Summary

Metal complexes of a wide variety of organic ligands have significantly contributed to the development of modern coordination chemistry. Among the forerunners of organic ligands, are the heterocyclic compounds and their derivatives, with a particular reference to Schiff bases. These derivatives and their metal complexes have received much attention by researchers mainly because of their synthetic feasibility, structural diversity, bonding variability, catalytic capability and varied bioactivity.

The literature survey reveals that sulfonamides, hydrazides and pyrazinamides and their derivatives have received attention as complexing agents. In addition, significant chelating abilities could be developed in these systems by introducing suitable substituents in the heterocyclic ring or benzene ring and further derivatizing them by reaction with appropriate moiety. Furthermore, these compounds have a wide range of applications in pharmacology, bacteriology and mycology. The biological activity of an organic compound having potential donor sites is often attributed to its ability to chelate metal ions present in the biosystem; in many cases, the metal ion association exerts a synergistic effect on the activity of the free ligand.

Considering the importance associated with this class of compounds, the author has considered it worthwhile to undertake the synthesis and characterization of metal complexes of Schiff bases derived from the systems aforementioned. Thus, the present thesis deals with the preparation and characterization of the ligand systems namely

4-((2-hydroxybenzylidene)amino)benzenesulfonamide (HBABS),

4-((furan-2-ylmethylene)amino)benzenesulfonamide (FMABS),

4-((thiophen-2- ylmethylene)amino)benzenesulfonamide (TMABS),

N-(thiophen-2-ylmethylidene)- pyridine-4-carbohydrazide (TMPCH) and

N-(thiophen-2-ylmethylidene)-pyrazine-2-carboxamide (TMPCA).

and their Fe(III), Ru(III), Co(II), Ni(II), Cu(II), Pd(II), Zn(II), Cd(II) and Hg(II) complexes on the basis of elemental analysis, conductance, thermal, magnetic and infrared, electronic, ^{1}H-NMR, mass and electron spin resonance spectral data. The work incorporated in the thesis also includes the results of investigations on the biological activity of the ligands: TMABS, FMABS and TMPCA and their Fe, Ru, Pd, Zn and Hg complexes against the two gram positive bacterial strains: *Basillus Subtillus*, *Staphylococcus Aurus* and two gram negative bacterial strains: *Escherichia coli*, *Salmonella typhi*, and two fungal strains: *Aspergillus niger and Penicillium rubrum* wherein the zone of inhibition was measured.

The contents of the thesis are presented in six chapters.

Chapter I is on introduction which begins with a brief account of the general aspects of the ligand systems highlighting their importance. This is followed in Chapter II by a survey of the literature on the synthesis and characterization of the metal complexes of substituted sulfonamide, hydrazide and pyrazinamide derivatives. The objectives of the present work and the systems investigated are stated in chapter III.

Procedural details concerning the preparation of the ligands and their metal complexes and a brief description of the instruments employed in the present investigations and the experimental details are given in Chapter IV.

Chapter V deals with the characterization of the ligand systems and the structural investigations of the metal complexes prepared.

It is divided in to four sections as fallows.

A. Characterization of the ligands

B. Characterization of the Fe(III), Ru(III), Co(II), Ni(II), Cu(II), Pd(II), Zn(II), Cd(II) and Hg(II) complexes of HBABS, FMABS and TMABS

C. Characterization of the Fe(III), Ru(III), Co(II), Ni(II), Cu(II), Pd(II), Zn(II), Cd(II) and Hg(II) complexes of TMPCH

D. Characterization of the Fe(III), Ru(III), Co(II), Ni(II), Cu(II), Pd(II), Zn(II), Cd(II) and Hg(II) complexes of TMPCA.

The results obtained from the techniques employed are discussed to arrive at the bonding characteristics and the probable structures of the complexes. In the first set of complexes presented in Section B, the discussion of the results is preceded, wherever necessary, by a brief introduction to the techniques.

The metal-organic ligand stoichiometry in the Fe(III) and Ru(III) complexes of HBABS has been found to be 1:3, while in the Co(II), Ni(II), Cu(II), Pd(II), Zn(II), Cd(II) and Hg(II) complexes it is 1:2. With respect to FMABS and TMABS, their Fe(III), Ru(III) and Cu(II) complexes have 1:2 and Co(II), Ni(II), Pd(II), Zn(II), Cd(II) and Hg(II) complexes 1:1 stoichiometry. In the case of TMPCH and TMPCA, the stoichiometry is 1:2 with

Fe(III), Ru(III) and Cu(II) complexes of the former and with Fe(III), Ru(III) Co(II), Ni(II) and Cu(II) complexes of the latter and is 1: 1 with rest of the complexes of both the ligands.

Thermal studies of the selected metal complexes of the TMABS and TMPCA ligands indicate that they are thermally stable to different higher temperatures. All the complexes lose weight on heating almost in a continuous manner, most of them attaining no constancy in weight at the higher temperature studied (700^0C). Where the constancy in weight has been observed, the final product of decomposition corresponds to metal oxide.

The ligand HBABS functions as a mononegative, bidentate one coordinating through phenolic oxygen and the C=N nitrogen and the ligands FMABS, TMABS, TMPCH and TMPCA function as netrual, bidentate ones coordinating through the free C=N nitrogen and oxygen of furan ring in FMABS and sulphur of thiophen ring in TMABS, TMPCH and TMPCA.

Based on the electronic spectral and other data obtained for the complexes, they have been assigned tentative probable geometry, for instance, octahedral geometry for the Fe(III) and Ru(III) complexes, square planar geometry for Ni(II), Cu(II) and Pd(II) complexes and tetrahedral geometry for Co(II), Zn(II)), Cd(II) and Hg(II) complexes. Co(II), Ni(II) and Cu(II) have also been found to have octahedral geometry with some ligands.

The ESR spectra of Cu(II) complexes indicate that the unpaired electron is present in the $d_{x^2-y^2}$ orbital giving $^2B_{1g}$ as the ground state.

Chapter VI incorporates the results of investigations on the biological activity of the ligands: TMABS, TMPCA and FMABS and their Fe, Ru, Cu, Pd, Zn and Hg complexes has been studied against the two gram positive bacterial strains: *Staphylococcus Aurus*, *Basillus Subtillus* and two gram negative bacterial strains: *Salmonella typhi*, *Escherichia coli* and two fungal strains: *Aspergillus niger and Penicillium rubrum*. The results obtained in this connection are discussed.

The results indicate that the complexes are in general more active than the free ligands. Further, Hg complexes, of all the compounds, exert highest activity on the bacteria as well as the fungi studied.

The results of antibacterial and antifungal screening of the compounds indicate that the activity profiles of the ligands and their metal complexes are varying in that some of the compounds are active either significantly or marginally while others are not.

It may be inferred from the results that the ligands are less antibacterial and antifungal than most of their complexes. There are reports that antimicrobial activity of organic compounds is considerably enhanced in association with transition metal ions. A possible mode of toxicity can be speculated in the light of chelation theory. Chelation lowers the polarity of the metal ion considerably, owing mainly, to the partial sharing of its positive charge with donor groups and possible π-electron delocalization over the whole chelate ring. The reduced polarity of the metal ion, in turn, increases its lipophilic character. This favours interaction with lipids and polysaccharides which are important components of cell wall and membrane. This increased interaction, most probably, leads to the breakdown of permeability barrier of the cell, resulting in interference with the normal cell processes i.e. toxicity.

However, chelation is not the only criterion for antimicrobial activity of a compound. Factors such as nature of the metal ion, geometry of the complex, steric and pharmacokinetic factors, etc. also play an important role in deciding the antimicrobial potency of a compound. The inactivity of certain of the present metal complexes may be traced to these reasons. For example, if the geometry and charge distribution of a compound is incompatible with that of the microbial cell wall, then the compound cannot penetrate the wall and hence the toxic action is prevented.

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