GENERAL INTRODUCTION
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The field of coordination chemistry, initiated by Alfred Werner and nourished by eminent inorganic and physical chemists like Jørgensen, Pfeiffer, Tschugaev, Ley, Bodlander, Jaeger, Mann, Bjerrum, Leden, Chernyaev and his group of Russian chemists, Ray, Feigel, Prodinger, Schwarzenbach, Calvin, Bailer, Nyholm, Chatt and several others, has witnessed spectacular developments in the last two decades. Several factors have been responsible for these advancements. The gradual development of the valence bond theory, and further the ligand field and molecular orbital theories combined with the introduction of new analytical techniques such as infra red and ultra-violet spectroscopy, nuclear magnetic and electron spin resonance, nuclear quadrupole resonance, X-ray absorption, Mössbauer effect etc., has immensely helped in correlating the structural and configurational aspects of complexes with their physical properties. This in turn has opened new avenues for basic and applied research, basic chemical applications, therefore, now include use of metal catalysts or chelate protective groups in the preparation of organic compounds, synthesis of inorganic compounds of predetermined properties, and the introduction of some new industrial processes like Zeigler-Natta polymerisation, the hydroformylation process and the Wacker olifine oxidation, and a better understanding of life process.
To incorporate the various aspects of modern inorganic chemistry mentioned above in the form of a short review would require great space and will also be the out of tune from the present investigations, it, therefore, seems reasonable to elaborate only those aspects which are pertinent to the problem, under study. A discussion of the modern valence concepts, and a survey of the chemistry of Cu(I), Ni(II) and Pd(II) and their substitution reactions, coordinating abilities of rare earths and, an account of the coordinating and chelating properties of sulphur and nitrogen containing ligands, have been included in this review.

1. Valence Theories

Sidgwick's concept\textsuperscript{1a,1b} of E.A.N, and later elaboration of the fact that the ligand species would be one which has a pair of electrons for sharing, is still the starting point for modern valence theories.

Since 1950, the crystal field theory, the molecular orbital theory and their admixture, the ligand field theory have been widely used to explain the behaviour of coordination compounds. The crystal field theory first proposed by Bethe\textsuperscript{2} in 1929, was successfully applied to explain the magnetic properties of the transition metal ions by Schlapp and Penney\textsuperscript{3} and by Van Vleck\textsuperscript{4}. The theory was further strengthened by Hartmann\textsuperscript{5} who used it to explain the so called d-d spectra of the complexes in the visible range. Orgel\textsuperscript{6} was the first to give its usefulness for explaining
the stability of coordination compounds of transition elements. Crystal field theory emphasizes the effect of the external electrical field, due to the ligands, on the energy levels of the d orbitals of the central atom or ion. These orbitals split into groups of different energy and nature of the splitting determines the electronic population of the various orbitals and, by implication, the magnetic and spectral characteristics of the central atom. A further area where crystal field theory provides a very direct prediction is in the distortion of regular coordination arrangements. It predicts which electronic configuration will be energetically favourable for distortion. Such predictions have been extensively verified from X-ray determinations of the structure of complex ions.

The application of molecular orbital theory to coordination compounds was first made by Van Vleck in 1935. The ligand and metal orbitals which are used to build up the molecular orbitals are combined to form new linear combinations which satisfy some symmetry requirements. In the event a given atomic orbital overlaps appreciably with only one other atomic orbital, the pair may be regarded as a localised molecular orbital, holding as many as 2 electrons. This would correspond to the usual conception of chemical bond. The d orbitals of the central metal ion which do not point towards the ligands become non bonding molecular orbitals e.g., orbitals in which the electrons have the same energy as they possess prior to coordination. Thus, the $d_{xz}, d_{yz}$ and $d_{xy}$ are non bonding molecular orbitals for an octahedral
complex, while for a square planar complex the non bonding orbitals are \( p_z \), \( d_{xz}, d_{yz}, d_{xy} \) and \( d_{z^2} \). For an \( n \) coordinated central ion there will be found \( n \) bonding orbitals e.g., orbitals having lower energy than they possess prior to coordination and \( n \) antibonding orbitals e.g., orbitals in which electrons possess higher energy than they possessed prior to coordination. The molecular orbital theory is most reasonable of the existing theories. It conveniently explains all type of bondings including \( \pi \) bonding. Furthermore, with a reasonable selection of atomic orbitals, the theory automatically includes all of the interactions which in the valency bond theory would require the inclusion of a large number of resonance forms.

The nature of the chemical bond in coordination compounds has also been explained currently on the basis of (i) electrostatic theory and (ii) valence bond theory. Although each theory has its own advantages and a single theory cannot be applied convincingly to all types of coordination compounds.\(^8a,8b\) However, the approach of molecular orbital theory is so far more logical and convincing.

2. Nucleophilic Reactivity

The effectiveness of a nucleophilic reagent, nucleophilic reactivity is often defined in terms of the basicity \( (B) \) of the nucleophile (towards the proton on water) and polarizability \( (\rho) \) which is a measure of the ease of distorting or removing the electrons in the nucleophile.\(^9\) The polarizability is calculated from the molar refraction \( (R) \), the electrode potential \( (L_n) \) or
the electronegativity.

Edwards\textsuperscript{10} correlated these terms by the equations:

\[ \log \left( \frac{k}{k_0} \right) = \alpha P + \beta H \]
\[ \log \left( \frac{k}{k_0} \right) = \xi E_n + \beta H \]

where \( \frac{k}{k_0} \) is the rate relative to water, \( P \) is defined as \( \log (R^N/RH_2O) \), \( H \) is a function of basicity \( (pK_a + 1.74) \), \( E_n = E^0 + 2.60 \), where \( E^0 \) is the standard potential for the process:

\[ 2Y \rightleftharpoons X_2^{2+} + 2e^- \]

For water, \( H \) and \( E_n \) are zero, \( \alpha \) and \( \beta \) can be determined experimentally from a series of related reactions.

The correlation of basicity with nucleophilic character may be understood by aligning the substitution reaction:

\[ S + X \rightleftharpoons Y = S + X \] (where \( Y \) is a nucleophile, \( S \rightarrow X \) is the substrate, and \( X \) is the leaving group) with an acid-base reaction. The basicity of \( Y \) (and similarly of \( X \)) is measured by the acid-base reaction:

\[ Y + H_3O^+ \rightleftharpoons YH^+ + H_2O \]

Obviously, to the extent the substrate atom \( S \) has a localised positive charge similar to that of a proton, the basicity of the nucleophile would play the main role and the rate of substitution will be correlated with basicity.

Some of the important coordinating groups such as thiourea, triphenyl phosphine and iodide are more nucleophilic than their basicities would warrant and this excessive reactivity is ascribed to polarizability.\textsuperscript{11}
In general, those nucleophiles that are strongly basic are often not very polarizable e.g., $F^-$ on tetrahedral phosphorus. Conversely, a large polarizable nucleophile may not be very basic e.g., thiourea, iodide ion. This situation is further exemplified by considering the stability order of the halide ions in presence of different cations. With $Be^{2+}$, $Mg^{4+}$ the order is $F^- > Br^- > I^-$ and with cations such as $Ag^+$, $Cu^+$ and $Hg^{2+}$ the order is reversed e.g., $I^- > Br^- > Cl^- > F^-$.\[12,13\]

The alteration of solvent is another factor that affects the order of nucleophilic reactivities.\[12,13\] In general, the most basic is often the most solvated in a protic solvent such as water and alcohol. The poor nucleophilicity of $F^-$ and good nucleophilicity of $I^-$ may be explained on considering the order of binding of halide ions $F^- > Cl^- > Br^- > I^-$ in hydroxyl solvents through hydrogen bonding: The strong solvation of the ground state is one reason why $F^-$ ion, the most basic halide ion, is a poor nucleophile whereas $I^-$ ion is a good nucleophile in displacements on saturated carbon in aqueous solution. In solvents that cannot hydrogen bond (e.g., acetone, dimethyl formamide, D.M.F.), the rate order is apparently reversed, for $Cl^-$ ion reacts more rapidly than iodide.

It has been found that some nucleophiles such as peroxyanions and hydroxylamine show higher reactivities than those expected from their basicities and polarizabilities, such groups are characterised by the presence of one or more unshared electron pairs on an atom adjacent to the nucleophile atom. The excess reactivity shown by this class of reagents is called the 'alpha
effect as proposed by Edwards and Pearson, with reference to the pair of electrons on the alpha atom. The magnitude of alpha effect may be estimated by the fact that perhydroxide ion $\text{OOH}^-$ is several times more reactive than $\text{H}^-$, even though the $\text{OH}^-$ ion is far more basic.

Some of the factors that influence reactivity of nucleophile have been listed by Jencks and Carruolo. These include (a) hydrogen bonding (b) proton transfer and general acid catalysis (c) electrostatic effects (d) steric effects (e) resonance and (f) relative bond strengths to proton and other substrate atoms. These factors, although are of limited applicability than basicity, polarizability and solvent effects, but are important in special cases.

3. **Hard and Soft Acids and Bases.**

A convenient and useful way to classify metal ions and ligands is according to their order of polarizability. In general, polarizable bases (or Lewis acids) are called soft bases (or acids) and non polarizable bases (or Lewis acids) are called hard bases (or acids). The above classification can be very well understood if we carry out the division of metals according to their tendencies: class (a) to form stable complexes with first ligand atom of each periodic group and, class (b) to form stable complexes with the ligand atom belonging to the second or subsequent member of each periodic group.
For class (a) metal ions the order of stability is

\[ F^- > Cl^- > Br^- > I^- \]
\[ O > S > Se > Te \]
\[ N > P > As > Sb > Bi \]

For class (b) metal ions, the order of stability is

\[ F^- < Cl^- < Br^- < I^- \]
\[ O < S ∼ Se ∼ Te \]
\[ N < P > As > Sb > Bi \]

In general, class (a) metal ions are Lewis acids of small size and high positive oxidation states, prefer to bind to small, non-polarizable ligands (containing least polarizable atom of a group) such as \( F^- \), \( O_2 \) and \( H_2O \), whereas class (b) metal ions, are Lewis acids of large size and low positive oxidation states, prefer to bind large, polarizable ligand (containing most polarizable atom of the group) such as \( I^- \), \( R_2S \) and olefins.

Class (a) Lewis acids are called hard acids and class (b) Lewis acids are known as soft acids. As a rule, soft acids always prefer to combine soft bases and hard acids prefer to combine hard bases.

According to the \( \pi \) bonding theory of Chatt\(^{17a,17b}\) the soft acids, class (b), have invariably closely held outer d orbital electrons which can form \( \pi \) bonds by donation to suitable ligands. Such ligands contain atoms having empty d orbitals acting as acceptor orbitals such as \( p \), As, S and I. Unsaturated ligands
such as CO and isonitriles would also act as acceptors of metal electrons by the use of empty orbitals provided the molecular orbitals formed are not too unstable. In class (a) Lewis acids, ligand atoms such as O and F could form bonds in the opposite sense, by donating electrons from the ligands to the empty orbitals of the metal. Thus the soft acids (class b) are potential d-p electron donors via π bonds. The hard acids are potential π bond acceptors. These effects are, in addition to σ bonding interactions.

4. General Considerations on Sulphur containing Ligands (especially thioalcohol and related compounds).

Ligands containing oxygen or nitrogen as donor atoms and ligands such as halide ion, cyanide ion and unsaturated compounds such as olefines, cyclopentadiene, carbon monoxide etc. have so far been studied in much detail. Ligands containing sulphur have less extensively investigated although in recent years considerable interest has been shown in sulphur ligands.

From a consideration of an electrostatic model, the coordinating ability of a unidentate ligand depends not only on its electronegativity but on total dipole moment, $\mu$. Thus the large size and small permanent dipole moment of $H_2S$ ($\mu_{H_2S}$, 1.1D, $\mu_{H_2O}$, 1.9D) reduces its coordinating ability below that of water for ions of low field strength. However, $H_2S$ is more polarizable than water (molar refractivity of donor atoms, $H_2O$: 3.7 cc., $H_2S$: 9.5 cc) and with ions of high field strength ($Cu^{+}, Ag^{+}, Hg^{++}$ etc.),
$H_2S$ coordinates readily and protons are forced off to give insoluble sulphides. Whereas both the permanent dipole moment and coordinating ability decrease in the series $H_2O > ROH > R_2O$, the reverse holds good for sulphur, both dipole moment and coordinating ability increase in the order: $H_2S < RSH < R_2S$.

Moreover, although polarizability is decreased by alkyl substitution, the decrease is much less (5%) in going from $H_2S$ to $R_2S$ than the corresponding decrease (24%) in going from $H_2O$ to $R_2O$.

Leaving aside a few potential ligands$^{21a,21b}$ e.g., $NO_2^-$, $2,2'$-bipyridyl, o-phenanthroline, dimethyl glyoxime etc., oxygen and nitrogen have no orbitals available to accept electrons from suitably placed d orbitals on the metal atom. However, sulphur has vacant d orbitals which can be used for d-π bonding, this usually occurs with latter transition metals in their normal oxidation states, Pd(II), Pt(II), Hg(II) etc., and with the early transition metals in their lower oxidation states, (Mo(0), W(0), Re(I) etc.). The extent to which such π bonding occurs is mere speculation but it does occur with ligands containing sulphur. Low spin $d^8$ ions, Pd(II), Pt(II), Ni(II), and Au(III), and $d^{10}$ ions, Cu(I), Ag(I), Au(I) and Hg(II) have the highest formation constants with heavy halides ($I^-$, $Br^-$) and with sulphur ligands. Being typically (b) they form strong π bonds with soft ligands and also d-π bonds by donation of a pair of electrons to the ligand.$^{15,17a,17b}$
The polarizabilities of sulphur ligands decrease in the order: \( S^{2-} > R S^- > R_2 S \) and therefore, it is necessary to have a distinction between sulphide ion, mercaptide ion and thioether while considering the bonding properties of sulphur ligands. In the above order, not only the polarizabilities but the number of lone pairs also decrease. Williams suggested that the principal difference between thiols and thioethers as ligands is that the former are highly polarizable but not as effective \( d_\pi \) electron acceptors as the latter. Thiols but not thioethers cause spin pairing in complexes of Co(II) and Ni(II). The ability to cause spin pairing in complexes of Co(II) and Ni(II) is confined to 'soft bases' which are relatively strong \( \kappa \) acceptors. The polarizability of the ligand is, however, the more decisive factor.

Livingstone has given an excellent review on metal complexes of sulphur containing ligands and described the chemistry by dividing the ligands into the following categories: (i) sulphide ions (ii) negatively charged unidentate ligands such as thiols, sulphite ion, thiosulphate ion and thiocyanate ion (iii) neutral unidentate ligands such as thioethers, thiourea, thio acetamide, thiobenzamide, triphenyl phosphine sulphide and dimethyl sulfoxide (iv) sulphur containing chelating agents such as thioether, thiol, alkyl xanthates, dialkyl-dithiocarbamate, thio derivatives of \( \beta \) diketones and \( \beta \) ketoesters and \( \alpha \) dithiols. The present discussion, however, will be limited to thiourea and related ligands.
Thioureas act as soft bases and unidentate neutral ligands, forming strong complexes with class (b) metals particularly with $d^{10}$ configuration e.g., Cu(I), Ag(I), Au(I) and Hg(II). In thiourea, sulphur atom unlike the nitrogen has vacant d orbitals, the latter may be used as $d_{\pi}$ acceptor orbital and therefore, the possibility of $d_{\pi} - d_{\pi}$ bond formation is not excluded. Another important characteristic with thiourea is its tendency to reduce some metals from higher oxidation states to lower oxidation states e.g., Cu(II) to Cu(I), Au(III) to Au(I), Pt(IV) to Pt(II), Ce(IV) to Ce(III), and Te(IV) to Te(II), and stabilising the lower oxidation state. This is not surprising since thiourea being highly polarized molecule and having sulphur atom with acceptor d orbitals, should have tendency to create conditions so as to make the metal ions favourable for coordination and this may be achieved by making the size of the ions larger and reducing the positive charge. This is of course not necessarily be true with all the ions since factors such as configuration of the metal, redox potential of the system and other environmental factors also play key roles in the stabilization of the oxidation state of a particular metal ion.

Thiourea forms complexes in which the coordination number of the metal ion usually varies from 2 to 4 and in a few cases the formation of higher coordinate species ($>4$) are also reported. Complexes with coordination number two are reported with Ti(IV), Ag(I), Au(I), Hg(II) etc. A coordination number of three is reported for Cu(I). There are numerous examples of 4 coordinate
species. The structures of a number of thiourea complexes have been determined by X-ray analysis and infra-red studies.

The nickel atom in $\text{[Ni(tu)$_4$Cl$_2$]}$ where $\text{tu} = \text{thiourea}$, is surrounded by four sulphur atoms at 2.45$\text{Å}$ and two chlorine atoms are at 2.4$\text{Å}$ in the trans octahedral sites. The structure of high spin compound has also been determined. $\text{Ni-S}$ is found to be 2.1-2.3$\text{Å}$ in the diamagnetic form whereas in 6-coordinate complex it is 2.4-2.6$\text{Å}$. This is in accordance with the ligand field theory which predicts that stronger field produced by the ligands closer to the nickel will cause the $\text{eg}$ electrons to pair in the $d^2$ orbitals, so producing a diamagnetic complex with no close neighbours in the $z$-direction.

The compound $\text{[Ni(tu)$_2$(NCS)$_2$]}$ is octahedral and polymeric, the sulphur atom of each thiourea molecule is bound to two nickel atoms. The compounds $\text{[M(tu)$_2$(NCS)$_2$]}$ ( $\text{M} = \text{Mn, Co, Cd}$ etc.), are isostructural with $\text{[Ni(tu)$_2$(NCS)$_2$]}$. In the compound, $\text{(Ni(py)$_2$(tu)$_2$Cl$_4$)}$ ( $\text{py} = \text{pyridine}$), the sulphur atoms of two of the four molecules are probably bridging as in thiocyanate complexes.

The compound $\text{[Ud(tu)$_2$Cl$_2$]}$ is tetrahedral but $\text{[Pb(tu)$_2$Cl$_2$]}$ has a polymeric structure in which lead atom is 7-coordinate, being surrounded by 4 bridging sulphur atoms, 2 bridging chlorine atoms and one non bridging chlorine. The complex $\text{[Mo(tu)$_3$Cl$_3$]}$ has a magnetic moment of 3.71, but the complex $\text{[Mo$_2$(tu)$_6$Cl$_6$]}$ has a moment of 0.59B.M. In the latter, two Mo octahedral are bridged by either 3 chlorine or 3 sulphur atoms (from the thiourea) and the low value of magnetic moment is ascribed to spin-spin coupling.
due to metal-metal interaction, either directly or via the bridging atoms,

Infra red spectra studies shown that thiourea coordinates through sulphur not only with class (b) metals but also with Sn(IV), Pb(II) and Te(II), however, in Ti(tu)₂Cl₂ the coordination is through nitrogen.

Complex of NN'-substituted thioureas(I), R=alkyl or aryl, R'=alkyl, aryl or H, has been extensively investigated. Cu(I) and Ag(I) form complexes containing 1, 2, 3 or 4 molecules of ethylene thiourea (II). Complexes of Cu(I) and Ag(I) are also known with other substituted thioureas.

Ni(II) forms an interesting series of complexes with substituted thioureas. The complexes [Ni(nu)₂X₂] (where X=Cl, Br, ntu=1-(1-naphthyl)-2-thioureia) are tetrahedral, the paramagnetic compounds, [Ni(ethu)₄X₂](X=Cl, Br) are octahedral and have been isolated in cis and trans forms but the iodo complex is six coordinate and is a rare example of tetragonal Ni(II) complex.
NN'-diethyl thiourea, NN'-diphenyl thiourea and NN-diphenyl thiourea behave as bidentate chelating agents, bonded through both nitrogen atoms.\(^3\) Bis chelate complexes of Co(II), Ni(II) and Cu(II) are formed by a number of NN'-diaryl-N-hydroxothioureas (III), the hydrogen of the OH group is replaced and the ligand is most probably coordinated through sulphur and oxygen\(^3\) (IV).

5. Stabilisation of Lowest Valencies of Transition Metal (Formation of complexes with \(\pi\) -Acceptor (\(\pi\) acid) ligands).

In metals in their lower valency states the coordination between the ligand and the metal usually takes place by the donation of electrons from the filled orbitals of the ligand to the empty orbitals of the metal.\(^4\) Such a process will naturally lead to extensive charge accumulation around the metal with the result that the chances of covalent bonding diminish. However, there is one way in which the effect of charge accumulation can be minimised, namely, by a mechanism involving the transfer of charge from the metal ion back to the ligand. This usually takes place by the \(p_\pi\) or \(d_\pi\) orbitals on the ligands which act as acceptor orbitals and cannot be done by \(\sigma\) bonding since \(\sigma\) orbitals of all the ligands are filled. Such type of acceptor ligands are also called \(\pi\) acid ligands.\(^3\)

The important ligands which are found experimentally to stabilise the lower valency states of the transition metals are:

\[
\begin{align*}
\text{C}_2\text{H}_4\text{CO}, \text{CN}^-, \text{PR}_3\text{P}_3\text{As}, \text{SC(NH}_2)_2\text{I}^-, \text{SCN}^-, \text{C}_5\text{H}_5\text{N}, \\
22'-\text{dipyridyl, o-phenantrhoiline etc.}
\end{align*}
\]
Each of these ligands has acceptor levels for $\pi$ electrons and is suitable for the stabilisation of lower valency states and other ligands though similar in each other way are less effective or incapable to stabilise these valency states. Thus phenanthroline, dipyridyl and thiourea with vacant $d$ orbitals and arsines with empty $d$ orbitals are more effective than ethylenediamine or aliphatic amines in stabilising lower valency states.

It is now recognised that the qualitative order of various ligands in their ability to function as $\pi$ acceptors is in the following order: $^{40a}$

$\text{NO} > \text{CO} \sim \text{RNC} \sim \text{PF}_3 > \text{PCl}_3 \sim \text{AsCl}_3 > \text{SbCl}_3 > \text{PCL}_2 \sim (\text{OR})_2 > \text{PCL}_3 \sim (\text{OR}) > \text{PR}_3 \sim \text{AsR}_3 > \text{SbR}_3 \sim \text{SR}_2 > \text{RCN} \sim \text{NR}_3 \sim \text{OR}_3 \sim \text{RCH} \sim \text{H}_2 \text{NCOR}$. 

6. Dipyridyl and o-phenanthroline as $\pi$ Acid Type Ligands.

$2,2'$ dipyridyl and o-phenanthroline form complexes with metal ions in their normal oxidation states e.g., $\text{Cu}^+\text{, Cu}^+\text{ etc.}$. They are supposed to form strong $\sigma$ donor bonds, supplemented by moderate degree of $\pi$ bonding as is the case with all ordinary complexes with similar ligands. However, in contrast to nearly all of the other complexes formed by metal ions in normal oxidation states, the dipyridyl and o-phenanthroline complexes, generally of the type $(\text{ML}_2)_n^+$ or $(\text{ML}_3)_n^+$ where $\text{L}$ is dipy or o-phen., can be reduced giving stable species with the same formulas but with charges of only $+1, 0$ or even $-1$. This is true for both
transition and non transition metals\textsuperscript{43,44} e.g., Ti(I), Ti(0), V(II), V(I), V(0), V(═I), Cr(II), Cr(I), Cr(0), Co(0), Cu(I), Fe(0), Zr(0), Mg(0), Be(0) etc.

There is no plausible explanation for the abnormal behaviour of these ligands to stabilise zero or negative oxidation states of the metals. However, the following approaches are worth mentioning although a convincing solution is yet to come.

According to Orgel\textsuperscript{40b} the source of stability of these complexes is due to synergic bonding in which electrons are transferred from the σ orbital on the nitrogen atoms to the empty d (\textit{e}\textsubscript{g}), s and p orbitals of the metal and from the d (\textit{t}2\textsubscript{g}) orbitals of the metal to the empty π molecular orbitals of the conjugate system. The acceptor properties of these amines, as indicated by their charge-transfer spectra, e.g., (Fe(phen)\textsubscript{3})\textsuperscript{2+}, (Cu(phen)\textsubscript{2})\textsuperscript{+}, do not seem to depend critically on the presence of the aromatic system, but rather than that of the 4 atom conjugate system.

\[\text{HN} = \text{CH} - \text{CH} = \text{NH}\]

The argument is not very convincing and moreover, not applicable to non d metal ions.

Another approach which Harzog\textsuperscript{44} used in his communications consists of assuming that the ligand, dipy or o-phen, is always formally neutral, thus making the formal oxidation state of the metal equal to whatever charge is carried by the complex as a whole. Using this formulation, it must be assumed that the dipy
molecules manifest their acidity by absorbing electron density from filled metal orbitals into the antibonding orbitals of the ring system. This view is perhaps suitable for the transition metal complexes but of course without any direct support from e.s.r. or any other electronic spectral study, but for the non-transition metal complexes it seems less appropriate than the following formalism. In this approach, the metal atom is assumed to remain in its normal oxidation state, while the dipy groups are assumed to be reduced to radical anions, dipy\(^{\bullet}\), with the extra electrons occupying antibonding antibonding orbitals. When the number of unpaired electrons is found to be less than the number of dipy\(^{\bullet}\) groups, there is sufficient dipy\(^{\bullet}\) - dipy\(^{\bullet}\) interaction to cause coupling of spins. Such formulations are equally applicable to \(\alpha\)-phenanthroline complexes.

7. Heterocyclic Amines as Ligands—Some recent studies.

Amongst the nitrogen containing ligands, the complexes of pyridine and related compounds have been extensively studied and this is perhaps due to their ease of preparation and their relatively uncomplicated reaction mechanism. Beech on the basis of magnetic and spectral studies classified these complexes into three main types:

1) Discrete, octahedral \(ML_4X_2\) (L = pyridine or substituted pyridine, X = halogen or pseudo halogen). The X groups are axial.
11) Discrete, tetrahedral $ML_2X_2$

iii) Polymeric, octahedral $ML_2X_2$ with bridging $X$ groups.

Nelson and coworkers,$^{49a,49b}$ have studied the configurational equilibria: $ML_4X_2$ (octahedral) $\rightleftharpoons ML_2X_2$ (tetrahedral) ($L$ is pyridine or its alkyl substituted analogue), present both in the solution and in the solid state. It was found that the heat of reaction could not be correlated with the basicity but is dependent on the alkyl side chain in $L$. Thus, for the system $X = I$, $M = Ni^{2+}$, $L$ = pyridine or 3-picoline in chloroform solution, enthalpy changes were +23.8 and 21.7 kcal/mol, respectively. Since the 3-methyl substituent directs charge on the 2,4 and 6 positions of the pyridine ring, it was inferred that metal to ligand $\pi$ bonding must exist in these complexes and was inhibited by the presence of 3-substituent. Also the relative value of the equilibrium constant for the reaction with 3-methyl pyridine, compared to pyridine, was found to depend on $X$ and it was possible to arrange $X$ in order of $\pi$ bond (L to M) promotion.

$$\text{NCS}^- \ll \text{Cl}^- \ll \text{Br}^- \ll I^-$$

Irving and de Silva,$^{50}$ calculated the equilibrium constants for the reaction, $Ag^+ + 2HL^+ = AgL_2^+ + 2H^+$; $L$ = pyridine or substituted pyridine. Jaffe and Jacobs$^{51}$ observed that enhanced stability in these complexes is reflected in changes from $\sigma$ bonding to $\pi$ bonding. Mortimore et al.$^{52a,52b,52c}$ have used differential
enthalpic analysis to study the thermal decompositions of the complexes of the type $ML_nX_2$ ($M =$ first transition series metal, $L$=quinoline, pyridine or a methyl pyridine, $X$=Cl, Br or I). For the reaction of the type $ML_4X_2$ (octahedral) $\neq ML_2X_2$ (tetrahedral) $+ 2L$, similar conclusions to those of Nelson (loc.cit.) were reached regarding the extents of $\sigma$ and $\pi$ bondings.

Baxendale and George$^{53}$ studied the stepwise reaction of $2,2'$-dipyridyl with Fe(II) and found that the order of stepwise equilibrium constants normally follows: $K_1(1.6 \times 10^{-4}\text{mol}^{-1}\text{lit}^{-1}) > K_2(<10^5) > K_3(2 \times 10^7)$ and reversal in order for Fe(II)-dipy system is thought to be related to change in spin state of Fe(II)$^{54}$ which results in an increase stabilization of the more substituted species. The overall equilibrium constant for the analogous reaction of Fe(III) with $2,2'$-dipyridyl was found to be $1.6 \times 10^{12}$ mol$^{-3}$lit$^{-3}$. The smaller value compared with that obtained for the Fe(II) complex, is not unexpected since no stabilization due to change in spin state is anticipated.

Dale and Banks$^{55}$ summarised the equilibrium constants data between divalent metal ions (except Ag$^+$) and $o$-phenanthroline. For the stepwise reactions:

$$M(aq)^{n+} + o\text{-phen.} \rightleftharpoons M(o\text{-phen})_{aq}^{n+}$$
$$M(o\text{-phen})_{aq}^{n+} + o\text{-phen} \rightleftharpoons M(o\text{-phen})_{2aq}^{n+}$$
$$M(o\text{-phen})_{2aq}^{n+} + o\text{-phen} \rightleftharpoons M(o\text{-phen})_{3aq}^{n+}$$

(where $M$ is Ag, Mn, Cu, Zn or Cd, and n=1 (Ag) or 2 for other metals)
In most cases the order of the equilibrium constants was found to be \( K_1 > K_2 > K_3 \) except \( M = \text{Ag}^+ \) for which \( K_3 \) was not recorded and \( K_2 > K_1 \). This reversal in \( K_1 \) and \( K_2 \) implies that the substitution sequence is different for \( \text{Ag}^+ \) than for other metal ions. The substitution in this case may take place either through linear coordination\(^{56,57} \) in which \( \text{c-phenanthroline} \) acts as a unidentate ligand resulting in a linear \( N-\text{Ag-N} \) structure of enhanced stability or by bridging or polymerisation as observed for ethylene-diamine complexes of \( \text{Ag}(\text{I}) \) in the solid state.\(^{58} \)

8. **Linear Coordination of \( d^{10} \) Ion.**

The formation of linear coordinated species (1, 2, or 2) is well known in \( d^{10} \) configuration. The simple ionic theory, however, predicts that these large ions (\( \text{Ag}^+, \text{Au}^+, \text{Hg}^{2+}, \text{Cu}^+ \text{etc.} \)) should occur in higher coordinate species.\(^{64} \)

An obvious explanation for linear coordination in \( d^{10} \) ion involves \( s-p \) covalent bonding in preference to ionic bonding. This explanation has, however, got its exceptions, e.g., \( \text{Au}^{2+} \) and \( \text{Cd}^{2+} \) where the order of \( s-p \) separation is more or less the same.

On the other hand a strong tendency of linear distortion is always associated with small \( d-s \) separation (Table-I) with the result that extensive hybridization of \( d_{2s} \) and \( s \) orbitals is made possible in case of \( \text{Cu}^+, \text{Ag}^+, \text{Au}^+ \) and \( \text{Hg}^{2+} \) as against \( \text{Cd}^{2+}, \text{Au}^{2+} \) and \( \text{Tl}^{3+} \). According to Orgel,\(^{6} \) this is essentially because the mixing of \( d \) and \( s \) orbitals can lead to a charge distribution strongly favouring
a linear arrangement by removing charge from the region between
the ligand and the metal ion.56,57

TABLE I

Energies (e.v.) of lowest d⁹ state above the d¹⁰ state

<table>
<thead>
<tr>
<th>Element</th>
<th>Energy (e.v.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu⁺</td>
<td>2.7</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>9.7</td>
</tr>
<tr>
<td>Ag⁺</td>
<td>4.8</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>10.0</td>
</tr>
<tr>
<td>Au⁺</td>
<td>1.9</td>
</tr>
<tr>
<td>Hg²⁺</td>
<td>5.3</td>
</tr>
<tr>
<td>Tl³⁺</td>
<td>9.3</td>
</tr>
</tbody>
</table>

The mechanism of hybridisation of d₉² and s orbitals
resulting in linear coordination may be explained on considering
the fig. 1. The electron pair initially in the d₉² orbitals occupies
\( \psi_1 \sqrt{2} (d_{x^2} - s) \) hybridised orbital giving a circular region of
relatively high electron density, from which the ligands are
somewhat repelled and regions above and below this ring in which
the electron density is relatively low. Ligands are attracted to
these regions. By further mixing of \( \psi_2 \sqrt{2} (d_{x^2} + s) \) with the \( p_z \)
orbital, two hybrid orbitals suitable for forming a pair of
linear covalent bonds can be formed.

Fig. 1

(Cotton and Wilkinson 'Advanced Inorganic Chemistry'
9. Some Aspects of the Chemistry of Copper(I).

The copper is the only member of first transition series giving some stable monovalent compounds. This characteristic is attributed to the higher second ionization potential of copper in comparison to other members as evident from the ionization data given in the table II.

<table>
<thead>
<tr>
<th></th>
<th>Ca</th>
<th>Sc</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>First I.P. (eV)</td>
<td>6.11</td>
<td>6.56</td>
<td>6.83</td>
<td>6.74</td>
<td>6.76</td>
<td>7.43</td>
<td>7.90</td>
<td>7.86</td>
</tr>
<tr>
<td>Second I.P. (eV)</td>
<td>11.87</td>
<td>12.80</td>
<td>13.57</td>
<td>14.65</td>
<td>16.49</td>
<td>15.54</td>
<td>16.18</td>
<td>17.05</td>
</tr>
<tr>
<td>Ni</td>
<td>Cu</td>
<td>Zn</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>First I.P. (eV)</td>
<td>7.63</td>
<td>7.72</td>
<td>9.39</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Second I.P. (eV)</td>
<td>18.15</td>
<td>20.29</td>
<td>17.96</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Another criterion generally applicable to the phenomenon of the variable valencies in the transition metals, is the overall
energy changes occurred during the formation of the compound in a particular valency state. If the (endothermic) ionization energy is sufficiently compensated by the increased (exothermic) solvation energy or electrostatic lattice energy of the solid compound, that particular oxidation state may be favourable.

Copper(I) ion with a $3d^{10}$ configuration is colourless, insoluble, diamagnetic, and with zero ligand field stabilisation energy. The instability of Cu(I) is explained in terms of the following potential data:

$$\begin{align*}
\text{Cu}^+ + e^- &= \text{Cu}, \quad E^0 = 0.52V \\
\text{Cu}^{2+} + e^- &= \text{Cu}^+, \quad E^0 = 0.153V
\end{align*}$$

whence

$$\begin{align*}
\text{Cu} + \text{Cu}^{2+} = 2\text{Cu}^+, \quad E^0 = -0.37V; \quad k = \frac{(\text{Cu}^{2+})}{(\text{Cu}^+)^2} = \sim 10^6
\end{align*}$$

The relative stabilities of Cu(I) and Cu(II) will depend very strongly on the nature of anions or other ligands present, on the dielectric constant of the solution and on the nature of neighbouring atoms in a crystal. The fact that these factors will play important role will be exemplified in the discussion in the proceeding paragraphs.

The potential data indicate that copper(I) ion can exist in aqueous solutions in exceedingly low concentrations, and in fact the compound like CuCl, CuBr and CuCN do exist in stable state in water but decompose readily to cupric state due to higher solution and lattice energies of the copper(II) ions.
The equilibrium $2\text{Cu}^+ \rightleftharpoons \text{Cu} + \text{Cu}^{2+}$, can be displaced in either direction depending upon the nature of the anion or the ligand introduced and on the dielectric constants of the media. The equilibrium, $[\text{CuI}_2(\text{H}_2\text{O})_2]^{-} \rightleftharpoons [\text{CuI}_2(\text{H}_2\text{O})]_2^+ + e^-$, with a large negative $E^o$ value, favours a copper $^+\text{Cu}^+$ state in which iodide forms easily polarized strong covalent bonds. Similarly, in the equilibria:

$[\text{Cu(CN)}_2]^{-} = \text{Cu}^{2+} + 2\text{CN}^- + e^-$, $E^o = 1.1$, CN$^-$ favours covalent bond formation and Cu(I) state is favoured. On the other hand, anions that cannot give covalent bonds or bridging groups such as ClO$_4^-$ and SO$_4^{2-}$ or ligands having greater affinity for Cu(II) than Cu(I) or Cu(I)-L is less covalent than Cu(II)-L (L is a ligand) e.g., NH$_3$, ethylene-diamine, hydrazine etc., Cu(II) state is favourable.

Another approach perhaps more logical and convincing, regarding the stability of copper(I) complexes is based on the behaviour of Cu(I) ion as a soft acid. Cu(I) being a Lewis acid of large size and low oxidation state will prefer to bind large polarizable ligands such as $I^-$, $R_3P, R_3As$ etc. (soft bases). As stated by Chatt (loc.cit) in his $\kappa$ bonding theory that soft acids contain loosely held $d$ electrons which can form $\kappa$ bonds by donation to suitable ligands (soft bases). Thus there will always be tendency of copper(I) ions to form $d_\kappa - P_\kappa$ or $d_\kappa - d_\kappa$ bonds to ligand atoms with empty or vacant $d$ orbitals, e.g., N, S, P, As, I etc. In fact copper(I) forms stable complexes with phosphines, arsines,
thiourea, iodide and unsaturated ligands such as Cu, C_2H_2, C_2H_4, propylene, butylene, butadiene etc.

The formation of halo complexes of copper(I) is another characteristic associated with copper(I) halides. Copper(I) halides are highly insoluble but, however, may be made soluble in presence of the excess of halide ions. Sufficient amount of work has been done on the behaviour of copper(I) halides in alkali halide solutions. The compounds more extensively studied are cuprous chloride and cuprous bromide. The complex species like CuX^2_2, CuX^3_2, CuX^3_3 (X = Cl⁻, Br⁻) are found to exist in solutions. With the higher concentrations of halide ions the lower species such as CuX^2_3 form the main bulk. Recently, the behaviour of copper(I) iodide in acetone-sodium iodide medium was studied and the main species present in the solution was found to be CuI^2-. An interesting aspect related to the coordination chemistry of copper(I) is the lower coordination number exhibited by copper(I) complexes. In general, Cu⁺ ion usually forms complexes with a coordination number one or two (NH₃, halides, pyridine and substituted pyridines, CN⁻ etc.), less commonly with a coordination number of three (thiourea) and the examples of tetra coordinated copper(I) are not very common (tris phosphines, tris arsines, dipy etc.). The small coordination number in Cu(I) complexes is related to the characteristic of d^{10} ion with large size and low oxidation state favouring a linear coordination due to small d-s separation (Orgel, loc.cit). However, more interesting is the observation
that there is always a tendency for copper(I) ion to achieve its coordination maximum. There are numerous examples in literature to illustrate this characteristic of copper(I) complexes. The complex, \((C_2H_5)_3 As CuI\) in which the apparent coordination number is two, the molecular weight determination indicates it to be a four fold polymer \((Et_3 As CuI)_4\). The crystal structure of this complex consists of four copper atoms disposed at the species of a regular tetrahedron, in such a way that each copper atom is itself surrounded tetrahedrally by three iodine atoms (each shared with copper atoms) and an arsine molecule. Similarly, the compound \(CuI\, 2P\,(C_2H_5)_3\) described by Argulow is a tetramer with the following structure.

![Diagram](https://via.placeholder.com/150)

10. **Some Aspects of the Chemistry of Ni(II).**

The complex formation tendency of Ni(II) is well known. The main stereochemical species of the Ni(II) complexes may be described in terms of octahedral \((C,N=6,\, para-magnetic, \mu_{eff}=3.0-3.3)\), tetrahedral \((C,N=4,\, para-magnetic, \mu_{eff}=3.45-4.0)\) and square planar \((C,N=4,\, diamagnetic)\) structures. Pentacoordinate (diamagnetic) trigonal bipyramidal form is also known. All these
complexes have characteristic electronic spectra and which can be interpreted in terms of d orbitals splitting under a particular ligand field usually governed by the spectrochemical series, the series for the common ligands is: $\Gamma^- < Br^- < Cl^- < F^- < OH^- < C_2\text{O}_4^2- < H_2O < NCS^- < py^- < NH_3 < en < dipy^- < o-phen^- < NO_2^- < CN^-$ and is arranged according to the capacities of the ligands to cause splitting.\(^6\)

Considering the distortion of d\(^8\) system in a tetragonally distorted octahedral field bringing about a singlet-triplet spin state isomerism. The theoretical interpretation of this type of behaviour was given by Maki\(^6\) for a weak ligand field and by Liehr and Ballhausen\(^7\) for a strong ligand field.

The first convincing example of spin state isomerism was given by Carlin et al., while studying dichloro tetrakis (N,N-diethyl thiourea) Ni(II) complex.\(^7\) The complex is spin paired below 194\(^0\)K but attains partial magnetism reversibly as the temperature is raised. The corresponding Br\(^-\) and $\Gamma^-$ are diamagnetic at room temperature but Br\(^-\) becomes slightly paramagnetic at 373\(^0\)K. The relative abundance of the triplet state among the two halides is that predicted by Maki and Ballhausen, and Liehr treatments of Ni(II) in D\(_{4h}\) symmetry, since the separation between the singlet and triplet states is the least for Cl\(^-\) which lies closest in ligand field strength to the substituted thioureas. Several other examples of spin isomerism are provided by Ni(VPP)\(_2\) (NO\(_3\))\(_2\)\(^7\) (where VPP is $P(\text{Ph})_2\text{CH=CHP(\text{Ph})}_2$)
and Ni(TAAB)\(X_2\)^{73a,73b} (where TAAB is tetra benzo (b,j,n) 1,5,9,13-tetra azacyclohexadecane) complexes.

The presence of Ni(II) with two different stereochemistries in a unit cell of a complex molecule has been reported in a number of cases. The complexes exhibit two types of behaviours, one in which the metal ion has the same coordination and same set of attached ligands but different stereochemistries and other in which the metal ion produces two different coordination numbers and hence different stereochemistries within the unit cell.\(^7^4\)

Kilbourn, Powell and Derbyshire\(^7^5\) isolated two crystalline forms of the complex compound dibromo bis (benzyl diphenyl phosphine) Ni(II), one red and diamagnetic, the other green with two unpaired electrons (\(\mu_{\text{eff}}=2.7\) B.M.). On the basis of X-ray studies of green complex, they showed that there are 4-coordinated atoms in the unit cell, one Ni(P(Ph,CH)\(_2\) Br\(_2\)) is square planar and two Ni(P(Ph,CH)\(_2\) Ph\(_2\)\(_2\) Br\(_2\)) units are tetrahedral. When allowance was made for only two of the three Ni atoms being high spin, the moment of the tetrahedral Ni atoms was calculated to be 3.3 B.M., in good agreement with the values generally observed for nickel in pseudo tetrahedral environment. Since the square and tetrahedral structures of a complex differ chiefly in the angles subtended by ligand atoms at the metal atoms, Powell\(^7^5\) suggested the term interallogon (allos-different, gonia-angle). An example of the second type of isomerism is provided by the yellow form of the Lifschitzs compound, bis-(meso-stibene diamine)
Ni(II) dichloroacetate 2/3 C₂H₃OH, 4/3 H₂O. The magnetic, spectral and x-ray studies of the complex indicate a magnetic moment of 2.58 B.M. at room temperature and the unit cell contains both 6-coordinate and 4-coordinate Ni atoms in the ratio 2:1.⁷⁶a,⁷⁶b

A large number of Ni(II) complexes which are diamagnetic in the solid state are found to be paramagnetic when dissolved in a variety of solvents, without decomposition. Such a phenomenon was explained on the basis of solute-solvent interactions thus depending upon the character of the solvent. In most polar solvents, a strong ligated atom such as nitrogen or oxygen is present and this may exercise a moderate perturbation with a resultant change in the coordination number and spin state of a particular species.⁷⁷

Several diamagnetic bis(salicylaldimine) Ni(II) complexes were found to be fully paramagnetic (μ_eff=3.0-3.2 B.M) in pyridine solution, a phenomenon which Wills and Mellon⁷³ attributed to the formation of 6-coordinate pyridine adducts. Basolo and Matouš, were later on able to isolate the pyridine adducts. Similar behaviour was observed in water, py and acetonitrile for the nickel complexes of the macro-cyclic ligand.⁷⁹ It was suggested that the origin of paramagnetism in all these cases is solvent dependent and may be represented by the equilibria:

\[
\text{Solvent} + \text{planar (diamagnetic)} \rightleftharpoons \text{pseudo octahedral(paramagnetic)}
\]
Later studies particularly by Sacconi\textsuperscript{30,32a,32b} and Holm\textsuperscript{31} and their coworkers conclusively proved that solvent is not the necessary condition for the development of paramagnetism. Sacconi\textsuperscript{30} on the basis of dipole moment studies and Holm\textsuperscript{31} on electronic spectral grounds showed that bis-(N alkyl-salicylaldimine) Ni(II) complex when dissolved in inert solvents like benzene, no tetrahedral species are present in significant concentrations although the solution is paramagnetic. Sacconi and coworkers\textsuperscript{32a,32b} further observed that besides in solutions, paramagnetism also occurs in the molten state. On the basis of these detailed investigations they arrived at the conclusion that experimental evidence can only be accounted by the two models (i) molecular association (solute-solute interaction) and (ii) planar-tetrahedral equilibria.

The studies on Ni(II)-N-n-alkyl salicylaldimine complexes, Ni(II)-N-aryl substituted complexes\textsuperscript{38,83} and Ni(II)-β diketone complexes\textsuperscript{90,91} provide some of the best examples related to anomalous magnetic behaviour of Ni(II) complexes arises by solute-solute interaction. An early indication that the anomalous magnetic moment of bis(N-methyl salicyldimine) Ni(II) in solution might be due to molecular association was provided by the isolation of a coloured, paramagnetic (μ\textsubscript{eff}=3.2 B.M.) form of the complex by heating the diamagnetic form to 150-200°C\textsuperscript{83,84}. In contrast to diamagnetic isomers, the paramagnetic form was observed to have a very low solubility in organic solvents. This
suggested that 6-coordination is attained by the stacking of the planar units in a manner that the oxygen atoms of adjacent molecules interact axially with the metal ions.\textsuperscript{23,25,26} In terms of solute-solute interactions Ni(II)-n-alkyl salicylaldimine complexes have been studied to the greatest extent. The evidence for solute association was provided by the observations: simultaneous increase in magnetic moment with increasing concentration, n.m.r. contact shifts, molecular weight in chloroform and benzene as well as by spectral data.\textsuperscript{31} Solute association in solutions of the higher N-n-alkyl substituted analogues is apparently less, these being monomeric and diamagnetic at ordinary temperatures.\textsuperscript{37} N-methyl complex is infact the best example of solute-solute interaction model.

As stated above the main reasons for abandoning the mechanism involving the equilibria planar(diamagnetic) $\rightleftharpoons$ tetrahedral (paramagnetic) in solution were the paramagnetism shown by bis-(N-methyl salicylaldimine) Ni(II) in non-conducting solvents and absence of tetrahedral species. One great difficulty in regard to the conclusive recognition of the presence of planar tetrahedral equilibria for solutions of diamagnetic complexes for many years was the fact that the stereochemical species had not been characterised spectrally till 1959.\textsuperscript{92} However, with the isolation and characterisation of planar and tetrahedral forms of (benzylidiphenyl phosphine) Ni(II) halides and related complexes, the planar $\rightleftharpoons$ tetrahedral equilibria model was again revived.\textsuperscript{93-95}
These complexes exhibit moments between 0 and 2.9 B.M. in benzene solutions. Although the planar ♦ tetrahedral model failed to explain the paramagnetism of bis-(N-methyl salicylaldimine) complex in solution, however, it was found to be suitable for accounting some of the properties of N-aryl substituted salicylaldimines complexes and infact the paramagnetism of α-branched N-alkyl substituted complexes appears predominantly due to the presence of tetrahedral species. Holm and Chakravorty studied a series of bis-(o-hydroxynaphthalimine) nickel(II) complexes and observed their magnetic behaviour as a function of ring substituent and R (alkyl) group, both in solid and in solution. The anomalous moments in solution have been found to arise from a planar ♦ tetrahedral equilibria. Spin density calculations were performed and thermodynamic data were obtained by the use of n.m.r. contact shift methods. A number of similar examples of Ni(II) complexes with nitrogen and/or oxygen donor systems showing configurational equilibria involving planar ♦ tetrahedral and in a few cases octahedral ♦ square planar via 5-coordinate paramagnetic form, have been cited in recent chemical literature.

A brief survey of the recent chemistry of Ni(II) complexes described above leads undoubtly to believe that the anomalous magnetic behaviour of Ni(II) complexes is one of the most fascinating problems in coordination chemistry. The mechanism namely, spin state isomerism, solvent-solute and solute-solute
interactions and configurational equilibria are although quite capable to explain the observed facts but, however, they are subjected to change as new informations are uncovered or new concepts in this area of chemistry are developed.

11. **Chemistry of Palladium(II) Complexes**

At this stage it will be worthwhile to discuss briefly the stereochemistry of Pd(II) complexes and to give certain salient features for comparison to its lower analogue, Ni(II).

Palladium(II) and Nickel (II) have similar chemical characteristics. There is extensive tendency to form square planar complexes although Pd(II) is kinetically less labile than Ni(II) (Pt(II) is inert) as is evident from numerous kinetic data.\(^{101,102}\) Ni(II) is commonly six coordinate, Pd(II) like its Pt(II) analogue is commonly 4-coordinate square planar and only in special circumstances five and six coordinate species are formed. The fact that the tendency to form square planar complexes increases from Ni(II) to Pt(II) may be attributed to increase bond strength in the heavier metals due to the ability of their more extended orbitals \(d_{xy}, d_{xz}, d_{yz}\) to overlap better with ligand \(\pi\) orbitals.\(^{103}\)

Although Pd(II) species are predominantly square planar, there are indications that additional weaker bonds may be formed in the vacant octahedral sites. In solutions, the vacant sites...
may be occupied by solvent molecules, and in catalytic reactions of these metal complexes or in ligand displacement reactions, initial attack presumably occurs in the axial positions. The dimethyl glyoxime complex, \( \text{Pd(DMGH)}_2 \) is an example of axial interactions in crystalline compounds between stacked square units. Unlike Ni(II) complex, the Pd(II) complex dissolves in bases again indicating additional coordination:

\[ \text{Pd(DMGH)}_2 + \text{OH}^- = \left[ \text{Pd(DMGH)}_2 \text{OH}^- \right] \]

There is also evidence of interaction of certain atoms of ligands bound to the metal with axial positions. The crystalline complex, trans-\( \text{PdI}_2 \left( \text{PMe}_2\text{Ph}_2 \right) \) in which the \( \alpha \) hydrogen of the phenyl groups of the coordinated phosphine occupy axial positions, the trans axial position being occupied by an iodine atom of an adjacent molecule with the formation of quasi 7 coordination complex. Basolo and Saddy studied the substitution reactions of \( \left[ \text{Pd(Lt}_4\text{dien)} \text{Cl} \right]^+ \) with various reagents and found that the complex reacts rather slowly \( (t_f = 6 \text{ min}) \), an example of the steric hindrance, the ethyl groups block off the axial positions of the plane to give a quasi octahedral structure a position which is frequently observed in chloro ammine Co(III) substitution reactions whereas the corresponding reactions with unsubstituted \( \text{Pd(dien)} \text{Cl}^+ \) are exceedingly rapid.
Like Ni(II) but less frequently, complexes with a trigonal bipyramidal structure have been obtained for Pd(II). Tris (o-diphenyl arsinophenyl) arsine (QAS), for example, gives the salts of the type Pd(QAS)\(^{X^-}\) which act as 1:1 electrolyte in solution. 109 With bis (o-diphenyl arsinophenyl) phenyl arsine (TAS), a 5 coordinate complex Pd\(_2\)(TAS) is obtained but this dissociates in nitro benzene to give Pd(TAS).\(^{110}\)

12. Coordination Chemistry of Rare Earth Ions.

The coordination chemistry of rare earth metal ions is not extensively investigated while compared to d block transition metal ions, this is evident from the scanty references available in chemical literature. Prior to 1950, the only approach to the coordination chemistry of rare earths was in connection with the separation of lanthanide ions from each other. However, during the last ten years or so considerable interest has been shown in this area of coordination chemistry due to the advancements in analytical techniques and enrichment in the field of theoretical chemistry in general.

Compared to d-type transition metals, the lanthanides form a few complexes, and are obtained only with strong chelating agents containing highly electronegative donor atoms e.g., oxygen. So it is not surprising to find a majority of rare-earth complexes belonging to oxygen containing ligands. The fact that the electronic configuration does play an important role in the rare
earth complex formation can be exhibited by the following considerations.

The formation and stability of a coordination compound of a 3d metal ion are related to the participation of the d electrons in the metal-ligand bond through hybridisation of metal electronic orbitals and overlapping of the hybrid orbitals with the appropriate ligand orbitals. The 4f electrons present in rare earth metal ions are effectively shielded by electrons in subsequent 5s and 5p orbitals and thus unable to interact with ligand orbitals. If rare earth ligand bonding is to occur, the hybridisation must involve normally with unoccupied high energy 5d, 6s and 6p orbitals and hybridisation of this type can be expected only with strong coordinating ligands. Such type of bond formation should be highly electrostatic in character and the complex species formed by these cations (rare earth) should resemble more closely with those of alkaline earth metal ions, Ba\(^{2+}\), Ca\(^{2+}\) and Sr\(^{2+}\) rather than that derived from the d block transition metal ions.

The absence of significant interaction between ligand and 4f orbitals is supported by magnetic and spectral measurements. It has been observed that complexing groups have only nominal effects upon the magnitude of the permanent magnetic moments of the tripositive ions or upon the positions of their sharply defined, characteristic absorption bands in the ultraviolet and visible regions. Indirectly this
is evidence for the ionic model, as is also the absence of a bonding. On the other hand, the possibility of covalent interactions cannot be completely excluded.

The lanthanide ions, in any oxidation state are large (radii: 0.85-1.06) compared with those of transition elements (e.g., Cr$^{3+}$ and Fe$^{3+}$ with radii of 0.60-0.65Å) forming most stable complexes. Strongly electrostatic attractions between rare earth metal ions will, therefore, be small in comparison to d block transition metals, but will increase in magnitude from cation to cation for a given oxidation state as cation radius decreases, and for a given metal as cation charge increases. The said viewpoint is confirmed by the observations: (a) the relatively small overall stabilities of the known complex species (b) generalised increase in stability with decreasing size of positive cation for species containing a common ligand and (c) the increase in stability for a given ligand with cation charge (e.g., Ce$^{3+}$ to Ce$^{4+}$, Lu$^{2+}$ to Lu$^{3+}$).

Summing up the above factors it may be concluded that the rare earths have reduced tendency to form complexes, the situation is here comparable to that existing in alkaline earth metal chemistry, where possible coordinated bonds are not strong enough to cause the metal ion to leave the solvation layer and enter into the complex. The 'chelate effect' overcomes this deficiency as is evident from the study of stable complexes of rare earths where a large majority belongs to chelate complexes.
Chelating agents increase the free energy change of the reaction through an entropy effect, a common feature of all chelation processes. The fact that entropy effect is operative in rare earth metal chelate is substantiated by a number of thermodynamic measurements which show that in many cases the entropy contribution of the free energy change of the process is the determining factor and the enthalpy term is very small or even opposed to the formation of the complex.

A big majority of rare earth metals chelates are formed by chelating agents containing oxygen as a donor atom and in a few cases nitrogen donor is also found to be active. The chelates with \( \beta \) diketone series of ligands such as acetyl acetone, dibenzoyl methane and thionyl trifluoro acetone have been much studied, they have the stoichiometry \( M(\beta \text{ diketone})_3 \) and generally crystallized with solvents. The chelate species in these cases is usually inner complex type. The water soluble chelates formed by hydroxy acids, aminoacids and polyamine polycarboxylic acids are extensively reported. The latter give simultaneously more than a single metal chelate ring involving a given metal ion, are most stable and probably the best characterized species. Although most of the chelates contain tripositive rare earth metal ions but a significant number are also derived from Eu(II) and Ce(IV), the two tripositive ions that are most stable in aqueous solution. These complexes have 6-coordinated octahedral structures in which
coordination numbers greater than six, are also reported.

The tripositive rare earth ions have little tendency to form halocomplexes. The fluoro salts containing tetra positive Pr, Nd, Tb and Dy are of particular importance in exemplifying the stabilization of this oxidation state by highly negative charged F ions.

Due to the high positively charge character the lanthanides have little or no tendency to form complexes with bonding ligands. The absorption spectra of solutions of certain rare earth metal laurates in mesitylene have been interpreted as indicating some association of the cations with hydrocarbon through electrons supplied by the latter, but there is no confirmatory evidence. Similarly, complexes with o-phenanthroline and 2,2'-dipyridyl are also known such as [phen₂HCl (H₂O) Cl₂], [Phen₃M (SCN)₃] and [dipy₂M(H₂O)₆]. The cyclopentadiene gives salts cyclopentadienides such as [M (cp)₃] and [M (cp)₂]Cl₃.

There are numerous experimental evidences which indicate the formation of complex species in which the coordination is larger than six. Thus the solid compound, M(Br₃)₃(H₂O)₉ contains the grouping M(H₂O)₆³⁺, which has a trigonal prismatic geometry with the water molecules opposite the rectangular faces. The compound, M(SO₄)₃·9H₂O contains the grouping M(H₂O)₆⁶⁻, which amounts to two interpenetrating prisms and requires a coordination number of eight. The formation of M(diket)₄ as the piperidina salt requires a coordination number of at least eight. The ability
of certain complex species to add additional ligands e.g., to form \( M(\text{HEDTA}) \) \( ^{137} \) \( M(\text{NTA})^{138} \) \(^2 \) \( M(\text{HEDTA}) (OH^-) \) \(^{139,140} \) also indicate coordination numbers larger than six. The insolubility of some lanthanide tropolonate also suggests cross linkages leading to coordination number exceeding six \(^{141} \) Recent crystal structure studies indicate ten coordination in the compound \( M(\text{EDTA}) (H_2O)_4 \), \(^{3H_2O_{142,133} \), nine coordination in the ion \([La(\text{EDTA}) (H_2O)_3]^{142,133} \) eight and coordination in \([\text{Eu(aaoa}_4])^{143} \)

**Problem Under Investigation:**

The thesis deals with the syntheses, structural studies and behaviour in solution of some new complexes of transition metals.

The complexes synthesised are those of copper(I), nickel(II), palladium(II) and some rare earth metal ions with nitrogen and sulphur containing ligands. The nitrogen containing ligands include delocalised systems such as pyridine and substituted pyridines e.g., picolines, lutidines, quinoline, acridine etc. The potential \( \pi \)- acceptor ligands 2,2'-dipyridyl and o-phenanthroline have also been used in these studies. Amongst the sulphur containing ligands only neutral unidentate ligands, thiourea and substituted compounds e.g., isopropyl, benzyl, naphthyl, diphenyl, allyl and o-tolyl thioureas have been used for the present investigations. Some complexes of 2-mercapto-benzthiazole with copper (I) and rare earths have also been synthesised.
The main emphasis has been laid on the mixed ligand complexes of Cu$^+$, Ni$^{2+}$ and Pd$^{2+}$. Some of the systems in this field have not been sufficiently explored especially those of copper(I). The studies in solution have been carried out with these mixed ligand compounds and detailed mechanisms have been put forward.

The kinetic studies are based on the potentiometric and spectrophotometric measurements and wherever possible the stereochemical evidence has been provided by the synthesis/or the preparation, of a particular substituted complex by adopting various paths.

The structural aspects in these studies are limited to the investigations on the geometry and the bonding in these complexes.
REFERENCES:


39. (b) See reference 39a, pp. 745-746
39. (c) See reference 39a, pp. 755-756
40. (b) See reference 40a, pp. 144-145
43. S. Harzog and H. Taube, Angew Chem., 79, 469 (1953), and references therein.


56. See Ref., 39a, p. 1041.

57. See Ref., 39b, p. 66.


60. See Ref., 40a, p. 12.

61. See Ref., 39a, p. 895.


66. See Ref., 62, pp.150-151


68. See Ref., 38a, pp. 630-681.


77. See Ref., 74, p. 483
92. See Ref., 74, p. 491 and the references therein.
103. See Ref. 39a, pp. 712 - 713.
110. See Ref., 39a, p. 1034.


121. See Ref., 111, p. 27.


128. See Ref., III, p. 5.
133. See Ref., III, p. 18.