CHAPTER I

INTRODUCTION

1a. HISTORICAL INTRODUCTION

1b. SURVEY OF LITERATURE
HISTORICAL INTRODUCTION

Although the discovery of the cobalt ammine by Tassart (1) marks the beginning of the coordination chemistry, the developments in the field were more pronounced in the next fifty years when numerous complex compounds of cobalt, platinum, iron, copper and nickel were isolated and attempts were made to assign suitable structures to them by using the then existing valence theories (2-9).

First systematic approach to the study of complexes was made by Alfred Werner in his paper entitled, "contribution to the theory of affinity and valence", in which he advanced the fundamental idea that valence can be divided into units of varying strength, depending on the species combining with an atom or ion (10). He distinguished two sorts of valences, primary and secondary, for every metal. Neutral or anionic groups are held by secondary valencies to produce a complex ion with a certain charge, which is satisfied by groups of opposite charge linked by primary valency. The number of secondary valencies for a metal ion is a fixed quantity for a particular oxidation state of that metal and the properties of the coordination compounds are mainly dependent on these.

In terms of the modern valence theory given by Sidgwick and Lowry (11-12), the secondary valence is considered to be a two electron bond, or coordinate bond. It is,
therefore, essential that all coordinating groups should contain at least one electron pair which can be donated partially to the metal ion. Such a group is called a donor or ligand and the metal ion is referred to as an acceptor.

Theories of metal to ligand bonding

At present usually four distinct approaches namely the valence bond theory, crystal field theory, the ligand field theory and the molecular orbital theory are available for the interpretation of bonding in coordination compounds.

(1) The Valence bond theory

This theory is an outcome of Pauling's attempt (13) and is largely based on quantum mechanics and takes into consideration three important basic ideas:

(a) the geometries of the complexes with different coordination numbers which can be explained by the hybridization of atomic orbitals.

(b) the magnetic criterion of metal to ligand bonding, and

(c) lastly a type of double bonding between metal and ligands which by spreading out the negative charge over whole of the coordination sphere can result in a more stable structure.
According to this theory the vacant metal orbitals overlap with filled orbitals on the ligands to form dative \( \sigma \)-bonds. For the formation of a strong dative bond the charge clouds must overlap to a maximum extent, and it thus introduces the idea of hybridization of the individual atomic orbitals with definite characteristic directions.

It was further suggested by Pauling (14) that the accumulation of an excess negative charge on the central metal atom produced by donation of one lone pair of electron by each ligand, can be minimised by assuming the formation of an additional multiple or pi- bond. This theory, however, fails to explain the spectra of complexes, their detailed magnetic behaviour and also the relative energies of the free state of metal (15).

(2) **Crystal Field Theory**

The electrostatic crystal field theory which was first expounded by Bethe (16), considers the attraction between the central metal and ligands as purely electrostatic. The ligands are arranged in a regular manner around the metal, thus producing a negative field around the metal and the changes which are brought about by this ligand field on the 'd' electrons of the metal are considered in this theory.

In the case of an octahedral complex where ligands
approach along the x, y and z coordinates, the originally degenerate 'd' orbitals split into an upper doublet (e\(_g\) orbitals) and a lower triplet (t\(_{2g}\) orbitals) as shown in the energy level diagram (fig. -Ia). The term \( \Delta 0 \) in the diagram is the ligand field stabilization energy. Its magnitude depends upon the strength of ligand and it governs the distribution of electrons in the two sets. For example in case of complex ions \([FeF_6]^{3-}\) and \([Fe(CN)_6]^{3-}\), in the former the ligand field is weak so the energy difference between two sets is not large enough to overcome the tendency of electrons to go into different levels with their spins parallel, so a spin free complex results, while in the latter the field is strong, so a spin paired complex is formed.

For a tetrahedral complex with the same ligands, as evident from the energy level diagram (fig. 1,b) the settings are reversed and \( \Delta t = 4/9 \Delta 0 \).

(3) **Ligand Field Theory**

This theory in principle is the same as the crystal field theory but allows some covalent interaction between the orbitals on the metal and the ligand. Three types of interactions involving \( \sigma \) overlap of orbitals, \( \pi \) overlap of orbitals and \( p\pi - d\pi \) bonding have been observed (18).
(4) Molecular Orbital Theory

In molecular orbital theory, bonding between metal and ligand is due to the ligand providing electron pairs which occupy bonding $\sigma$ molecular orbitals in the complex. According to this theory the molecular orbitals fulfil the same function for molecules as the familiar s, p, and d orbitals do for atoms. The only orbitals which can transform as the same representation of the molecular point group can combine together to give molecular orbitals (19,20).

In case of an octahedral complex the metal ion has ns, np, and (n-1)d orbitals, available for bond formation. Generally the number of new molecular orbitals formed is equal to the number of combining orbitals. The energy level diagram of an octahedral complex involving only $\sigma$-bonding can be drawn as shown in fig.2. It is consistent with the elementary molecular orbital theory arguments.

It has been observed that $t_{2g}$, d-orbitals are unaffected by $\sigma$-bonding while the $e_g$ orbitals combine with the corresponding separating ligand orbitals to give double-degenerate bonding and antibonding molecular orbitals, provided the ligand orbitals are more stable than the metal orbitals. The bonding orbital is mainly a ligand orbital and the antibonding orbital mainly a metal orbital. This follows from
the theory which shows that a molecular orbital formed from two component orbitals includes a larger contribution from that component which is closer in energy.

In square planar complexes only $dx^2-y^2$ and $dz^2$ orbitals can form bonds with the ligands. Exhaustive calculations have shown that the $dx^2-y^2$ orbital is much more affected by such bonding than $dz^2$ orbital and hence the antibonding combination of the $dx^2-y^2$ orbital with the ligand orbital is much less stable than any other d-orbital.

This theory is applied to tetrahedral complexes also but in a very much complicated manner and hence is usually not of much use.
Energy level diagram showing splitting of a set of d orbitals by octahedral and tetrahedral electrostatic crystal fields.

Molecular-orbital energy-level diagram for an octahedral complex involving only $\sigma$ bonds.
SURVEY OF LITERATURE

The chemistry of complex compounds of cobalt and iron is almost as old as the discovery of these compounds. Both the metals are found to coordinate very readily with different aliphatic and aromatic amines to produce complexes possessing wide varieties of structures and properties. In the following pages a survey of the existing literature on such complex compounds of the above two metals is presented. For convenience the discussion is written under following subheads:

(i) Ammonia complexes of cobalt(II) and iron(II)
(ii) Aromatic and heterocyclic amine complexes of cobalt(II) and iron(II).
(iii) Chelating amine complexes of cobalt(II) and iron(II).

Ammonia Complexes of cobalt(II) and Iron(II).

The ammonia complexes of cobalt(II) and iron(II) have been extensively studied and it is reported that because of the small stability difference between the two structural types i.e. octahedral and tetrahedral, many instances are known in which both types are obtained with the same anions(21). Nelson and Shephard have thus reported the formations of...
octahedral $[\text{Co(NH}_3\text{)}_6]^{2+}$ and tetrahedral $[\text{Co(NH}_3\text{)}_4]^{2+}$ ions (22).

Clark and Williams (23) have examined the infrared spectra in the region 4000 - 200 cm$^{-1}$ of several complexes of the type $\text{M(NH}_3\text{)}_2\text{X}_2$ where $\text{M} = \text{Co(II)}$ and $\text{Fe(II)}$; $\text{X} = \text{Cl}^-$, $\text{Br}^-$, $\text{I}^-$ or $\text{CN}^-$$. Assignments of $\text{NH}_3$ deformation, $\text{M-N}$, and $\text{M-X}$ stretching frequencies were made to establish the structure of the ammonia complexes.

A number of tetrahedral, planar and polymeric six coordinate complexes were studied and certain relationships between their structures and the $\text{M-N}$ and $\text{M-X}$ frequencies were established. Nuclear magnetic resonance studies further indicated some kind of pi- hyperconjugation between the ligand and metal (24).

The black crystalline compound nitrosyl pentaammine cobalt(II) chloride was prepared in pure form by saturating an ammonical solution of cobaltous chloride with NO. It is found to decompose in water even at 0°C (25).

The formation of some molecular addition compounds of cobalt(II) oxalate with primary aliphatic amines and ammonia of the type $\text{CoC}_2\text{O}_4\cdot\text{RNH}_2$ has recently been reported (26). These compounds behaved as electrolytes, which has been confirmed by their molecular weight measurements.
Iron(II) has a lower tendency to form tetrahedral complexes than cobalt(II). The compounds of bivalent iron with ammonia having the molecular formulae \([\text{Fe(NH}_3\text{)}_2\text{X}_2]\) and \([\text{Fe(NH}_3\text{)}_4]^{2+}\) have been prepared (27), while the stability constant of several ammine complexes of the type \([\text{Fe(NH}_3\text{)}_n\text{X}_2]\) where \(n = 2, 4\) or 6 have been determined by Biltz (28).

The reaction of the ammine complexes of iron(II) with benzoylhydrazine has been recently studied thermogravimetrically (29).

Iron(II) halides combine with gaseous ammonia, forming several ammoniates of which the highest has been shown by x-ray studies to be the hexa-ammoniate: (30). On the other hand, cobalt(II) chloride yields pentammine complex in ethanol and diammine in either acetone or methyl acetate media (31-33).

Ammonia complexes of organic salts of these metals have comparatively been less extensively studied, and it has been reported that the number of ammonia molecules coordinated to the metals decreases with an increase in molecular volume of the anions (34).
AROMATIC AND HETEROCYCLIC AMINE COMPLEXES OF COBAL(T(II))
AND IRON(II)

Excellent donating properties possessed by pyridine and its substituted derivatives have made them one of the most thoroughly studied ligands. The structure of the base clearly shows that its nitrogen atom is incorporated in a conjugated pi-system, and hence the possibility of back donation of non-bonding metal 'd' electrons into vacant acceptor antibonding pi-orbitals of the pyridine ring is well pronounced. Although the degree of this type of pi-bonding is not much, many properties of pyridine complexes can only be accounted for in terms of this back donation (35).

In general the transition metals are found to form complexes of the general formula \( M^{2+} \text{py}_2X_2 \) (\( M \) = Transition metal; \( \text{py} \) = pyridine, and \( X \) = halogen or pseudohalogen). It is also reported that the complex \( [\text{Co(py)}_2\text{Cl}_2] \) is crystallized in two isomeric violet and blue i.e., \( \alpha \) - and \( \beta \) - forms respectively which are interconvertable (36,37). Similarly, the \( \alpha \) - (yellow) and \( \beta \) - (black) forms of \( [\text{Fe(py)}_4\text{(SCN)}_2] \) have been prepared and both are shown to have similar magnetic behaviour (38).

Weinland et al have studied a number of pyridine complexes involving different salts of cobalt(II) and iron(II). The complexes possess the general molecular formula \( M^{2+}(\text{py})_4X_2 \).
where $M = \text{Co}^{2+}$ or $\text{Fe}^{2+}$, and $X = \text{SO}_4^{2-}$, $\text{Cl}^-$, $\text{Br}^-$, and $\text{I}^-$ (39,40).

Some bis pyridine salts of fatty acids have been prepared by refluxing cobalt(II) carbonate for several hours with fatty acids and then treating with pyridine (41). Upon the addition of a saturated alcoholic solution of cobalt(II) halides to a saturated alcoholic solution of 3-carboxamido pyridine, a lilac coloured compound, $\text{CoCl}_2 \cdot 2\text{C}_6\text{H}_6\text{ON}_2$ is formed (42).

Spectrophotometric study of complexes formed between cobalt(II) chloride and pyridine or piperidine indicate the formation of 1:2 complexes, which are intense blue in colour giving an absorption band at 650 m$\mu$ (43).

$\left(\text{Fe(\text{OAc})}_2\right)$ in pyridine on cooling gives crystals of $\left[\text{Fe(\text{py})}_4(\text{OAc})_2\right]$ which on heating to 100$^\circ$ in inert atmosphere gives yellow $\left[\text{Fe(\text{py})}_2(\text{OAc})_2\right]$. Both compounds decompose in air to basic Acetate (44).

The thermal decomposition of cobalt(II) and iron(II) halide complexes with pyridine; $\alpha$, $\beta$, $\gamma$ -picolines; 2,6-lutidine and 2,4,6-collidine has been studied by Allan et al. (45). Logan and Costa have reported oxalatobispyridinecobalt(II), $[\text{Co(py)}_2(\text{C}_2\text{O}_4)]$, while the pyridine complexes of cobalt(II) nitrate have also been studied by Biagetti and Haendler (46,47).
Cobalt(II) complexes with piperidine, 4-vinyl pyridine and many other substituted pyridines have been thoroughly studied (48-50).

\[ \text{[Fe(py)\textsubscript{6}]^{2+} has been reported to have a regular octahedral configuration with the pyridines oriented in three mutually perpendicular planes, such that each pair of trans pyridine ring is planar (51), while the existence of [Co(py)\textsubscript{6}]^{2+} ion in pyridine solution of [Co(py)\textsubscript{4}]BF\textsubscript{4} has been established by electronic spectral studies and the ligand field parameters have been evaluated to be at 1017 cm\textsuperscript{-1} and 0.82 cm\textsuperscript{-1} (52).} \]

The magnetic properties, the electronic and Mössbauer spectra of some new and several previously prepared iron(II) complexes of the types \[ \text{[Fe(py)\textsubscript{4}X\textsubscript{2}], [Fe(py)\textsubscript{2}X\textsubscript{2}] and [Fe(py)X\textsubscript{2}] have recently been interpreted in terms of tetragonally distorted octahedral structures (53).} \]

The equilibrium and thermochemical studies on the complexes of M\textsuperscript{2+} (py)\textsubscript{4}X\textsubscript{2} and M\textsuperscript{2+}(py)\textsubscript{2}X\textsubscript{2} (where M = Co\textsuperscript{2+} or Fe\textsuperscript{2+} and X = Cl\textsuperscript{-}, Br\textsuperscript{-}, or NCS\textsuperscript{-}) have been conducted. The splitting of the \( ^5\text{T}_{2g} \) level is attributed to weaker pi-acceptor capacity of the NCS\textsuperscript{-} ion (54).

Mössbauer spectra have recently been employed to solve the problems of the Cis- trans isomerism of \[ \text{[Fe(py)\textsubscript{4}(NCS)\textsubscript{2}] (55,56). The magnetic properties, electronic,
infrared and Mossbauer spectra of some iron(II) complexes of quinoline and 3-methyl quinoline have also been studied (57).

Cobalt(II) chloride when refluxed with piperidine and 2-acetyl pyridine gives tetracoordinated complexes (58), but the amines like pyridines and isoquinoline give complexes containing only two molecules of the ligand per molecule of cobalt(II) oxalate (59).

Roy et al have reported that chlorination and bromination of ethanolic suspension of several non-electrolyte cobalt(II) complexes of the formula CoL₂X₂ gives 2:1 electrolyte complexes of the type L₂(CoX₂Y₂) where L=isoquinoline, β-picoline, γ-picoline and 3,5-butidine; X and Y = Cl⁻ or Br⁻. The complexes were characterized by analysis, conductance, magnetic susceptibility, infrared and electronic spectral data and a tetrahedral structure was proposed (60).

Some complexes of cobalt(II) salts with pyridine carboxylic acids have been reported by Ellis et al (61). The far infrared, magnetic moments and diffuse reflectance spectra have been discussed with reference to their structures (62).

The complexes of cobalt(II) halides with 2-amino- methyl pyridine (2-AMP) of the type [Co(2-AMP)₂X₂] where X = Cl⁻, Br⁻, I⁻, have been synthesised and their magnetic moments and diffuse reflectance spectra are discussed to establish their structures (63).
N-hydroxy methyl-3-carboxamidopyridine (I) has also been complexed with cobalt(II) chloride and bromide to give complexes $[\text{CoL}_2X_2]$ (64). A bidentate ligand of similar type is 2-acetamidopyridine which gives many complexes with cobalt(II). The structures of these complexes have been established by infrared, magnetic susceptibilities and reflectance spectral studies (65).

Very recently Zygmunt has prepared some cobalt(II) halide and pseudohalide complexes with isonicotinamide (I), $\text{CoL}_2X_2$ ($X = \text{Cl}^-, \text{Br}^-$ ) (66), while the complexes of 3-carboxamidopyrine and diethyl-3-carboxamidopyridine have also been prepared and studied spectroscopically (67).

Some complexes of 2- and 4-vinyl pyridines with iron(II) halides and pseudohalides have been reported recently and bridged octahedral structures have been suggested for these (68). Similarly the cobalt(II) complexes with the same ligands have also been reported (69).

Quinoline, substituted quinolines, and 3-quinoline-8-carboxamide react with cobalt(II) chloride, bromide or perchlorate to give hexa and tetracoordinated complexes. The magnetic and electronic spectral studies clearly indicate octahedral and tetrahedral structures (70-71). Very recently the studies on the interaction of sodium-pentacyano-ammine Ferrate(II) with pyridine and quinoline have been made by Malik et al (72). The resulting complexes have been found to
be diamagnetic. Mixed ligand complexes of bis(ethylaceto acetate) Co(II) with quinoline and isoquinoline have been synthesised. On the basis of analysis, conductance, magnetic moments (4.90 - 5.0 B.M.), infrared and electronic spectral studies, a high spin octahedral configuration has been proposed for these complexes (73).

Many other aromatic amines like aniline, toluidines anisidines and their substituted derivatives have also been employed for preparing complexes of cobalt(II) and iron(II) salts. Ahuja et al. have reported the preparation and properties of some complexes of the sulphates and nitrates of the above metals and their possible structures have been deduced on the basis of spectroscopic measurements (74).

The reaction of aniline with dimethylglyoximate cobalt(II) has been studied and the composition of the complex was shown to be $\text{Co} \left( O_2N_2C_2\text{Me}_2 \right) \left( \text{PhNH}_2 \right)_4 \text{Cl.3H}_2\text{O}$ (75). The preparation has been described of some complexes of 2-methoxyaniline with chloride and bromide of cobalt(II). These complexes are reported to have tetragonal structures (76).

During the first attempts in the study of weak unidentate type of linkages, the ligand benzene -1,2-diamine or (o-phenylenediamine) was used, which has now been shown to act as a bidentate ligand for cobalt(II) and iron(II) halides (77-79). Recently Duff has reported the synthesis of some
complexes of o-phenylenediamine (L) with cobalt(II). These complexes fall into three types viz. \( \text{CoL}_2 X_2 \) \((X = \text{Cl}^-, \text{Br}^-)\); \( \text{CoL}_2 X_2 \) \((X = \text{Cl}^-, \text{Br}^-, \text{NO}_3^-, \text{ClO}_4^-, 0.5\text{SO}_4^{2-})\) and \( \text{CoL}_3 X_2 \) \((X = \text{Cl}^-, \text{Br}^-, \text{NO}_3^- \text{or ClO}_4^-)\), and the ligand in these complexes either behaves as a bidentate chelating or a bridging agent (80).

Synthesis of some six coordinate cobalt(II) complexes containing 2 and 3 moles of the aromatic diamines e.g. 0-phenylenediamine, 1,8-diamino-naphthylene and 2,2'-diaminobiphenyl has been described by Kakazol and Nelson. The complexes have been characterized by the magneto-chemical, vibrational and electronic spectral studies. The complexes containing 2 moles of diamine are assigned trans-structures and their visible and near infrared spectra are explained on the basis of tetragonal distortion (81).

A survey of the literature shows that complexes of m- and p-phenylenediamines have been much less studied. Their complexes with cobalt(II) and iron(II) salts have been prepared and the ligands are only monodentate in nature probably due to symmetry reasons (82-85).

Very recently some iron(II) complexes with \( N-(2\text{-pyridyl methylene})-4\text{-methyl aniline}\) of the types \( \text{FeL}_3 X_2 \) \((X = \text{Cl}^-, \text{Br}^-, \text{I}^-; \text{ClO}_4^-)\); \( \text{FeL}_2 X_2 \) \((X = \text{Cl}^-, \text{Br}^-, \text{I}^-)\) and \( \text{FeL}_X X_2 \) \((X = \text{Cl}^-, \text{Br}^-, \text{I}^-)\) have been reported. These complexes were characterized by elemental analysis, magnetic measurements
and infrared spectral studies (86).

**CHELATING AMINE COMPLEXES OF COBALT(II) AND IRON(II)**

Complexes of this class of ligands are the ones, best studied. Such complexes have been prepared by using ligands e.g. 2,2'-dipyridyl (dipy) and 1,10-phenanthroline (phen), containing an α-di-imine group, which is capable of inducing spin-pairing and also stabilizing low oxidation states.

Pfeiffer and Tappermann prepared the compounds $\text{M(phen)₃XₙH₂O}$ (where $\text{M} = \text{Co}^{2+}$ and $\text{Fe}^{2+}$, $X = \text{Cl}^-$ and $n = 6-14$ and $\text{am} = \text{dipy}$ and phen ) and studied their structures (87), while the magnetic susceptibilities and many other properties of the cobalt(II) and iron(II) salts with dipy have also been studied (88,89). The resolution of tris (dipy) iron(II) complexes through iodide antimonyl tartarate has been attempted by Dwyer and Gyarfas (90).

Absorption spectra of mono complexes of cobalt(II) and iron(II) with dipy of the type $[\text{M(dipy)}]^{2+}$ has been studied. The spectra are explained on the basis of electrostatic complex model, and the term shifts for the ligand in the field of the central ion have been derived (91).

Magnetic properties of the three complexes of cobalt viz. $[\text{Co(phen)}₂(CN)₂]$, $[\text{Co(phen)}(\text{NO}_₂)_₂]$ and
[Co(dipy)(CN)₂] have been studied and the magnetic moments are 1.75, 1.71 and 1.67 respectively. These values show the presence of one free electron and thus suggest a low spin state for the metal (92).

Some mixed cobalt(II) salts containing 1 mole of dipy or phen and 1 mole of dimethylglyoxime (H₂D) of the type [Co(H₂D)(dipy)Br₂] and [Co(H₂D)(phen)Br₂] have been isolated by Paglia (93).

Stability of cobalt(II) and iron(II) complexes of these ligands and their derivatives like 5,6-dimethyl, and 4,7-dimethylphenanthrolines were determined by the partition method. It was found that basicity of the ligands confers an increased stability on the complexes (94-96).

It is found that the spin multiplicity of the ground state in a series of complexes of the type [Fe(phen)₂X₂] depends on the position of X in the spectrochemical series. The spin equilibrium \( ^1A_1 \rightleftharpoons ^5T_2 \) is interpreted by the study of the Mossbauer spectra (97).

Structural studies of mono 2,9-di methyl-1,10-phenanthroline complexes of cobalt(II) and iron(II) sulphates have been made by Hall et al (98). The complexes of cobalt(II) and iron(II) with various substituted dipyridyls and phenanthrolines, have also been prepared and studied spectroscopically (99,100).
Coordination compounds of iron(II) phthalimide with dipy, phen and 5-nitrophenoanthroline have been prepared. On the basis of conductivity, infrared and magnetic susceptibility measurements, the structures of these complexes have been resolved (101).

\[ \text{[Fe(phen)\textsubscript{2}(CN)\textsubscript{2}] \cdot 2H\textsubscript{2}O} \] was prepared by adding K\textsubscript{2}CN to a hot solution of Fe(NH\textsubscript{4})\textsubscript{2}(SO\textsubscript{4})\textsubscript{2} and phen and was crystallised from concentrated H\textsubscript{2}SO\textsubscript{4}. When dipy was used, \[ \text{[Fe(dipy)\textsubscript{2}(CN)\textsubscript{2}] \cdot 3H\textsubscript{2}O} \] was obtained (102).

A novel series of bis complexes of iron(II), employing the bidentate ligand 2-methyl-phen(L), of the type \[ \text{[FeL\textsubscript{2}X\textsubscript{2}]} \] (\(X = \text{Cl}^-, \text{Br}^-, \text{NCS}^-\)) have been reported recently (103), while some bis-phenoanthroline cobalt(II) complexes have been reported by Hennig et al (104). The far infrared spectral studies of some phen and dipy complexes of iron(II) have been made by Ghosh et al (105).

Some cobalt(II) pseudo-octahedral complexes containing two triazine-1-oxide moieties and one dipy or phen have been reported. Conductance, magnetic moments and molecular weights of these complexes have been determined (106).

Piperazine and its substituted derivatives have received proper attention only recently and a large number of complexes using these ligands have been synthesised and their structures have been established using various physico-
chemical methods (107-109).

Hendra et al have reported the infra red spectra of piperazine and some methyl substituted piperazines and their compounds (110); while the compounds of the type $\text{CO}(L)X_2$ (where $L$ stands for $1,4$-bis(3-aminopropyl)piperazine and $X$ for $\text{Cl}^-$, $\text{Br}^-$, and $I^-$) have been prepared and studied spectroscopically (111).

Two series of solid complexes namely $\text{CoL}_2X_2$ and $\text{CoLX}_2$ (where $L =$ piperazine and $X =$ $\text{Cl}^-$, $\text{Br}^-$, $I^-$) have been synthesised by interaction of piperazine with cobalt(II) halide in alcoholic media (112).

Pellaconi et al have prepared various adducts of piperazine and methylpiperazine ($L$) with Cobalt(II) acetylacetonate, cobalt(II) benzoylacetonate and cobalt(II) dibenzoylmethanate ($X$) of the type $[\text{Co}(X)_2(L)_2]$. They have studied the infrared spectra, magnetic moments and electronic spectra of these complexes and assigned an octahedral structure to them (113).

Very recently Marcotrigiano et al have prepared $N$-methyl piperazine-4-carbodithioate complexes of cobalt(II) and iron(II) and characterized them by elemental analysis, infrared, magnetic moments and electronic spectral studies. An octahedral structure has been proposed for the iron(II) complex while a square-planar structure has been suggested
for the cobalt(II) complex (114).

The usual mode of coordination of another chelating ligand i.e. ethylenediamine is through both the nitrogens but under certain conditions only one nitrogen is bonded (115).

Complexes of ethylenediamine with some iron(II) halides have been prepared by Brevil by adding ethylenediamine to iron(II) halides in anhydrous methanol in an atmosphere of hydrogen. These compounds are unstable in air (116).

Fowls and Mc-Gregor have reported that on addition of ethylenediamine (en) to iron(III) chloride; the iron(III) chloride is first reduced to iron(II) and subsequently forms the outer orbital complex \([\text{Fe(en)}_3\text{Cl}_2]\) (117).

Haschke and Wendlandt have studied the thermal decomposition of \([\text{Co(en)}_3\text{C}_2\text{O}_4]\) by thermogravimetric or differential thermal analysis, and high temperature reflectance spectroscopy. The thermal dissociation reaction \([\text{Co(en)}_3\text{C}_2\text{O}_4] \rightarrow [\text{Co(en)}]\text{C}_2\text{O}_4\) takes place in the temperature range 200-300°C (118).

Bhat et al reported some cobalt(II) arsenate complexes with ethylenediamine in 1965 (110), while recently Joshi (120) has determined the stability constants of some cobalt(II) and iron(II) complexes with 2-hydroxy-5-methyl-propiophenone-ethylenediamineanil, 2-hydroxy-5-methyl
benzophenone-ethylenediamineanil and 2-hydroxy-5-chloro-
benzophenone-ethylenediamineanil potentiometrically. The
change in free energy of the complex formation has also
been calculated.

The complex formation between N-methyl sulphonic
acids of ethylenediamine with cobalt(II) has been studied
by Achilles and Uhlig. In these complexes ethylenediamine
acts as a bidentate ligand (121).