ABSTRACT

The Chemistry of Co-ordination compounds embraces the study of metal ligand interaction and formation of complex in solution as well as their isolation and characterization in the solid phase. Metal complexes of Schiff bases have played a central role in the development of coordination chemistry and are known over a century for their increasing use as biochemical, industrial and antimicrobial agents. Thus the coordination chemistry has become the most obvious crossroad between organic, inorganic and theoretical chemistry. This also deals with the intrinsically interesting compounds having intellectual challenge because of their structural problems.

Metal complex chemistry has become now an exciting field of research. Many of these metal complexes are formed through organic ligands containing nitrogen, oxygen or sulphur as donor atoms. Among nitrogen donors, Schiff bases have been used as ligands for a large number of transition metals. The coordination compounds find a large number of applications though they have yet to be explored for variety of uses and structures in depth. The complex compounds are of special significance in the chemistry of transition metals because of their academic and economic importance.

The phenomenon of chelation helps in stabilizing the free ligands and metal ions. Present studies covers synthesis and characterization of some ligands viz. Schiff bases and their chelates with some 3d-transition metals.
The following Schiff bases (ligands) have been synthesized viz. 4-Chlorobenzylidene-2-aminothiazole (CAT), 4-Chloro-benzylidene-2,6-dichloro-4-nitroaniline (CDN), 2-Nitrobenzylidene-4-amino acetanilide (NAA), 2-Nitrobenzylidene-2-aminothiazole (NAT) and 3-Nitrobenzylidene-thioacetamide (NTA). The above Schiff bases were reacted with Co(II)-, Ni(II)- and Cu(II)- chlorides in order to get various Schiff base-metal complexes (Table-1).

The synthesized complexes have been analysed and characterized on the basis of elemental analysis, molar conductance, magnetic measurements, infrared and UV-VIS spectroscopy. Five of the copper (II) complexes have been studied for their ESR properties. Some ligands and their complexes have been screened for their antimicrobial activities. Five Schiff base-complexes are studied by thermogravimetric analysis and four Schiff base- complexes are studied by X-ray powder diffraction. Non-isothermal solid-state degradation based, Kinetic parameters (E*,Z,ΔS*) of the relevant Schiff base complexes have also been calculated by Coats-Redfern (C-R) and Piloyan-Novikova (P-N) methods. Ligand field parameters have also been evaluated for some of the Schiff base Co(II), Ni(II) and Cu(II) complexes.

Ultrasonic studies of four Schiff bases and their metal complexes have also been done.

The results of the above investigation will be presented in the form of thesis entitled "SYNTHESIS, PHYSICO-CHEMICAL AND ANTIMICROBIAL STUDIES OF SOME ORGANIC LIGANDS AND THEIR METAL COMPLEXES".
The description in the thesis have been divided into five main chapters.

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 co-ordination theories.

Section 2: It gives an introductory idea about various physico-chemical methods, viz. magnetic, conductance, electronic, infrared and ESR spectroscopy, TGA and X-ray diffraction; which have been employed for characterization of complexes during present studies. Account of Ultrasonic studies have also been given.

Section 3: This section describes the significance of metal ions, various ligands and complexes.

CHAPTER – II

This chapter is again divided into two sections.

Section 1: This section covers the general introduction and relevant literature survey of the Schiff base-metal complexes.

Section 2: 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 and characterizational experimental aspects of all the fifteen Schiff base-metal complexes.
Synthesis of Schiff bases (Ligands)

The ligands (Schiff bases) have been synthesized by adding the methanolic solution of the aldehydes -CHO (0.01 mole) to the amines -NH₂ (0.01 mole) in 1:1 ratio. The reaction mixture was then refluxed on a water bath for about 2-6 hours. The condensation product was washed and recrystallized, dried and characterized. The purity of the synthesized compounds have been monitored by T.L.C. & M.P.

Preparation of the metal complexes

The metal complexes have been prepared by adding the methanolic solution of the appropriate metal salts, MCl₂.xH₂O (0.01 mole) to the alcoholic solution of Schiff base (0.01 or 0.02 mole) in 1:1 or 1:2 ratio and the resulting mixture was then refluxed on a water bath for about 2-7 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 two sections.

Section 1: This section contains the discussion relating to structural elucidation of all the synthesised ligands (Schiff bases) and their metal complexes on the basis of various physico-chemical characterization studies.
Section 2: Account of ESR studies of five copper (II) complexes have been discussed.

CHAPTER V

This chapter has been divided into four 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 have been tested by filter paper disc method / pouring method on the human pathogenic bacteria viz. Escheria coli, Solmonella typhi and Bacillus subtilis and the fungi viz. Fusarium oxysporum, Aspergillus niger and Candida albicans. 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 the same 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.

Section 4: This section deals about the physico-chemical behaviour of these complexes in solution using techniques; Ultrasonic velocity and density. The measurements have been made in non-aqueous medium. With the help of these data, a number of acoustical parameters have been calculate such as; adiabatic compressibility, apparent molar volume, molar sound velocity, inter molecular free length and apparent molar compressibility. These parameters provide useful information regarding solute metal ions/ligands/complex ions interaction in solvent (methanol).
The effect of metal ion on such solute-solvent interaction may be recorded in the form of change in volume of activations and mechanism of ligand exchange etc. The parameters thus derived may be useful for understanding the associated phenomenon viz. kinetics, conformational properties and mechanism of ligand exchange, in coordination chemistry.