CHAPTER I

INTRODUCTION

Immensely exciting and monumental developments in coordination chemistry have taken place ever since Alfred Werner profounded his theory\(^1\) of coordination compounds in 1893. The advent of highly sophisticated physico-chemical techniques of very high precision and capability have led to the developments that have turned up fascinating ideas and materials. These have considerably enriched our understanding of the metal-ligand bond, their structure and stereochemistry of metal complexes, their stabilities, etc. The invention of new synthetic methods of importance, the increasing use of metal complexes commercially as catalysts, their involvement in vital biological processes such as oxygen transport and storage and electron transfer etc. have greatly contributed to the rapid developments in coordination chemistry. An increasingly large number of studies have also been devoted to the dynamics and mechanism of reaction of metal complexes. The classical applications of complex formation in analysis and other laboratory practices are refined and sophisticated to such a degree that it is now possible to monitor concentration of species at unbelievably low levels, viz. in the range of a fraction of a microgram per milliliter of solution based on several physico-chemical characteristics such as colour, catalytic activity etc. Indeed, such techniques are now extremely useful in monitoring hazardous metals, which are serious environmental pollutants.

Coordination compounds, because of their wide range of properties, find extensive use in everyday life. They play a vital role in analytical chemistry, in chemical industries and in biological processes. The complexes and complex formers have been in use in medicine since a long time; for example gold complexes are used in the treatments of tuberculosis (since 1917) and arthritis (since 1927). Some ligands are used to selectively extract metal ions from
biological tissues; several significant researches during the last 30 years have unequivocally proved the effective usefulness of metal complexes in biology, in the treatment of several diseases, including the dreadful diseases like cancer and for metal detoxification in the case of metal poisoning. The rapidly developing field of bio-inorganic chemistry in recent years, is centered on the presence of coordination complexes in living systems.3-6

Complexes find invaluable uses in agriculture, corrosion and chemical cleaning, detergents, electroplating, environmental problems, geosciences, metallurgy, oceanography etc. Some recent and exciting applications of metal complexes are found in the photolytic splitting of water producing hydrogen, a process which has an immense potential for generating a non-polluting fuel which may be an ultimate solution for saving the world from a severe crisis in the future due to non-availability of fossil fuels. Knowledge of the nature of metal-ligand bond provides a fundamental basis for understanding the behaviour of metal complexes.

Though in the early stages of development of coordination chemistry complexes of only a few metals like Pt, Co and Cr with coordination numbers four and six were considered, today complexes of nearly all the metals in the periodic table, with a range of coordination numbers from two to twelve in many oxidation states7 are synthesized and studied. Metals, which were once thought to be non-complex formers, are now known to form stable complexes with special types of ligands, such as the alkali metal complexes formed by crown ethers and cryptates. As such, now the coordination chemistry constitutes a major part of the Inorganic Chemistry curriculum in various universities. In accounting for the existence and describing the behaviour of such a wide range of complexes with widely differing properties and complicated patterns of structure and reactivity we need to resort to certain aspects of Physical Chemistry notably thermodynamics, electrode potentials, electronic structure of atoms, molecular bond theories and reaction kinetics.
Various aspects of transition metal complexes are very widely studied. The transition metals are characterized by their ability to form a wide range of coordination compounds in which the octahedral, tetrahedral and square-planar geometries are predominant. Based on this, several complexes of the Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pd(II) are characterized.

Cobalt exhibits various oxidation states ranging from +1 to +5. The most common oxidation states are +2 and +3. The coordination compounds of Co(II) exhibit diversity in coordination number, geometry, stability, lability and other aspects of their chemistry.

The chemistry of cobalt is associated with three different types of stereochemical configurations such as tetrahedral, octahedral, square-planar and trigonal bipyramidal. The tetragonal is a rare possible one. The different types of geometries are more often discussed in terms of magnetic and spectral data than on the basis of isomerism. Nicholls\textsuperscript{8} has reviewed biological importance of cobalt compounds.

Nickel exhibits various oxidation states ranging from +1 to +4. The most common oxidation state is +2 in which it has [Ar] 3d\textsuperscript{8} electronic configuration. Numerous interesting studies on Ni(II) complexes have been reported in the literature.\textsuperscript{(9-12)} Ni(II) complexes mainly exist in square-planar structures. These forms are capable of manifesting complicated equilibria that are dependent on the nature of the solvent, concentration and temperature.

Ni(II) can also form several pentadentate complexes. Five coordinate Ni(II) complexes with a trigonal bipyramidal\textsuperscript{13,14} and square pyramidal geometry have been characterized.\textsuperscript{15} Ni(II) chelates with distorted trigonal prismatic structures\textsuperscript{16}, have also been reported. One of the exciting features of Ni(II) complexes is their ability to change from one geometry to other. Nickel can also form complexes in +3 and +4 oxidation states but the number of such complexes is limited.
Copper having a single electron outside its completed 3rd shell, exhibits oxidation states of +1, +2 and +3. The dipositive state is the most important one for copper. The 3d⁹ configuration makes Cu(II) susceptible to John-Teller distortion when placed in an environment of cubic symmetry (i.e. regular octahedral or tetrahedral), and this has profound effect on its stereochemistries. In six-coordinated octahedral geometry, octahedron is severely distorted. The typical distortion is an elongation along a four-fold axis, so that there is a planar array of four short Cu-L bonds and two trans long bonds. This kind of distortion may lead to a situation where an octahedral geometry becomes indistinguishable from square planar coordination. Hence, the complexes of tetragonally distorted octahedral coordination and square planar coordination cannot be easily differentiated. All the hexa-coordinated Cu(II) complexes, structures of which have been established by X-ray technique, are found to be affected from tetragonal distortion due to John-Teller distortion. The predominant coordination number observed with Cu(II) are 4, 5 and 6, but variation of each structure occurs through bond length or bond angle distortion. Another major factor, which is significantly responsible for the distortion, is the steric effect. Copper is also known to form complexes in mono and trivalent states, which are not so common as bivalent copper. The compounds of copper find applications in Organic Chemistry for carrying out oxidations, coupling, halogenations, etc. reactions. Oxidation of phenol by copper-amine complexes provide a model for phenol-oxidizing enzymes. Copper is also found to play a significant role in biological processes. For instance, Cu(DMG)_2 shows some activity against cancer and shows increasing life span to the extent of 200-300 %. Binuclear Cu(II) complexes provide useful simple models for the study of the magnetic interactions of two unpaired d electrons, and models of biological copper systems.

Zinc is a constituent of enzyme carbonic anhydrase, which is involved in the conversion of CO₂ to carbonic acid in plants. It is also found in horse-liver alcohol dehydrogenase. Deficiency of zinc in animals result in stunted growth
and male sexual immaturity. The toxicity of zinc is very low. Zinc shows oxidation states of +1 and +2. Zinc(I) does not occur in the normal conditions, only spectroscopic species have been detected. Like mercury $\text{Zn}^{2+}$ exist.\textsuperscript{23} Zn(II) complexes are essentially diamagnetic due to filled $d^{10}$ configuration. The complexes of Zn(II) can be 4, 5 and 6 coordinated. It is seen that zinc forms invariably only tetrahedral complexes with coordination number 4. Five coordinated complexes either possess square pyramidal or trigonal bipyramidal structures. Complexes are octahedral when coordination number is 6. Many polymeric structures involving bridging groups are reported. Certain complexes show even coordination number 7. Most of the zinc is utilized in the form of alloy to prepare containers, as its toxicity is low.

The presence of cadmium in living organism is highly toxic. It has not been found as an essential trace element in biological system. It affects the kidney and liver. Cadmium shows +1 and +2 oxidation states. Cd(I) has been isolated in solid state in which it is present as $\text{Cd}^{2+}$. Cd(II) is well known to form a large variety of compounds and complexes. Complexes of cadmium are 4, 5 and 6 coordinated. Four coordinated complexes are tetrahedral. Five coordinated complexes are not found as frequently as in zinc. Six coordinated complexes have octahedral structure and are of common occurrence. Use of cadmium as an alloy metal is very less because of its high toxicity. Cadmium is used in control rods and shielding for nuclear reactors because of its high neutron-absorbing capacity.

Palladium is used in jewellery and in the formation of white alloy with gold, which serves as a substitute for platinum. It is also used as a catalyst in several hydrogenation reactions. Palladium exists in the +2 state in most of its compounds such as oxide, chloride, sulphate etc. The $\text{PdCl}_2$ exists as a linear polymer in the solid state. A number of complex compounds of divalent palladium are known. Amongst the various amine complexes, mention may be made of tetrammine palladium(II) chloride which is a pink solid and
dichlorodiammine palladium (II) which is a yellow solid and exists in -cis and -trans forms. The complexes of tetravalent palladium are not very stable. The square-planar palladium complexes are diamagnetic and octahedral complexes are paramagnetic.

A survey of literature reveals that though a lot of work has been done in the case of dithizone, its oxygen analogue diphenylcarbazone (DPC), though it was introduced as an analytical reagent much earlier than dithizone, has received very little attention. DPC is an orange-yellow solid with m.p. 127 °C. It is soluble in ethyl alcohol, chloroform, benzene etc., and is insoluble in water. The crystal and molecular structure of DPC were reported by Balton et al. This reagent was employed as a suitable analytical reagent in the detection of heavy metals, Hg, Cu, Fe, Cd, Mo, Cr, (25-28) Balt and Van Dalen (29,31) and Geering et al (32) showed that DPC acts as a monoprotic acid and it forms 1:2 (M:L) complexes with Ni(II), Zn(II), Pb(II), Cd(II), Fe(III) and Co(II). A few studies relating to DPC have been made mainly by spectrophotometric and solvent extraction techniques (29,30,33-41) where in the formation constants of a few metal complexes have been reported, mainly from our laboratory. The pKₐ values of these reagents and stability constants of some metal complexes and their thermodynamic parameters are also reported. (41,42) The formation of adducts (or mixed ligand complexes) is of very much analytical importance as it enhances the extractability of neutral metal chelates from organic phase upon the addition of nitrogen bases, a phenomenon known as synergism. The uses of DPC as an antibacterial agent against mycobacterium tuberculosis (43), as an indicator in complexometric determination of mercury (44) and Mo (45) and in the determination of Mn (46), Cu (47) and fatty acids (48) in blood serum are reported. DPC is also used to determine zinc and iron in zirem, ferbem and Zineb (49). DPC is also used in the preparation of etching solution (50), thermographic materials (51), copy writing and recording materials (52), and in the preparation of photochromic masks. Apart from this, there are so many reports...
on analytical and other uses of DPC based on its sensitivity towards metal ions, which have been published in the journals of different nature.

Siddalingaiah et al have reported, in a number of papers, the $pK_a$ values of several substituted diphenylcarbazones and their stability constants with the d-transition metals and their thermodynamic parameters.\(^{53-55}\) They have also synthesized several metal complexes (mainly transition metals) and have characterized them by elemental, magnetic and spectral analyses. The various substituted diphenylcarbazones and some of their metal complexes were tested \textit{in vitro} against human malignant cell lines\(^6\) and \textit{mycobacterium tuberculosis}. The studies on adduct formation of Ni(II) chelates of these substituted diphenylcarbazones with various heterocyclic nitrogen bases in chloroform to examine the influence of steric factor, basicity and resonance effect on adduct formation have been reported.\(^{57-59}\) Some of the metal complexes of substituted diphenylcarbazones were characterized by using Time Domain Reflectometry technique and dielectric measurements.\(^6\)

**PRESENT WORK**

In the present work the complexing behaviour of some of the substituted DPC towards transition metals such as cobalt, nickel, copper, zinc, cadmium and palladium have been investigated using elemental and spectral analyses.

The thesis comprises of 7 chapters including the introduction of the work carried out in the present investigation.

The experimental technique such as synthesis and purification of DPC derivatives and their metal complexes, instrumentation and analyses of the DPC derivatives and their metal complexes, are presented in chapter (II).

The characterization of DPC derivatives and their metal complexes by elemental and spectral analyses are reported in chapter (III). The chapter IV deals with thermogravimetric studies. The data on decomposition kinetics are
reported for some selected metal complexes. The chapter V deals with the Cyclic Voltammetric studies wherein the electrochemical investigation of Cu(II) complexes of substituted diphenylcarbazones are reported. The ground state and excited state dipole moments are presented in chapter VI. The antimicrobial and the pharmacological activities of the compounds synthesized for the present investigations are given in chapter VII on biological studies.
References


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