11 GENERAL INTRODUCTION AND THEORIES OF COORDINATION COMPOUNDS:

The twentieth century has been regarded as an active era of chemistry. Modern inorganic chemistry is more than a descriptive science. In recent decades inorganic chemistry has had an impressive renaissance. The coordination chemistry has widened its scope in the latter half of the present century. In the modern era coordination chemistry forms an integral part of several interdisciplinary researches. In a brief period of about four decades of growth in chemical sciences, no other field has received as much attention as the study of coordination compounds. The noteworthy recent experimental developments coupled with extensive theoretical treatments are the significant highlights of the subject. Over recent years, there has been considerable progress in our understanding on the reactivity of the coordinated ligands with transition and non-transition metal ions. New types of complexes displaying remarkable properties are being continuously turning up. It should soon be possible to "tailor make" any type of individual metal complex to suit any purpose with the help of suitable complexing agents.

Compounds now considered to be coordination compounds have been known for over a century.\(^1\)\(^-\)\(^6\) No satisfactory explanation for complex formation was available till 1893 (Werner's theory).\(^7\) The word 'complex' employed by
Albert acquired a new meaning and significance with the enunciation of coordination theory by Alfred Werner. Werner, who was trained as an organic chemist, suggested that every metal-ion has two types of valencies, the primary and secondary. The secondary valences remains directed in space in a fixed manner. The central metal and the fixed number of groups attached to it by these secondary valencies constitute a 'coordination complex'. Very little was known about the origin of chemical bonds and the basis of molecular shapes at that time. Werner was an experimentalist and a synthetic chemist of rare ability who went on translating his predictions into practice. He predicted and experimentally proved that optical activity is not a special feature of carbon compounds but is a general property of unsymmetrical polyhedral binding.

A metal complex consists of a central atom or ion which is surrounded by atom or group of atoms, charged or neutral known as ligands. These ligands are united to the metal atom by a coordinate bond. The complex compounds do not give up their identity in solution. They may dissociate only partly into their constituents and the extent of dissociation determines their stability. In ordinary complexes the ligand or donor groups are mono functional. In 1920, Morgan and Drew introduced the term 'Chelate' to designate complex of cyclic structure in which a metal ion gets bound by at
least two bonds to a donor substance (chelating ligand) possessing two or more lone pairs of electrons. Multidentate ligand may be bi-, tri- or quadridentate with two three or four electron donating group, respectively. The formation of inner complex compounds involving a ring structure received recognition by earlier workers viz. Werner and Ley, who realised that chelated structures were stabler than simple complex and the chelation was the cause of extra stability.

The picture of coordination link (secondary valency) became considerably clearer with the idea of electronic theory of valency formulated by Lewis (1916) and it was applied extensively to coordination compounds by Sidgwick and Lowery. Sidgwick suggested the donation of a pair of electron from each group (so called ligand), gives rise to secondary valency; while the primary valencies are simple ionic bonds. The number of ligands so attached was called the coordination number of the metal and the resulting complex had a definite geometrical shape. The concept of effective atomic number (E.A.N.) by Sidgwick also helped in qualitative explanation of magnetic behaviour of some of the complexes.

Sidgwick's idea of coordinate bond was extended by Pauling, who applied quantum mechanical principles to elucidate the valence bond theory (VBT) and metal ligand
bonding. The theory concentrated on the stereochemistry and magnetic properties of the central atom in the complex but had very little to do in properties of complexes. Most structures can be understood on the basis of repulsion between pairs of electrons or the use of hybridised orbitals. Pauling's theory rendered valuable service in understanding the main features of coordination chemistry for nearly twenty years (1930-1950). The main weaknesses of valence bond theory as applied to complexes were:

(i) Its failure to consider the existence of excited states and an explanation for the spectra of the complexes;
(ii) Though specifying the number of unpaired electrons, it provides no further explanation for magnetic behaviour. In brief this theory offers only qualitative interpretation of stereochemical and allied properties and bond type.

The crystal field theory (C F T) was initiated by Bethe\textsuperscript{19} in 1929, and in the following years it was applied to transition metal complexes by Penny and Schlapp,\textsuperscript{20} and by Van Vleck.\textsuperscript{21} It was however, more than two decades later, that the theory came to be popularly accepted by coordination chemists, mainly due to the contribution of Hartmann and Orgel and was popularised as ligand field theory by the work of Ballhausen, Orgel, Nyholm, Figgis and Jorgensen, in the later years. 22-27
The essential assumption of CFT is that the ligands which are treated merely as point charges or point dipoles, produce, a negative field around the central metal ion and thus the five "d" orbitals which were originally degenerate and equal in energy in a free transition metal ion, become differentiated in the presence of electrostatic field giving sets of orbitals higher and lower in energy depending upon the crystal field geometry around central metal ion. The advantages of CFT lie in its capability of explaining magnetic, spectral, thermodynamic, kinetic and stereochemical properties of the complexes on the basis of the splitting of d-orbitals. Since the CFT lays total emphasis on the metal orbitals and does not consider ligand orbitals at all, it fails to explain (i) Intraligand, metal to ligand and ligand to metal charge transfer bands associated with the ligand orbitals, (ii) Bonding found in a large number of complexes, (iii) Covalency in metal ligand bonding, (iv) Relative strength of various ligands.

The more pragmatic method of molecular orbitals was originally conceived by Hund and Mulliken. The molecular orbital theory envisages the combination of various metal orbitals with the ligand group orbitals of similar symmetry giving rise to pairs of bonding and antibonding molecular orbitals. Some orbitals fail to interact due to unfavourable symmetrical considerations.
resulting in nonbonding orbitals. According to this theory, the ligand electrons are accommodated in the bonding molecular orbitals and "d" electrons are accommodated in the nonbonding and an antibonding molecular orbitals. This corresponds to the splitting of "d" orbitals as in the crystal field theory but the significant difference between the two approaches is that metal orbitals are not pure and the extent of overlap determines covalency. Thus it may be concluded that CFT and VBT are special cases of two extremes i.e. zero covalency and 100% covalency.

Molecular orbital theory, inspite of its utility, suffers from the limitation that the calculations involved are rather tedious and lengthy. Therefore, a via media, LFT or ACFT has been evolved which is essentially based on crystal field treatment but at the same time it also takes into consideration a moderate amount of overlapping of orbitals by adjusting various parameters in a suitable manner. A number of evidences based on electron spin resonance (ESR), nuclear magnetic resonance (NMR), nuclear quadrupole resonance (NQR) and d-d absorption bands leads the conclusion mentioned above. Ligand field theory has been able to interpret or predict for complexes the most favourable coordination number, stereochmical reaction paths for substitution and magnetic and thermodynamic properties. This theory involves the use of interelectronic
interaction parameters like spin orbital coupling constant $\lambda$ and the two Racah parameters $B$ and $C$ which are regarded as variables in the complexation process. Racah parameters $B$ and $C$ measure the energy separations between various Russel-Saunders states. The treatment envisages that overlapping on metal electrons are dragged out to some extent under the influence of the nuclei of the ligand atoms, thereby reducing their mutual interaction. It has been found that the magnitudes of the parameters are reduced in complexes in comparison to their free ion values. From magnetic and spectral studies, it has been inferred that good agreement between theory and experiment exists if all the three parameters are taken to 70-80% of their free ion values.

Studies in the field of coordination chemistry in solid state and solution have engaged the attention of workers. Solid study comprises preparation of solid complexes, their elemental analysis, magnetic study, thermal analysis, spectral analysis viz. infrared, ultraviolet-visible, electron spin resonance, nuclear magnetic resonance, Mossbaur, X-ray etc. Solution study comprises thermodynamic and kinetic aspects. Kinetic studies deal with rate and mechanism of chemical reaction while thermodynamic studies mainly includes the stabilities of complex species formed in solution, under variety of conditions. There are several electrometric
techniques viz. pHmetry, Polarography, Amperometry, Voltametry, Conductometry, Electrophoresis, Chromatography etc, which are being frequently employed for discovering the physicochemical phenomena of active chemical species.

1.2 PHYSICO-CHEMICAL METHODS IN THE CHARACTERIZATION OF COMPLEXES:

The characterisation of a coordination compound normally involves the identification as well as structural determinations. Among various physico-chemical techniques the elemental analysis, magnetic susceptibility, thermal and conductance help in deciding the molecular formulae of the complexes; while the sophisticated spectral methods help to establish the actual site of bonding of ligands to metal and also the stereochemistry of the complex. The choice of method depends upon the physical state of the complex. The present investigation is concerned with the structural characterisation of coordination compounds with the help of following well known techniques.

1. Elemental analysis.
2. Molar conductance
3. Magnetic susceptibility
4. Infrared absorption spectrophotometry
5. Electronic spectroscopy

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5. Electronic spectroscopy

(Visible absorption spectrophotometry)
6. Electron spin Resonance spectroscopy
7. Thermogravimetric analysis
8. X - Ray diffraction

1.21 **ELEMENTAL ANALYSIS**: The molecular formula of the coordination compound can be deduced from elemental analysis. For the determination of the metal and sulphur contents, the complex was decomposed by heating with concentrated nitric acid and the contents were estimated by well known standard analytical methods. The percentage of C, H & N have been estimated microanalytically at Central Drug Research Institute (RSIC), Lucknow.

1.22 **MOLAR CONDUCTANCE**: The electrical conductivity measurements have been used to determine the charged type of the complex molecules. In most cases molar conductance and not the equivalent conductance of charged complex falls in a predictable range, at a given concentration.

As a result of the passage of electric current, an electrolyte gets decomposed into ions. These ions in solution are responsible for the conductance. The standard unit of which is the specific conductance i.e. reciprocal of specific resistance. A molar conductance may be defined as the conducting power of all the ions produced by one gram mole of an electrolyte in a given solution and it can be expressed by the following relation

\[ \lambda = 1000 \ k/C \]

where \( \lambda \) is molar conductance, \( k \) is specific conductance
and C is the concentration in gram mole per litre.

In context with the coordination compounds, the determination of molar conductance value is quite meaningful as it assists in deciding whether a negative group is inside or outside the coordination sphere. Most ions, with the exception of those having long chains (H⁺, OH⁻) & some complex ions have ionic conductance of about 60 ohm⁻¹ cm² mol⁻¹ at 25°C in water. As a first approximation, one should expect the contribution of an ion iⁿ⁺ to the molar conductivity to be about 60 mhos(S) and accordingly for uni-univalent salt MA type 120 ohm⁻¹ cm² while for a uni-bivalent electrolyte MA₂ or M₂A will be about 240 ohm⁻¹ cm². The approximate values of the conductance varies with the change in size of ion, temperature, dielectric constant relative velocity of ion and viscosity of the solvent. 43-48

1.23 MAGNETIC SUSCEPTIBILITY:

Magnetic measurements are of importance in solving the stereochemical problems of inorganic complexes. The magnetic susceptibility provides direct information about the oxidation states, geometry and bond types of the complexes.

The intensity of magnetisation (I), induced at any point in a body is directly proportional to the magnetising
field (H) i.e. I \propto H and I=KH, where K is a proportionality constant and is known as the magnetic susceptibility of the medium. As I, the intensity of magnetisation is the magnetic moment per unit volume, K is likewise called the volume susceptibility, which is defined as the ratio of intensity of magnetisation produced in the material to the magnetising force. The molar susceptibility is the susceptibility per gram mole, represented as \chi_m. Two important groups associated with complexes are as follows:

**DIAMAGNETISM**: Diamagnetic substances are repelled by magnets when placed in a magnetic field. The diamagnetic susceptibility is a negative quantity.

**PARAMAGNETISM**: The substances which are attracted by the force of magnetic field, which is proportional to the field strength are known as paramagnetic substances. Unpaired electrons present in the system are responsible for the paramagnetic behaviour and its susceptibility is a positive quantity.

Magnetic moments are expressed in Bohr magneton and are calculated by the equation:

$$\mu_{\text{eff}} = 2.839 \left( \chi_m T \right)^{1/2}$$

where, T is the absolute temperature. The effect of magnetic moment of transition elements is the summation of spin and orbital moment, i.e.
\[ \mu_{\text{eff}} = (\mu_S + \mu_L)^{1/2} = \left[ 4S(S+1) + L(L+1) \right]^{1/2} \]

The normal paramagnetic behaviour of the complex ion depends upon -

(I) The number of unpaired electrons.

(II) spectroscopic group state and the energy levels that lie within KT of the lowest possible ground level.

(III) Occupancy of the various levels at a given temperature and

(IV) Strength and symmetry of the ligand field present.

1.24 INFRARED ABSORPTION SPECTROSCOPY :55-59

The most fundamental information that may be obtained from infrared spectra is the knowledge of interatomic force in terms of force constant within a molecule which gives important information about electronic structure and bonding in molecule. Absorption of infrared radiation in the frequency range of 10000-200 \text{ cm}^{-1} \text{ by the inorganic molecules is used for their molecular vibrations. These vibrations comprise of motions of the atomic masses in the material about centers of vibrations. Electromagnetic radiation can induce transition among the vibrational energy levels only when the dipole moment changes either in magnitude or in the direction of the molecule and a vibrational spectrum can then be expected. The two important modes of vibration for a molecule are possible stretching and bending vibrations. The former requires more energy}
In stretching vibrations atoms vibrate along the bond axis. The two types of stretching vibrations are observed (a) symmetric stretching vibrations and (b) asymmetric stretching vibrations.

In bending vibrations, atoms vibrate perpendicular to the bond axis. The four types of bending vibrations are assigned which are-(a). Scissoring, (b). Rocking, (c). Twisting and (d). Wagging.

From the observation of infrared spectra of a number of compounds having a common group it has been found that a particular group absorbs a narrow range of frequency called the group frequency. The observation of particular band is a strong evidence for the presence of a specific group. Sometimes the band may be weak and difficult to observe or it may be masked by a strong neighbouring band. There are certain limitations for the concept of group vibration as it rests on the assumption that the vibrations of the particular group are relatively independent of the molecule. But in some systems it is not possible to isolate the group frequencies, because since frequencies coupling, the symmetry of the molecule affects its vibrational mode because it has been observed that the molecule having more symmetrical structure exhibits fewer distinct vibrational modes. Hence, sufficient caution is necessary for the assignment of bands of the various
groups. Moreover, the physical state and temperature of some of the substances have direct effect on their frequencies.

Thus, infrared spectroscopy provides one of the useful technique for determining the mode of coordination of the ligand to the metal ion and is often used as a technique to provide fingerprints for identification which is a function of the constituent atoms, bond lengths and bond angles. As a result of coordination of a metal ion with a ligand usually the following changes takes place, in the context of infrared spectra; (i) A appearance of new bands and splitting of degenerated modes due to lowering of the symmetry, (ii) shifting of the frequency bands, and (iii) Increase in the intensity of the spectra. The coordination of the ligand with metal, lowers its symmetry which results in splitting of forbidden vibration. The stronger the metal-ligand bond, larger will be the splitting of the degenerated mode. The shifts in frequency, the magnitude of splitting and the intensity of newly permitted bands are useful as a measure of the effect of coordination.

In the infrared spectra of complexes formed by Schiff bases, the most important is the azomethine vibrational frequency, because it changes on
complexation. It may either increase or decrease depending upon various factors such as coordination, extent of pi-bonding, presence or absence of substituents in the adjacent position and also on the type of the compound being studied. This vibration in free schiff bases usually occurs in the region 1640-1470 cm\textsuperscript{-1} and on coordination a negative shift is theoretically expected. But in some complexes it may also be found that the extent of pi-bonding between ligand and metal ion is so large that the effect of coordination is not seen in the shifting of the frequency to lower wave number but rather to high wave number although the azomethine group is involved in coordination. Various other bands due to stretching vibrations of aromatic rings, C-H, N-H, metal-oxygen, metal-nitrogen and deformation vibrations of CH, NH or CH are also observed in the spectra.

1.25 ELECTRONIC SPECTROSCOPY \textsuperscript{32,38,52,60-630}

When a molecule absorbs visible or ultraviolet radiation, an electron in the molecule undergoes a transition from a lower to a higher energy level. There is correlation between the nature of an electronic transition and the magnitude of the absorption intensity with the help of selection rules. We can predict whether a transition will be allowed (intense band) or forbidden (weak band). But the intensity of absorption has to be considered only as a
guideline to the nature of transitions.

The study of electronic absorption spectra of transition metal complexes has constituted one of the major efforts to understand electronic structure and bonding in the complexes, because most of the complexes are coloured and they usually provide absorption bands in the visible region of the spectrum, depending upon the number of 'd' electrons.

Electronic spectra for a compound may be obtained in solution or mull, fused salt or crystal states. For complexes which do not have a suitable solvent, a modified technique known as diffuse reflectance spectra (drs) is used.

In metal complexes three main types of spectra are obtained:

(I) **Ligand Spectra**: Organic molecules frequently act as ligands in transition metal complexes and they exhibit characteristic spectra. On complexation, the ligand spectral bands are shifted to a lower wave number. The magnitude of the shift is a measure of the oxidation state of the metal atom. These intraligand transitions usually occur in ultraviolet region.

(II) **Charge Transfer Spectra**: Transition involving transfer of an electron from ligand to metal or vice-versa, is known as charge transfer transition and
certain ligands show distinct charge transfer bands of high intensity. This phenomenon can not be explained by crystal field theory and represent the tendency of ligands to reduce the metal ion or vice-verse.

(III) **d-d OR LIGAND FIELD SPECTRA.** This occurs in the near infrared, visible and ultraviolet region (1000-30000 cm⁻¹ or 1000-333 nm). Lower frequencies are not easily accessible at experimental level and the higher frequencies though accessible are over shadowed by the charge transfer and the intraligand transitions. This has limited the study of the d-d transitions only in the visible region of spectrum. These transitions are considered to be totally within the metal ion in the crystal field theory model, though some ligand contribution is included in ligand field theory or adjusted crystal field theory models. Molecular orbital theory treats these transitions as arising due to the excitation of the electron from the t²g level to the eg levels belonging largely to the metal itself. These d-d electronic transitions are weak because of the reason that the transitions of the same quantum shall be forbidden.

**SELECTION RULES FOR ELECTRONIC TRANSITION:**
Quantum mechanics imposes restrictions on electronic transition in terms of selection rules that arise from the properties of the wave function.
(i) **Spin Selection Rule**: Transition in which the spin multiplicity changes, are not allowed. Thus the transition $S^2-S^1 P^1$ is allowed only if the spin of the two electrons in the $S^1 P^1$ state is +1/2 and -1/2 (singlet state); the transition to the triple state $(3_p)$ is forbidden.

(ii) **LaPorte's Selection Rule**: Any electron transition is allowed only if $\Delta l = \pm 1$. Thus only the transition between an even state (g) and uneven state (u) are permitted, i.e. $g <---u$ but $g <---1----> u$ and $u <---1----> u$.

The strictness of the selection rules is slightly violated or diluted because of the slight mixing or coupling of the orbitals or states in some cases resulting slightly enhanced intensity of the observed bands.

From the number, position and intensity of the bands in the spectrum, it is possible to obtain information on the symmetry around the central metal ion, relative orders of energy levels, 10 Dq and other parameters. In addition to this, when the ligand also absorbs the visible region, the change in absorption bands indicate the complex formation.

1.26 **Electron Spin Resonance Spectroscopy**: 64-69
A molecule or an ion having the unpaired electron(s) \( m_s = \pm 1/2 \) absorbs electromagnetic radiation of microwave frequency (wavelength \( 10^{-1} \sim 100 \text{ cm} \)) under the influence of a magnetic field. This phenomenon is known as electron spin resonance (ESR) and it is exhibited by a paramagnetic species. It is also often referred to as electron paramagnetic resonance (EPR). ESR is shown by free radicals, molecules (such as \( \text{O}_2^\cdot \), \( \text{NO} \) and \( \text{NO}_2 \)) and transition metal complexes. Bulk susceptibility and electron spin resonance play complementary roles in elucidating the structure of a coordination complex.

An electron has a spin quantum number \( S = 1/2 \), it can have two orientations, one with spin angular momentum of magnitude \( + (1/2) \hbar /2\pi \) and the other with \( -(1/2) \hbar /2\pi \).

The magnetic spin momentum quantum numbers corresponding to these orientations are \( m_s = +1/2 \) and \( m_s = -1/2 \). In the absence of magnetic field, the two \( m_s \) states remain degenerate. On application of magnetic field, the two \( m_s \) states split. The \( m_s = +1/2 \) state is of an energy higher than the \( m_s = -1/2 \) state. The former does not get aligned with the direction of the applied magnetic field \( (H) \), but the latter does. This can be easily appreciated when we consider that the energy of an electron in a magnetic field is given by \( E = -\mu \hbar \), where \( \mu \) is the magnetic moment in a specified direction,
i.e. \( \mu \) is the projection of it in the direction of \( H \). We have \( m = g/\hbar m_s \), where the symbols have their usual meaning. Then for the \( m_s = +1/2 \) state, \( E = (1/2) g/\hbar H \), and for the \( m_s = -1/2 \) state, \( E = -(1/2) g/\hbar H \). Thus, the two otherwise degenerate \( m_s \) states in a field-free situation get separated by \( g/\hbar \) on the application of magnetic field. Now, if an energy corresponding to microwave frequency \( \nu \) is fed to the electron and the applied magnetic field is such that \( g/\hbar = h\nu \), the energy will be absorbed by the \( m_s = +1/2 \) state and a transition between the two \( m_s \) states will take place.

When an unpaired electron comes in vicinity of a nucleus with a spin \( I \), an interaction takes place which causes the absorption signal to be split into \( 2 I + 1 \) components (due to nucleus spin electron spin coupling). The energies of the levels are given by the following expression:

\[
E = g/\hbar m_s + A m_s m_I
\]

where, \( A \) is reflected as the hyperfine coupling constant.

It has now become one of the most important tool for the study of paramagnetic substance because ESR spectrum is extremely sensitive to surrounding of the paramagnetic ion in the system. It provides information about the symmetry of surrounding, the nature and strength of bonding, extent of delocalization of unpaired electrons,
relative energies of various filled and unfilled molecular orbitals in the bonding scheme in both solid and solution.

1.27 THERMOGRAVIMETRIC ANALYSIS:

The thermogravimetric analysis is concerned with the change in weight of sample being heated as a function of temperature or time. The curve so produced is termed "thermogram" or "pyrolysis" curve. The historical aspects of thermogravimetry had been described by Duval and others.

Solids which undergo two general type of reaction can be studied by thermogravimetry viz.

Reactant (s) \rightarrow Products (s) + gas
Reactant (s) + gas \rightarrow Products (s)

The process in which association or dissociation in mass with temperature does not occur, cannot be studied by thermogravimetry.

In thermogravimetric analysis, the mass is monitored as the temperature is increased, when \( \Delta G \) for the process becomes zero or negative, the reaction starts, which is indicated by change in mass from initial plateau. At the end of the reaction a new plateau will be observed. The nature of curve so obtained depends upon many factors such as rate of heating, heat of reaction,
furnace atmosphere, amount of sample, particle size and packing of sample. The study of weight change vs. temperature gives information about thermal stability, composition of residue, kinetics of decomposition, energy of activation and rate of reaction. It is also helpful in understanding the mechanism of formation of some unknown compounds by following its way of degradation. For complexes containing water molecules it has been possible in some cases to differentiate between lattice and coordinated water as well as to determine dehydration and decomposition temperature.

When the thermogravimetry is used in association with other physico-chemical techniques, such as magnetism, electronic and infrared spectrophotometry, its field of application widens and it provides a clear geometry for the complex.

1.28 X-RAY DIFFRACTION:

In recent years X-Ray methods have been increasingly used for fundamental studies of the properties and structures of various classes of inorganic compounds. X-Ray diffraction is perhaps the only reliable and hence widely used physical procedure for the complete determination of molecular structure of crystalline compounds.

The instrument for extending normal vision is the
optical microscope (resolution 1000 Å). The electron microscope takes over and extends the resolution limit some 25 Å; but a single atom is barely 1 Å in diameter, so even the electron microscope is limited to a study of atomic aggregates. Clearly some other technique i.e. X-Ray, may ascertain the exact location of the individual atoms constituting the matter. It is not possible to really see the atoms in samples but through the interaction of X-rays with these atoms, the position of the latter can be assigned.

Most solids are constructed from some elementary spatial unit duplicate over and over at regular intervals. Crystal structure analysis by X-ray diffraction provides the complete electron distribution in the molecule and its environments. It also provides all bond lengths and bond angles which help in the determination whether a bond is a single, double or triple or any one of the intermediate nature.

X-Ray were discovered by W.C. Rontgen in 1895. It is an electromagnetic radiation similar to light but with a very short wavelength. Since the spacing between atoms in a crystal (10^-8 cm) is comparable to the wavelengths (10^-8 cm) of X-rays. Von Laue (1912) suggested that crystals might be used as three dimensional gratings for X-rays. This prediction was confirmed in the next year by W. Friedrich and P. Knipping who were able to produce
the diffraction pattern (which depends upon the geometrical arrangement of atoms in the crystal) on photographic plates. In the same year (1913) W.L. Bragg and W.H. Bragg first employed X-ray to study the internal structure of crystals. He pointed out that every lattice plane behaves to X-rays first as does a line in a diffraction grating and the nature of the X-ray diffracted by a crystal will be determined by the spacing between successive planes. He showed that:

\[ n \lambda = 2d \sin \theta \]

Where \( n \) is an integer number, \( \lambda \) is the wavelength for maximum diffraction of X-Rays, \( d \) is the spacing between layers and \( \theta \) is the angle of diffraction.

This equation is called Bragg's equation. For a homogenous phase \( \lambda \) is fixed, and for a set of lattice planes \( d \) is fixed, hence the extent of diffraction will depend on the glancing angle \( \theta \). The Bragg's equation thus permits the calculation of \( d \), if \( \theta \) is measured. It has now become customary to refer the diffraction maxima as reflections.

There are several experimental methods for the determination of crystal structure, namely Laue method, rotating crystal method (Polany : 1921), oscillating crystal method (Weissenberg : 1924) and Powder method (Debye & Scherrer : 1916, Hill 1917). There are many
application of powder method but two of them are of primary importance. Fundamentally, the powder method provides a way of investigating within limits of the crystallography of the crystal in powder. Secondarily, the powder diffraction diagram produced by a crystalline substance is a characteristic of that substance in the same way as a finger print is to a human being.

X-rays in essence permits one to look inside the crystal and this provide a potent tool for studying the ultimate structures. Before X-rays can be used for this purpose, some knowledge of crystallography is necessary. Besides Bragg's equation, some basic concepts are: (i) space lattice, (ii) unit cell (iii) crystal systems (iv) space groups (v) elements of symmetry (vi) miller indices (vii) point groups. Their details are available, in standard text book of physical chemistry mineralogy and crystallography.
13 SIGNIFICANCE:

Since the appearance of the earth, aqua complex ions of metals must have existed. The subsequent appearance of life depended on, and may even have resulted from interaction on metal ions with organic molecules. Attempts to use consciously and to understand the metal-binding properties of what are now recognized as electron-donating molecules or anions (ligand) date from the development of analytical procedure for metals by Berzelius and his contemporaries. Since the time the progress in studies of metal complex chemistry was rapid, perhaps partly because of the utility and economic importance of metal complex chemistry, but also because of the intrinsic interest of many of the structural problems to be solved.

The applications of coordination compounds appear distinctly increased in past three decades. In recent years coordination compound are being used in the field of medicine, biology, industry and agriculture. However the most important application of these occurs in the areas of catalysis electrochemistry, dyes & pigments, photography, extractive metallurgy, geochemistry, nuclear fuel cycle & radiopharmacy, analytical chemistry, bio-medical and therapy.84-86

Nickel compounds are of great industrial importance and can be used in heterogeneous catalysis, electroplating,
batteries, pigments, ceramics and hydrogen storage. [Ni(NH$_3$)$_6$]Cl$_2$ have been shown to be potentially applicable in heat pumps. One nickel dithiabenzil complex has been used in laser technology. Nickel complexes are applicable as stabilizers and antioxidants for polymers of various kinds. Salicylaldiminato and dithiocarbamato complexes of Ni(II) have been found significantly active in photostabilization and in thermal oxidative degradation of certain polymeric materials.

The application of copper complexes are extremly varied and of great importance. Cu$_2$O is used as an antioxidant in lubricants, as an absorbent for carbon monoxide and in helium purification. Cu(OH)$_2$ and CuO finds applications as a plastic stabilizer, in rayon production and in antifouling paints. Several other copper compounds are used in oil industry, catalysis, as corrosion inhibitor and wood preservator. Copper halides may be used in lubricants as a stabilizer for polymers, as a decolonizer for ceramics and as an antioxidant. CuI is of potential interest in the initiation of rainfall by cloud seeding and in the production of conducting films. Copper (II) soaps, mainly the oleate and stearate, find application in antifouling paints and as fungicides for textiles. Copper acetylacetatonato chelate has been used as a source of copper in copper vapour lasers, and it has been investigated as substitute for silver iodide as an ice-nucleating agent for the initiation of rainfall.
Copper complexes are effective smoke retardant for polystyrene and polyvinyl chloride. The complex of copper diethyl dithiocarbamate has been shown to be extremely effective scavenger for peroxyl radicals and can be used to inhibit the autoxidation of hydrocarbons.

Various natural colouring matters contained a chelating system e.g. azocompounds, azomethins, O-hydroxynitro compounds, hydroxyanthraquinone, amino compounds etc. Copper complexes are important as dye-stuff for cotton materials. Copper -phthalocyanines have been a good pigment material for cotton, wool & Nylon etc. Azomethines bear a formal resemblance to azo compounds and many parallelisms exists in the coordination chemistry of the two series of compounds. Some nickel complexes of porphyrazines, O-phenylenediamine and 3-formyl pentane-2, 4-dione have been stated to be purple and red-violet pigments. In silver-dye-bleach process of photographic dyes & imaging chemistry the copper and nickel azo dyes are used. In photothermography bis(salicylaldoximato) nickel(II) complexes are used. In catalytic hydrogenation & carbonylation processes several nickel carbonyl compounds have been used. Metal schiff-base chelates acts as catalyst with dioxygen. Dioxygen is generally completely reduced by copper(I) salt. Copper oxygen compounds are used as catalyst for oxidation of alkene & alkynes, arenes, phenols, alcohols, amines & activated
double bond.\(^8\)

The effect of metal ions on the acid and base hydrolysis of imines is of considerable biological interest. The decomposition or cleavage of water into its elements (photolysis) may be achieved by using some metal complexes of nickel (IV) or copper (III) in acidic medium. Coordination chemistry helps us also in understanding the phenomenon of geochemical and prebiotic significance. Metal ions and ligands are used in mutual extraction and estimation of their presence in a sample.\(^8\)

Metal ions in biology will usually be bound by much larger and more complicated ligands than the relatively simple ones usually encountered in coordination chemistry. The fact that such complicated ligands are used in biology is reflected in the remarkable and subtle ways in which these ligands control the function and reactivity of a particular metal in biology. Thus the ligand may control the coordination number, the geometry, the spin state, redox potential and rate of electron transfer of a bound transition metal ion. It may provide a hydrophobic environment around the metal centre that will control various electrostatic interactions and the reactivity of the group. The ligands which are found in nature generally belong to the groups carboxylate, amines, amino acids, imidazole, imines, pyridine,
pyrimidine, amide, thiols, hydroxamic porphyrins etc.
coordinating through N, O or S donor atoms. Study of
physicochemical behaviour of some matching ligands and
their metal chelates may be considered as a convenient
biomimetic step for getting an insight into the ways of
nature.

A number of nickel & copper complexes have been shown to
possess fungicidal activity. \( \text{Ni(salicylate)}_2 \text{(amine)}_2 \)
have been tested on a range of fungi, where amines were
pyridines, \( \beta \)-picolin, 8-hydroxyquinoline and nicotinic
acid Schiff-base complexes of nickel and copper were
found to show both fungicidal and bactericidal
activity. The complexes were found to be many times
more active than the free ligands. Six coordinate
thiadiazole complexes of the type \( \text{NiL}_2(\text{H}_2\text{O})_2 \) showed
fungicidal activity against rhyzopus nigracans and
curvularialunata and were more active than the free
ligands. Bis(8-hydroxyquinolinate) copper is used in
the protection of fabrics, mainly cotton against
fungicidal attack. Copper complexes of the ligand
N-benzoyl-N -( 2-aminophenyl) thiocarbamide are
effective fungicides for Aspergillus niger, Fusarium
oxysporium and Helminthosporium oryzae. A number of
benzothiazole Schiff-base base complexes of the type
have been evaluated against helminthosporium oryzae.
The four main areas of the fungicidal activity of copper
are as crop protection, the protection of wood and that
of cotton, and their use in antifouling paints. 85,86,90,91

Dithiocarbamates have found a variety of applications in agriculture as pesticide and in rubber industry as vulcanisation accelerators and anti-oxidants. 92 Foye 93 investigated the metal binding abilities of heterocyclic thiones as antibacterial agents. Katz 94 studied 2-(hydroxyphenyl) benzothiazole and its copper complexes as an antitubercular agent. Some metal complexes of a tridentate schiff base derived from 2-amino-5-chlorobenzophenone have been screened for their bio efficacy by recording their antibacterial and pharmacological activities. The series of compounds derived from this moiety are reported to act as potential antianxiety 95 and antiepileptic agents. 96

Coordination chemistry can find a use in medicine in a number of ways. Coordination compounds can be used in the treatment, management or diagnosis of disease. Complexes can be formed in the body to handle dysfunction due to metal poisoning. Specifically four principal areas may be for the use of metal chelation therapy: (1) The use of coordination compounds or metal based drugs to treat disease (2) The use of chelating or complexing agents to treat metabolic dysfunction (3) The use of complexing chelating or sequestering agents to remove heavy metal poisons from the body (4) The use of
coordination complexes to transport metals to specific sites in the body to aid in imaging.\textsuperscript{6}

It is well known that majority of 3d-transition elements play a dominant role in many biochemical systems and hence also remembered as life essential elements, though their occurrence is in traces. These elements even in traces affect significantly by their excess or deficiency. In biological systems these metallic cations are incapable of independent existence. The metal ions cannot enter the cell by themselves. They are however carried by the chelating agents, which are sufficiently lipid soluble. The use of chelating agents depends upon the formation of stable and soluble metal chelates with metal ions in circulation or their competition with chelating biological sites having bound metal ion and thus dislodging the bound metals, exerting as soluble chelate from the system.\textsuperscript{64,85,90,97,98}

Nickel is now firmly established as an essential nutritional requirement for many eukaryotic and prokaryotic organisms. It is particularly well known as a component of the enzyme urease in plant cells growing on urea as a nitrogen source. Nickel is now recognised to be involved in a number of microbiological processes involving gases such as the carbon monoxide dehydrogenases in acetogenic bacteria, the methyl cofactor M-reductase in methanogenic bacteria and in
hydrogenases from several different types of bacteria. A number of antibiotics appear to require a transition metal ion as a cofactor. Copper is widely distributed at trace levels in living systems. Highest levels in man are found in the liver, brain, lung and kidney in decreasing amounts. High levels of copper are associated with certain diseased states, notably Wilson's disease (hepatolenticular degeneration). Menke's disease is an inborn error of copper metabolism. Copper has an essential role in a number of enzymes, notably those involved in the catalysis of electron transfer and in the transport of dioxygen and the catalysis of its reactions. Thyrosinase, blue copper proteins and hemocyanin are important biocompounds which involve copper.  

It's a remarkable fact that certain physical and chemical properties of Furin, Vanillen, Dimethyl aminobenzaldehyde and Benzophenone and of their derivatives have aroused interest with respect to their biochemistry and pharmacology. Several derivatives of these compounds after suitable structural modifications, are being used as drugs or materials of industrial importance. A number of metal complexes have been documented which are biologically active as bactericidal, fungicidal, antiviral and antitumour agents.
The applications of schiff bases and metal chelates in the field of industry, agriculture, medicine are well known. The aldehyde and amines selected for present studies viz. furan-2-aldehyde, vanillin, 4-dimethylamino benzoaldehyde, isoniazide, 4-aminoantipyrine, 2-amino-pyridine, 4-bromoaniline, 4-chloroaniline, 3-nitroaniline, phenyl hydrazine and anisidine, are known for their biological potential. \(^91,100\)

The chelation studies of these synthesized schiff bases with the metal ions i.e. copper(II) & nickel(II) have been taken up. The phenomenon of chelation help to stabilize the ligand and in several cases even make rather persistant & important action of schiff bases due to its metallic counterpart. Terephthalate are known in industry for their polymeric resistance and tolerant nature.

Certain mixed ligand complexes of nikel & copper terephthalate with salicylaldoxime, diethyl-dithiocarbamate, mercaptobenzothiazole, 8-hydroxy-quinoline and dimethylglyoxime have been prepared. Besides industrial and biological significance, mixed ligand chelates have their theoretical chemical importance where we interpret the phenomenon of ligand-ligand and metal-ligand interaction in solution as well as in isolated solid state. It further reflects about the mechanism of ligand competition,
stereochemical conversions and their co-stabilization mediated through a metal ion. Thus it can serve as simple models for various complex natural systems.

The coordination chemistry, with its growing list of applications, has paved the way to the preparation of new compounds which may possess some definite predetermined properties and thus show promising prospects for molecular designing in the realm of biology & industry. Here certainly we are justified in thinking that chemical principles should give us an insight into the ways of nature.