Introduction

The heterocyclic NO donor Schiff base ligands play an important role in the development of coordination chemistry as they readily form complexes with most of the transition metal ions [1-4]. The synthesis, structure and properties of coordination complexes still arouse considerable research interests because of their potential applications in material science [5]. Transition metal complexes with Schiff bases are of particular interest for their ability to possess unusual configurations, structural lability and their sensitivity to molecular environments [6]. The heterocyclic Schiff bases are of particular interest because of their versatility in coordination to metal ions, the flexibility in adopting different conformations, the possibility of tautomerism and their ability to coordinate either in the neutral or in the anionic form [7, 8]. Also the unsymmetrical Schiff bases are very important as they can bind one, two or more metal centers, involving various coordination modes and allow successful synthesis of homo and/or heteronuclear metal complexes with interesting stereochemistries [9, 10]. The field of Schiff base complexes is fast developing on account of the wide variety of possible structures for the ligands depending upon the aldehydes and amines.

The synthesis and characterization of metal–organic supramolecular networks with beautiful shapes and chemical environments have achieved considerable progress in supramolecular chemistry, coordination chemistry and materials chemistry. Recently, there has been much interest in the construction of coordination complexes through crystal engineering due to their fascinating structural topologies as well as their potential application such as functional materials in the fields of molecular magnetism, catalysis, gas sorption and optoelectronic devices [11]. The key to the design of intriguing metal–organic supramolecular networks lays in the intelligent ligand design, the proper choice of metal
center and counter ions. The metal–organic supramolecular networks are the result of spontaneous supramolecular self-assembly process of ligands and metal centers via metal–ligand coordination and many other non-bonded interactions. Hydrogen bonding plays a crucial role in the crystal engineering of organic solids. Hence the combination of both metal–ligand coordination bonding and hydrogen bonding results in the possibility of various structural topologies in metal–organic supramolecular networks. However, the final outcome of these supramolecular structures is dependent on many parameters such as the dynamic nature of metal–ligand bonds, various coordination geometries of the metal centers, the nature and ligating topologies of the ligands, the metal–ligand ratio, the nature of the counter ions and the various experimental conditions such as solvents, temperature and crystallization methods.

**Scope and objectives of the present study**

The variety of possible Schiff base metal complexes with wide choice of ligands and coordination environments has prompted us to undertake research in this area. Our approach is to design, synthesize and characterize the coordination complexes derived from heterocyclic NO-donor Schiff bases and utilize these building blocks for the construction of ordered structures. The aim of our studies is to get a better insight into the most relevant factors determining the course of complex formation, including the choice of metal ions (cation) or anions, the ligand/metal ratios, temperature and solvent. Among them, the choice of metal ion (cation) and anion is the key factor governing the topology of coordination complex. The coordination geometry and the size of the cation are the two key effects upon the structure of the final product. The anion has two main effects on the final topology. Firstly, the coordinative ability of the anion can clearly influence the coordination sphere of the metal ion used. Secondly, the size of the anion can influence the long-range order and degree of interpenetration [12]. A typical geometry can be extended throughout the crystal if suitable
ligands are designed that carry sites suitable for participation in non-covalent interactions with nearest neighbors [13]. Hence, with the aim of obtaining information about the chemical and structural properties of the metal complexes, especially with regard to the stereochemistry and the effects of coordination on the conformation of the coordinatively flexible Schiff base ligands, we have undertaken the study of Fe(III), Co(II), Ni(II) and Cu(II) complexes of two Schiff bases, 4-(1-H-1,3-benzimidazole-2-yl)-1,5-dimethyl-2-phenyl-1,2-dihydro-3-H-pyrazol-3-one (Opdac) and 4-isopropylbenzaldehyde[N-(3-oxo-3,4-dihydro-2-quinoxalinyl) hydrazone] (Ipbh). The analytical tools employed for the characterization of the compounds include CHN elemental analysis, spectral techniques like FTIR, UV-visible, EPR, $^1$H NMR and $^{13}$C NMR, magnetic susceptibility measurements, TG/DTA analysis and single crystal X-ray diffraction technique.

**Structure and contents of the thesis**

The thesis is presented in VI chapters. Chapter I consists of an introduction to the present research work, scope and objectives of the present study and a brief review of the literature showing the importance of the Schiff bases complexes of different transition metal ions along with some of their applications. Some basic aspects of the coordination chemistry of Fe(III), Co(II), Ni(II) and Cu(II) as well as their electronic and magnetic properties are also discussed in this chapter.

Chapter II presents details on various reagents and methods employed for our study along with the essential theoretical principles involved in some of the experimental techniques we have used.

Chapter III describes the synthesis and characterization of the two novel heterocyclic NO donor Schiff bases 4-(1-H-1,3-benzimidazole-2-yl)-1,5-dimethyl-2-phenyl-1,2-dihydro-3-H-pyrazol-3-one (Opdac) and 4-isopropylbenzaldehyde[N-(3-oxo-
3,4-dihydro-2-quinoxalinylhydrazone] (Ipbh). The Opdac has three donor sites which are pyrazolone carbonyl oxygen (O1), benzimidazole imine nitrogen (N4) and benzimidazole -NH nitrogen (N3). The crystal structure of Opdac reveals that the the pyrazolone carbonyl oxygen (O1) and the benzimidazole imine nitrogen (N4) are $trans$ oriented while pyrazolone carbonyl oxygen (O1) and the benzimidazole -NH nitrogen (N3) are $cis$ oriented. Therefore Opdac can acts as bidentate ligand either coordinating through the pyrazolone carbonyl oxygen (O1) and the benzimidazole imine nitrogen (N4) or through the pyrazolone carbonyl oxygen (O1) and the benzimidazole -NH nitrogen (N3) forming a six membered ring around the central metal ion. The ligand Ipbh has quinoxaline carbonyl oxygen (O1), azomethine nitrogen (N4) and hydrazone -NH nitrogen (N3) as three potential donor sites. The crystal structure of Ipbh indicates that quinoxaline oxygen (O1), azomethine nitrogen (N4) are in opposite plane while the quinoxaline oxygen (O1) and hydrazone –NH nitrogen (N3) are in same plane. Therefore Ipbh can acts as bidentate ligand coordinating through either the quinoxaline carbonyl oxygen (O1) and the azomethine nitrogen (N4) or the quinoxaline carbonyl oxygen (O1) and the hydrazone -NH nitrogen (N3) forming a six or five membered ring respectively around the central metal ion. The single crystal X-ray diffraction study reveals that in solid state, the Opdac and Ipbh molecules are stabilized through a network of weak hydrogen bond interactions which result in a one dimensional assembly.

In Chapter IV we present our attempts to synthesize the Fe(III), Co(II), Ni(II) and Cu(II) complexes of the Schiff base 4-(1-H-1,3-benzimidazole-2-yl)-1,5-dimethyl-2-phenyl-1-2-dihydro-3-H-pyrazol-3-one (Opdac). All the mononuclear complexes were characterized by various physicochemical methods. It is interesting to compare the structure of the free ligand Opdac with that of its complexes (1 – 19). In the free ligand moiety Opdac, the imine nitrogen (N4) and pyrazolone oxygen (O1) are $trans$ oriented to each
other. During chelation, they rearrange to *cis* fashion in all the complexes by an $180^\circ$ rotation of the carbon-carbon (C17 and C18) single bond. Therefore in all the complexes (1 – 19) the metal ion is coordinated by the imine nitrogen (N4) and pyrazolone oxygen (O1) donor sites of the Schiff base Opdac. We could develop good quality single crystals of the complexes [Co(Opdac)Cl$_2$] (6), [Co(Opdac)Br$_2$] (7), [Co(Opdac)$_2$NO$_3$]NO$_3$ (9) and [Ni(Opdac)$_2$(CH$_3$OH)$_2$]Br$_2$(CH$_3$OH)$_2$ (12) by vapour diffusion method. The mononuclear units in 6 and 7 are engaged in weak intermolecular C–H…X and N–H…X (X = Cl or Br) hydrogen bonds to give a two dimensional structure. The complex 9 was found to be involved in weak hydrogen bonding via N-H…O interactions leading to the formation of one dimensional hydrogen bonded network. The single crystal X-ray diffraction study of the complexes 6, 7 and 9 reveal that intermolecular hydrogen bonding interactions play an important role in the different dimensional assembly of these complexes because of the presence of organic ligand and various anions. The complex 12 forms a two dimensional network structure which is supported by the O–H…O, O–H…Br and N–H…Br hydrogen bonds involving the coordinated as well as lattice methanol molecules, benzimidazole nitrogen and bromide counter anion.

Since the crystallographic data demonstrated that the complex 6 has a two dimensional microporous hydrogen bonded network we have selected this molecule for the hydrogen gas sorption studies. The ideal pores of the complex 6 have no disturbing molecules such as counter ions or any solvent molecules so that the skeleton of the complex is neutral. The hydrogen adsorption-desorption isotherm exhibits Type-I sorption behavior according to Brauner classification, typical for adsorption in microporous materials [14, 15]. This type of isotherm shows an initial steep increase, corresponding to progressive filling of the micropores, and then a plateau is reached at higher pressures, corresponding to monolayer coverage. Indeed, for microporous materials the small pore dimensions of the adsorbent limit
the adsorption only to one or a few molecular layers [16]. The Langmuir model describes Type-I isotherms with a kinetic approach assuming that the adsorption enthalpy is independent from the coverage [17]. The hydrogen adsorption isotherm was reversible with pressure which means that the adsorbed hydrogen can be easily desorbed by reducing the pressure. The hydrogen adsorption isotherms at 77 K confirmed the permanent porosities of the complex 6. Also the shape of isotherm shows that hydrogen sorption capacity is not saturated at 1 bar pressure; higher hydrogen sorption capacities can be obtained by increasing the hydrogen adsorption pressure.

In Chapter V we present our attempts to synthesize the Fe(III), Co(II), Ni(II) and Cu(II) complexes of the Schiff base 4-isopropylbenzaldehyde[4-oxo-3,4-dihydro-2-quinoxalinyl]hydrazone (Ipbh). All the mononuclear complexes were characterized by various physicochemical methods. It is interesting to compare the structure of complexes (20 – 38) with that of the unchelated analogue, Ipbh. It is observed that during chelation the hydrogen atom from the hydrazone nitrogen (N3) is shifted to the quinoxaline nitrogen (N2) resulting in the formation of double Schiff base form of the ligand, which is coordinated to the central metal ion in all the complexes (20 – 38) through its quinoxaline oxygen (O1) and imine nitrogen (N3). We could develop good quality single crystals of the complex [Ni(Ipbh)2.(CH3OH)2](NO3)2.(CH3OH)2 (33) by vapour diffusion method. The single crystal X-ray diffraction study of the complex 33 reveals that intermolecular hydrogen bonding via N–H…O and O–H…O interactions play an important role in its two dimensional assembly because of the presence of coordinated organic ligand, solvated as well as coordinated methanol molecules and counter nitrate anions.
Summary and Conclusion

A feasible route for constructing Schiff base transition metal complexes could be established in good yields from cheap, eco-friendly and commercially affordable reagents. The two novel heterocyclic NO donor Schiff bases (Opdac and Ipbh) have been exploited to study the effect of conformation dependent ligating topology, the coordination ability of various transition metal ions and counter anions of various size and shape. Thirty eight new coordination complexes with varied structures were successfully synthesized by the reaction of different metal salts with the two heterocyclic NO donor ligands in non-aqueous solvents. The results revealed that the nature of the ligand, metal ion, counter anion and solvent medium play important roles in determining the structure and topology of coordination compounds. The ligands Opdac and Ipbh exhibit various coordination modes in these complexes, which result in various coordination geometry around different metal centers. The crystallographic data reveals that the complex 6 is found to be a 2D microporous supramolecular network with hydrogen gas adsorption property, while the complexes 7, 9, 12 and 33 are 1D and 2D network structures with different topologies. The successful preparation of these coordination complexes provides a potential sense into the rational design and synthesis of metal–organic supramolecular networks with interesting structures and properties in the future.

In recent years, metal complexes with Schiff bases have attracted considerable attention due to their remarkable antifungal, antibacterial and antitumor activity. Many Schiff base transition metal complexes are reported to have anticancer activities. It is reported that some drugs have greater activity when administered as metal complexes than that as free ligand. So, Schiff base transition metal complexes may be an untapped reservoir for drugs. Metal chelation is involved in many important biological processes where the coordination can occur between a variety of metal ions and a wide range of ligands. The
Schiff base complexes derived from heterocyclic compounds have found increased interest in the context of bioinorganic chemistry. The Schiff base complexes with many transition metal ions have attracted considerable interest because of their growing importance as model molecules for biological systems such as oxygen carriers.

References


