characteristic of the functional groups comprising the molecule and the overall configuration of the atoms as well. Two conditions are to be fulfilled for an infrared absorption to occur. First, the energy of radiation must coincide with the energy difference between the excited and the ground states of the molecule so that the absorbed radiation will increase the natural vibration of the molecule. Secondly, the change must be associated with a change in the dipole moment. Stretching vibrations involve changes in the frequency of vibration of bonded atoms along the bond axis. Bending and deformation vibrations occur when three electrons system is part of a larger molecule which indicate the movement of atoms out from the bonding axis. There can be four types of bending vibrations.

(a) Deformation or scissoring, where the two atoms connected to a central atom move towards and away from each other with deformation of the valence angle.
(b) Rocking or inplane bending, where the structural unit swings back and forth in the symmetry plane of the molecule.
(c) Wagging or out of plane bending, where the structural unit swings back and forth in a plane perpendicular to the molecule's symmetry plane.
(d) Twisting, where the structural unit rotates back and forth around the bond which joins it to the rest of the molecule.

The number of possible vibration modes to absorb infrared radiation are \((3n-5)\) and \((3n-6)\) for linear and non-linear molecules, respectively, where \(n\) is the number of atoms in the molecule. In general, the frequency of vibration, \(\nu\), can be calculated from the equation

\[
\nu \text{ (cm}^{-1}\text{)} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \approx 1307 \sqrt{\frac{k}{\mu}}.
\]

where \(c\) is the velocity of light, \(k\) is force constant and \(\mu\) is the reduced mass of atoms involved. The reduced mass of the molecule may be obtained from the relationship \(\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}\) where \(m_1\) and \(m_2\) are the true masses of the involved atoms.

When a ligand is coordinated, at least one additional atom - the atom to which the ligand coordinates - is introduced into the ligand's vibrating system and bond lengths and angles, and interatomic forces within the ligand would be expected to alter slightly. This means that the infrared spectrum of a coordinated ligand will differ from that of the free ligand, and it should be possible to correlate the changes in spectra with the changes in geometry. In this way information about the structure of the complex may be obtained.
The qualitative identification of a compound can be made by comparing directly its spectrum with that of the ligand. The differences between the spectra of free ligand and complex fall into three categories.

(i) Band positions may change.

(ii) Relative band intensities may change.

(iii) Single peaks in the free ligand may split into several, closely spaced, bands in the complex.

Changes in band position

Vibrational bands associated with the stretching of bonds involving the coordinated atom(s) usually move to longer wavelength (lower energy) on coordination. Thus, the carbonate ion may function either as a unidentate or bidentate (chelating) ligand. A vibration of the free CO$_3^{-2}$ anion which absorbs at $\sim 890$ cm$^{-1}$ appears at 850 cm$^{-1}$ and $\sim 830$ cm$^{-1}$ when CO$_3^{-2}$ functions as a unidentate and bidentate ligand respectively, and is indicative of the mode of coordination. An example of a ligand frequency which moves to higher energy or coordination is provided by the cyanide anion. In KCN this shows absorption at 2080 cm$^{-1}$, but on coordination it appears anywhere from 2040 cm$^{-1}$ to 2170 cm$^{-1}$, although usually above 2100 cm$^{-1}$.

When linkage isomerism occurs, infrared spectroscopy may provide a simple method of determining the coordination. Thus, when the thiocyanate anion is S-bonded the C-S stretching vibration commonly occurs at ca 700 cm$^{-1}$, but for N-bonding it appears at ca 820 cm$^{-1}$. Similarly, N-O stretching mode of the NO$_2^{-}$ anion occurs at ca 1300 cm$^{-1}$ when N-bonded, but at ca 1050 cm$^{-1}$ when O-bonded.
Altered band intensities

Coordination usually reduces the effective symmetry of the ligand and so alters the vibrational selection rules. As a consequence vibrations which were infrared inactive in the isolated ligand may become active in the coordinated ligand, although seldom do they appear with great intensities. Although band intensities have been used to predict the molecular geometries of metal carbonyls this technique has been applied only rarely to other systems.

Band splittings

Just as a lowered symmetry on coordination may cause the appearance of new bands, so it may cause the splitting of bands which are degenerate in the isolated ligand. So, the free sulphate anion shows a band at 1104 cm\(^{-1}\) which is triply degenerate. In \([\text{Co(NH}_3\text{)}_6]_2(\text{SO}_4)_3\cdot5\text{H}_2\text{O}\) this appears as a broad double headed peak with a separation of ca 20 cm\(^{-1}\). The complex \(\text{Co(NH}_3\text{)}_5\text{SO}_4\cdot\text{Br}\) in which the sulphate is coordinated, shows a much larger splitting, ca 90 cm\(^{-1}\), with double headed bands at ca 1040 cm\(^{-1}\) and 1130 cm\(^{-1}\). Similarly, ionic perchlorate gives rise\(^{58}\) to a broad absorption band in the region 1050 - 1170 cm\(^{-1}\) and coordinated perchlorate shows\(^{59}\) three distinct bands at 1155, 1080 and 1005 cm\(^{-1}\).

5. Electronic spectra

A coordination compound may exhibit ultra-violet and visible absorption spectra due to any one of the following types of electronic transitions,
a) Transitions involving electrons of the central metal ion.
b) Transition involving promotion of ligand electrons and
c) Charge transfer spectra.

The transition metal ions contain an incomplete 'd' shell of electrons. The spectra of transition metal complexes do usually have one or more weak absorption band at long wave lengths (chiefly in the visible but some also appear in the near IR and UV regions) due to d-d transitions, i.e. transitions between the levels of a single d<sup>n</sup> configuration. In fact, the colours of most, but not all, transition metal compounds are due to these d-d transitions. The 'd' shell in an atom or ion is five fold degenerate in the absence of an external electric or magnetic field. In such case an electron may jump from one of these orbitals to another without any absorption or emission of energy. When a certain numbers of ligands are attached to the central metal ion the degenerate 'd' orbitals split up into groups of different energies and electronic transition from one set of orbitals to the other can take place without absorption of energy.

From the energy level diagram it can be easily deduced that a d<sup>1</sup> ion in an octahedral environment of ligands will have an absorption band due to the transition of electron from <sup>2</sup>T<sub>2g</sub> to <sup>2</sup>E<sub>g</sub> level. In the case of Ti(H<sub>2</sub>O)<sub>6</sub> <sup>+3</sup>, such band is actually observed and the separation between T<sub>2g</sub> and E<sub>g</sub> levels corresponds to the value of 10 D<sub>q</sub> for this complex.
Divalent copper has the electronic configuration (3d^9). The structure of the complex can be either a distorted octahedron, which in the limit goes to the square planar configuration, or a tetrahedron.

The d-d spectrum of a d^9 ion can be interpreted as simply as in the case of the d^1 ion. This follows from the well known hole formalism principle in spectroscopy, according to which a d^{10-n} configuration will have the same behaviour as for a d^n system except that the signs of the energy terms are different. For the d^1 (in octahedral field) the ground state is triply degenerate as the electron can occupy any of the three t_{2g} orbitals, while the excited state is doubly degenerate. But for d^9 in octahedral field the ground state is t_{2g}^6 e_g^2 which is doubly degenerate as the unpaired electron can occupy either d_{x^2-y^2} or d_{z^2} orbital. Similarly the excited state is triply degenerate (t_{2g}^5 e_g^4, unpaired electron in any of the three t_{2g} orbitals). This accounts for the inverted pattern of the orgel diagram for d^9 compared to that of d^1. Thus, the d^9 ion in an octahedral environment can be viewed as an ion containing one position in an octahedral field and hence in the ground state the positron will occupy an e_g orbital from which it may be excited by absorbing radiation of suitable frequency.
Fig. 3  The energy diagram for $d^3$.

Fig. 4  Orgel Diagram

(a) No Jahn-Teller distortion (hypothetical case).
(b) Medium Jahn-Teller distortion present.
(c) Strong Jahn-Teller distortion present.

Fig. 5  Energy states for the $d^9$ configuration in an octahedral field.
(h = 10 D_q) to a t_{2g} level. Absorption spectrum of Cu^{+2} ion in aqueous solution, which contains \( [\text{Cu} (\text{H}_2\text{O})_{6}]^{2+} \), however, consists of three nearly superimposed bands with the maximum at \( \sim 12500 \text{ cm}^{-1} \), i.e. \( \sim 800 \text{ nm} \) (\( \varepsilon_{\text{max}} \sim 11 \)). This is due to Jahn-Teller distortion which causes a further splitting of the energy levels into a set of four levels and clearly three bands, corresponding to the transitions from the lowest to the three upper levels are possible the frequency separation of which will depend on the extent of splitting caused by the ligands. When the ligand field is weak the splitting is small and hence the three bands are nearly superimposed to produce a broad absorption band as in the case of Cu(\text{H}_2\text{O})_{6}^{+2} ion. Spectra of most Cu(II) complexes reveal three absorption bands, one of which may be pushed so that much into the UV region as to escape detection due to the presence of strong charge transfer bands in that region.

**Six coordinate complexes**

Since the ground state in an octahedral field is \( 2E_g \), it is subject to considerable Jahn-Teller distortion and the majority of Copper(II) complexes which are usually green or blue are tetragonally distorted with four short metal ligand bonds in one plane (\( \text{xy} \)) and two longer metal-ligand bonds lying along the z-axis above and below this plane. In the limit, which is not generally reached, the molecule would be four coordinated and square planar.
Such complexes give rise to one absorption band in the visible region near $16000 \text{ cm}^{-1}$ which can often be resolved into at least three components, the band often exhibits a broad "tail" into the near infrared region. The relative order of these transitions will depend upon the extent of axial metal ligand interaction.

Certain trigonally distorted copper derivatives such as the tris(dipyridyl) and tris(o-phenanthroline) copper(II) ions give rise to two well defined absorption bands near 6000 and 15,000 cm$^{-1}$. These persist both in the solid state and in aqueous solution, and also appear when the ion is crystallised in a lattice with Zn(Bipy)$_2$.

Spectral data for many copper(II) complexes in solution have been given by Bjerrum et al and by Jørgensen. The absorption spectrum of blue crystalline Cu$_2$Si$_6$F$_6.6H_2O$ has been given and interpreted by Pappalardo, who assumed a regular octahedral configuration with spin-orbit coupling included.

Five coordinate complexes

Two limiting pentacoordinate geometries for copper(II) and other transition metals are trigonal bipyramidal and square pyramidal. Within this coordination numbers the square based pyramidal stereochemistry occurs much more frequently than does the trigonal-bipyramidal. Trigonal-bipyramidal copper(II) complexes normally exhibit two distinct bands in the near I.R and visible regions. Square pyramidal copper(II) complexes on the other hand, show only one asymmetric absorption maximum in this region.
A number of copper(II) compounds exhibit five coordination, the most simple derivative being the trigonal bipyramidal \( \text{CuCl}_5^{2-} \) ion in \( \text{Co(NH}_3)_6\cdot\text{CuCl}_5 \). This has two absorption bands lying at 8200 and 10,200 cm\(^{-1}\).

However, it is difficult to say the types of geometry these five coordinate complexes will adopt only from the electronic spectra.

**Tetrahedral**

Regular tetrahedral derivatives of copper(II) are very uncommon, there is usually a flattening of the tetrahedron leading to a molecule of \( D_{2d} \) symmetry, presumably as a consequence of the Jahn-Teller effect lifting the degeneracy of the \( ^2T_2 \) ground state. In general tetrahedral copper(II) derivatives, are expected to give a single broad band of about 10\(^2\) molar intensity in the near infrared region, and to be blank between 10,000 and 20,000 cm\(^{-1}\). The pseudo-tetrahedral bis(N-isopropylsalicylideneaminato) copper(II) has d-d transitions at 8500 and 13500 cm\(^{-1}\).

**Square planar**

Square planar complexes of bivalent copper are well established. In the spectra of \( \text{Cu(acetylacetonate)}_2 \), which is square-planar, there are bands at 15,000 cm\(^{-1}\) and 18,000 cm\(^{-1}\) and band of charge transfer at higher energies. The d-d transitions show marked polarisation in single crystals. The two bands may be assigned as probably, the transitions

\[ ^2A_{1g} \rightarrow ^2B_{1g} \quad \text{and} \quad ^2E_g \rightarrow ^2B_{1g} \]
Chromium(III) is the best known representative of d\(^3\) and its spectrum with very many different ligands is known. In hexacoordinated Cr(III) complex, the nearest neighbour atoms are arranged in an octahedral or nearly octahedral array. Two quartet states, \(4\Gamma\) and \(4\Pi\), and five doublet states, \(2\Pi, 2\Sigma, 2\Delta, 2\Pi,\text{ and } 2\Phi\), are derived from the \(d^3\) configuration\(^71\). In an octahedral ligand field \(4\Gamma\) is split into the \(4\Pi_2, 4\Pi_1,\text{ and } 4\Pi_2\) states. The only other ligand field states that have been observed in Cr(III) spectra are \(4\Pi_1\text{ and } 2\Pi, 2\Pi,\text{ and } 2\Pi_2\) derived from \(2\Sigma\).

A complete ligand field calculation has been made by Liehr\(^72\).

The salts of trivalent chromium give, in water, a light green solution. The colour is the result of absorption in the yellow and blue parts of the spectrum. The spectrum shows bands at 17000, 24000 and a weak band which appears as a shoulder at 37000 cm\(^{-1}\). The three stronger bands are due to the three expected spin-allowed d-d transition. These bands can be assigned\(^73\) to the transitions from the \(4\Pi_2\) ground term to the three excited quartet terms of Fig. 3:

\[
\begin{align*}
4\Pi_{2g}(F) & \rightarrow 4\Pi_{2g}(F) \quad ( = 10D_q ) \quad 17000 \text{ cm}^{-1} \\
4\Pi_{2g}(F) & \rightarrow 4\Pi_{1g}(F) \quad 24000 \text{ cm}^{-1} \\
4\Pi_{1g}(F) & \rightarrow 4\Pi_{2g}(F) \quad 37000 \text{ cm}^{-1}
\end{align*}
\]
There are also very weak bands at about 15000 and 22000 cm$^{-1}$ which are spin forbidden. However, the weak additional bands are due to quartet-doublet transitions ($^4\text{A}_{2g} \rightarrow ^2\text{E}_g$, $^4\text{A}_{2g} \rightarrow ^4\text{T}_{1g}$, and $^4\text{A}_{2g} \rightarrow ^2\text{T}_{2g}$).

**Spectrochemical series**

It has been found by experimental study of the spectra of a large number of complexes containing various metal ions and various ligands, that ligands may be arranged in a series according to their capacity to cause d-orbital splittings. The series, for the more common ligands, is $\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{F}^- < \text{CN}^- < \text{C}_2\text{O}_4^{2-} < \text{H}_2\text{O} < \text{NCS}^- < \text{Py} \sim \text{NH}_3 < \text{en} < \text{dipy} < \text{o-phen} < \text{NO}_2^- < \text{CN}^-$ and is referred as 'spectrochemical series'. The spectrochemical series for metal ions as arranged by Jorgensen is $\text{Mn(II)} < \text{Ni(II)} < \text{Co(II)} < \text{Fe(III)} < \text{Cr(III)} < \text{Co(III)} < \text{Mn(IV)} < \text{Mo(III)} < \text{Rh(III)} < \text{Pd(IV)} < \text{Ir(III)} < \text{Re(IV)} < \text{Pt(IV)}$.

**Nephelauxetic series**

A coordination compound is formed by the overlap of bond orbitals, thus bringing about a 'covalent tendency' between the metal ion and the ligand. For a particular metal ion the covalent tendency of the ligand, with respect to the bond formation depends upon the extent of overlap of the ligand electron cloud on that of the metal. Schaeffer and Jorgensen described a method for estimating the expansion...
of the d orbitals of the central atom under the influence of the ligands. These calculations are based on the smaller term values for the complexed ions as compared with the free ions. The varies from ligand to ligand in what is called the 'Nephelauxetic series'. For example, such a series of the order of increasing ability to produce d cloud expansion is, \( F^- < H_2O < \text{urea} < NH_3 < C_2O_4^{2-} < en < NCS^- < Cl^- < CN^- < Br^- < I^- \). This series measures a tendency towards increasing covalency in the metal-ligand bond.
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