ABSTRACT

Coordination chemistry encompasses a great diversity of substances and phenomena. It deals with the study of the metal–ligand interaction, synthesis, isolation and characterization of the metal complexes. In a brief period of about past three decades of growth in modern chemical sciences, no other field has received as much attention as the study of coordination compounds, due to emerging applications in biology and industry.

Chemistry of metal complexes has progressed enormously perhaps because of their possible applications in the thrust areas like biotechnology, nanotechnology and material science. Many of the metal complexes are formed with the organic ligands containing nitrogen and oxygen donor atoms. The central metal in these complexes act as active site and thereby successfully mediate and catalyse the chemical reaction. Association of a metal ion with an organic ligand through a coordinate bond changes drastically the properties of ligand or metal ion alone. The design and synthesis of metal chelated multidentate Schiff bases have received attention because of recent development of supramolecular chemistry, where ligand geometry and coordination propensity of the metal ion play a significant role.

Coordination compounds are known to play a vital role in the field of medicine. The cis-platin and carboplatin work as anticancer agents. The metal-chelates may exhibit antitumor, antiviral and antimalarial activities which are
reported to be due to chelation. The discovery of such compounds and other chelating agents capable of eliminating excessive intake of metal ions from the human body, have made important contribution in chelation therapy.

Study of mixed ligand chelates give an insight into the interactions between ligand –ligand and metal ligand coordination compounds. Homogeneous and heterogeneous catalysis is another significant area where metal-chelates may perform wonderful conversion and synthesis. Thus the chemistry of coordination compounds has become a bridge to combine closely and logically inorganic, organic and theoretical chemistry as the science dealing with the structure and properties of the matter. The phenomenon of chelation helps in stabilizing the free ligands and metal ions.

Present studies covers synthesis, characterization and antimicrobial studies of some ligands (Schiff bases) and their chelats with some 3d- transition metals viz. Ni(II), Cu(II).

The following Schiff base ligand have been synthesized viz. Methyl isobutylketone- nicotinamide (MKN), 2-Hydroxyacetophenone- nicotinamide (HAN), 2-Hydroxyacetophenone- isonicotinic acid hydrazide (HINH), Methyl isobutylketone– 2-amino- 4-chlorophenol (MAP), Furfurylidene-3, 4-dichloroaniline (FCA), 4-Dimethylamino- benzylidene-3, 4-dichloro-aniline (DCA), 4-Dimethylamino- benzylidene– 3-chloro-4- fluoro-aniline (DFA), 2-Pyridine carboxylidene-isonicotinic acid hydrazide (PINH), 2-Pyridine carboxylidene- 4-amino benzoic acid (PAB).
The synthesized complexes have been analysed and characterized on the basis of elemental analysis, molar conductance, magnetic measurements, infrared and electronic absorption spectroscopy. In all, eighteen complexes have been synthesized and characterized.

Five of Copper (II) complexes have been studied by ESR. Some Schiff base ligands and their complexes have been screened for their possible antimicrobial properties. Five complexes have been studied by TGA for their non-isothermal degradation behaviour. X-ray diffractogram of three complexes have been recorded and studied. Non- isothermal solid state degradation based kinetic parameters ($E^*, Z, \Delta S^*$) of the relevant Schiff base complexes have also been calculated by Coats-Redfern (C-R) and Pilyan-Novikova (P-N) methods. FAB mass of only three complexes could be done as representative case. Ligand field parameters have also been evaluated for some of the Ni(II) and Cu(II) complexes. To record optical behaviour polarimetric studies of all the Schiff bases and their metal complexes have been done. The results of the above investigation have been presented in the form of thesis entitled “SYNTHESIS AND PHYSICO-CHEMICAL INVESTIGATION ON SOME 3d-METAL COMPLEXES”. The description in the thesis have been divided into five main chapter.
CHAPTER - I

This chapter has further been divided into three sections.

Section - 1

This section is a brief historical review of the background introduction of complexes and coordination theories.

Section - 2

It gives an introductory idea about various physico-chemical methods viz. magnetic, conductance, electronic absorption, infrared, ESR spectroscopy, TGA and X-ray diffraction, which have been employed for characterization of complexes during present studies.

Section - 3

This section describes the significance of metal ions, various ligands and complexes.

CHAPTER - II

This chapter is again divided into three sections.

Section - 1

This section covers the general introduction and brief historical review of Schiff bases and their complexes.

Section - 2

This section deals with the relevant literature survey of various ligands and their metal complexes.
Section - 3

It gives a brief description of the work and systems undertaken for present studies.

CHAPTER - III

This chapter has mainly been divided into two sections.

Section - 1

This section covers the synthetic characterizational and experimental aspects of all the 18 Schiff bases (ligands) and their metal complexes.

Synthesis of Schiff bases (Ligands)

The ligand (Schiff bases) have been synthesized by mixing the methanolic solution of the aldehyde/ketone (0.01mole) with methanolic solution of amine (0.01mole) in 1:1 ratio. The reaction mixture was then refluxed on a water bath for about 4-6 hours. The condensation product was filtered, thoroughly washed with ethanol and ether and dried under reduced pressure over anhydrous CaCl₂. The purity of the synthesized compounds was monitored by TLC using silica gel G.

Preparation of the Metal Complexes

The metal complexes have been prepared by adding the methanolic solution of the appropriate metal salts MCl₂ × H₂O (0.01mole) to the methanolic solution of Schiff base (0.01 or 0.02mole) in 1:1 or 1:2 ratio and the resulting mixture was then refluxed on a water bath for about 6-10 hours. A coloured product appears on cooling the solution. It was filtered, washed and dried under reduced pressure over anhydrous CaCl₂ in a dessicator and later in an electric oven.
Section - 2

This section contains account of the experimental data relating to the microanalysis, magnetic, spectral and thermal studies. (in Tabular form.)

CHAPTER - IV

This chapter has further been divided into three sections.

Section -1

This section contains the discussion relating to structural elucidation of all the synthesized ligand (Schiff bases) and their metal complexes on the basis of various physico-chemical characterization studies.

Section - 2

This section covers the reactivity of the metal complexes against aquo, hydroxо, amine, thiocyanato, oxalato ligands and polarimetric optical studies of the synthesized Schiff bases and their metal complexes. The measurements have been done in methanol/ethanol. These investigations provide useful information about their substitution pattern and optical behaviour.

Section – 3

Accounts of ESR studies of five Copper(II) complexes have been discussed.

CHAPTER - V

This chapter has been divided into three sections.

Section –1

This section deals the general introduction and discussion of antimicrobial activities in the context of present studies. The antibacterial and antifungal
activities of the synthesized selected compounds (7,9,10,12) have been tested by Agar well diffusion method on the human pathogenic bacteria viz Escherichia coli, Staphylococcus aureus, Streptococcus fecalis and the fungi viz Aspergillus niger and Trichoderma polysporum. The results have been interpreted in the light of role of chelation in biological activity.

Section - 2

It gives the introductory theoretical account and discussion relating to solid-state non-isothermal decomposition kinetics. TGA plots and kinetic parameters of some complexes have also been discussed.

Section - 3

This takes into account an introduction and discussion of X-ray powder diffraction data of some Schiff base metal complexes.

CONCLUSION

Studies made in present context are focussed mainly on structure elucidation of Ni(II) and Cu(II) complexes. Ni(II) and Cu(II) –ONO, N₂, NO donor complexes have been synthesized and characterized by elemental analysis, molar conductance, magnetic measurement, thermal, UV-VIS, ESR, IR spectroscopic and XRD powder method. The proposed geometry for the Ni (II) and Cu (II) complexes are square planar or octahedral. The reactivity and substitution behaviour of the synthesized complexes against aquo, amine, chloro, hydroxo and thiocynato ligands have been studied. Polarimetric studies reflect optical behaviour of the Schiff bases and their metal complexes. Some of the
Schiff bases and their Cu(II) complexes act as antimicrobial agents. The Schiff base transition metal complexes may be of attractive oxidation catalyst for a variety of organic substrates because of their cheap and easy synthesis and their chemical and thermal stability; thus, may be of great academic and commercial interest.