SECTION-3
GENERAL SURVEY OF TRANSITION METAL COMPLEXES

(a) Brief outline about coordination complexes:

The branch of coordination chemistry took its birth in 1798 by discovery of cobaltamines by Tossaert\(^1\) which are known as coordination compounds or metal complexes. This type of compounds contain a central atom or ion usually a metal surrounded by a cluster of ions or molecules. It is the characteristic of the complex that it retains its identity, more or less, even in solution though partial dissociation may occur sometimes. The complex may be nonionic or a cation or an anion depending on the charges carried by the central atom and the coordinating groups, which are called "ligands", and the total number of attachment to the central atom is called coordination number.

According to Sidgwick and Lowry\(^2\), a coordinate bond in a coordination compound takes place between any atom or ion, which can accept a pair of electrons (the acceptor) and any atom or ion which can furnish a pair of electrons (the donor). The donor may be nonmetallic or a neutral molecule like CO, H\(_2\)O or NH\(_3\) or an ion like Cl\(^-\), CO\(_3\)^{2-} or NH\(_2\)COO\(^-\).

In 1893, Alfred Werner\(^3\) explained the formation of complex compounds and developed the concept of "primary" and "secondary" valence. Lewis\(^4\) in 1916 put Werner's view of secondary valency or coordination in terms of electrons. Thus the bond between central ion and each of the attached group involve a pair of
electrons and is represented as a coordinate or dative bond, \( M \leftarrow L \) or \( M:L^+ \). The electronic configuration of metal ions is often such that they can accommodate as many as twelve electrons or even more which means that coordination number of six or more are also possible. It has been suggested that ions tend to add a sufficient number of electrons by coordination, so that the ion in the resulting complex has an effective atomic number (E.A.N) of the next inert gas. This rule can be given qualitative significance, as there are a very large number of exceptions.

In 1919, the stage was set for renewed activity in this field, prompted by the availability of physico-chemical methods and by the valence bond theory developed by Pauling. The coordination number of a metal ion may differ depending on the nature of the coordinating groups viz., Nickel(II) forms compounds in which it has coordination number either four, five or six. The polarisability, size and ability to form sigma bonds of a ligand, all seem to play an important role in fixing coordination number of a metal ion. A classification of central ions, somewhat depend on electronegativity was proposed by Ahrland, Chatt and Davis. Class (A) acceptors form their most stable complexes with first ligand atom in each group, i.e. with N, O, F. Class (B) acceptors form their most stable complexes with the second or a subsequent ligand atom. The oxidation states of the metal affects the degree of (B) character which is strongest for the transition metals in low oxidation states, i.e. metals having nonbonding d-electrons.
and thus capable of forming $d_{π}−p_{π}$ and $d_{π}−d_{π}$ bonds. Craig and Nyholm have given a semi-quantitative explanation of Class (A) and (B) behaviour towards halide ions. Pearson's hard and soft acids correspond roughly to Chatt's (A) and (B) metals respectively. Jorgenson has suggested that, some metals may have (B) character in a low and high oxidation state, yet (A) character in an intermediate oxidation state.

Ligands:

Ligands using one atom at a time as a donor are known as monodentate ligands. They are classified as:

1. Those with one or more unshared pair of electrons:
   a. That contains no vacant orbitals for receiving electrons from the metal, e.g., $H_2O, NH_3, F^−, OH^−, NH_3$;
   b. Containing vacant orbital or orbitals that can be vacated for receiving pi-bonding electrons from the metal, e.g., $CN^−, CO, NO_2^−, R_3P, R_3As, R_2S$;
   c. Containing two or more electron lone pairs, one of which may become pi-bonding by donation to vacant metal orbitals, e.g., $OH^−, NH_2^−, Cl^−, Br^−$.

2. Those having no unshared pair of electrons, but with electrons already involved in pi-bonding, e.g., olefins, benzene, alkynes, and cyclopentadienyl ions.

3. Those that may act as bridging groups between two metal atoms.

Ligands having two or more donor atoms are called polydentate ligands. Chelate ligands permit the attachment of two or more
donor sites to the same metal ion thus choosing one or more rings. From the consideration of an electrostatic model, it can be said that for a unidentate ligand, the coordinating ability will depend not only on the electronegativity, but on the total dipole moment \( \mu = P + P' = P + \sum \varepsilon \), where \( P \) = permanent dipole moment, \( P' \) = induced dipole moment, \( \varepsilon \) = the polarizability, \( \varepsilon \) = induced electrostatic field.

Whereas, both permanent dipole moment and coordinating ability decreases in the series \( \text{H}_2\text{O} \succ \text{ROH} \succ \text{R}_2\text{O} \), the reverse order holds for sulfur. The spectrochemical series of ligands arranged according to the spectroscopic splitting parameters, roughly follows the order of decreasing radii of the ligand atom, i.e. \( \text{I} \succ \text{Br} \succ \text{Cl} \succ \text{S} \succ \text{F} \succ \text{O} \succ \text{N} \). The nephelauxetic series is a measure of the covalent tendency of the ligand. The repulsion between the d-electrons decreases by complex formation from 5 to 40 percent for 3d complex. \( \beta = (B'/B) \) is the ratio of electronic repulsion parameters for the complex (\( B' \)) and for the free gaseous ion (\( B \)). The nephelauxetic series of ligands is arranged according to increasing values of \( 1-\beta \) as \( \text{F} \prec \text{H}_2\text{O} \prec \text{Urea} \prec \text{NH}_3 \prec \text{en} \prec \text{C}_2\text{O}_4^{2-} \prec \text{NCS}^- \prec \text{Cl}^- \prec \text{CN}^- \prec \text{Br}^- \prec \text{S}^{2-} \prec (\text{EtO})_2\text{PS}^- \prec \text{I}^- \prec (\text{EtO})_2\text{PSe}^- \).

Preparation of the complex compounds:

1. Substitution Reaction in Aqueous Solutions: This method involves a reaction between an aqueous solution of a metal salt
and a coordinating agent (ligand). Most of the silver complexes are prepared by this method, as the silver salts are fairly soluble in water $[\text{Cu}(\text{NH}_3)_4]_2\text{SO}_4$ is readily prepared by the reaction between an aqueous solution of CuSO$_4$ and excess NH$_3$.

(2) Substitution Reaction in Nonaqueous Solvents: In most cases water can not be taken as a solvent, as either the ligand of choice is insoluble in it or the metal under consideration coordinates strongly with the oxygen of water molecule. Hence in some cases, the reaction is carried out in nonaqueous solvents and water is avoided completely. Thus if cobalt halides are dissolved in water, the complex $[\text{Co}((\text{H}_2\text{O})_6)^{+2}$ is formed, whereas, the reaction between cobalt halides and a ligand say, 4-methyl pyridine is carried out in ethanolic medium, a blue complex Co(4-MePy)$_2X_2$ is formed.

Sometimes, a mixture of several nonaqueous solvents are taken to decrease the solubility of the complex in a particular solvent. For example, in the preparation of thiourea complex of zinc, a mixture of ethanol and CCl$_4$ are used.

(3) Substitution Reaction 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 large excess also serve as a solvent for the reaction mixture. In certain cases, the presence of solvent is undesirable, because the complex may not separate out in presence of solvent or it may decompose after it is being formed. Preparation
of \( \text{Cu(acac)}_2(\text{Q}) \) and \( \text{Cu(acac)}_2(4-\text{MePy}) \) was done in absence of solvents\(^{11}\).

(4) **Thermal Dissociation of Solid Complexes**: Thermal dissociation amounts to a substitution reaction in the solid state. At some elevated temperature, volatile coordinated ligands are lost and their places in the coordination sphere is taken by the anions of the complex. Dash and Raman Rao\(^{12}\) have reported that \( \text{Mn(I.Q)}_2\text{X}_2 \) undergoes thermal decomposition at 120°C to \( \text{Mn(I.Q)}\text{X}_2 \). They have also reported the same behaviour in case of \( \text{Mn(4-Vinyl Pyridine)}_2\text{X}_2 \), \( \text{MnPy}_2\text{X}_2 \) and other cobalt complexes. This method was also used in the preparation of some zinc thiocyanate complexes by Guru and Raman Rao\(^{13}\).

(5) **Oxidation-Reduction Reactions**: The oxidation states of many ions are raised or lowered by complex formation. The trivalent and tetravalent states of nickel are stabilised by coordinating with ligands containing phosphorous and arsenic donor atoms. The use of ligand o-phenylene bis-dimethyl ditertiary arsine has also made possible the stabilization of the tetravalent state of iron. The compound \( \text{Fe(diarsine)}_2\text{Cl}_2 \) \( \text{[FeCl}_{3}]_2 \) is formed in which the iron atom is tetravalent. Univalent cobalt is also known in complex formation. Reduction of the complex \( \text{K}_2\text{[Ni(CN)}_{12}] \) by metallic potassium in solution in liquid ammonia gives nickel complex \( \text{K}_4\text{[Ni(CN)}_4] \). The preparation of complexes by reduction of the metal ion is less common than the preparation by oxidation.

**Coordination number and Stereochemistry**: Werner assumed that
certain metals possess characteristic coordination number, their coordination sphere have certain definite shapes or symmetries. There is now sufficient amount of direct evidence from X-Ray diffraction studies and indirect evidence from dipole moments, magnetic properties and electronic spectra concerning coordination number and geometries.

**Coordination number 2:**

Elements in Group I of the periodic table and Hg(II) seem to have a consistent tendency to exhibit coordination number 2. In a few cases, elements in other periodic groups, which can exist with a valence of one, may also be two coordinate. There are only two possible geometrical configurations, linear, O-M-O and angular O-M O. Rosenheim and Lowenstam reported the preparation of \( \text{Cu} \{ \text{SC(NH}_2 \}_2 \text{Cl}_2 \) in which they believe the thiourea is coordinated to the copper atom through sulfur. Spacu and Murguleseu reported a number of compounds in which Copper(I) has coordination number two. Silver(I) forms the linear diamine Silver(I) \( \text{Ag(NH}_3 \}_2 \) and dicyano silver(I) \( \text{[Ag(CN)}_2 \) ions. Fyfe prepared Silver(I) diamine with acridine, quinoline, isoquinoline and pyridine. Patel and Raman Rao have reported a number of two coordinated Silver(I) complexes having the composition \( \text{[AgL}_2 \text{ClO}_4 \), where L = alpha-picoline, beta-picoline, gamma-picoline, 2,6-lutidine, and 4-vinyl pyridine.

**Coordination number 3:**

On the basis of theoretical considerations Kimball offers
the trigonal plane, unsymmetrical plane and trigonal pyramid as possible structure of 3-coordinated complexes. Silver(I) and Copper(I) in addition to being two coordinate also forms a number of compounds in which they are apparently three coordinate. Compounds containing ethylenethiourea like $\text{[Ag\{SC(NH)\_2(CH\_2)\_2\}_3Cl]}$ and $\text{[Cu\{SC(NH)\_2(CH\_2)\_2\}_32SO\_4]}$ are known. The reddish chlorocuprate, the chloro cadmate and chloromercurates $\text{[CuCl\_3]}^\text{2-}$, $\text{[CdCl\_3]}^\text{2-}$ and $\text{[HgCl\_3]}^\text{2-}$ are well known.

**Coordination number 4:**

Two geometrical configurations for the coordination number 4 are now generally accepted, the regular tetrahedral and the square planar.

**Tetrahedral coordination:**

The evidence for a tetrahedral arrangement is found largely in complete structure determinations, either by X-Ray or by electron diffraction. Usually, Co(II), Ni(II), Zn(II), Cd(II), Hg(II) and in some cases Pd(II), Pt(II) forms tetrahedral complexes. All the four coordinate Zn(II) complexes are tetrahedral. Purely tetrahedral copper(II) complexes are not much known. $\text{[CuCl\_4]}^\text{2-}$, $\text{[CuBr\_4]}^\text{2-}$ ions have a distorted tetrahedral stereochemistry.

**Planar Configuration:**

Mellor has discussed the subject of square planar coordination thoroughly. Diekinson demonstrated a square planar arrangement of the chloride ions about the platinum or palladium
atoms in $\text{K}_2\text{PtCl}_4$, $\text{K}_2\text{PdCl}_4$ and $(\text{NH}_4)_2\text{PdCl}_4$. A few years latter, Pauling$^{21,22}$ explained the planar structure which had been observed for Platinum(II) and Palladium(II) compounds and predicted that dimagnetic compounds of Ni(II), Au(II), Cu(III) and Ag(III) are also planar. While Pauling's prediction that dimagnetic Nickel(II) and Gold(II) compounds would be planar was verified, it was also found that some Silver(II) and Cu(II) compounds are planar. For Ni(II) and Cu(II), it is very common and important. Both cationic and anionic Ni(II) and Cu(II) complexes are known.

Coordination number 5:

From theoretical considerations, a coordination number of five should be the least likely to exist, although there are many examples in which atoms are apparently five coordinate. Kimball$^{23}$ gives the following as geometrical possibilities, trigonal bipyramid, square pyramid, pentagonal plane, and pentagonal pyramid. Copper is reported to be five coordinate in the black crystalline compounds $\text{K}_3\left[\text{Cu(NO}_2\right)_5], \text{Rb}_3\left[\text{Cu(NO}_2\right)_5].$ Copper is five coordinate in the complexes$^{24,25}$ $\text{Cu(acac)}_2\text{Q}, \left[\text{Cu(acac)}_2\text{MePy}\right].$ NiBr$_2$-triarsine, NiI$_2$ triarsine are known as five coordinate square pyramidal complexes. Both iron and ruthenium form penta carbonyls of the general formula $\text{M(CO)}_5$. Tribromo bis-(triethyl) phosphine) nickel(III) is an unusual compound in two respects, it contains nickel(III) and exhibits coordination number five. Zinc is reported to be five coordinate in $\text{Zn(ter.py)Cl}_2^{26}$, $\text{Zn(acac)}_2$ adducts with 2-methyl and 4-methyl
pyridine. Both Co(II) and Ni(II) form five coordinate complexes with a triphosphine ligand bis-(3-diphenyl phosphino-propyl) phenyl phosphine.

**Coordination number 6:**

Most of the elements of first transition series form complexes of this coordination number. Many of the halide complexes with pyridine and substituted pyridines of the composition ML₄Cl₂, ML₂Cl₂ are six-coordinate octahedral complexes (involving halogen bridges in second case) where M is Co(II), Ni(II), Cu(II) and Zn(II). Copper(II) complexes are distorted octahedral. Similarly, adducts of bis-(β-keto-enolates) of Co(II), Ni(II), Cu(II) and Zn(II) with 2 molecules of nitrogen base are six-coordinated octahedral complexes. Bis-(acetylacetonate) dipyridine cobalt(II) was shown to be octahedral by X-Ray analysis.

**Coordination number 7:**

This coordination number is quite rare and appears generally in the heavier atoms such as Zr, Nb, Tl and Iodine. The halogens in general (especially fluorine) seem to favour this coordination number. At least two geometrical arrangements are associated with seven coordination. The ions UF₇⁻³, ZrF₇⁻³ have the shape of pentagonal bipyramid whereas the ions NbF₇⁻² has the shape of a distorted trigonal prism by addition of a seventh ligand atom along the normal to one face. Other compounds reported to contain seven coordinate atoms are the black (CH₃NH₂H)₃[Pt(IV)I₂], dark
Coordination number 8:

It is known at least in two geometrical forms -
(1) square antiprism found in $[\text{TaF}_6]^{-3}$ and $[\text{Sr(H}_2\text{O)}_8]^{+2}$ ions,
(2) dodecahedron arrangement is found in $\text{Mo(CN)}_8^{-2}$. This can be regarded as a distorted cubic arrangement. Fluorine seems to favour eight coordination as exhibited in the compounds $(\text{NH}_4)_2\text{H}[\text{PbF}_6]$, $\text{H}_3[\text{SbF}_6]$ $\text{Na[TaF}_6]$ and the well known highly volatile osmium(VIII) fluoride. Other compounds reported in which the central atom apparently has a coordination number eight are the octammines, $\text{MX}_2\text{SNH}_3$, where $\text{M}$ is Ca, Sr, Ba or Pb, metal acetylacetonates $\text{M(C}_5\text{H}_7\text{O}_2)_4$ where $\text{M}$ is Zr, Hf, Th, U, Po or Ce tetrakis (en) Cr(III) chloride and tetrakis (en) Cd(II) iodide. Guru and Raman Rao$^{35,36}$ have reported a number of eight coordinated Mn(II) complexes.

**Stability of the Complex Compounds**

Complex compounds are often described quantitatively as stable or unstable. The term 'stable complex' is defined in terms of the equilibrium constant for the formation of complex. The relative stabilities of many complexes can be understood in terms of a simple electrostatic model. Since oppositely charged particles attract one another, it is expected that the most stable complexes would be made-up of oppositely charged ions. Much of the data on stability has been correlated with varying success with ionisation potentials of the metals, the $(\text{charge})^2/\text{radius}$ ratios for the various ions and the electro-
negativity of the metals. Thus, the stabilities of the metal complexes increase with high charge on the central ion and a large electron affinity of the metal ion. This means that the alkali metal ions have the least tendency to form metal complexes and that the highly polarising transition metal ions have greatest tendency. Irving and Williams have reported the order of increasing stabilities for the bivalent metal ions of the first transition series as Mn < Fe < Co < Ni < Cu < Zn irrespective of the nature of the ligands. Similar orders had been previously observed by various authors, who also included other nontransitional ions in their series, but the order in which these 'outside' ions appear differs from one ligand to another. The process of coordination involves the 'donation' of a pair of electrons from each ligand to the metal ions.

If the bond formed was a perfect covalent bond, this would result in the effective transfer of one unit of charge to the metal atom for each coordinate bond formed. For a six-coordinate divalent cation, this would lead to an accumulation of four negative charges on the metal atom. Such a system would clearly be expected to be unstable and it is evident that in stable systems, the coordinate bonds must have considerable polarity. It is thus found that stabilities of complexes of any particular ion increases with increasing polarisability of the ligand, but that there is a limit to this increase, because ligands of too high polarisability would cause the accumulation of too much negative charge on the central atom. For the divalent metal
cations from Mn$^{+2}$ to Zn$^{+2}$ stabilities of complexes are found to increase with changing donor atom in the order F$^\text{O}$, O$^\text{N}$, S$^\text{P}$ donor atoms of the second short period evidently producing too great a transfer of charge to the metal atom.

It has been suggested that the balance of polarisability of the ligand and ionic potential of the metal cation is ideally such as to produce electrical neutrality on the metal atom and this is probably near the truth for typical transition metal ions.

The stabilities of complexes are greatly increased by the coordination of polydentate ligands. The coordination of such ligands produces ring structures, the metal atom forming a part of the ring. This process is known as 'chelation'. Bjerrum and Nelson observed that the chelate effect is larger for transition metal ions. Spike and Perry found that the chelate effect for nontransition metal ions (Zn$^{+2}$, Cd$^{+2}$) is almost entirely an entropy effect, but that for transition metals (Cu$^{+2}$) it is in part of an enthalpy effect. The enthalpy effect may result from the greater crystal field strength of ethylenediamine compound with ammonia which in turn has a greater stabilising effect on transition metal than on nontransition metal complexes.

In chelation, size of the ring produced is one of the most important factors and stabilization occurs only when the ring formed is five or six membered. It is seen from a comparison of the coordinating properties of the anions of the first four dicarboxylic acids. Usually, there is no much difference in the
stabilising effect of five or six membered rings, but the preference is for the five membered structure under conditions of direct competition. In fact, it may be said that the stability of a complex will depend upon the charge and radius of the central ion and its electron affinity and some characteristic properties of the ligand. Among the characteristics of the ligand which influence the stability of complexes are:

(1) Basicity of the ligand, (2) the number of metal chelate rings per ligand, (3) the size of the chelate ring, (4) steric effects, (5) resonance effects and (6) the ligand atom.

(b) Metal Ligand Bond in Coordination Compounds:

In modern times, three methods have been used to explain the nature of metal ligand bond and to account for other properties of the complexes:

(1) The valence bond theory, (2) i. Crystal field theory, ii. Ligand field theory, (3) Molecular Orbital theory.

1. The Valence Bond theory: This theory was developed by Prof. Linus Pauling. It is useful for qualitative explanations of stereo-chemistry and magnetic properties of the metal complexes. It deals with the electronic structure of the ground state of central metal ion. In the valence bond approach to bonding, it is assumed that electrons in atomic orbitals (often hybridised) overlap to form bonds. Despite its various defects, it is the simplest, and many chemists still find it useful in interpreting and correlating their results. Pauling's theory is based on the
following assumptions:

1. The central metal atom will make available a number of orbitals equal to its coordination number for the covalent bond formation with these ligand orbitals.

2. A covalent sigma-bond is formed from the head on overlap of a vacant metal orbital and a filled orbital of a donor group. The resulting bond axis lies in the direction in which the atomic orbitals are pointing. This bond called 'a coordinate link' is seen to be simply a covalent bond involving the characteristic overlap of two orbitals.

3. In addition to the sigma-bond, a pi-bond may be formed if the metal atom contains suitable d-electrons in an orbital which can overlap with a vacant orbital on the donor atom. This bond will change the charge distribution on both the metal and the ligand to strengthen the sigma-bond.

The strongest covalent bond is formed when there is maximum overlap between the two orbitals. Pauling has pointed out that the original atomic orbitals should be hybridised to form a new set of equivalent bonding orbitals having definite directional characteristics.

In an octahedral complex, where each of the ligand is considered as the donor of an electron pair to the metal ion in order to accept these pairs the metal ion must make available
a set of six equivalent orbitals with their lobes directed towards the apices of an octahedron. Such a set of orbitals can be obtained by hybridising the orbitals $S, P_x, P_y, P_z, dx^2-y^2, dz^2$.

When the required number of orbitals are not available, they are, generally made available by a process of spin-pairing. Pauling called them covalent complexes as opposed to ionic compounds where spins are free.

The main defects of the Valence Bond theory:

It only explains in a qualitative way and does not interpret the spectra or magnetic behaviour beyond the level of a specified number of electrons. It does not account for relative energies of different structures and splitting of the $d$-energy levels. There are also a number of aspects of which it does not give a satisfactory explanation. The valence bond theory is able to propose a $dsp^2$ hybridisation suitable for square planar structure, but this does not explain, why this structure is preferred. The formation of square planar cupric complex involving $dsp^2$ bond hybridisation and promotion of electron from $3d$ to higher level is another weakness.

2. (a) Crystal Field Theory: In 1929, Bethe while studying the effect of the symmetry and strength of a crystalline field upon the electronic levels of the gaseous metal ion, laid down the foundations of crystal field theory. In 1932, Van Vleck successfully applied the theory to the study of magnetism of the
complexes. The recent interest in CFT since 1951 is due to Ilse and Hartmann\(^{49}\) who applied it to the weak visible absorption band, shown by Ti(III) hexaquo ion. In the last twenty years valuable contribution to the theory and its applications have been made by Jorgenson\(^{50}\), Ballhausen\(^{51}\), Bjerrum, Griffith\(^{52}\), Nyholm\(^{53}\), Orgel\(^{54}\) and others. This theory is concerned with the effect of the electric field produced by ligands on the orbital energies of d-electrons of central metal ion. In the absence of the field, five d-orbitals are degenerate. This degeneracy is removed in the complex ion and split into one set of triply and a second set of doubly degenerate levels. The group of orbitals d\(_{xy}\), d\(_{yz}\) and d\(_{xz}\) are often referred to as the t\(_{2g}\)(d\(_{x^2-y^2}\)) orbitals. The two orbitals d\(_{x^2-y^2}\) and d\(_{z^2}\) are referred to as the e\(_{g}\)(d\(_{x^2-y^2}\)) orbitals. The energy difference between the t\(_{2g}\) and e\(_{g}\) levels is symbolically represented by the term 10D\(_{q}\) or \(\Delta\).

The magnitude of D\(_{q}\) varies with different complexes. In an actual complex, a spherical field is never obtained. Metal-electron, ligand-electron repulsions are decreased by a splitting of orbitals into t\(_{2g}\) and e\(_{g}\) sets. The splitting occurs in such a way as to result in an average energy for the five d-orbitals which is equal to that in the spherical field. Two orbitals are raised (6D\(_{q}\) each) and three are lowered (4D\(_{q}\) each) with respect to the energy of the d-orbitals in the hypothetical spherical field.

In an octahedral complex, MX\(_6\), because of the presence of six X\(^-\) ions, the metal ion orbitals split into two types, i.e., t\(_{2g}\) and
e_g orbitals. This splitting is just that which would be obtained by crystalline field of cubic symmetry(Oh). The crystal field splitting is the energy difference between d_e and d_y orbitals and is measured in terms of parameter D_q which is a measure of the crystal field strength. The magnitude of splitting is arbitrarily set at 10D_q or \( \Delta \) or \( \Delta E \) or \( E_1-E_2 \).

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 are further split-up and in the limiting case d_{xy} orbital crosses over the d_{z}^2 orbital, ultimately setting up a square planar environment. Crystal field splittings of the d-orbitals of a central ion in complexes having different geometries are shown in figure-1. Crystal field theory has been of great help in explaining magnetic properties and absorption spectra of the complexes.

2. (b) Ligand Field Theory: According to the crystal field theory, the metal ion orbitals do not mix with ligand atom orbitals. This assumption can never be true in a real chemical compound. On the other hand, ligand field theory, which uses the basic electrostatic approach and the methods of calculations of crystal field theory, includes the modified view that some mixing of ligand and metal ion orbitals always occurs even in those cases where C.F.T.approach is best. Following experimental observations provide evidence for the overlap of orbitals.
APPROXIMATE d-ELECTRON ENERGIES IN FIELDS OF DIFFERENT SYMMETRIES

Tetrahedral free ion Octahedral Tetragonal Square planar (square prism)

FIG. 1.
1. Electron spin resonance data is the most direct evidence for this modified approach. The pattern of sub-bands, called hyperfine structure has been clearly explained by assuming that certain of the iridium d-orbitals and certain orbitals of the surrounding chloride ion overlap to such an extent that the single unpaired electron is not localised only on the metal ion, but about 5 per cent localised on each Cl⁻ ion. The hyperfine structure is caused by the nuclear magnetic moments of chloride ions. The electron is thus only 70% an iridium 4d-electron instead of 100 per cent that is assumed in the purely electrostatic crystal field theory.

2. Nuclear magnetic resonance experiments also suggest that electron spin density is transferred from metal orbitals into orbitals of ligand atom. Even in MnF₆⁻² octahedra, where metal ligand bonding is expected to be electrostatic, fluorine nuclear resonance spectra shows delocalisation of the spin-density of the metal ion d-orbitals to the extent of 2 - 5 per cent.

3. The intensities of the absorption bands of d-d transition indicate that metal ion and ligand orbitals overlap with the result that the d-orbitals of the metal ions are not pure metal ion d-orbitals. The increased intensity of the bands can be explained by an additional process of overlap and mixing of the metal d-orbitals with various ligand orbitals.

4. In the study of energy level diagrams for transition metal ions with two to eight d-electrons, a modified assumption has
to be made to the effect that the d-electron cloud has expanded in the complex thus increasing the mean distance between the d-electrons and decreasing the inter electronic repulsions. This expansion of the d-electron cloud occurs at least partly, because the metal ion d-orbitals overlap with ligand atom orbitals. This effect of ligands in expanding the d-electron clouds is known as Nephelauxetic effect. The common ligands can be arranged in order of their ability to cause cloud expansion. The order is:

\[ \text{F}^- \text{H}_2\text{O}^- \text{NH}_3^- \text{Oxalate} \sim \text{en}^- \text{NCS}^- \text{Cl}^- \text{CN}^- \text{Br}^- \text{I}^- \]

Also the antiferromagnetic behaviour of most ionic salts, oxides and chalcooxides is attributed to some overlap between metal ion d-orbitals and anion orbitals.

3. Molecular Orbital Theory: The molecular orbital theory was first applied to complex ions by Van Vleck. The theory assumes that overlap of orbitals will occur to some extent whenever symmetry permits. It, thus includes the electrostatic approach of no overlap, maximum overlapping of orbitals and all intermediate degrees of overlap in its scope. The molecular orbital theory uses the same orbitals of the central ion as employed by Pauling method, but it also uses the available orbitals of the coordinating ligands directed towards the central atom. The linear combination of atomic orbitals method may be used to construct orbitals for the complex.
Bonding Scheme for an Octahedral Complex

The linear combination of atomic orbitals will be of use in the construction of molecular orbitals.

**Metal Orbitals:** Nine valence shell orbitals of the metal ion should be considered. Six of these $d_{z^2}, d_{x^2-y^2}, S, P_x, P_y, P_z$ have lobes lying along the metal ligand bond directions thus suitable for sigma-bonding, whereas, three $d_{xy}, d_{yz}, d_{zx}$ are so oriented as to be suitable for pi-bonding. These metal orbitals fall into one of four symmetry classes: (a) totally symmetric $a_1g$, (b) triply degenerate $t_{1u}$, (c) doubly degenerate $e_g$, (d) triply degenerate $t_{2g}$.

**Ligand Orbitals:** Each of the six ligands possess one sigma-orbital. These individual sigma-orbitals are combined into six symmetry orbitals which fall into the three symmetry classes $a_1g, e_g, t_{1u}$. The final step to obtain molecular orbitals is to allow each metal orbital to overlap with its matching symmetry orbital of the ligand system. Two combinations are to be considered, one in which the matched orbitals unite with maximum positive overlap thus giving a bonding molecular orbital and the other in which they unite with maximum negative overlap to give the corresponding anti-bonding molecular orbital.

In figure-2 is depicted the bonding scheme for an octahedral complex. Each of the ligand sigma-orbitals contains two electrons. Hence, these twelve electrons plus the electrons from the central ion must be accommodated in the bonding scheme. For example for
BONDING SCHEME FOR AN OCTAHEDRAL COMPLEX. (a) ENERGY LEVELS FOR THE GASEOUS METAL ION (b) ENERGY LEVELS FOR THE LIGANDS (c) ENERGY LEVELS FOR THE COMBINED METAL AND LIGAND ORBITALS

Fig. 2
one lone-pair of electrons on each water molecule are taken to be sigma-electrons, the metal atom on the other hand has only one 3d-electron. The molecular electronic configuration for this complex is thus \((a_{1g})^2 (t_{1u})^6 (e_g)^4 (t_{2g})^1\). The 12 sigma-electron occupy all of the bonding orbitals, while single electron goes to the non-bonding \(t_{2g}\) orbital. The level above the \(t_{2g}\) orbital is the anti-bonding \(e_g\) orbital. In molecular orbital theory, \(10D_q\) must be interpreted as the energy difference between non-bonding \(t_{2g}\) level and anti-bonding \(e_g\) level.

When the donor atoms of the ligands possess vacant orbitals in addition to lone-pairs, these vacant orbitals accept electron density from filled metal orbitals to form a type of pi-bonding, which strengthens the sigma-bonding arising from lone pair donation. The molecular orbital theory can thus explain the influence of pi-bonding on the stability of metal complexes and on the magnitude of crystal field splitting due to ligands.

(c) **Physical Methods Useful in Structural Investigation:**

The physical methods used for structural investigation of complex compounds are discussed below:

1. **Dipolemoment:** Dipolemoment measurements of coordination compounds help the chemists in drawing some conclusions regarding their structures.

    The molecules of a compound may be considered as being composed of positively and negatively charged particles. The
number of positive charges will be numerically equal to the number of negative charges resulting in electroneutrality of the compound. Each molecule has what may be thought of as centres of +Ve and -Ve charges, much as masses have centres of gravity. If the centres of +Ve and -Ve charges coincide, the molecule is non-polar. Otherwise, it is polar and the measure of the degree of polarity is the dipole moment, ($\mu$). Dipole moment is defined as the product of the net charge of either sign and the distance between the centres of charge. Dipole moments are usually quoted in Debye units, where 1 Debye unit = 1 D = $10^{-8}$ e.s.u.cm.

With complexes of coordination number two, i.e. $MA_2$, the two possible bonding arrangements produce different resultant dipole moments, the linear arrangement $A-M-A$ would have zero dipole moment, while the angular structure $A--M\_\_\_\_A$ would have a finite dipole moment. We can represent this by vector diagrams thus,

$$\begin{align*}
A & \xrightarrow{M} A \\
\text{and} & \\
A & \xrightarrow{M} A
\end{align*}$$

A similar distinction between planar (zero dipole) and angular (finite dipole) arrangements can be made for complexes of coordination number 3.

The complexes of coordination number four with general formula $Ma_2b_2$ may have a cis-planar or a tetra-hedral structure.
The cis-structure will have a large dipole, the trans-structure a zero or very small dipole and the tetrahedral structure quite a large dipole moment, although not as great as that of the cis-planar.

\[
\begin{align*}
\text{cis-structure} & \quad \text{trans} \\
\begin{array}{c}
M \\
b \quad a \\
\end{array} & \quad \begin{array}{c}
M \\
b \quad b \\
\end{array} & \quad \begin{array}{c}
M \\
a \quad b \\
\end{array}
\end{align*}
\]

cis-planar \hspace{1cm} \text{trans} \hspace{1cm} \text{tetrahedral}

Dipole moment measurements are particularly useful for distinguishing between the possible structure for coordination number 5.

2. Magnetic susceptibility measurements:

While electrical dipoles result from unbalanced distribution of +Ve and -Ve charges within molecule of a compound, magnetic dipole results from unbalanced electronic spin and orbital contributions to molecular magnetism. All substances display some sort of magnetic disymmetry in contrast to the existence of electrical nonpolarity. Most of the compounds of the transition metals are paramagnetic because of the presence of incomplete shells of electrons which are isolated from each other. Valency bond theory enables us to correlate more confidently the valency, bond type and stereochemistry of an atom with its effective magnetic moment and as such much of our understanding of transition metal chemistry has been derived from magnetic data.
The paramagnetic susceptibility due to uncompensated electron spin is given by:

\[ \mu = \frac{4s(s+1)}{U} \]

where 's' is the sum of the spin quanta, and as such, electron has a spin quantum of \( \pm \frac{1}{2} \), this can be expressed as:

\[ \mu = \frac{n(n+2)}{U} \]

where 'n' is the number of unpaired electrons. The magnetic moment of the paramagnetic atom is given by:

\[ \mu = \sqrt{\frac{3RT X_M}{N}} \]

where 'N' is Avogadro's number, 'T' is the absolute temperature and 'X_M' is the molar susceptibility of the molecule. It is expressed in units called B.M. In practice, most transition metal compounds are 'magnetically dilute', i.e. the atom with a permanent magnetic moment is surrounded by other atoms without any permanent moment. So, it is necessary to correct the molar susceptibility of the compound and this correction is known as diamagnetic correction. It is possible to estimate the diamagnetism for a molecule simply by summing up the known diamagnetism for each component atom. So by replacing the molar susceptibility by \( X_M \) by the corrected molar susceptibility \( X'_M \), the magnetic moment is given by:

\[ \mu_{\text{eff}} = \sqrt{\frac{3RT X'_M}{N}} = 2.84 \sqrt{(TX'_M)} \]
Some of the theoretical and observed values of $\mu_{\text{eff}}$ are listed by Nyholm. It can be seen that agreement between the theoretical and observed values is excellent in the ions containing up to five electrons, but that abnormally high values are observed in the ions with six to nine electrons.

**Application of Paramagnetism**

In inorganic chemistry, these measurements are useful for three main purposes. Provided that the number of unpaired electrons can be deduced from the magnetic moment, it is possible to infer from the former - (1) valency, (2) the bond type, and (3) the stereochemistry of the metal atom. Use can be made of the size of orbital contribution to the moment, in case of first row transition elements to obtain information concerning the stereochemistry of metal atom.

(1) **Valency Problem**: We can distinguish between different possible valency states provided they contain different numbers of unpaired electrons. The decision is specially easy with first row transition elements because Hund's rule is obeyed for the simple ions. Thus $\text{Fe}^{3+}$ contains five unpaired electrons whilst $\text{Fe}^{2+}$ has only four, these correspond to moments of 5.9 B.M and 4.9 B.M. respectively. Similarly, $\text{Cu(I)}$ and $\text{Cu(II)}$ may be distinguished because the former is diamagnetic. When electron-pairing occurs, valency states of iron can be distinguished since one is
diamagnetic (Fe\(^{2+}\)) and the other (Fe\(^{3+}\)) contains one unpaired electron, i.e. \(K_4[Fe(CN)_6]\) and \(K_3[Fe(CN)_6]\).

(2) Bond types: Magnetic moments can be used to distinguish between two types of bonding in metal complexes namely - ionic and covalent, which gives rise to spin-free and spin-paired states respectively. They are also called outer-orbital, and inner-orbital complexes. In these two situations, if the number of unpaired electrons is different, it can be differentiated by magnetic measurements.

(3) Stereochemistry of metal atom: For a metal ion in a particular valence state, after knowing the spin state of the complex (whether spin-free or spin-paired) from the magnetic moment value, its stereochemistry can be predicted, as the same metal ion in the same valence state gives rise to different magnetic moments according to the geometry of the complex molecule. For example, octahedral Cobalt(II) complexes have magnetic moments ranging from 4.7 to 5.2 B.M., whereas tetrahedral complexes have values in the range of 4.4 to 4.8 B.M. Similarly, Nickel(II) octahedral complexes have moments in the range of 2.9 to 3.4 B.M., whereas, tetrahedral compounds have the moment ranging from 3.5 to 4.2 B.M. Distinction can be made between a high-spin paramagnetic and low-spin diamagnetic Nickel(II) square planar complex from the study of magnetic moment data.
(3) Infra-red Spectra:

Absorption of radiations in the infra-red range is attributed to molecular vibrations of the absorbing material. The two atomic masses represent the bodies which are displaced during vibration and the strength of the bond corresponds to the restoring force. Thus each such system has a characteristic vibrational frequency depending upon those factors and it absorbs infra-red radiations of that frequency. In general, only vibrations of an unsymmetrical nature are detected by infrared absorption. Conclusions of general nature are feasible with respect to ligand chain length, presence or absence of certain functional groups, multiple bonding, isomerism, free or bound state of a ligand and degree of molecular symmetry.

Molecular vibrations absorb light in the infrared region of the spectrum, which includes light of wave lengths 1.0 to 200/\mu, where /\mu represents the micron, which is 10^{-4} \text{cm}. Thus, the position of infra-red absorption band can be specified in units of /\mu. An alternative unit is of wave number, reciprocal of wave length in cms. The infrared region covers the range from 10,000 \text{ cm}^{-1} (1/\mu) to 50 \text{ cm}^{-1} (200/\mu).

**Force Constant:** The difference in energy \Delta E between two adjacent levels, \(E_v\) and \(E_{v+1}\) is given by the equation:

\[
E = \left( \frac{\hbar}{2\pi /\mu} \right)^{1/2} \text{ for a harmonic oscillator.}
\]
where $K$ is the stretching force constant and $\mu$ is the reduced mass, $\mu = \frac{m_A m_B}{m_A + m_B}$ for the diamagnetic molecule $A-B$. The relationship between energy and frequency, $E = h\nu = \hbar\nu$. The symbol $\nu$ will be used interchangeably for frequency (sec$^{-1}$) or wave number (cm$^{-1}$). Stretching force constants for various diatomic molecules are summarised in the following table.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$C_m$</th>
<th>$K$(dynes/cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>3958</td>
<td>$8.8 \times 10^5$</td>
</tr>
<tr>
<td>HCl</td>
<td>2885</td>
<td>$4.8 \times 10^5$</td>
</tr>
<tr>
<td>HBr</td>
<td>2559</td>
<td>$3.8 \times 10^5$</td>
</tr>
<tr>
<td>HI</td>
<td>2230</td>
<td>$2.9 \times 10^5$</td>
</tr>
<tr>
<td>CO</td>
<td>2143</td>
<td>$18.7 \times 10^5$</td>
</tr>
<tr>
<td>NO</td>
<td>1876</td>
<td>$15.5 \times 10^5$</td>
</tr>
</tbody>
</table>

A large force constant is often interpreted as being indicative of a stronger bond. Triple bonds have stretching force constants of the order of magnitude of $13$ to $18 \times 10^5$, double bonds about $8$ to $12 \times 10^5$ and single bonds below $8 \times 10^5$ dynes/cm$^{-1}$. In general force constants for bonding modes are much less than those of stretching modes.

By convention the highest frequency totally symmetric vibration is called $\nu_1$, the second highest $\nu_2$ etc. When the symmetric vibrations have all been assigned, the highest frequency asymmetric vibration is counted next followed by the remaining in order of decreasing frequency. Another common
convention involves, labelling stretching vibrations \( \nu \) bending vibrations \( \delta \) and out of plane bending vibrations \( \Pi \). Subscripts 'as' for asymmetric, 's' for symmetric and 'd' for degenerate are employed with these symbols.

For the region 5000 - 650 cm\(^{-1}\), rock-salt optics are used, while for the region 600 - 250 cm\(^{-1}\), cesium bromide prism is used. Potassium bromide is used also for the region 5000 - 400 cm\(^{-1}\). The spectra recorded using either KBr dises or mulls made with Nujol or hexachlorobutadiene.

The principal uses of infra-red spectroscopy are (1) the qualitative identification of compounds through the use of the finger-print technique, (2) identification of certain features of composition (C-H, N-H, O-H, C=O, C=N, -COOR, etc), (3) study of overall symmetry of a molecule.

The O-H stretching vibration occurs around 3600 cm\(^{-1}\). Hydrogen bonding lowers the frequency and broadens the band. The N-H stretch occurs in the 3300 - 3400 cm\(^{-1}\) region, as sharp peaks. The group C\(=\)N gives rise to a strong sharp absorption in the 2200 to 2300 cm\(^{-1}\) region (2500 - 2000 cm\(^{-1}\) for triply bonded). The region 2000 to 1600 cm\(^{-1}\) contains stretching vibrations for doubly bonded molecules and bending vibrations for the O-H, C-H and N-H groups. The carbonyl group in a ketone absorbs around 1700 cm\(^{-1}\). Conjugation in an amide R-C-N(CH\(_3\))\(_2\) decreases the C-O force constant and lowers the
highly coupled (C=O) carbonyl absorption to the 1650 cm\(^{-1}\) region. Stretching vibrations for C=C and C=O also occur in this region. The region below 1600 cm\(^{-1}\) is referred to as the fingerprint region for many organic compounds. This is the single bond region and it is very common to get coupling of individual single bonds which have similar force constants and connect similar masses (e.g. C=O, C=C and C-N stretches often couple).

**Change in Spectra of Ligand upon Coordination:**

A decrease in the stretching frequency and bond order results on coordination of the donor atom involved in a double bond. Sometimes also there is an increase in cases depending on the acidity of the ligand. Usually, the carbonyl stretching frequency decreases on coordination. Similarly the P=O stretching frequency in phosphine oxides and S=O stretching frequency in sulfoxides decrease on oxygen coordination, whereas increase in stretching frequency indicates sulphur or phosphorous coordination. C=WN stretching frequency in thiocyanates decrease on N-coordination. In lactums, the decrease in \(\nu(C=O)\) and increase in \(\nu(C-N)\) is indicative of oxygen coordination. There is also a decrease of \(\nu(C=O)\) in metal acetylacetonates, but when this chelate forms an adduct with one or more nitrogen donor ligands, \(\nu(C=O)\) may increase due to feeding back of electrons by the sigma-bonding ligand to ring system, whereas, if the ligand has more of pi-character, the \(\nu(C=O)\) should decrease more in the adducts. There are many such examples, which can help to determine the bonding site in an indirect manner from the study of infra-red spectra.
Change in Spectra Accompanying Change in Symmetry upon Coordination:

Evidence to support coordination of the nitrate ion to metal ions can be obtained from infra red studies. Free nitrate ion has $D_{3h}$ symmetry but upon coordination of one of the oxygens, the symmetry is lowered to $C_{2v}$. The asymmetric stretch in the nitrate ion is split up into high frequency $N-O$ asymmetric stretch and a lower frequency symmetric stretch. These occur at 1460 and 1280 cm$^{-1}$. An additional $N-O$ stretch corresponding roughly to the inactive symmetric stretch in nitrate ion also appears. The sulfate and perchlorate ions are the other examples to demonstrate the effect of change in symmetry on spectra.

Far Infra-red Spectra:

Metal ligand vibrations recorded in the far infra-red region give direct evidence regarding the nature of bonding between the metal ion and the ligand donor atoms. In a complicated molecule, the informations obtained from both the regions help in deciding the bonding scheme and the stereochemistry of the complex compounds. Usually, $\nu(M-O)$, $\nu(M-N)$, $\nu(M-S)$, $\nu(M-X)$ frequencies occur in the 500 - 180 cm$^{-1}$ regions. Far infra-red spectra can be used to assign unambiguously the metal-ligand stretching frequencies and determine the bonding sites. Even information about the presence of bridging halogen can be obtained from metal-halogen stretching frequencies and in many cases stereochemical environment of the metal ions can be determined with the help of such observations.
Electronic Spectra:

Transition metal ions exhibit various colours arising out of different electronic transitions. The same metal in the same oxidation state often gives rise to different colours in the presence of different complexing agents. Attention has been drawn to the origin of this change in colour only since 1951 when Ilse and Hartman tried to explain the absorption spectrum of $\text{Ti(H}_2\text{O)}_6^{3+}$ on the basis of crystal field theory. Then followed a remarkable period of intense investigation and theoretical advance by Orgel and Jorgenson and others, rationalising the absorption spectra of the transition metal ions and their complexes. The transition metal ions contain an incomplete 'd' shell of the electrons and the colours of transition metal ions and their complexes are due to electronic transitions involving d-electrons. The d-shell in an atom or ion is five-fold degenerate in the absence of an external electric or magnetic field. For a free ion in the gaseous state, an electron can jump from one of these orbitals to the other without any absorption of radiation. When a certain number of ligands is attached to the central metal ion, the degenerate 'd' orbitals split up into groups of different energies and electronic transitions from one set of orbitals to the other can take place with absorption of energy. The magnitude of energy separation is such as to produce the well known colours of these complexes.

Most applications of electronic spectroscopy have been made in the wavelength range from 2100 to 7500Å, for this is the range
accessible with most recording spectrophotometers. A number of common types of molecules have no absorption in this range and may thus be commonly used as solvents. Hydrocarbons, particularly, hexane, and heptane are useful below 2500Å° and water, alcohols, and even halogenated solvents such as chloroform may be used down to about 2400Å°. U.V.Spectra are generally characterised by the position of maximum absorption and the molar extinction coefficient at this wave length defined by the equation \( \varepsilon = \frac{E}{c_l} \), where 'E' is the optical density, 'C' is the concentration in moles/litre and 'l' is the cell depth in cms. U.V.Absorptions are frequently very intense, allowing work to be carried out in very dilute solutions. (10^{-3}M).

Brasted and Cooley have discussed the theories of absorption in terms of three bands, first band in the range 450 - 550 m\(\mu\)u., the second band in the range 320 - 400 m\(\mu\)u., and the third band in the range 195 - 250 m\(\mu\)u. The greatest single factor leading to absorptions in the first range is vibration of the nonbonding electrons of the metal ion. The coordinate bond electron are thought to be responsible for the second absorption band. The presence of third band has been described by Tsuchida as a polarisation phenomena. The position of second and third bands are useful in determining geometric configuration.

For a configuration (Ti^{3+}), only one transition \( ^2E_g \leftarrow ^2T_{2g} \) is predicted and only one is observed, which occurs at 20,400 cm\(^{-1} \) in \([\text{Ti(H}_2\text{O)}_6]^{3+}\) complex corresponding to a \(D_q\) value of 2040 cm\(^{-1}\).
For a $d^9$ complex in an octahedral field, the energy level diagram is obtained by inverting that of $d^1$ complex.

The inversion results, because the ground state of a $d^9$ configuration is doubly degenerate and the excited state is triply degenerate. Therefore, the transition is $E \rightarrow T_2$.

The results are often summarised by Orgel diagram.

Since the tetrahedral splittings for $d^1$ is just the opposite that for octahedral splitting, $d^1$ tetrahedral and $d^9$ octahedral complexes have similar Orgel diagrams.

The splitting of the state as a function of $D_q$ for octahedral complexes with electron configurations $d^1$ and $d^6$ for tetrahedral, $d^4$ and $d^9$ complexes is described by right half. The spectra of the complexes contain only one band arising from $d$-$d$ transitions and this is assigned $T_{2g} \rightarrow E_{g}$. The left hand side of the Orgel diagram
applies to octahedral $d^4$ and $d^9$ as well as tetrahedral $d^1$ and $d^6$ complexes. The single d-d transition that occurs is assigned as $E - T_2$.

According to Hole formalism in a poly electronic system, a configuration of $d^{10}$ will have the same behaviour in a crystal field, except for certain changes in the signs of energy terms, as a $d^n$ configuration. Hence a similar but inverted spectral pattern will be observed. Thus Cu(II)($d^9$) ion will have a similar pattern as Ti(III)($d^1$) ion. But the former, in an aqueous solution, gives two or three nearly super-imposed, symmetrically shaped bands. This has been traced to the distortions of the octahedral environment as required by Jahn-Teller theorem.

In 1937, Jahn and Teller advanced a theory which states that "in any non-linear molecular system, a degenerate electronic state will be unstable and will undergo some kind of distortion which will lower its symmetry and split the degenerate state." In $O_h$ symmetry, the octahedral groups are regularly placed. The Teller group states are stable for $d^3(t_{2g}^3)$, high-spin $d^5(t_{2g}^3e_g^2)$, low-spin $d^6(t_{2g}^6)$, high-spin $d^8(t_{2g}^6e_g^2)$ and $d^{10}(t_{2g}^6e_g^4)$ systems. Among unstable Jahn-teller states, a weak order distortion for unsymmetrically field $t_{2g}$ orbitals, i.e. $d^1$, $d^2$, low-spin $d^4(t_{2g}^4)$ and $d^5(t_{2g}^5)$, high spin $d^6(t_{2g}^4e_g^2)$ and $d^7(t_{2g}^5, e_g^2)$ systems and a stronger distortion for unsymmetrically field $e_g$ orbitals, i.e. high-spin $d^4(t_{2g}^3e_g^1)$, low-spin $d^7(t_{2g}^6e_g^1)$ and $d^9(t_{2g}^6e_g^3)$ systems are observed. The latter type of complexes (as also low-spin
d^8) develop tetragonal symmetry to such large extent that most complexes appear square planar. The complex decreases its energy by a splitting of these equivalent orbitals t_{2g} or e_g letting one or two have lower energy and the rest higher energy. The splittings due to these distortions appear as separate absorption maxima.

Spin-orbit coupling in a complex gives rise to a number of fine structures in the spectrum of a metal complex. The parameter that expresses the magnitude of spin-orbital coupling is either \lambda or \delta, the former applying to a single term while the latter to a single electron parameter, which has a particular value for the whole configuration. The magnitude of \delta 3d increases steadily from about 80 cm\(^{-1}\) for Sc(II) to about 830 cm\(^{-1}\) for Cu(II).

Different types of notations have been used to represent the various energy levels obtained from the contributions from central field forces, inter-electronic repulsions and spin-orbital coupling forces. Mulliken symbols are more common to represent the various energy levels. The table below gives the Mulliken symbols used for O\(_h\), D\(_{4h}\) and Td symmetry.

| Mulliken symbols representing various energy levels in different crystal fields |
|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| Octahedral field (O\(_h\) symmetry) | Square planar field (D\(_{4h}\) symmetry) | Tetrahedral field (Td symmetry) |
| A\(_1\)g | A\(_1\)g | A\(_1\) |
| A\(_2\)g | B\(_1\)g | A\(_2\) |
| E\(_g\) | A\(_1\)g + B\(_1\)g | E |
| T\(_1\)g | A\(_2\)g + E\(_g\) | T\(_1\) |
| T\(_2\)g | B\(_2\)g + E\(_g\) | T\(_2\) |
The transitions observed in various symmetry for the Ni(II) (d⁸) ions are mentioned below as Ni(II) is one of the well-studied ions. Large spin-orbit contributions of nickel has interested many workers. This generalisation gives a very good impetus to study the electronic spectra of Ni(II)(d⁸) complexes with various ligands.

Octahedral Symmetry(Oh): Six regularly placed groups constitute the octahedral symmetry. Three bands arise in the visible region attributable to transitions ³A₂g —> ³T₂g(F), —> ³T₁g(F) and → ³T₁g(F). For [Ni(H₂O)₆]²⁺ and [Ni(en)₃]²⁺ complexes, these bands appear approximately at 9,000, 14,000 and 25,000 cm⁻¹ and 11,000, 18,500 and 30,000 cm⁻¹ respectively. They appear usually as well defined bands of molar absorbance between 1 and 10. The middle band of the former appear as being split in the middle to two bands. This arises out of spin-orbit coupling, which mixes ³T₂g(F) and ¹Eg states which are very close in energy. Ethylene diamine causes a stronger ligand field and hence the bands being well separated, no such significant mixing occurs as to cause spin-orbit coupling. In the case of an intense ligand field, such as the ligand o-phenylene-bis-(dimethyl arsenic) might give in [Ni(diars)₃]²⁺, a singlet level or originating in a Russell-Saunders state of a d⁷s or d⁷p configuration could drop down and become the ground state. The diamagnetism arising here is out of the d⁴sp³ bonding.
Square Planar Symmetry ($D_{4h}$): The planar complex of Ni(II) may be diamagnetic or paramagnetic depending on the energy separation, i.e., whether the ligand field splitting is greater or less than the energy necessary to cause electron pairing. This property depends upon the effect of the surrounding ligands—the effect of the trans ligands on the plane of the four other ligands. As the two trans-ligands are taken farther apart from the planar field of the other four ligands of an $O_h$ symmetry, the symmetry gets distorted and finally assumes a $D_{4h}$ symmetry in the extreme case. The distorted octahedron (which has also an apparent $D_{4h}$ symmetry) shows bands arising out of transitions:

\[
3B_1g \rightarrow 3E_g(P), \rightarrow 3B_1g(F), \rightarrow 1A_1g, \rightarrow 1B_2g(D) \rightarrow 3A_2g(F) \rightarrow 3E_g(F) \rightarrow 3A_2g(P) \text{ and } 3E_g(P) \text{ approximately at } 9,000, 12,000, 13,000, 14,500, 18,000; 25,000; \text{ and } 28,000 \text{ cm}^{-1} \text{ respectively as studied for the pyridine type of complexes of Ni(II).}
\]

In a perfectly square planar field (diamagnetic) the well-defined bands are obtained due to $1A_1g \rightarrow 1B_1g$ and $1A_1g \rightarrow 1B_2g$ at about $20,000 - 25,000 \text{ cm}^{-1}$ as in bis-dimethyl glyoximato nickel(II).

Various $n$-alkyl salicylaldimine and substituted salicylal dimine nickel(II), have been known to be paramagnetic square planar, but the transitions have not yet been characterised.

Tetrahedral Symmetry ($T_d$): Three absorption bands in the visible and near infrared regions are observed in the case of
tetrahedral Ni(II) compounds. The bands arise out of transitions \(3\Sigma_1^-(F) \rightarrow 3\Sigma_2^+(F), \rightarrow 3\Sigma_2^+(F)\) and \(\rightarrow 3\Pi_1^-(P)\). The former two bands appear at \(5000 \text{ - } 7000\) cm\(^{-1}\) and \(7000 \text{ - } 8000\) cm\(^{-1}\). But the band at about \(15,000\) cm\(^{-1}\) is of very high intensity (molar absorbance \(\sim 200\)) and is usually split into two components due to larger spin-orbit coupling which lifts the degeneracy of the \(3\Sigma_1^-(P)\) state. Such bands have been observed in case of Ni(Ph\(_3\)P)\(_2\)Cl\(_2\) and \([\text{Ph₃As}]_2[\text{NiCl}_4]\).

Besides these three common types of complexes, there are also other symmetries which have been studied less. But the ligand influence is the major criterion in explaining the preference of various symmetries. According to the relative influence of these ligand fields in the complexes the ligands have been placed in 'Spectrochemical' and 'Naphelauxetic' series.

**Spectrochemical Series:** An electrostatic perturbation causes in splitting of the degenerate orbitals of the ions. Therefore, the C.F.S.E.\((\Delta)\) is taken as a measure of such splitting, resulting out of perturbation caused by the ligand field on the metal ion orbitals. The position of the ligand, in this series is determined by the order of \(\Delta\) value. As discussed earlier, the C.F.S.E. value can be obtained directly from the lowest transition, i.e. from the ground state the first excited state, in a field of cubic symmetry. But in case of lower symmetry, more number of transitions occur with splittings of various energy levels. It
then becomes difficult to find out the ligand field parameters.

Since, $\Delta$ is a complex quantity, its value and hence the order of the spectrochemical series for ligands depends upon:

(a) Purely electrostatic perturbation,
(b) effect of lone pairs belonging to the ligand,
(c) effect of the metal $\rightarrow$ ligand $d_{\Pi} - p_{\Pi}$ bonding,
(d) effect of ligand $\rightarrow$ metal $p_{\Pi} - d_{\Pi}$ bonding,
(e) the positions and the extent of disimilar ligands present in the complex,
(f) the transition series of the metal, and
(g) the charge or oxidation number of the metal ion.

The effect of (a), (b), and (c) act towards increasing while that of (d) acts in opposite direction. Effect of (e) depends upon the net effects of the mixed ligands. It is also found that increases both according to oxidation number, i.e. $0, (+1) \leq (+2) \leq (+3) \leq (+4)$ as in (g) and also according to the order of the transition series as in (f), i.e. $3d \leq 4d \leq 5d$. The value of $\Delta$ for bivalent ions is $\sim 10,000$ cm$^{-1}$ and for trivalent ion is $\sim 20,000$ cm$^{-1}$. The spectrochemical series for metal ions as arranged by Jorgenson is as follows:

- Mn(II) $\leq$ Ni(II) $\leq$ Co(II) $\leq$ Fe(III) $\leq$ Cr(III)
- Co(III) $\leq$ Mn(IV) $\leq$ Mo(III) $\leq$ Rh(III) $\leq$ Pd(IV)
- Ir(III) $\leq$ Re(IV) $\leq$ Pt(IV).
Naphelauxetic 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. Schaffer and Jorgensen arranged the ligands according to the increasing tendency of such overlap in a series called 'Naphelauxetic' (Cloud-expanding) series. It is seen that interelectronic repulsion forces between d-electrons are decreased by complex formation, and the decrease being anything between 5 - 40 per cent for the 3d series of metal complexes. This is correlated with the extend to which covalent bond formation occurs. The index for such inter-electronic repulsing power, $\beta$ is given by:

$$
\beta = \frac{B'}{B}.
$$

where $B$ and $B'$ are the Racah parameters for the free gaseous ion and the complex respectively. The values of $B$ are given in table for different 3d metal ions are obtained directly from the atomic spectroscopy. The series of decreasing order of $\beta$ is given by:

$F^- > H_2O > Urea > NH_3 > C_2O_4^{2-} > en > NCS^-$

$Cl^- > CN^- > Br^- > I^-.$

This series gives the order of the inter-electronic repulsion forces and the quantity of direct dependence on the covalent
tendencies is given as \( (1-\beta) \) and for this the given series reverses. It is found that the series for \( (1-\beta) \) is nearly of the same order as Pauling's electronegativity series:

\[
F > O > N > Cl > C > Br > S > I.
\]

Accordingly, \( H_2O \) and \( F \) are known to form least covalent complexes of a given central ion as \( \beta \) is nearer to unity.

The naphelauxetic series enables the chemists to detect the presence of some complex species in solution and also, at times, the type of bonding in the complex. For example, \( \left[ \text{Co(NH}_3)_3\text{NO}_2 \right]^{2+} \) has red colour when there is M-O linkage, but yellow when only M-N linkages are there. To make the series more useful, coordination chemists are trying to make the series bulkier by collecting more data regarding different ligand systems.

The electronic spectra can be obtained from either the use of absorption or reflectance spectra of the incident monochromatic beam falling on the sample, or by passing the incident beam through a solution of the compound in a suitable solvent. But since in some cases, the compounds are insoluble or change the coordination species in solution, either due to decomposition or by coordinating with the solvent, it is very essential to record the spectra of solid samples.

**Structural Evidence From Electronic Spectra:**

From the observation of absorption bands due to d-d transitions, the stereochemical configuration of the metal ion is
predicted. Four coordinate square planar complexes of Copper(II) has an absorption band in the region 17,000 cm\(^{-1}\), whereas tetrahedral or distorted tetrahedral complexes have the characteristic band below 10,000 cm\(^{-1}\). Octahedral or distorted octahedral Copper (II) complexes give rise to a number of absorption bands in the region 13,000 to 15,000 cm\(^{-1}\) or else a number of bands are present in a single broad band envelop in this region. Similarly, Nickel(II) octahedral complexes have three characteristic absorption bands in the regions 9,000 - 11,000, 14,000 - 18,000 and 25,000 - 30,000 cm\(^{-1}\). A truly tetrahedral Cobalt(II) species have an absorption band in the 16,000 cm\(^{-1}\) region due to the transition \(^{4}A_2 \rightarrow ^{4}T_1(P)\). But the fine structure and complexity of this band is caused due to spin-orbit coupling effects which splits the \(^{4}T_1(P)\) state and allows the transitions to the neighbouring doublet states to gain same intensity. Thus position of the absorption bands, their intensity and calculation of \(D_q\) and values help in elucidating the geometry of the complex to a fair degree of accuracy.

**Conductivity studies:** Conductivity measurements will indicate whether the compound is nonionic or ionic and if it is ionic, then the number of ions present in it. The data obtained experimentally may be compared with standard values in drawing the conclusions in this respect. For example, the standard values for univalent electrolytes measured in different media are presented by Robinson and Stokes\(^{68}\) to be as follows:
\[ \Lambda_m \] value for 1:1 electrolytes (Robinson & Stokes)

<table>
<thead>
<tr>
<th>Substance</th>
<th>Conductance (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrobenzene</td>
<td>25 - 35</td>
</tr>
<tr>
<td>Acetone</td>
<td>150 - 200</td>
</tr>
<tr>
<td>Pyridine</td>
<td>60 - 80</td>
</tr>
<tr>
<td>Ethyl dichloride</td>
<td>50 - 70</td>
</tr>
<tr>
<td>Ethylidene chloride</td>
<td>90 - 115</td>
</tr>
<tr>
<td>Water</td>
<td>90 - 130</td>
</tr>
</tbody>
</table>

Conductance helps to draw conclusions regarding the coordination number and the nature of the involved bonds.

**Molecular Weight Determination:** Molecular weight determination which may be carried out by Freezing point method or any other convenient method is helpful in indicating whether the compound is a monomer, dimer or polymer or whether the compound is ionic or nonionic. This measurement coupled with other physical measurements gives a fair amount of certainty to the structural inorganic chemist to draw safer conclusions.

**X-Rays:** A quick and relatively simple method of X-Ray analysis employs crystallising powders, rather than large crystal. Powder patterns sometimes serve to identify unknown substances by comparison with known pattern. X-Ray and electron diffraction studies on complex compounds have yielded valuable information concerning properties of symmetry, spatial configuration, orientation of complex ions and molecules in crystal lattices, differentiation between racemates and optically inactive forms, determination of bond angles and distances, estimation of
molecular weight of complexes, differentiation between mixture and single phase crystals and identification of bridging groups.

Though the physical methods described below have not been used in the present investigation, it is thought worthwhile to mention briefly some of the important tools used in structural investigation.

**Raman Spectra:** The emission spectra resulting from the Raman effect are attributable to molecular vibrations which are symmetrical in nature. Raman spectra thus complement infrared spectra as means of studying molecular structure. The Raman effect is produced when a molecule is irradiated with a beam of monochromatic light of wavelength greater than the size of the molecule. The radiation undergoes interaction with the molecule, loses some of its energy and then scatters. The wavelength of the scattered light is greater than that of the incident light unless the molecule is in an excited state. The scattered light may be passed through a spectrometer and received on a photographic plate. The spectrum of the plate contains a strong central line corresponding to the incident beam and removed at various distances are the less intense Raman lines. The numerical values of these shifts are in the same range of the frequencies of the IR absorption. Krishnamurti \(^{70}\) used the Raman method to study the formation of chloro complexes of mercury. An extensive investigation of the structure of complexes has been carried out by Mathieu and Corniavin \(^{71}\).
Electron Spin Spectroscopy: E.S.R. is a branch of absorption spectroscopy in which radiation of microwave frequency is absorbed by molecules possessing electrons with unpaired spins. The energy $E$ of the transition is given by $E = \hbar \nu = g \beta H_0$, where $\hbar$ is Planck's constant, $\nu$ the frequency of radiation, $\beta$ the Bohr magneton, $H_0$, the field strength (applied) and $g$ the spectroscopic-splitting factor. For a free electron $g$ has the value of 2.0023. In general, the magnitude of $g$ depends upon the orientation of the molecule containing the unpaired electron with respect to the magnetic field. The value of $g$ for an unpaired electron in a gaseous atom or ion for which Russell-Saunders coupling is applicable is given by the expression:

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

For the halogen atom in the gas phase, $g$ values predicted by the above equation have been found to agree exactly with experimental values. But no such agreement is found when the unpaired electron is placed in a chemical environment in a transition metal ion complex crystal lattice. In such a case, the orbital motion of the electron is strongly perturbed and the orbital degeneracy is partly removed or quenched. The properties of the transition metals are determined to a large extent by the relative magnitudes of the crystal field and spin-orbit coupling. These two interactions have opposite effects on the orbital degeneracy. For octahedral Nickel(II) complexes, calculations, which include
mixing of the $^3A_{2g}$ ground state with the $^3T_{2g}$ excited state, give the following equation for the $g$ value.

$$g = 2 - \frac{8\lambda}{10D_q}$$

where $\lambda$ is the spin-orbit coupling constant. In hexaaquo nickel (II), it is found experimentally that $g = 2.25$, hence $8\lambda/10D_q$ must equal $-0.25$. From the electronic spectrum one can calculate $10D_q = 8,500$ cm$^{-1}$ producing $\lambda = -270$ cm$^{-1}$. In a molecular orbital description, the extent to which $\lambda$ is lowered from the free ion value is a measure of the extent of mixing of metal and ligand orbitals. This example illustrates how both spin-orbital coupling and $D_q$ can affect the magnitude of the $g$ value. From the E.S.R spectra of complexes studied usually by variation of field strength $g$ values may be obtained and on analysis of the $g$ value, the extent of spin-orbit coupling and $D_q$ values may be obtained.

**X-Ray photoelectron Spectroscopy:** X-Ray photoelectron spectroscopy, also called E.S.C.A. is the study of the energy distribution of electrons emitted from X-Ray irradiated compounds. In principle, all electrons, from the core to the valency level can be studied. In this respect, the technique differs from ultraviolet photo-electron spectroscopy, in which only $\alpha$ the valency electrons can be studied.

The photoelectric interaction between monoenergetic X-rays and a solid or gaseous sample causes electrons to be ejected with discrete kinetic energy. The observable quantities in photoelectronic spectroscopy are thus the kinetic energies corresponding to
discrete electron lines. The energy conservation for the photo-emission process can be expressed by:

\[ E_{\text{h}} = E_k + E_\phi + E_B(i) \]

where \( E_{\text{h}} \) is the X-ray energy, \( E_k \) = photoelectron kinetic energy, \( E_\phi \) is a small correction for solid effects and \( E_B(i) \) is the electron-binding energy of the \( i^{\text{th}} \) level. An electron energy analyser is used to scan the kinetic energy spectrum and to record the \( E_k \) value. The binding energies can be determined by the use of above equation.

The power of photoelectron method lies in the fact that the measured quantity, the electron-binding energy of an atom is a function of the chemical environment of the atom.

The application of X-ray photoelectric spectroscopy is illustrated by the study of nitrogen spectra of some transition nitrosyl complexes.
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