Chapter V

Summary and Conclusion

Extensive studies have been conducted on complexation of Schiff bases with metals due to the attractive physicochemical properties of metal complexes and broad range of utilization in various areas of science. The data available for Schiff bases in literature embrace very wide and diversified subjects comprising vast areas of organo-metallic compounds and multiple aspects of bioinorganic chemistry.

The Schiff bases of antipyrine-4-carboxaldehyde are considered to be pyrazolone derivatives and are reported to be very important compounds in biological, clinical, pharmacological and analytical applications. Their metal complexes are of great interest because of their applications in analytical chemistry, industry, modeling in some biosystems, transport processes, stabilization of higher oxidation states and catalysis. It is reported that pyrazolone based ligands display variable complexing behaviour and variety of coordination possibilities to metal ions.

Chromones are compounds which contain γ-pyrene nucleus fused to benzene ring. Molecules which contain chromone ring in their structure have attracted much attention because of their interesting biological properties. Schiff bases of 3-formylchromone and its complexes also have a wide range of applications in biological clinical and pharmacological areas. Moreover organic molecules containing π electron conjugation systems like chromones can produce NLO materials.
The work incorporated in this thesis deals with the synthesis and characterization of Fe(III), Co(II), Ni(II) and Cu(II) complexes of Schiff bases

a) 2,3-dimethyl-4-formyl-[2'-(aminomethyl)pyridine]-1-phenyl-3-pyrazolin-5-one (DFAPP), and

b) Ethylenediaminobis(chromone-3-carbaldehyde) (FCED)

The physicochemical methods adopted for characterization of complexes are elemental analysis, molar conductance in non-aqueous solvents, FT-IR, UV-Vis and EPR spectra, magnetic susceptibility measurements as well as TG/DTA. In addition to these methods single crystal X-ray diffraction technique was also employed in the characterization of a few complexes. The thesis is presented in V chapters.

Chapter I consists of introduction to the work presented in this thesis, scope and objectives of the present work, a discussion of general chemistry, coordination chemistry, electronic and magnetic properties of Fe(III), Co(II), Ni(II) and Cu(II), applications of Schiff base transition metal complexes and a brief review of studies on Fe(III), Co(II), Ni(II) and Cu(II) complexes derived from pyrazolones and chromones.

Chapter II presents the materials and methods employed for the present study. It contains the procedural details of the synthesis of Schiff bases and essential theoretical principles involved in the experimental techniques used.

Chapter III describes the synthesis and characterization of a series of mononuclear complexes of Fe(III), Co(II), Ni(II) and Cu(II) ligated by a Schiff base 2,3-dimethyl-4-formyl-[2'-(aminomethyl) pyridine]-1-phenyl-3-pyrazolin-5-one (DFAPP) derived from antipyrine. Detailed spectral and structural
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Investigation of the complexes have also been carried out. Various stages of thermal decomposition of the complexes were also studied using TG/DTA. In all the complexes, DFAPP acts as a neutral bidentate ligand coordinating through pyrazolone carbonyl oxygen and imine nitrogen. The metal to ligand ratio in all the complexes was found to be 1:2. The iron(III) complexes may be formulated as [Fe(DFAPP)$_2$X$_2$]X (where X = Cl$^-$, Br$^-$ or CNS$^-$) and [Fe(DFAPP)$_2$X]$_2$ (where X = NO$_3^-$ or ClO$_4^-$). The Fe(III) complexes are found to have a high spin octahedral geometry around the central metal ion. TG/DTA analysis shows that all the complexes follow a two-stage decomposition pattern. The chloride complex is thermally least stable and nitrate complex is most stable among the series. The cobalt(II) complexes may be formulated as [Co(DFAPP)$_2$Cl$_2$] and [Co(DFAPP)$_2$] X$_2$ (where X = Br$^-$, NO$_3^-$, ClO$_4^-$, or I$^-$). Chloride complex have octahedral geometry while all other complexes have tetrahedral geometry around central metal ion. The complexes undergoes a two-stage thermal decomposition pattern. The iodide complex is thermally least stable and perchlorate complex is most stable among the series. The Ni(II) complexes may be formulated as [Ni(DFAPP)$_2$X$_2$] (where X = Cl$^-$ or Br$^-$), [Ni(DFAPP)$_2$(X)]X (where X = NO$_3^-$ or ClO$_4^-$) and [Ni(DFAPP)$_2$]I$_2$. In the series Ni(II) chloride, bromide, perchlorate and nitrate complexes have octahedral geometry while iodide complex has tetrahedral geometry around central metal ion. The complexes undergo thermal decomposition in two stages. Thermal decomposition studies shows that the perchlorate complex is most stable and chloride complex is least stable among the series. The copper(II) complexes may be formulated as [Cu(DFAPP)$_2$X$_2$] (where X = Br$^-$ or Cl$^-$) and [Cu(DFAPP)$_2$] X$_2$ (where X = NO$_3^-$ or ClO$_4^-$). The geometry around Cu(II) is octahedral in chloride and bromide complexes while it is square planar in nitrate and
perchlorate complexes. All the complexes undergo a two stage thermal decomposition pattern. The bromide complex is least stable and perchlorate complex is most stable among the series.

Chapter IV presents the synthesis and characterization of Fe(III), Co(II), Ni(II) and Cu(II) ligated by the Schiff base ethylenediaminobis (chromone-3-carbaldehyde) (FCED) derived from chromone. Detailed spectral and structural investigation of complexes has been carried out. A few complexes were characterized by single crystal X-ray diffraction technique. Thermal decomposition stages of the complexes were also studied using TG/DTA. Studies shows that FCED acts as a tetradeinate N₂O₂ donor chelating through two carbonyl oxygens and two imine nitrogens in all the complexes. The perchlorate complexes undergo explosion when heated to high temperatures so their thermal decomposition pattern cannot be studied. The iron(III) complexes may be formulated as [Fe(FCED)X₂]X (where X = Cl⁻, Br⁻ or CNS⁻) and [Fe(FCED)X]X₂ (where X = NO₃⁻ or ClO₄⁻). All the complexes have an octahedral geometry around central metal ion and the complexes undergo a two stage thermal decomposition pattern.

The cobalt(II) complexes may be formulated [Co(FCED)]X₂ (where X = Cl⁻, Br⁻ or I⁻) and [Co(FCED)X]X (where X = NO₃⁻ or ClO₄⁻). Among the complexes chloride, bromide and iodide complexes have tetrahedral geometry while nitrate and perchlorate complexes have octahedral geometry around central metal ion. All the complexes undergo a two stage thermal decomposition pattern.

The nickel(II) complexes may be formulated as [Ni(FCED)X]X (where X = Cl⁻, I⁻ or ClO₄⁻) and [Ni(FCED)(H₂O)₂]X₂.H₂O (where X = NO₃⁻ or Br⁻). The complexes have a square pyramidal geometry around the central
The nickel(II) ion in both the complexes is coordinated by neutral tetradeinate ligand FCED and two water molecules. The equatorial positions of Ni(II) metal center are occupied by two carbonyl oxygen atoms and two imine nitrogen atoms of the tetradeinate chelating ligand while trans axial positions are occupied by the oxygen atoms from two water molecules. Thus FCED forms a six membered chelate ring around Ni(II) metal ion. One lattice bound water molecule per metal also is present in both the complexes. A hydrogen bond scheme is present in both complexes interlinking hydrogen atoms of coordinated water molecules with counter ions and crystal bound water molecules. Intermolecular hydrogen bonds present in crystal of complexes form one dimensional chain structure and adjacent chains are connected by intermolecular hydrogen bonds to form an infinite double chain structure. The chloride and perchlorate complexes undergo a two stage thermal decomposition pattern while bromide and nitrate complexes undergo a three stage thermal decomposition pattern.

The copper(II) complexes may be formulated as [Cu(FCED)X]X (Where X = Cl\(^-\), Br\(^-\) or NO\(_3\)\(^-\)) and [Cu(FCED)](ClO\(_4\))\(_2\). Among the Cu(II) complexes, all the complexes except the perchlorate complex have a square pyramidal geometry while the perchlorate complex has a square planar geometry around central metal ion. The nitrate complex has been characterized by single crystal XRD. The Copper(II) ion is coordinated by two carbonyl oxygen atoms (O1,O2) and two imine nitrogen atoms (N1,N2) of tetradeinate chelating ligand FCED with trans angles $\angle O1$-Cu-N2 = 167.86 (10), O(2)-Cu-N(1) = 172.82(10) which are less than expected for perfect square
pyramidal geometry, while the fifth position is occupied by monodentately coordinated nitrate ion (O6). Trigonal index defined by $\tau = (\beta - \alpha)/60$ (where $\beta$ and $\alpha$ are largest angles in metal coordination sphere with $\beta > \alpha$) is only 0.083 indicating the existence of a distorted square pyramidal metal coordination sphere, taking into account that this angular parameter has an ideal value of zero for square pyramidal geometry with $C_{2v}$ symmetry and one for trigonal bipyramidal geometry with $D_{3h}$ symmetry. Such a type of distorted square pyramidal geometry is observed in similar type of Cu(II) complexes ($\tau = 0.08 - 0.58$). Weak $\pi-\pi$ interactions have been observed with the carbon atoms present in the adjacent chromone ring via C(7)--C(17) interaction [C(7)--C(17) = 3.395 Å] resulting in the formation of a dimer. Each dimer extent to form 3D stacks through weak hydrogen bond interactions via ionic as well as coordinated nitrates to form a herringbone picking network. The bromide and nitrate complexes undergo thermal decomposition in two stages while chloride complex decomposes in three stages.

It is established that the biological activity of a Schiff base is altered many fold on coordination with suitable metal ions. The introduction of nitrogen atoms into the structure of organic compounds often resulted in important changes in their behaviour towards metal ions. Schiff base complexes with heterocyclic molecule and/or containing heteroatoms such as N and O show diverse biological activity. The findings on the structural studies are of great interest in the sense that the Schiff base ligands can control the stereochemistry of complexes and provide us numerous examples of different geometry around central metal ion. The role of metal ions in altering the coordination environment which is supposed to be further responsible for the properties of the complexes, has been extensively studied through various analytical tools in the present investigation.