# SUMMARY

Schiff bases and their metal complexes have found a multitude of uses, apart from being instrumental in the development of coordination chemistry. The real impetus towards developing the coordination chemistry of these potential ligands were probably provided by the remarkable antitumour, antiviral and antimalarial activity observed for some of the metal derivatives of these ligands.

Our attention is mainly focussed on the reactive ability of some Schiff bases derived from certain β-diketones, thiosemicarbazones and benzoin. Seven new ligands viz., acetylacetone aminofluorene (AAAF), dibenzoylmethane anthranilicacid (DBMAA), dibenzoylmethane-5-bromoanthranilicacid (DBM5-BrAA), dibenzoylmethane aminophenol (DBMAP), dibenzoylmethane thiosemicarbazone (DBMTSC), nitrofluorenone thiosemicarbazone (NFTSC) and benzoin aminofluorene (BAF) and their metal chelates have been synthesised and characterised.

The thesis is divded into 3 parts. Part I deals with synthesis and characterisation of various complexes derived from the above ligands. Part I consists of 8 chapters. The first chapter consists of an introduction and a critical review of published work on

the topic. In the second chapter, materials, methods and instruments utilised for the various studies are described.

Chapter III deals with the preparation and characterisation of Co(II), Ni(II), Cu(II), Pd(II), La(III) and Ce(IV) complexes of AAAF. Formulation of these complexes have been made on the basis of microanalytical, spectral and magnetic data. These data suggest that AAAF behaves as a bidentate ligand for the metal ions. Based on the above physicochemical studies, octahedral structures are suggested for Co(II), Ni(II), La(III) and Ce(IV) complexes, and square planar geometry has been assigned for Cu(II) and Pd(II) complexes.

Chapter IV deals with the preparation and characterisation of Mn(II), Fe(III), Co(II), Ni(II), Cu(II), La(III) and Ce(IV) complexes of DBMAA and DBM5-BrAA. The i.r. spectral data reveal that the ligand acts as a bivalent tridentate ligand in the complexes. The Ni(II) complexes are diamagnetic and Co(II) complexes are paramagnetic. These data suggest their square planar configuration. Fe(III) complexes show subnormal magnetic moment and are likely to have a structure with considerable metal-metal interaction. Mn(II), La(III) and Ce(IV) complexes possess octahedral configuration. Dimeric structures have been assigned for the Cu(II) complexes.

Chelates of DBMAP with Mn(II), Fe(III), Co(II), Ni(II) and

Cu(II) were prepared and characterised and the results are presented in chapter V. The complexes were characterised on the basis of analytical, conductance, magnetic susceptibility, i.r. and electronic spectral data. The data are consistent with square planar stereochemistry for Co(II), Ni(II) and Cu(II); octahedral geometry for Mn(II) and a 1:1 dimeric structure for Fe(III) complexes.

Chapter VI covers the description of synthesis and characterisation of Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Pd(II) complexes of DBMTSC. All these complexes possess 1:1 stoichiometry. Spectral magnetic and analytical data suggest octahedral geometry for the Mn(II), Co(II) and Ni(II) complexes. Fe(III) and Cu(II) complexes possess dimeric structure, while Pd(II) complex is square planar in nature.

Chapter VII describes the physicochemical investigation on some metal complexes of NFTSC. These metals include Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Pd(II). Characteristic i.r. stretching frequencies (4000-200 $cm^{-1}$) are reported for each complex. It is found from the elemental and i.r. data that NFTSC behaves as a monovalent bidentate ligand in these complexes. Based on the magnetic and spectral data square planar structure has been assigned for Co(II), Ni(II), Cu(II) and Pd(II) and an octahedral structure for Mn(II) complexes. Fe(III) and Cu(II) complexes possess dimeric configuration which has been supported by a subnormal magnetic moment.

Chapter VIII comprises the preparation and characterisation of three complexes of the ligand BAF. The data are consistent with octahedral stereochemistry for Co(II) and square planar geometry for Ni(II) and Cu(II) complexes. Part I ends with bibliography.

Part II deals with thermal studies of a few selected complexes of the above Schiff bases. Part II consists of 5 chapters. The first chapter gives an introduction about the thermal studies and the various methods used to determine the kinetic parameters. The second chapter gives a description of the materials, methods and instruments used for thermogravimetric studies.

Chapter III contains results of thermogravimetric studies of La(III) and Ce(IV) chelates of AAAF and DBMAA. Order of reaction, energy and entropy of activation are calculated on the basis of mechanistic and nonmechanistic equations. The methods based on Coats-Redfern, Horowitz-Metzger, MacCallum-Tanner equations were used. The above parameters were also calculated from DSC curves using Rogers method.

Thermal decomposition kinetics of Co(II) and Ni(II) complexes of four Schiff bases namely AAAF, DBMAA, DBM5-BrAA and DBMTSC are described in the fourth chapter. The parameters calculated are n, E, A and $\Delta S$. Based on initial decomposition temperature of relative thermal stabilities of the chelates can

be given as: $[NiL''''(H_2O)_3] > [CoL''(H_2O)] \approx [NiL''(H_2O)] > [CoL'''(H_2O)] \approx [NiL'''(H_2O)] > [NiL'_2(H_2O)_2] > [CoL'_2(H_2O)_2] > [CoL''''(H_2O)_3]$.

The fifth chapter deals with the thermal decomposition of Cu(II) complexes of AAAF, DBMAA, DBM5-BrAA and DBMAP. Interpretation and mathematical analysis of data, and evaluation of order of reaction, energy and entropy of activation based on Coats-Redfern, Horowitz-Metzger and MacCallum-Tanner are also presented. Part II concludes with references.

Part III deals with biological studies of the above complexes. This part consists of 3 chapters.

The first chapter begins with an introduction about the anti-cancer studies of the metals and ligands. In the second chapter the instruments, materials and methods utilised for the anticancer studies are described.

The third chapter deals with the anticancer studies of the complexes. Studies were evaluated in vitro using cytotoxicity and tissue culture methods, and in vivo in mice using Ehrlich ascites tumour cells grown as ascites form. Haematological analysis like haemoglobin, total WBC count were found out. These compounds were found to be cytotoxic to tumour cells at conc. 1-20 µg/ml using Trypan Blue Exclusion method. L929 Cells were used for

determining the cytotoxicity in cultured cells at a conc. 0.5-5 μg/ml. These compounds increase the life span in tumour bearing Swiss albino mice. Pathological studies were found to be nontoxic.

References are given in serial order at the end of part III.