Summary and Conclusions

Metallo-organic chemistry, incorporating the frontiers of both inorganic and organic chemical aspects, is a topic of utility concern. The first exploration of coordinated metal complexes dates back to the nineteenth century, during the days of Alfred Werner. Thereafter, the inorganic chemistry witnessed a great outflow of coordination compounds, with unique structural characteristics and diverse applications. The diversity in structures exhibited by the coordination complexes of multidentate ligands have led to their usage as sensors, models for enzyme mimetic centers, medicines etc. The ligands chosen are of prime importance in determining the properties of coordination compounds. The presence of more electronegative nitrogen, oxygen and sulfur atoms attached to the ligands increases their denticity thereby enhancing the coordinating possibilities of ligands. Moreover, the presence of these atoms in the coordination sphere leads to their biological activity.

Schiff base ligands are able to coordinate metals through imine nitrogen and another group, usually linked to the aldehyde/ketone. Well-designed Schiff base ligands are considered ‘privileged ligands’ because they are easily prepared by the condensation between aldehydes and amines. Synthetic catalysts which are enantioselective over a wide range of different reactions were defined as ‘privileged’ by
Jacobsen. Schiff base ligands are able to coordinate many different metals, and to stabilize them in various oxidation states, enabling the use of Schiff base metal complexes for a large variety of useful catalytic transformations. Metal complexes of Schiff bases are useful in the catalysis of many reactions like carbonylation, hydroformylation, reduction, oxidation, epoxidation and hydrolysis etc.

Antimicrobial and antifungal activities of various Schiff bases have also been reported. Many Schiff bases are known to be medicinally important and are used to design medicinal compounds. It has been shown that Schiff base complexes derived from 4-hydroxysalicylaldehyde and amines have strong anticancer activity, e.g. against Ehrlich Ascites Carcinoma (EAC).

The pseudohalogen azide and thiocyanate have been demonstrated to be versatile bridging ligands. They are excellent candidates for the design of molecule based magnetic materials. In addition, the azide and thiocyanate anions are observed to inhibit several enzymes like ATPases, cytochrome C oxidase, human carboxy peptidase etc. This makes the study of the metal complexes of these anions very useful for the understanding of biological processes. The use of these anions in conjugation with the Schiff bases for the synthesis of metal complexes can bring about interesting results.

Chapter 1 depicts a brief introduction on Schiff bases, the pseudohalogen azide and thiocyanate and their transition metal complexes. The survey of the previous research works in the field of
Schiff bases and their complexes with azide and thiocyanate, their properties and applications is also included. The chapter also contains the objectives of the present study and the details of the different analytical and spectroscopic techniques used for the analysis of the metal complexes.

Chapter 2 deals with syntheses of seven Schiff base ligands. The ligands synthesized are:

1. Pyridine-2-carbaldehyde-aniline (paa)
2. Pyridine-2-carbaldehyde-1-phenylethylamine (papea)
3. Pyridine-2-carbaldehyde-2-aminopyrimidine (paap)
4. 2-Benzoylpyridine-aniline (bzpa)
5. Di-2-pyridyl ketone-aniline (dpka)
6. Quinoline-2-carbaldehyde-aniline (qaa)
7. 2-Hydroxy-4-methoxybenzaldehyde-aniline (Hhmba)

The ligands paa, papea, bzpa and qaa are neutral bidentate ligands with \(N, N\) donor atoms. The ligands paap and dpka are also neutral ligands, but they have additional \(N\) donors, which may or may not be coordinated. If all the \(N\) atoms of the ligands coordinate to the same metal centre, paap and dpka becomes quadridentate and terdentate respectively. The involvement of the additional \(N\) atoms in coordination to the same metal is less probable because of its spatial disposition and the distance from the metal centre. All the above mentioned ligands were obtained as yellow oils and could not be isolated in the solid form even after repeated trials. The ligand Hhmba
could be isolated in the solid form and is a monoprotic bidentate \( N, O \) ligand, which usually coordinates to the metal through deprotonation. This ligand was characterized by \(^1\)H NMR, IR and electronic spectral studies.

**Chapter 3** contains the discussion of the thirteen Cu(II) complexes synthesized and characterized by various spectroscopic techniques such as IR, electronic spectral studies and EPR. The magnetic susceptibility measurements reveal some of the complexes to be diamagnetic and many to have low magnetic moments at room temperature. The diamagnetic nature and the low magnetic moments are probably due to an effective antiferromagnetic exchange coupling occurring through the bridging ligands which gives rise to a net spin-pairing effect. In the electronic spectral studies, the broadness of the d-d transitions restricted the assignment of the three d-d transitions. IR spectral studies revealed the coordination of the azomethine N to the Cu(II) centre in the complexes. IR spectroscopy could be used as a very valuable tool to get information regarding the coordination mode of the pseudohalogens. The EPR spectra of all the Cu(II) complexes were recorded both in polycrystalline state at 298 K and in DMF at 77 K. The g values and the various EPR spectral parameters are calculated. The g values calculated indicate that in most of the complexes the unpaired electron in Cu(II) resides in the \( d_{x^2-y^2} \) orbital. Some of the complexes were found to be EPR silent in the polycrystalline state, while some others in the powder state displayed very weak Cu\(^{2+}\) signals. We could isolate X-ray quality single crystals for one copper
complex and it was found to be a one-dimensional polymer with Cu(II) in an tetragonally elongated octahedral geometry. In the above complex, the ligand papea is found to have undergone metal assisted oxidation and cleavage to give deprotonated pyridine-2-carboxamide, which coordinated to the metal.

Chapter 4 deals with the synthesis and characterization of four Mn(II) complexes. The compounds were characterized by IR, UV-Vis and EPR studies. It was possible to isolate single crystals for two complexes of manganese and in both Mn(II) is in a distorted octahedral geometry. The EPR spectrum of most of the complexes in the polycrystalline state were very broad and it is a characteristic feature of Mn(II) complexes in the polycrystalline state, which arises due to dipolar interactions and enhanced spin lattice relaxation. In the polycrystalline state, two Mn(II) complexes showed two g-tensors, while the remaining two gave three g values. This revealed less zero field splitting (ZFS) effects in former complexes while appreciable ZFS in the latter. The spectra in DMF revealed hyperfine splitting consisting of six lines. In addition to the hyperfine pattern, a pair of low intensity lines is found in between each of the two main hyperfine lines. These are the forbidden lines corresponding to $\Delta m_I \neq 0$, transitions which arise as a result of the mixing of the nuclear hyperfine levels by the zero-field splitting factor.

Chapter 5 describes the synthesis and characterization of six nickel complexes. All the compounds were characterized by various spectral studies. Magnetic susceptibility measurements revealed three of the
nickel complexes to be diamagnetic and hence square planar. We could successfully isolate the single crystals of one nickel complex and the X-ray diffraction studies revealed Ni(II) to be in a distorted octahedral environment in the complex.

**Chapter 6** deals with synthesis and characterization of ten cobalt(II/III) compounds. Magnetic susceptibility investigations indicate four complexes to be having cobalt in the $+3$ oxidation and the remaining to be in the $+2$ oxidation. Single crystals of two complexes were isolated. The studies reveal one to be having Co(II) and other to be Co(III). The geometry of cobalt in both the compounds is found to be distorted octahedron. The Co(III) complex had two independent molecules in the asymmetric unit.

**Chapter 7** describes the synthesis and characterization of seven Cd(II) compounds using various spectral studies like IR and electronic spectra and $^1$H NMR. The single crystal of one cadmium complex could be isolated. Single crystal X-ray diffraction studies of the compound revealed Cd(II) centres in a distorted octahedral geometry.

Based on the present work, we would like to conclude that the transition metal complexes of Schiff bases and pseudohalides like azide or thiocyanate are promising materials for applications in science and technology. Also, depending up on the metal and the Schiff base used, pseudohalides azide and thiocyanate are found to exhibit different coordination modes in the complexes.