Chapter VII

Concluding remarks

In the present dissertation syntheses of single crystals of some metal-organic hybrid complexes containing Cu(II) ion as the metal centre have been described using both the hydrothermal and conventional methods. Chapter I is the introductory one and chapter II deals with the experimental section. Chapters III to V describe hydrothermal syntheses, structural characterization and properties (mainly magnetic properties) of single crystals of some Cu(II) hybrid complexes.

In chapter I a general introduction to crystal its various feasible and popular synthetic routes has been given with special focus in the hydrothermal method of crystal growth. It also includes the novelty/driving force behind the synthesis of metal-organic hybrid complexes using hydrothermal method.

Chapter II involves the experimental section briefly describing the chemicals and materials used in completing this research. This chapter also describes the novelty behind choice of organic linkers/ligands used in the works embodied in this thesis. The details of the instruments used for the physico-chemical characterization of the synthesized complexes were discussed briefly.

In chapter III, hydrothermal synthesis, structural characterization and magnetic properties of a unique Cu(II) hybrid complex was presented. The complex, characterized using different physico-chemical techniques like single crystal X-ray diffraction, FTIR spectroscopy, EPR, SQUID, TGA and FESEM, was found to be three-dimensional, monoclinic with distorted octahedral coordination geometry. The zigzag channels present within the crystal structure is attributed due to the interesting extensive hydrogen bonding existing between the two O-atoms of SO_4 bridges of one chain and the H-atoms of the coordinated H_2O moieties of another chain leading to its three dimensional polymeric sheet structure. The structure and stoichiometry of the complex was also supported by FTIR and TGA study. SQUID and EPR study suggested paramagnetic behavior of the complex. Crystalline morphology as studied by FESEM also supported the regular crystalline geometry of the complex.

A newly synthesized metal-organic hybrid complex [{Diaquo(3,5-dinitrobenzoato-κ^1O^1)(1,10-phenanthroline-$\kappa^2N^1:N^{10}$)}copper(II)] 3,5-dinitrobenzoate, containing Cu(II) central atom, has been discussed in chapter IV. The crystal is blue colored needle shaped monoclinic with space group $P12_11$. The assymetric unit of the crystal was found to contain a penta-coodinated Cu(II) ion in a distorted square pyramidal geometry due to steric hindrance caused by the phen ligand with a dihedral angle of 5.73° between the plane of the phen ligand and the plane of dnb^- moiety. The crystal is a three-dimensional structure and stable due to extensive inter- and intra-molecular hydrogen bonding interactions. Thermogravimetric and magnetic studies revealed its thermal stability and paramagnetic nature, respectively.

In chapter V, hydrothermal synthesis of a tetra-coordinated with slightly distorted square planar Cu(II) hybrid complex, [Bis(picolinate-$\kappa^2N:O$)Copper(II)] di(benzene-1,3,5- tricarboxylic acid) was reported. The complex was found to crystallize in monoclinic crystal system with space group P1 21/c 1. The physico-chemical characterization of the single crystals revealed that the Cu(II) ion is coordinated to two picolinate moieties leading to a square planar complex with slight distortion in geometry. The stability of the complex is due to the existence of hydrogen bonding interactions involving trimesic acid co-ligands. The thermogravimetric analysis and DFT studies justified the exceptional stability of the complex. The ferromagnetic nature is supported by EPR and SQUID studies of the synthesized complex.

Chapter VI discusses the synthesis of the blue colored single crystals of metal-organic hybrid complex [Diaquo{bis(*p*-hydroxybenzoato-κ^1O^1)}(1-methylimidazole- κ^1N^1)}copper(II)] using conventional method. The parallelopiped orthorhombic crystals with space group $P2_1\ 2_1\ 2_1$ was found to be three-dimensional stabilised by extensive inter- molecular hydrogen bonding interactions. Thermogravimetric and magnetic studies revealed its thermal stability and weak paramagnetic behaviour, respectively. The purity of the synthesized complex was well supported by FESEM, X-ray diffraction and DFT study. The synthesized complex acts as good catalyst in benzimidazole synthesis with good recyclability as catalyst up to 5^{th} run.

Synthesis of dislocation free single crystals of hybrid materials involves both challenges and opportunities. It is always challenging to synthesize hybrid combinations by keeping or enhancing the best properties of the components while eliminating their limitations. Such challenges always bring the opportunities to develop unique materials having synergistic behaviour. The synergistic behavior leads to improved performance of materials and also leads to the discovery of new complexes with fascinating properties.

In the present dissertation, an attempt has been undertaken to synthesize and physico-chemical characterization of single crystals of metal-organic hybrid complexes of Cu(II) using both hydrothermal and conventional methods. It has been found that the hydrothermal method is superior to conventional methods in terms of time and quality of crystals prepared. It has been found that the hydrothermal synthetic method is environmentally benign, cheap and can lead to the synthesis of dislocation free single crystals on a large scale. More useful hybrid single crystals may be synthesized by selecting suitable ligands, metal ions and reaction conditions. The potential applications/properties of the hybrid complexes can be explored using various physico-chemical techniques. Although the poor solubility of such complexes in common solvents pose a great problem in the exploration of their potential properties/applications especially in solution phase, the synthesis of single crystals of metal-organic hybrid complexes using hydrothermal technique can open up a new horizon of opportunities that can be grabbed with patience and intelligence in order to synthesize more useful compounds/devices and attempts in this regard is underway in our laboratory presently.