CHAPTER-I

INTRODUCTION

SCOPE

&

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CHAPTER-I

1. A. INTRODUCTION:-

The development of chemistry and in turn co-ordination chemistry was hampered by the idea of vital force theory which attempts to fit into the imperfect valency theories. But co-ordination chemistry makes clear distinction between valency and co-ordination number and prove useful in the development of inorganic chemistry. Alfred Werner’s co-ordination theory in (1893) paved way for the present development. He showed that factor determining the structure of co-ordination compounds was not the valency of the central metal atom, but the number of groups of any kind attached directly to it. i.e. it’s co-ordination number. Any groups over and above these must be outside the co-ordination sphere of the central atom and exist as ions, attached only by electrostatic forces. Latter he resolved certain co-ordination compounds into optical isomers and was able to demonstrate in the classical manner that the co-ordination compounds had the shapes.

Werner’s ideas and the earlier valency theories of inorganic and organic chemistry were finally accepted by G.N.Lewis in the electronic theory of valency, which was extensively applied to co-ordination chemistry by N.V. Sidgwick.

Co-ordination chemistry for its full development needed the methods of physical, theoretical and organic chemistry. The theories of chemical bonding, especially as developed by L. Pauling and the theories and methods of physical chemistry had reached the stage where they could be fruitfully applied to problems on co-ordination chemistry. Pauling’s principles achieved success in explaining stereochemistry, magnetic behavior and some other physical and chemical properties but it did not function well in ascribing the charge transfer
from the site of ligand donor atom towards the metal ion and the formation of II - bond. The Pauling’s principle was successful because of back donation of electron density from the metal atom to vacant orbitals of the ligand.

The limitations of Pauling’s Valance Bond Theory were subsequently removed by crystal field theory, Ligand Field Theory and Molecular orbital Theory. The crystal Field Theory was modified by Van Vleck’s Ligand Field Theory which explains the covalent nature of metal ligand bonds.

The interaction between metal and ligands can be explained in terms of molecular orbitals formed by overlapping of ligand and metal orbitals. As a whole these theories are equally important for several aspects of co-ordination compounds like synthesis, characterization, stability, thermodynamics, and stereochemistry, magnetic and spectral properties.

The ultraviolet and visible spectra provide an experimental basis for the application of crystal Field Theory in co-ordination chemistry and all spectral data proves a great value in the structural analysis. The magneto chemistry has also its great importance in the study of transitional metal complexes. As the search for complex compounds continues we try to solve the puzzle and frame new laws in this multifaceted discipline.

B. SCOPE

Complex chemistry, with the synthesis of new ligands and a large number of complex compounds has captivated the imagination of the whole scientific community. Their vast and extensive applications in several fields have brought the attention of many eminent chemists. Following are the few important applications in a variety of disciplines.
1. METALLURGY

The metal extraction process from their purified ores depends upon their ability to form coordination compounds with various ligands. This principle has been widely used to separate gold, beryllium, silver, nickel, cobalt and copper from their ores as amine complexes by using aqueous ammonia as solvent. The selective precipitation process is applied for the separation of niobium and tantalum, when these two metals are isolated by preferential hydrolysis of their fluoride complexes.

2. ORGANOMETALLICS

The organometallic compounds like cyclopentatriene, orene complexes, trophylum complexes, non-aromatic olefin and acetylene complexes are enormously used in chemistry. Some of the complexes like zinc dithiocarbamates are served as accelerators in the vulcanization of rubber. Alumino siloxanes are used because of their thermal and hydrolytic stability.

3. SEQUESTERING (Water Softening)

Ethylene diamine tetraacetic acid (EDTA$_4$) has been used for softening water which does a lot of harm in industrial boilers and other equipments by forming a scale between them. Ethylene diamine tetracetic acid is added to the boilers in which EDTA$^{-4}$ ion forms water soluble chelated complex ion, [M$^{2+}$ (EDTA)]$^{-2}$ where M = Ca$^{2+}$ and Mg$^{2+}$ion present in hard water and thus, these ions are removed.

4. POLYMERS

Certain polymers are commercially important because they are used to make plastic, fibers and film articles of different types. In order to form polymers of high molecular weight and well defined structures,
the combination of titaniumtrichlorides and triethyl aluminium brings about the polymerization of organic compounds having carbon-carbon double bonds under mild conditions.

Some of the polymeric ethylenediamine, bis (acetylacetone) and bis (thiopicolylamidato) metal\textsuperscript{II} complexes of Cu, Zn and Ni have been reported to have thermal stability and resistance to attack by organic compounds due to co-ordination of the metal ions.

5. INHIBITION AND POLSONING

The inhibition actions of the enzymes for certain ligands co-ordinate to an active centre in an enzyme and thus prevent co-ordination by the substrate. The activity of the enzyme is destroyed by the co-ordination of the azo enzyme to metal like Hg\textsuperscript{2+} ion. Azide ion inhibits the action of carbonic acid anhydrase to a moderate extent and as little as 4x10\textsuperscript{-6}M cyanide or hydrogen sulphide inhibits the enzymatic activity up to 85%.

6. AGRICULTURE

Some of the synthetic complex compounds are used to protect the agricultural products in the crop field. The Te, Fe, Mn, Zn – dithiocarbamates are used as agricultural fungicides. The compounds having B-O-Hg and B-O-Sn type of linkages have been proved to be efficacious against agricultural bacteria. The toxic effect of silicon moiety has got special recognition in the form of (CH\textsubscript{3})\textsubscript{3} Si-as it provides solubility in non-polar solvent and allows easier penetration across the hydrophilic membrane.

7. PHOTOGRAPHY

After the exposure of a photographic plate the unwanted residual silver halide was found that should be removed in the form of soluble silver
thiocyanate complex. Macrocyclic metal chelates of Co\textsuperscript{II}, Ni\textsuperscript{II}, Mn\textsuperscript{II}, Cd\textsuperscript{II}, Pt\textsuperscript{II} and Cu\textsuperscript{II} serve as photoconductors.

8. **RAYON INDUSTRY**

   The copper amine complex ion in solution called Schweitzer’s solution, dissolves cellulose and is used in the manufacture of rayon.

9. **FOOD PRESERVATION**

   Fruit juices and many other foodstuffs are preserved by the addition of EDTA and numerous other chelating agents.

10. **CHEMICAL ANALYSIS**

    The complex compounds are enormously used for certain chemical analysis purpose, viz,

    (a) Separation and purification of metal salts, lanthanides and actinides by simple estimation and ion-exchange methods and methods involving EDTA, versene, sequestrene nullapon and trilon etc. as industrial chelating agents.

    (b) Chelating ligands find a number of applications as reagents and masking agents in various titrimetric, spectrophotometric, chromatographic, polarographic and electrophoretic methods of evaluation.

    (c) Separation of radio-active metals by using chelating agent in connection with cation exchange and solvent extraction processes.

11. **CATALYSTS**

    Titanium-aluminium metals are used as catalyst in Ziegler-Natta process, originated from German and Italian chemists, in order to manufacture super quality polyethylene industry. Secondly, oxoreaction process utilizes octacarbonyl (Co\textsubscript{2} (Co)\textsubscript{8} and water gas to make numerous alcohols from olefins.
12. **DYES**

At present, metal complexes having azodyes of aromatic and heterocyclic amines are being significantly applied in pharmacology, leather technology and food stuff technology.

The possession of one or more donor atom like N, O and S bonding with the heterocyclic intermediates like pyrrole, pyridine, thiophene, imidazole, azine pyrimidine, oxazole, thiazole, thiazine, triazine, carbazole etc. are capable enough to form metal complexes in the variety of structures and uses.

13. **PHTHALOCYANINES**

The phthalocyanine compounds have been greatly used as compounds for the biological porphyrins. The intense coloured metal complexes are of great commercial values as dyes and pigments. The phthalocyanines are used as insecticidal and antifungal reagent because of their smaller size.

14. **PHARMACOLOGICAL ACTIVITY**

Cis-[Pt (NH$_3$)$_2$Cl$_2$] complex is used as antitumor agent in the treatment of cancer. Also few metal complexes of thisemicarbazone ligands posses anticancer properties and they are more carcinostatic than the free ligands. Amino halides and amino acids with various metals have been successfully used against carcinoma. The antibacterial activity of isonicotinic acid hydrazide is potentiated by copper$^{II}$ (Albert 1953, crfaigental1955). The antibacterial action of oxine is increased many fold by ion (III) chelates.

15. **BIOINORGANICS**

The role of metal complexes in biological system is indispensable. Certain enzymes, which play a significant role in regulating biological processes, are metal complexes. For example, a hydrolytic enzyme serves useful purpose in digestion, carboxy peptidase contains zinc atom co-ordinated to
several amino acid residues of the protein. The other enzymes catalase, very efficient catalyst for the decomposition of H₂O₂, contains iron prophyrin complexes. Again chlorophyll (a magnesium porphyin complex) and vitamine-B₁₂, a complex of cobalt with a macro cyclic ligand are co-ordination compounds, equally important in biological processes.

C. OBJECTIVES

The metal complexes reached its highest peak because of varied application. Chalcogens, azodyes and schiff bases have been immensely indispensable for the pharmacological intermediate for the preparation of broad spectrum chemotherapeutic drugs. Synthetic chemists have been inspired to prepare new type of azodyes, Schiff bases by the investigation of antibacterial, antifungal, antiseptic, herbicidal, anticancerial and pesticidal properties. The new avenues in investigating the application side are left for the future scholars to explore and make it sound and complete.

The main objective of the present investigation is to adopt various preparative techniques for the isolation of complexes from active azodye ligands and to establish the most probable structure of the complexes. The different physical methods of investigation have been used for the confirmation of feasible stereochemistry of the complexes. However, it is left to the future investigators or contemporary researchers to be more devoted to the application side to make the field by large assignable and concrete.

The multidentate azodyes reported here for the first time behave as bidentate, ligands having N-O donor atoms, bis-bidentate (tetratdentate) ligands having O-O-N-N donor atoms, bis-tridentate (hexadentate) ligands having O-O-N-N-O-O donor atoms, and bis-tetratdentate (octadentate) ligands having donor atoms.
By using the above multidonor azodyes as ligands, a good number of interesting monomeric and polymeric complex compounds have been isolated. The newly synthesized complex compounds are then analyzed to establish the composition by using various physico-chemical techniques usually adopted for structural diagnosis. The physico-chemical and biological methods undertaken in the present work are as follows.

(a) Molar conductance
(b) Magnetic susceptibility
(c) Infrared spectra
(d) Electronic spectra
(e) $^1$H n.m.r. spectra
(f) E.S.R. spectra
(g) Atomic absorption spectra
(h) XRD study
(i) Antibacterial and Antifungal study