CHAPTER 8

SUMMARY AND CONCLUSIONS

The thesis gives the summary of the work done on transitional metal complexes of nitrogen containing ligands in general and the substituted pyridines in particular. Literature survey of the metal complexes of alkyl, aryl and aromatic heterocyclic group mono and disubstituted pyridine were premeditated for carrying out this research work. Analytical applications of substituted pyridines and their metal complexes have also been briefly specified. The thesis is embodied the results of investigations on isolation and structural elucidation of complexes of nicotinamide/nicotinic acid as primary ligands and the nitrite/cyanate as secondary ligands with the metal ions viz., Cr(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II). Preliminary in vitro antimicrobial studies of the ligands and their metal complexes have also been carried out in order to understand the toxicity of ligands and metal complexes against microbes.

Chapter I presents the introduction, summary of the previous work done on the metal complexes of nicotinamide, nicotinic acid and relevance for carrying out this work. It has been formulated in the following sequence. The first part highlights the importance of inorganic chemistry and coordination compounds. The second part deals with the synthetic strategy of the microwave methods, microwave effects and the mechanism of microwave assisted synthesis. The next part deals with the synthetic approach to prepare metal complexes and the survey of the substituted pyridines. The third, fourth and fifth parts deal with the coordination tendencies of nicotinamide and nicotinic acid followed by the literature survey and the importance of the metal complexes of the pyridines.

Chapter II deals the aim and scope of the present research work.

Chapter III takes care of the various experimental techniques that were employed to probe the structures and characterisation of the ligands and their metal complexes for the biological and chemical nuclease applications.

The metal complexes deal with the various physical techniques that were employed in the characterisation and structural elucidation of the complexes. The following techniques were used:

1) Molecular weight determination.
2) Elemental CHN analysis
3) Electrical conductivity measurements
4) Magnetic susceptibility measurements
5) Infrared spectral measurements including far infrared
6) Electronic spectral measurements
7) Proton magnetic resonance studies
8) Electron paramagnetic resonance studies
9) Thermal decomposition studies (TG, DTA & DSC)
10) Cyclic voltammetric studies
11) X-ray powder and single crystal diffraction studies

The procedure for carrying out the biological applications like antibacterial and antifungal studies and their methodology were discussed. The methodology of DNA cleavage studies of gel electrophoresis like photo cleavage, viscosity measurements, absorbance and voltammetric studies were also discussed.

Chapter IV consists of three parts. The first part deals with the synthesis of the complexes with Nicotinamide and nitrite ion as ligands. The second part treats the general properties of the synthesised complexes.

The third part of this Chapter explicates the results and discussions of the prepared complexes and this part consist of characterisation and application techniques. The metal complexes were isolated from non-aqueous media. The electrical conductivity measurements made on \(\sim 10^{-3}\) M solutions of the complexes in DMF showed that all the complexes were non-electrolytes. The characterisation ranging from elemental analysis to various spectral studies confirms the formation of the complex. The elemental analyses and various spectral studies indicate the chemical formulae of the complexes.

The stoichiometry of the complexes were found to be consistent with the formulae, the nicotinamide tends only one bonding mode upon coordination with the metal ions. The mode of coordination was suggested based on the shifts observed in the stretching and bending frequencies of various donor atoms of the ligand on complexation. The nicotinamide acts as non-chelating monodentate coordination through pyridine ring nitrogen in all the complexes and not through the carbonyl oxygen. The far IR spectral data evidence, the existence of M-N and M-O bonds. From the broad peak around 3400 cm\(^{-1}\), it was concluded that the complexes were hydrated.

The magnetic susceptibility measurements made on the complexes showed that the Cr(III), Co(II), Ni(II), Cu(II) complexes were paramagnetic while Zn(II), Cd(II) and Hg(II) complexes were diamagnetic. The low effective magnetic moment values of Cr(III) complex indicates the presence antiferromagnetic coupling. The number of
unpaired electrons calculated, using the magnitude of magnetic moment buttresses the stereochemistry as proposed by electronic spectral studies.

Electronic spectral measurements both in solution as well as diffused reflectance spectra were carried out in order to ascertain the stereochemistry around the metal ion. The number and energy position of absorption bands indicate that the complexes possess a hexa coordinate geometry except Cd(II) ion and Cd(II) forms hepta coordination with the \([\text{Cd(ONO)}_2\text{O(NA)}_2]\) pentagonal bipyramidal geometry. The various electronic spectral parameters like \(B\), \(B'\), \(\beta\), \(\beta\%\) and \(Dq\) were calculated and they predicts the octahedral geometry for the complexes.

To further substantiate the nature of bonding in the Cu(II) complexes, EPR spectral studies were undertaken and they showed well defined parallel and perpendicular parts. The EPR study revealed that metal ligand bond possessed considerable covalent characters. From the thermo analytical studies it was concluded that some of the complexes contain crystallisation water and were thermally stable.

The results of the screening of biological applications for the nicotinamide and its complexes were undergone in vitro studies. The antimicrobial assay of the nicotinamide and its representative complexes were carried out against the bacterial strains such as \(B.\ subtilis\), \(S.\ aureus\) (gram positive) \(E.\ coli\), \(P.\ aeruginosa\) and \(P.\ vulgaris\) (gram negative) by disc diffusion method. The 30 and 200\(\mu\)g/mL concentrations of the compound were taken for the investigation. It has been observed that the increase in concentration concomitantly increases the potential. It has also been found that the metal complexes have higher antimicrobial activity than the free ligands and Cu(II), Cd(II) and Cr(III) complexes were found to be more active than rest of the complexes.

The results of the antifungal activities of the nicotinamide and the complexes against the fungal strains such as \(C.\ Albicans\), \(A.\ Nigier\) and \(A.\ fumigates\) were done by disc diffusion method. It was found that complexation enhances the activity. The nature of the metal ion, the ligand, the coordinating sites, the geometry of the complex, the anionic part (counter anion) of the metal etc., play important role in deciding the activity.

Electrochemical properties of the metal complexes revealed the quasi-reversible one electron/two electron transfer redox process. The DNA binding study takes place via an intercalative mode; copper complex has stronger binding strength as compared to the other metal complexes. Noticeably, metal complexes have been found to promote cleavage of SC CT-DNA from the supercoiled Form I to the open circular Form II or the linear Form III in the presence of AA.
Chapter V deals with the synthesis, characterisation and biological applications of the metal complexes of Cr(III), Co(II), Ni(II), Cu(II), Zn(II) and Hg(II) with nicotinamide as primary and the cyanate as secondary ligand. Among the complexes isolated, mercury complex was found to be free from coordinated water. The rest of the complexes were hydrated. This Chapter consists of three subdivisions. The first subdivision presents the synthesis of the metal complexes and the second subdivision describes the general characteristics of the complexes. The third subdivision explains the constitution of the derivative which has been elucidated using a variety of spectral techniques.

Based on the electrical conductance value for the ~10^{-3}M solutions of the complexes in DMF, all were found to be non-electrolytes. The elemental analyses and other spectral studies indicate the chemical formulae of the complexes. The IR spectral studies indicate that all the complexes were mono-nuclear and the ligand nicotinamide acts monodentate coordination through pyridine ring nitrogen atom. The mode of coordination was suggested based on the shifts observed in the stretching and bending frequencies of various donor atoms of the ligand on complexation. The far IR spectral data evidence the existence of M-N and M-O bonds. The characteristic bands in the IR spectra showed the presence of water molecules in the crystal lattices.

The electronic spectral data coupled with the magnetic moment data indicate that the complexes were found to have six-coordinate geometry. The ligand field parameters calculated were also in consistency with the covalent character of the M-L bonds. The various electronic spectral parameters like B, B', β, β% and Dq were calculated and they predicted the octahedral geometry for the complexes.

To further substantiate the nature of bonding and geometry in the Cu(II) complexes, EPR spectral studies were undertaken and various spectral parameters were calculated. The g\| and g\perp and G values of the Cu(II) complexes indicate the covalent nature of the complexes. Among the complexes, few only exhibit the lowest Dq value, cyanate being more polarisable than other anions. Calculation of percentage covalence reveals that the M-L bond in the complexes was less ionic. Based on the anisotropic 'g' factor, the Cu(II) complex assigned a tetragonally distorted octahedral.

To further ascertain the mode of coordination proposed based on IR data, ^1H NMR studies were also carried out for these complexes. The chemical shift values of the complexes registered a downfield shift for the protons which were directly attached to
the donor atom due to the electron shift from the atom involved in coordination to the metal ion.

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It has been observed that the increase in concentration increases the activity, also the metal complexes have higher antimicrobial activity than the free ligand. In the case of metal complexes, Cu(II), Zn(II) and Hg(II) complexes were found to be more active than rest of the complexes.

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**Chapter VI** deals with the synthesis and characterisation and biological applications of the metal complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with nicotinic acid as primary and the nitrite as secondary ligand. The first part deals with the synthesis of the mixed ligand complexes, the second part treats the general properties of the synthesised complexes.

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