CHAPTER I

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I. INTRODUCTION

I.a. HISTORICAL INTRODUCTION

Coordination compounds which constitute one of the main subjects of chemistry were initially studied in the Scandinavian countries towards the end of the nineteenth century. Later the investigations shifted to Werner's laboratory at Zürich, and then to other countries. Probably, the earliest complex compound on record is prussian-blue having the composition $\text{K}_4\text{Fe(CN)}_6$, obtained by the artistic colour maker, Diebach in Berlin, at the beginning of the eighteenth century.

Systematic study of transition metal complexes may be said to date back to 1798 when chemists started studying the reactions of metal salts with ammonia. Many metal salts interact with ammonia and give complexes in which they exhibit unusual valencies. It is thus found that when ammonia is added to copper(II)chloride solution, beautiful blue-green crystals having the composition $[\text{Cu(NH}_3)_4]\text{Cl}_2$ are formed. What intrigued the early chemists was as to how ammonia molecules were held to copper when both the valencies of the copper(II) ion were already used up in the bonds with chloride ions. Scientists like Berzelius$^1$, Graham$^2$, Claus$^3$, Tassaert$^4$, Blomstrand$^5$ and Jorgensen$^6$ discussed the formation and structure of such metal complexes. However, their explanations
fell short of giving a comprehensive postulate.

This mystery was later solved by Werner in his immortal and revolutionary paper "contribution to the theory of affinity and valence" who therein, gave a theory, now commonly referred to as "Werner's coordination theory". The fundamental postulate of his theory stated in his own words is:

"Even when to judge by the valence number, the combining power of certain atoms is exhausted, they still possess in most cases, the power of participating further in the construction of complex molecules with the formation of very definite atomic linkages. The possibility of this action is to be traced back to the fact that besides the affinity bonds designated as principal valencies, still other bonds on the atoms, called auxiliary valencies, may be called into action".

II. THEORETICAL ASPECTS OF COORDINATION CHEMISTRY

This concept of Werner's gave rise to a few essential principles like that of fixed coordination number for the metal, a direct M→L bond and of simple stereochemistry. The octahedral, tetrahedral, planar and linear arrangements were predicted for complexes and finally established by classical methods.

It was only in the year 1916 that Werner's theory got full support and acceptance by the work of Lewis. Werner's primary valencies were interpreted as arising from electro-
valency or electron transfer and secondary valencies resulting from covalency or electron-pair sharing. Later, Lewis's work was extended by Lowry and Sidgwick, and the formation of complex compounds was explained on the basis of the concept of effective atomic number.

Sphraim suggested that an important condition is the attainment of a symmetrical structure irrespective of the actual number of electrons available. Sidgwick's electronic interpretation of coordination failed because of the fact that the lone pair of electrons donated by neutral molecules (e.g. H₂O, NH₃) to the central metal ion belongs to the 2s level and thus has no binding characteristics and to excite it to a higher level requires more energy than is usually available in bond formation.

An obvious flaw of the theory is that the acceptance of many electron pairs by metals would cause them to have a formal negative charge. This paradox was considered by Pauling who, later, provided quantum mechanical basis for qualitative ideas of Sidgwick which resulted in new knowledge of the basis of stereochemistry of complexes.

The modern treatment of the coordinate bond, in electronic terms, is based on quantum mechanics, proposed by Schröedinger and Heissenberg and at present, the following four theories are used for the interpretation of bonding in transition metal complexes:
Valence bond theory
Crystal field theory
Ligand field theory
Molecular orbital theory

Valence bond theory

Pauling has developed this theory on the basis of quantum mechanics and is simply the development of Sidgwick's electron-pair bond theory. In principle, this theory pictures that the electron-pair bond is formed when two atoms are brought together in such a manner that appropriate atomic orbitals interact. Since the electron clouds are directed in space, the concept of directed valency follows. The normal quantisation can be changed or broken down and new equivalent bonding orbitals called "hybridised orbitals" directed symmetrically in space are formed in atoms or ions in which several of the outer electronic levels differ little in energy.

This theory can be successfully applied to the transition metal complexes and it is suggested that the metal atom makes available a number of "hybrid orbitals", equal to its coordination number, for the formation of covalent bonds with ligand orbitals. The overlap of these with the filled donor ligand orbital gives rise to a covalent sigma bond. The excess negative charge so accumulated on the electro-positive metal atom is minimized by the formation of pi bonds between filled 'd' orbitals of the metal and vacant orbital on ligand.
This process which is known as back donation changes the charge distribution on both, i.e. the formal negative charge on metal atom is now spread over many atoms instead of being concentrated on one and this strengthens the sigma bond.

The formation of $\sigma \rightarrow \pi$, pi bond depends upon the number of filled d-orbitals of the central atom. The pi bonds can be of two type, $d\pi - p\pi$ bond resulting from the overlap of d-electrons of the metal atom and empty p-orbitals of the ligand and $d\pi-d\pi$ bond which arises by overlap between d-electrons of metal with d-orbitals of ligand.

The valence bond theory is quite satisfactory qualitatively for explaining the bonding in coordination complexes, and this is perhaps the reason for its wide application, but due to lack of precision in quantitative interpretations, it has been criticised by many workers. The defects pointed out by them are listed below:\textsuperscript{15-19}

1. It interprets neither absorption spectra of complexes nor reaction paths for the substitution reactions.
2. It fails to explain in detail the magnetic behaviour and other properties of the complexes.
3. It fails to account for the relative energies of different structures.
4. It does not take into account the splitting of d-orbitals.
Crystal field theory

This theory has been so called as it was first applied to the solid ionic type crystalline substances. It regards the metal ion as situated under the influence of an electrostatic (crystalline) field caused by surrounding molecules or ions and thus, considers the changes which are brought about by this negative field on the 'd' electrons of the central metal ion.

It was developed by Bethe\textsuperscript{20}, and was first applied to transition metal complexes by Schlapp, Penny\textsuperscript{21} and VanVleck\textsuperscript{22}. Recent renewed interest in the theory is due to the work of Ilse, Hartmann\textsuperscript{23} and Orgel\textsuperscript{24}. Crystal field theory thus becomes an alternative approach for the theoretical interpretation of the absorption spectra and the magnetic properties of the complexes as shown by Basolo, Ballhausen, Bjerrum, Jorgensen\textsuperscript{25-27}, Griffith\textsuperscript{28}, Nyholm\textsuperscript{29}, and Cotton\textsuperscript{30}.

In case of an octahedral complex where ligands approach along the x, y and z coordinates, the degenerate d-orbitals split into an upper doublet (e\textsubscript{g} set of orbitals which points towards the direction of ligands) and a lower triplet (t\textsubscript{2g} set which points inbetween the direction of ligands) as shown in the energy level diagram (Fig. 1a).

The magnitude of the ligand field stabilisation energy, represented by the term $\Delta_{o}$, depends upon the strength of
ligands and it controls the distribution of electrons in the $e_g$ and $t_{2g}$ sets. Taking the example of the complex ions $[\text{FeF}_6]^{-3}$ and $[\text{Fe(CN)}_6]^{-3}$, we find that in the former the ligand field is very weak so the energy difference between $e_g$ and $t_{2g}$ sets is not large enough to overcome the tendency of electrons to go into different levels with their spins parallel which results in a spin-free complex, while in the latter the field is strong so that all the electrons will occupy the $t_{2g}$ set with their spins-paired, and a spin-paired complex results.

For tetrahedral complexes with the same ligands, the settings are reversed and it has been shown with the help of appropriate calculations that $\Delta_t = \frac{1}{3} \Delta_o$. In this case the $t_2$ set is less stable than a set of orbitals as is evident from the energy level diagram (Fig. 1b).

The splitting of d-orbitals in distorted octahedral and planar complexes may now be considered. In an octahedral complex, if two trans ligands along z-axis are gradually withdrawn, new energy differences result. The degeneracy of $e_g$ set is lifted, $d_{z^2}$ orbital becoming more stable than $d_{x^2-y^2}$. The three fold degeneracy of $t_{2g}$ set is also lifted, doubly degenerate $d_{yz}$ and $d_{xz}$ become more stable than $d_{xy}$, since they are sensitive to changes along z-axis.

If the two trans ligands along the z-axis are completely withdrawn, we have the limiting case, i.e. a square planar structure. The $d_{z^2}$ orbital drops so far below $d_{x^2-y^2}$ that
it becomes almost as stable as \( d_{x^2-y^2}, d_{yz} \) pair. These results are shown in the energy level diagram (Fig. II).

The main shortcoming of this theory is that it does not take into consideration direct covalent bond or electron-pair bond between the ligand and the central metal atom. As a result of this it fails:

1. To account for the formation of complexes involving pi bond.

2. To account for the resolution of asymmetric complexes into their optically active modifications.

3. To explain properly, the relative strengths of the ligands.

4. To represent the total energy picture of complexes\(^{31}\).

**Ligand field theory**

This theory is really an outcome of the combined ideas of Bethe\(^{20}\), VanVleck\(^{32}\) and Mulliken\(^{33}\). There is general agreement that in addition to the perturbation of the orbitals by the electrostatic field of ligands, there is also overlapping between the orbitals of the metal ion and the ligand. It thus accounts for the observed covalency in the metal ion-ligand bond, as evidenced by the observations on the intensities of the d-d transitions in the absorption spectra,
electron spin resonance and nuclear magnetic resonance spectra of the complexes. The two theories, i.e. crystal field and ligand field, differ only in this respect otherwise the essential treatment is the same. Three important parameters of interelectronic interactions namely, the spin-orbit coupling constant λ', and the two Racah parameters B' and C are taken into consideration for the orbital overlap.

Molecular orbital theory

This theory assumes that a pair of bonding electrons is not confined to a single bond but participates in all bonds. A necessary consequence of this picture is that all bonds are inter-related and changes in one bond will be propagated to all other links in the complex. The molecular orbital theory makes it possible to predict the energy separation, E, as a function of the stereochemistry of the complex. It can be seen that the structural configurations predicted by molecular orbital method are the same as those predicted by valence bond method.

Molecular orbital theory employs the same orbitals of the central metal ions as does the Pauling method but it also uses the available ones of the coordinating ligands that are directed towards the central atom. The orbitals of the metal ion and the ligand which can transform as the same representation of the molecular point group can combine together to give molecular orbitals.
The metal ion has ns, np and (n-1)d sigma orbitals, in case of an octahedral complex, available for bond formation. Usually, the number of molecular orbitals obtained is equal to the number of combining orbitals. The energy level diagram of an octahedral complex involving sigma bonding can be drawn as shown in fig. III. If the coordinating ligands also possess pi orbitals, these can also be combined with their proper symmetry orbitals on the metal ion to give a similar set of bonding and antibonding pi molecular orbitals.

It has been observed that the metal t_{2g}, d-orbitals are unaffected by sigma bonding and are suitable only for pi bond formation. The ligand electrons supply the bonding electrons and the d-electrons originally present in the metal ion are accommodated in the non-bonding d-orbitals and the anti-bonding molecular orbitals. This corresponds to the splitting of d-orbitals of the crystal field theory. The energy separation of the non-bonding d-orbitals and the anti-bonding molecular orbitals, Δg, as well as, the energy required for the pairing of the originally unpaired electrons determine the formation of the coordinate link.

In case of square planar complex, only d \( x^2-y^2 \) and d \( z^2 \) orbitals can form bonds with the ligands. Appropriate calculations have shown that the d \( x^2-y^2 \) orbital is affected a great deal more by bonding than d \( z^2 \) orbital and hence the anti-bonding combination of the d \( x^2-y^2 \) orbital with the ligand
Fig. I

Octahedral Complex

S Tetrahedral Complex

Fig. II

Octahedral MX₆

Square MX₄

Fig. III

Metal ion orbitals

Ligand orbitals

Molecular orbitals
orbital is much less stable than other d-orbital.

The molecular orbital theory is also applied to tetrahedral complexes but in a much complicated manner and hence is usually not of much use. However, the qualitative aspect of this theory for complexes needs further development. Recent efforts have been made in this direction by Fanske, Basch, Gray and Cotton.

II. SURVEY OF LITERATURE

Transition metals in general are known to form complexes very easily and a survey of the literature shows that a large number of complexes of copper(II), nickel(II) and cobalt(II) with different nitrogen donor ligands have been studied, with almost all possible types of anions. However, no systematic work on the amine complexes of these metals with some bigger inorganic anions like selenates, tungstates and oxalates has been done so far. The work already reported on such complexes is briefly reviewed in the following pages and for convenience it has been classed under the following heads:

Ammonia complexes
Aliphatic amine complexes
Aromatic and heterocyclic amine complexes
Chelating amine complexes
AMMONIA COMPLEXES OF COPPER(II), NICKEL(II) AND COBALT(II).

Reaction of copper(II)sulphate with ammonia gives a tetrammine complex in the solid form, whereas penta- and hexammine complexes are formed in aqueous solution. Bhatnagar, Mata Prasad and others reported the existence of pentaammine-copper(II)sulphate. A large number of copper(II)-ammonia complexes have also been characterized with the help of x-ray, electronic, electron spin resonance and infrared spectra. Cyanuric acid (HL) in aqueous ammonia reacts with copper(II)sulphate pentahydrate to give CuL₂(NH₃)₂, which has been characterized by infrared spectra and thermal decomposition studies. Nickel(II)sulphate forms hexammine complex having the composition [Ni(NH₃)₆]SO₄, in aqueous solutions only. Complexes of cobalt(II)sulphate with ammonia in an organic solvent have also been investigated, as well as the reactions of nickel(II)oxide and cobalt(II)oxide in liquor ammonia.

Anhydrous nickel(II)nitrate reacts with gaseous ammonia in the absence of air, a solvated form of complex of the type Ni(NO₃)₂·xNH₃ (where x = 3 or 4) has been obtained. Cobalt(II)nitrate hexahydrate gave with gaseous ammonia Co(NO₃)₂·6NH₃ but with liquid ammonia, Co(NO₃)₂·4NH₃ is obtained. Thermal decomposition of [Co(NH₃)₆](NO₃)₂ under vacuum resulted in the formation of [Co(NH₃)₂(NO₃)₂]. The magnetic susceptibility data, infrared and electronic spectra have shown the presence of bidentate nitrato groups.
In aqueous ammonium halide solution, ammine-copper(II)halide complexes have been identified. Dark-blue $\text{Cu}_3\text{Cl}_4(\text{NH}_3)_4\cdot\text{H}_2\text{O}$; brown-violet $\text{Cu}_3\text{Br}_4(\text{NH}_3)_4$ and black $\text{Cu}_3\text{I}_4(\text{NH}_3)_4$ crystals have been obtained when the filtrate from a mixture of CuO, Cu and $\text{NH}_4X$ or $\text{C}_2\text{H}_5(\text{NH}_2)_2+\text{HX}$, is heated for a few hours. The reaction between copper(II)chloride and bromide with ammonia has also been studied. When ammonia is passed through a solution of nickel(II)chloride in an organic solvent, two complexes with 3 and 5 ammonia molecules are separated. Hexammine complexes of the type $[\text{Ni}(\text{NH}_3)_6]^x_2$ (where $x = \text{Cl}^-, \text{Br}^-$) underwent dissociation into two steps. Hetero-type mixed crystals of hexammine-cobalt(II)iodide are also known. Hexammine cobalt(II)chloride was prepared by boiling cobalt(II)chloride hexahydrate in a nitrogen atmosphere and adding hot aqueous ammonia. Robert has also reported the formation of several ammonia complexes of cobalt(II) chloride.

Magnetic susceptibility and visible absorption spectra of the coordination complex formed from the treatment of copper(II)oxalate in chloroform with ammonia, have been reported. The infrared spectra and magnetic data indicated a square planar configuration. Some tetrammine nickel(II) oxalate complexes have been prepared and their infrared spectra reported. Hexacoordinated non-electrolyte complex of nickel(II)oxalate with ammonia has been prepared and studied. The complex has been characterized by absorption
spectra and magnetic data\textsuperscript{66,67}.

A complex formed between copper(II)chromate and ammonia has been reported. It decomposed gradually, when exposed to air and loses ammonia and is found to be paramagnetic\textsuperscript{68,69}. By shaking the reaction mixture containing nickel(II)chromate in acetone and stoichiometric quantity of ammonia, coordination complex of the type \([\text{Ni(NH}_3\text{)}_4\text{]}\text{CrO}_4\), has been prepared and characterized. The yellow colour, electronic. Spectrum and diamagnetic nature indicated a square planar geometry around the nickel(II) ion\textsuperscript{70}.

Copper(II) acetate reacted with ammonia to form a complex \([\text{Cu(NH}_3\text{)}_2(\text{CH}_3\text{COO})_2]\)\textsuperscript{71,72}. Nickel(II) acetate bisamine and tetrammine complexes have been characterized by various physicochemical methods\textsuperscript{73,74}. Cobalt(II) acetate tetrahydrate and ammonia in an organic solvent yielded the ammoniate of cobalt(II)\textsuperscript{51}.

Visible absorption spectral data of complex formed by treating nickel(II) ferrocyanide with ammonia were obtained and bands near 10,800, 12,190, 18,000 and 28,000 cm\(^{-1}\) have been assigned to various transitions\textsuperscript{75}.

It has been observed that copper(II) thiocyanate reacts with ammonia to give a tetrammine. Physicochemical studies on the formation of nickel(II) thiocyanate-ammonia complexes in solution have been reported\textsuperscript{76}. Nickel(II) sulphate heptahydrate and barium thiocyanate dissolved in ammonium hydroxide yielded
a complex of the type $[\text{Ni(NH}_3)_4(\text{NCS})_2]$ at room temperature. It lost ammonia when exposed to air. The influence of different modes of preparation on the stoichiometry and thermal decomposition of isothiocyanato-ammine-nickel(II) complex was studied and electronic and infrared absorption spectra obtained have been analysed.

Copper(II) di- and tetra-thionates gave tetrammine complexes whereas copper(II)pentathionate yielded a pentammine complex. Nickel(II)tetrathionate has been observed to give hexammine complex with ammonia.

Crystals of blue-octammine copper(II)perchlorate which decomposed at 100°C to give tetrammine, have been prepared by the reaction of very concentrated solution of copper(II) and ammonium perchlorates in ammonia, whereas nickel(II)perchlorate formed hexammine complex on saturation with ammonia.

Nickel(II)chlorate and iodate formed either hexa- or tetramminnes. Some cobalt(II)iodate-ammonia complexes have also been reported. Complexes of the type $[\text{Ni(NH}_3)_6]^{2+}(\text{ClO}_4)_2$ (I) and $[\text{Co(NH}_3)_6]^{2+}(\text{ClO}_4)_2$ (II), were prepared by saturating simple perchlorates. Hydrogen bonding is clearly indicated in $[\text{M(NH}_3)_x]^{2+}(\text{ClO}_4)_2$ complexes.

Ammine-cyanide-copper(II) complexes with the formula $[\text{Cu(NH}_3)_2][\text{Cu}_2(\text{CN})_4(\text{NH}_3)_2]$ have also been reported. Reactions of ammonia with nickel(II)cyanide gave unstable $\text{Ni(CN)}_2$. $\text{Cu}(\text{CN})_2\cdot2\text{H}_2\text{O}$ (I) and stable $\text{Ni(CN)}_2\cdot\text{NH}_3\cdot\text{H}_2\text{O}$ (II) complexes. (I)
was found to be stable in concentrated ammonia solution but decomposed in air to form (II)\(^88\). Purple crystalline complex of the type Ni(CN)\(_2\).NH\(_3\) has also been reported, which has been synthesized from nickel(II)sulphate, potassium cyanide and ammonia \(^89\).

Ammones of basic copper(II) and nickel(II)carbonates have been investigated while the existence of the carbonato and bi-carbonato-pentammine-cobaltate ions have also been reported \(^90-92\). The complex of copper(II)azide with ammonia has also been obtained and characterized \(^93\).

**ALIPHATIC AMINE COMPLEXES OF COPPER(II), NICKEL(II) AND COBALT(II).**

In general, primary aliphatic amines have been shown to form complexes more readily than the secondary and tertiary amines \(^94,95\).

Copper(II) complexes with primary aliphatic amines have been studied \(^96\). With increasing size of the amine ligands and with varying anions, Cl\(^-\) to I\(^-\), the different degradation stages for \([Ni(RNH\(_2\))\(_6\])X\(_6\)\) (where R = methyl, ethyl, propyl, butyl and \(X = Cl^-\), Br\(^-\) and I\(^-\)) complexes have been observed. Dinuclear structure of \([Ni(RNH\(_2\))\(_3\])X\(_2\)\) and octahedral polymer of \([Ni(RNH\(_2\))\(_{1,5}\])X\(_2\)\) have been demonstrated \(^97\).

Coordination number four for copper(II)bisamine
complexes was found maintained even when long chain aliphatic amines were used. This indicated that the chain length of the amine affects only the solubility in organic solvents and the physical properties of the complex. The acid radicals, chloride, bromide, acetate, succinate, carbonate and sulphate, which controlled the colour and stability of the complexes, were covalently bonded to the metal. Solid complexes such as copper(II)chloride—1/2-amine and copper(II)chloride—2-amine have been reported. Copper(II)chloride reacting with methylvamine or ethylamine in suitable solvents yield mono-, complexes while copper(I)iodide formed a complex containing two amine and two water molecules. A nickel:amine ratio of 1:6 is found in hexacoordinated complexes of nickel(II)halides with primary aliphatic amines (e.g. methyl, ethyl and propylamines) and the structure of these complexes has been confirmed by magnetic and spectrophotometric measurements. Treatment of nickel(II)chloride with tertiary butylamine(I) formed polymeric complexes of the type $[\text{NiCl}_2]_n \cdot 1.5\text{H}_2\text{O}$, which lost water at $70^\circ\text{C}$ and butylamine at higher temperatures. Ethylamine has been shown to form stable coordination compounds with cobalt(II)halides. It has been observed that only two molecules of ethylamine are added per molecule of salt. The magnetic and spectral data indicated tetrahedral structure for cobalt(II) complexes. 

Magnetic susceptibility, infrared and visible absorption spectra of copper(II)oxalate complexes with methyl- and
ethylenamines confirmed a square planar configuration. Complexes of the type $[\text{Ni(C}_2\text{O}_4)_2L_2]$ (where $L =$ methyl, ethyl, propyl and butylamines) have been prepared and characterized by magnetic moments and infrared spectra.

Para-magnetic compounds of the type $[\text{CuL}_4]^{2+}$ (where $L =$ ethyl and ethylenamines) and $[\text{CuL}_2(H_2O)_2]^{2+}$ (where $L' =$ propyl, butyl, and amylamines) have been prepared and characterized with the reported values of $\alpha_{\text{eff}}$ in the range 1.77 - 1.86. The assignment of the vibrational bands of the ligand and their shifts in frequency on coordination with copper(II) ion have also been discussed.

Aliphatic amines in methanol, when added to methanolic solutions containing potassium thiocyanate or potassium selenocyanide and nickel(II) nitrate hexahydrate gave complexes of the type $[\text{Ni(RNH}_2)_4(\text{NCX})_2]$ (where $R =$ methyl, propyl or butyl; and $X =$ S or Se). These complexes have octahedral structure with the bonding of $\text{NCX}^-$ and $\text{NCSe}^-$ ligands through the nitrogen atom. The infrared spectra also showed that only one $\text{NCX}^-$ or $\text{NCSe}^-$ ligand is coordinated in $[\text{NiL(NCX)}]^{+}$. The magnetic moments have also been determined and reported.

Some cobalt(II) thiocyanate aliphatic amine complexes have also been isolated and studied.

Nickel(II) complexes of the type $[\text{Ni(RNH}_2)_6]^{2+}(\text{ClO}_4)_2$ (where $R =$ butyl, iso-butyl, pentyl, iso-pentyl etc.) with long chain primary amines have been prepared and characterized.
by magnetic moment, infrared and electronic spectra. These complexes have been found to be paramagnetic with 0h symmetry. Cobalt(II)perchlorate complexes with amines have been characterized with the help of magnetic, spectral, molecular weight and molar conductance data. The acetato and formate amine complexes of copper(II) and nickel(II) have been prepared. The infrared, metal ion spectra and magnetic susceptibility have also been reported.

Complexes of copper(II) azide and aliphatic amines have also been studied and reported.

AROMATIC AND HETEROCYCLIC AMINE COMPLEXES OF COPPER(II), NICKEL(II) AND COBALT(II).

Aromatic amines or heterocyclic bases have a strong tendency to coordinate with metals as the latter contain a tertiary nitrogen atom and their complexes resemble the corresponding complexes formed with metals and ammonia.

Aniline complexes

Complex compounds of the type Cu(NO$_3$)$_2$.2PhNH$_2$ have been prepared by dissolving 6 moles of aniline in 300 ml ethyl alcohol and 25 ml alcoholic copper(II) nitrate. Their infrared studies and effect of the various nitrogen containing ligands on the N-H bond strength have also been discussed. Ultraviolet, visible reflectance and far infrared spectra of solid
aniline complexes of copper(II) and nickel(II) halides have also been reported to determine the probable coordination arrangement about the metal atoms in each complex\textsuperscript{114}. Addition of aniline to an alcoholic suspension of nickel(II) nitrate and potassium thiocyanate results in the formation of some polymeric complexes with thiocyanate bridges\textsuperscript{115}. Complexes of aniline with cobalt(II) dichromate and chromate have been prepared, which behave as binary electrolytes as indicated by their conductivity values\textsuperscript{116}. The thiocyanate complexes of aniline with cobalt(II) have been studied with the help of infrared and electronic spectra and the bridging nature of thiocyanate is clearly indicated\textsuperscript{117}. A wide range of some substituted aniline complexes have also been prepared with nickel(II) thiocyanate. The complexes are assigned ionic octahedral structures\textsuperscript{118}.

**Pyridine complexes**

Bi-, tri- and tetra-pyridine complexes of copper(II) sulphate, obtained by adding aqueous solution of copper(II) sulphate into hot alcoholic solution of pyridine, have been reported\textsuperscript{119,120}. Blue-crystals of [Ni(py)_4]SO_4, obtained by adding a saturated solution of nickel(II) sulphate dropwise to boiling pyridine, have been reported. The complex changed to Ni(py)_2SO_4·2H_2O in air and finally to NiSO_4·2H_2O at 140°C. Similarly, [Ni(py)_4]SeO_4 complex has been prepared and is stable only under pyridine vapour. In air, it changes to
\[
[\text{Ni(py)}_3]\text{SeO}_4 \text{ and finally to } [\text{Ni(py)}_2]\text{SeO}_4^{121}.
\]

Reactions of anhydrous nickel(II) and cobalt(II) nitrates with pyridine in non-aqueous solution, gave complexes of the types \([\text{Ni(py)}_3(\text{NO}_3)_2]\) and \([\text{Co(py)}_3(\text{NO}_3)_2]\). 3py, \([\text{Co(py)}_3(\text{NO}_3)_2]\) and \([\text{Co(py)}_3(\text{NO}_3)_2]\). 3py, whose thermal, magnetic, conductometric and spectral data show that tris(pyridine) complexes have octahedral structure with both mono- and bidentate nitrate groups\(^{122-124}\).

Copper(II) halide-pyridine system has been investigated. Copper(II) chloride and bromide-pyridine complexes were found to be yellow and black in colour respectively\(^{125-127}\). Equivalent amounts of anhydrous copper(II) chloride and pyridine in absolute alcohol or dry acetone formed, light-blue \(\text{CuCl}_2.2\text{C}_5\text{H}_5\text{N}\) complex, which slowly changed to grey having the composition \(\text{CuCl}_2.6\text{C}_5\text{H}_5\text{N}\) complex has also been prepared from copper(II) chloride and a large excess of pyridine within ten days at a temperature not over 12-15°C\(^{128}\). Many stable complexes of copper(II) and nickel(II) halides with pyridine are known\(^{129}\). Magnetic susceptibility studies of complexes such as \([\text{M(B)}_2(\text{H}_2\text{O})_2]\text{Cl}_2\) and \([\text{M(B)}_4]\text{Cl}_2\) (where \(\text{M} = \text{Cu(II)}\) or \(\text{Ni(II)}\); and \(\text{B} = \text{pyridine}\)) showed that paramagnetism of copper(II) complexes remains unchanged whereas that of nickel(II) complexes, decreased with increasing hindrance around the metal\(^{130,131}\). Magnetic and electronic spectral properties of complexes of nickel(II) halides (Cl\(^-\), Br\(^-\) and I\(^-\)) with pyridine have been reported and the assignment of the
spectra of tetrakis-amine complexes $[\text{Ni(py)}_4] X_2$, confirmed $D_{4h}$ symmetry of the complex molecule $^{132,133}$. Some substitution reactions in the bipyridine complexes of nickel(II) and cobalt(II) of the type $\text{MPy}_2\text{Cl}_2$ showed that $\text{Cl}^-$ ion can be readily replaced by $\text{Br}^-$, $\text{I}^-$, $\text{NO}_2^-$, $\text{CNS}^-$, and $\text{C}_2\text{O}_4^{2-}$ ions $^{134}$. Complexation of cobalt(II)chloride and bromide with pyridine in acetone solution has also been studied and discussed $^{123,135-137}$. Some mixed ligand complexes of cobalt(II)halides with pyridine and thiourea have also been investigated $^{138}$.

Infrared and electronic spectra and magnetic data of $[\text{MC}_2\text{O}_4 L_2]$ (where $M = \text{copper(II)}, \text{nickel(II)}$ and cobalt(II); $L = \text{pyridine}$) type complexes have been obtained and the structures assigned. The infrared spectra confirmed the presence of covalently bonded oxalate group in the complexes $^{64,67,139}$.

Some halogen substituted copper(II)acetate complexes of pyridine have been obtained and their structures discussed, for example, complexes of the type $[\text{CuL}_x(\text{CF}_3\text{OOO})_2]$ (where $x = 2$ or 4 and $L = \text{pyridine}$) have been prepared and characterized by spectroscopic methods. It has been found that hexacoordinated complexes are formed having either mono- or bidentate trifluoroacetate group $^{140,141}$. The addition of pyridine to copper(II)acetate, substituted acetates and formates has also been studied by electron spin resonance $^{131}$.

The formation, magnetic and spectral properties of some blue copper(II) and nickel(II)thiocyanate complexes containing 2,4 and 6-molecules of pyridine have been studied $^{133,142,143}$. 
Addition of potassium selenocyanate to copper(II) and nickel(II) salts and pyridine yielded corresponding pyridinated selenocyanates of these metals. Cobalt(II) thiocyanate has been combined with pyridine to give a complex of the type Co(py)$_2$(SCN)$_2$. The structural configuration has been confirmed with the help of magnetic and spectral properties along with molecular weight and molar conductance data.

Pyridine complexes with the general formula M(L)$_4$(ClO$_4$)$_2$ or M(L)$_4$(Br$_4$)$_2$ have been prepared with copper(II), nickel(II) and cobalt(II) perchlorates and tetrafluoroborates. Their infrared ultraviolet, visible reflectance spectra and magnetic properties have also been discussed.

Quinoline and iso-quinoline complexes

A very stable penta-coordinated complex of copper(II) sulphate and quinoline has been isolated and investigated. Heating anhydrous copper(II) sulphate, nitrate, chloride and bromide in quinoline yielded the respective complexes on cooling. Absorption spectra of these complexes have been reported in the range 450 - 1600 nm. The magnetic moments of nitrate and chloride complexes are found to be 1.37 and 0.75 B.M. respectively, while the Cu(quin)$_3$Br$_2$ complex has been found to be diamagnetic. The complexes of the type L$_2$M(NO$_3$)$_2$ (where M = copper(II), nickel(II) and cobalt(II); and L = quinoline or isoquinoline) and L$_4$M(NO$_3$)$_2$ (where M = nickel(II) and cobalt(II); and L = isoquinoline) have been synthesized. The
infrared, electronic, magnetic, conductometric, molecular weight and X-ray powder data have been obtained in order to determine the structure of these complexes. Several complexes of copper(II) and nickel(II) halides with quinoline and isoquinoline have been investigated. The nickel(II) halide-quinoline complexes have been found to be paramagnetic except the iodo-complex, which is green in colour and diamagnetic due to a planar structure. Halide complexes of the type CoLₙX₂ (where L = quinoline or isoquinoline; and X = halide or pseudo-halide ion), have also been reported. It has been observed that chlorination or bromination of ethanolic suspension of several non-electrolyte cobalt(II) complexes containing nitrogen donor ligands yielded 2:1 electrolyte complexes of the type [{LH}_2][CoX₂Y₂] (where L = quinoline or isoquinoline; X and Y = Cl⁻ and Br⁻). The electronic spectra have provided evidence for a tetrahedral configuration for these complexes.

Magnetic susceptibility, visible and infrared absorption spectra of the complexes with general formula MCo₂L₂ (where M = copper(II), nickel(II) and cobalt(II) and L = isoquinoline), obtained from the reaction of metal(II) oxalate in chloroform with isoquinoline, have been reported. The infrared spectra indicated the presence of covalently bonded oxalate group.

Copper(II) cyanate complexes with quinoline and isoquinoline having the composition Cu(OCN)₂L₂ or L' have been prepared. The magnetic susceptibility of Cu(OCN)₂L₂ obeyed
Curie Law, hence negative values of the constant were obtained. The diffuse reflectance spectra indicated a polymeric distorted octahedral structure. In case of Cu(ON)₂⁻L complex, the magnetic susceptibility followed Curie-Weiss law with negative values of the constant. The diffuse reflectance spectra confirmed a polymeric trigonal bipyramid structure ¹⁵⁶, ¹⁵⁷. At room temperature, stirring of finely ground copper(II)thiocyanate with an ethanolic solution of quinoline, formed a complex of the type Cu(NCS)₄. The infrared spectrum indicated the presence of two oxidation states of copper. It has also been found that thiocyanate is nitrogen bonded ¹⁵⁸. Magnetic and electronic spectral properties of the complexes of the type Ni₄⁺X₂⁻ (where n = 1, 2 or 4; X = NCS⁻ and L = isoquinoline) have been reported ¹³³.

Quinoline and isoquinoline complexes of copper(II), nickel(II) and cobalt(II) have been prepared by dissolving the metal(II)perchlorate or tetrafluoborate in excess ligand, warming the solution and leaving overnight in a desiccator and removing excess of ligand by washing with acetone or chloroform ¹₂⁶, ¹₅₄, ¹₅₉.

The synthesis and properties of complexes having the composition ML₄X₂ (where M = nickel(II) or cobalt(II); L = quinoline or isoquinoline and X = dicyanamide or tricyanomethanide) obtained from the reaction of metal(II) salt solutions with NaCN in the presence of excess ligand, have been described. The electronic spectra and magnetic
measurements indicated the following sequence in the nepheleuxetic series, $C(N)\geq N(CN)_2\sim NCS^{160,161}$.

The complex formation from combination of quinoline and copper(II) formate, acetate or substituted acetates has been studied by electron spin resonance$^{131}$.

**CHELATING AMINE COMPLEXES OF COPPER(II), NICKEL(II) AND COBALT(II).**

Diamines e.g. ethylenediamine(en) and propylenediamine(pn) and some tertiary di-amines e.g. 2,2'-dipyridyl(dipy) and 1,10-phenanthroline(phen) show maximum complexing tendencies to give very stable chelate complexes because of the formation of the five-membered ring in the coordination sphere.

**Ethylenediamine and propylenediamine complexes**

Morgan and Burstell in 1927, reported complexes of the type $Cu(en)A_2$ (where $A =$ sulphate, persulphate, nitrite, hyponitrite, hypophosphite, carbonate, thiosulphate, di-, tri- and tetra-thionate and selenocyanate)$^{162}$. Later, some homogeneous and heterogeneous salts of copper(II) and nickel(II) were prepared with ethylenediamine$^{163}$. During the study of structural elucidation of nickel(II) diamine complexes, workers failed to resolve $[Ni(en)_3]Cl_2$ into optical isomers$^{164}$. Violet-red prismatic crystals of trisethylenediaminonickel(II) bisulphate and nitrite have also been investigated$^{165,166}$.
Crystallography and structure of copper(II) complexes with ethylenediamine (e.g. \textit{enCuCl}_2 and \textit{enCuBr}_2) have been reported by Werner, Spruck, Grossmann and Schuck. Coordination complexes like blue-violet \textit{Cu}_4\text{Cl}_5(\textit{en})_2, violet \textit{Cu}_3\text{Br}_4(\textit{en})_2, red-brown \textit{Cu}_3\text{I}_4(\textit{en})_2, which changed to steel-blue \textit{Cu}_2\text{I}_3(\textit{en})_2 on heating, have been prepared and characterized.

The reaction of \([\textit{Cu}(\textit{en})_2](\text{ClO}_4)_2\) with anion \((\text{N}_3^-)\) and halide ions \((\text{Cl}^-, \text{Br}^-, \text{I}^-)\) in aqueous solution, caused a continuous shift in the electronic absorption maxima towards red, which indicated the formation of \([\textit{Cu}(\textit{en})_2\text{X}]^+\) (where \(\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{N}_3^-\)). This information confirmed that copper(II) in solution has a maximum coordination number of five.

Square planar complex of the type \textit{CuC}_2\text{O}_4.\textit{en} prepared from the treatment of copper(II) oxalate in chloroform with ethylenediamine, has been confirmed by infrared, electronic absorption and magnetic data. Equilibrium constants of \([\text{NiC}_2\text{O}_4.\textit{en}]\) and \([\text{NiC}_2\text{O}_4.\textit{en}_2]\) have been reported and the structure elucidated. Some mixed ligand complexes of the type \([\text{Ni}(\text{pm})_2\text{C}_2\text{O}_4]_2\text{X}_2\cdot\text{H}_2\text{O}\) and \([\text{Ni}(\text{en})_2\text{C}_2\text{O}_4]_2\text{X}_2\) (where \(\text{X} = \text{ClO}_4^-, \text{Br}^-\) or \(\text{I}^-\)) have also been reported.

Suspension of nickel(II) chromate in acetone and the addition of stoichiometric quantity of ethylenediamine or propylenediamine yielded yellow coloured complexes of the type \([\text{Ni(dam)}_2]\text{CrO}_4\). The yellow colour, diamagnetic nature and
electronic spectra suggested a square planar geometry around the nickel(II) in the complexes.  

Copper(II), nickel(II) and cobalt(II) acetate-ethylenediamine or propylenediamine complexes have been prepared and characterized by many workers. The d-d transitions observed have been used to discuss the structure of the complexes. 

Bisethylenediaminecopper(II)hexacyanoferrate(II) and the corresponding propylenediamine complexes have been prepared and characterized. The conductance values of the complexes have been found to be 238 and 250 mhos, respectively. The visible absorption bands at 648 and 650 nm, respectively, suggested a square planar configuration. The corresponding octahedral complexes of nickel(II) ferrocyanide with ethylenediamine and propylenediamine have also been isolated and characterized.

Complexes of the type CuL₂X₂ and [Cu₂(SeCN)₄]NO₃, isolated by treatment of ethanolic solution of copper(II) nitrate with propylenediamine(L) and solid ammonium pseudohalide (X = NCS⁻, NO₂⁻) clearly indicated the presence of S- and N-bonded thiocyanate and cyanate groups, respectively. The ionic nature of the nitrate group and the octahedral symmetry of the selenocyanate complex showed that selenocyanate functioned as a bridging group. Complexes with the formula [Cu(en)₃]X₂, [Cu(en)₂]X₂, [Ni(en)₂]X₂ and [Ni(en)₃]X₂ (where X = thiocyanate or selenocyanate) have been isolated and characterized on the basis of infrared spectra. Mixed
ligand complexes of nickel(II) thiocyanate with propylenediamine and coordinated nitrate, oxalate or perchlorate have been isolated and the structures assigned on the basis of infrared, electronic absorption, magnetic and X-ray data\textsuperscript{172,182,183}. Crystalline sample of Cu\textsubscript{3}(en)\textsubscript{2}(CN)\textsubscript{4} has been prepared. The infrared and visible spectra have shown the coordination of copper(II) with nitrogen base\textsuperscript{184}.

Complexes of nickel(II) perchlorate or Ph\textsubscript{4}B with ethylenediamine have been isolated and their physical properties discussed. In the solid state, [Ni(en)\textsubscript{2}(OH)\textsubscript{2}]\textsuperscript{+2} can have cis- or trans-configuration. Two forms of the anhydrous complex Ni(en)\textsubscript{2}(ClO\textsubscript{4})\textsubscript{2} have been investigated. The infrared spectral data have shown that the orange form has ionic perchlorate, whereas the blue form bidentate perchlorate\textsuperscript{185}.

Dark-blue complex, Cu\textsubscript{2}P\textsubscript{2}O\textsubscript{7}.2en.2H\textsubscript{2}O (I), has been obtained by adding a slight excess of Cu\textsubscript{2}P\textsubscript{2}O\textsubscript{7} to a 5% solution of ethylenediamine. Similarly, a purple complex with the formula Cu\textsubscript{2}P\textsubscript{2}O\textsubscript{7}.4en.6H\textsubscript{2}O (II), has been precipitated by ethanol from Cu\textsubscript{2}P\textsubscript{2}O\textsubscript{7}.2H\textsubscript{2}O and 20% solution of ethylenediamine. Lustrous-blue plates of the complex of the type Cu\textsubscript{2}P\textsubscript{2}O\textsubscript{7}.3en.6H\textsubscript{2}O(III), has also been isolated from a solution of I and II by precipitation with ethanol\textsuperscript{186}.

Coordination complexes with general formula
\[ [CuL\textsubscript{2}]\textsubscript{3} (X)\textsubscript{2}, \text{ where } L = \text{en or pn and } X = \text{PO}_4^{3-} \text{ or AsO}_4^{3-}, \] have been isolated by suspension of powdered copper(II) phosphate or
arsenate in acetone, followed by addition of little excess of stoichiometric quantity of diamine. The complexes have blue to violet colour and are electrolytes. The infrared and visible absorption spectra confirmed the square planar structure\(^{187}\).

The interaction of copper(II)tellurite with aqueous ethylenediamine has also been investigated\(^{188}\).

### 2,2'-Dipyridyl and 1,10-phenanthroline complexes

Copper(II) and nickel(II) salts readily form stable chelates with 2,2'-dipyridyl and 1,10-phenanthroline because of the formation of the five-membered ring\(^{149}\) and a large number of such complexes have been prepared and studied\(^{189,190}\).

Combination of nickel(II)sulphate, nitrate, chloride and bromide with 1,10-phenanthroline yielded complexes with the general formula \([\text{Ni(phen)}X_2]\)^{191}. A complex with the formula \(\text{CoSO}_4\cdot3.5\text{H}_2\text{O}\) has been prepared by heating aqueous solution of cobalt(II)sulphate and 1,10-phenanthroline(L) in 2:1 molar ratio. The infrared and differential thermal analysis data have shown that the complex is a dimer with sulphato-bridging groups\(^{192}\). Crystalline complexes of the type \(\text{Co(phen)}_2X_2\cdot\text{nH}_2\text{O}\) (where \(X = 0.5\text{SO}_4^{--}, \text{NO}_3^-, \text{NO}_2^-, \text{Cl}^-, \text{Br}^-, \text{SCN}^-, 0.5\text{CO}_3^{--}\)) have been isolated by mixing solutions of the corresponding cobalt(II) salts with 1,10-phenanthroline. Cobalt(II)nitrate reacted with 1,10-phenanthroline in the presence of potassium iodide to give \([\text{Co(phen)}_3]^\text{I}_2\cdot5\text{H}_2\text{O}\) only. The \(\text{CO}_3^{--}\) ion is shown to act as a
monodentate ligand in the complex, \([\text{Co(phen)}_2(\text{H}_2\text{O})(\text{CN})]_2 \cdot 6\text{H}_2\text{O}\)^{193}. Mixed-ligand complex having composition \([\text{Co(phen)}(\text{NH}_3)_2]\text{SO}_3\) has been isolated by coordination of 1,10-phenanthroline with disulphitotetramminecobaltate(II)^{194}.

Coordination complexes like \([\text{Qu(phen)}X_2]\) (where \(X = \text{NO}_3^-,\text{Cl}^-,\text{Br}^-,\text{I}^-,\text{SCN}^-\) and \(1/2\text{S}_2\text{O}_3^-\)) and \([\text{Qu(phen)}_2]X_2\) (where \(X = \text{NO}_3^-,\text{Cl}^-,\text{Br}^-\) and \(1/2\text{S}_2\text{O}_3^-\)) have been prepared and characterized^{195,196}. Several paramagnetic copper(II) complexes of empirical composition \([\text{Qu(AA)}(X)_2]\) (where \(\text{AA} = 2,2'\)-dipyridyl or 1,10-phenanthroline and \(X = \text{NO}_2^-\), \(\text{NCS}^-\) or \(\text{N}_3^-\)) have been isolated in pure crystalline forms, green or dark-green in colour. The magnetic moments of the complexes are in the range 1.7 - 1.9 B.M. The infrared spectral data demonstrated N-coordination for both the \(\text{NO}_2^-\) and \(\text{NCS}^-\). The reflectance spectra and solution spectra in acetone suggested distorted octahedral structure^{197}. \([\text{Co(phen)}(\text{NO}_3)_2]_4\text{H}_2\text{O}\) complex has been isolated by the reaction of cobalt(II)nitrato hexahydrate in ethanol with 1,10-phenanthroline. The infra-red spectra and differential thermal analysis confirmed a dimeric structure with bridging \(\text{NO}_3^-\) groups^{198}.

The isolation of \([\text{Qu(dipy)}_3]\text{Cl}_2\) and \([\text{Ni(dipy)}_3]\text{Cl}_2\) has been reported^{199}. The mono-complexes of 2,2'-dipyridyl and 1,10-phenanthroline with nickel(II) and cobalt(II)halides have been prepared in good yield by reaction of these bases with an excess of anhydrous metal(II)halide in boiling dimethylformamide solution. Complexes of the types \(\text{Ni(dipy)}\text{Cl}_2\cdot\text{H}_2\text{O}\), \(\text{Co(dipy)}\text{Cl}_2\cdot\text{H}_2\text{O}\) and \(\text{Co(dipy)}\text{Cl}_2\cdot2\text{HCl}\) have been obtained. The
structures have been assigned on the basis of analytical data, reflectance spectra, magnetic moments and X-ray powder patterns\textsuperscript{200,201}. Treatment of aqueous solutions of cobalt(II)halide-2,2'-dipyridyl or 1,10-phenanthroline complexes with thiourea or selenourea resulted in the formation of new complexes, but the infrared spectra clearly showed that neither thiourea nor selenourea are coordinated\textsuperscript{202}.

MC\textsubscript{2}O\textsubscript{4}L type complexes (where M = nickel(II), cobalt(II), and L = 1,10-phenanthroline or 2,2'-dipyridyl) have been isolated by treating the chloroform suspension of metal(II)oxalates with the ligand. The complexes showed paramagnetic properties and has further been characterized by infrared spectra\textsuperscript{139}.

From aqueous and non-aqueous systems, a series of coordination complexes with general formula\textsuperscript{[M(phen)(NCS)\textsubscript{2}]} (where M = copper(II), nickel(II) and cobalt(II)) has been reported. Their behavior on combination with acids has been examined to determine whether or not the thiocyanate ligand could be protonated\textsuperscript{203,204}. Reactions of metal(II)cyanates with 2,2'-dipyridyl or 1,10-phenanthroline in aqueous methanol solution yielded\textsuperscript{[M(dipy/phen)\textsubscript{2}(NCO)\textsubscript{2}]} (where M = nickel(II) and cobalt(II)). The NCO\textsuperscript{-} ion is coordinated to metal(II) via the nitrogen atom\textsuperscript{205}. Dithiophosphinate complexes of nickel(II) and cobalt(II) containing 1,10-phenanthroline have been prepared and investigated\textsuperscript{206}. Cobalt(II) cyanide-2,2'-dipyridyl and 1,10-phenanthroline complexes have also been isolated and studied\textsuperscript{207}. 
Some five-coordinate complexes of copper(II) containing 2,2'-dipyridyl and 1,10-phenanthroline of the type 
\[ \text{Cu(dipy/phen)}_2(ClO_4) \] X (where X is any halide or nitrate ion) have been obtained. Conductivity in nitrobenzene ranges from 27 - 29 mbos and magnetic moment varies from 1.8 - 2.0 B.M.

Bis-1,10-phenanthrolinecopper(II) and tris-1,10-phenanthroline-nickel(II)perchlorate complexes have been prepared by the reaction of copper(II) and nickel(II)perchlorates respectively, with 1,10-phenanthroline

\[ \text{Cu(P}_2\text{O}_7)\text{L} \] (where \( L = 2,2'\)-dipyridyl, or 1,10-phenanthroline) type complexes have been prepared and characterized spectroscopically. The pyrophosphate anion has been shown to act as a bidentate ligand.