

PREFACE

A great deal of the recent attention in the coordination chemistry of sulphur donor ligands such as dithiocarbamate ligand based complexes has been driven by their involvement in a number of processes which include electrical conductivity, molecular magnetism, electrochemistry, optoelectronic properties and biological processes. In particular, dithiocarbamate have drawn a lot of attention since its first derivative tetramethylthiuram disulfide, more commonly known as thiram has achieved prominence fungicidal properties. Compounds having dithiocarbamate group, were proven medicinally significant and utilized as microbicidal, spermicides, anesthetic, anti-HIV, mono glyceride lipase inhibitors, anti-tumour agents. The unique redox properties of the sulfur atom in dithiocarbamate make it a key residue for enzyme catalysis, protein folding, and redox signaling and regulation, which are important for cellular energy metabolism, motility and subsistence of cellular systems. The above properties of the dithiocarbamate group make it a versatile pharmacophore and hence, it is used in the compounds of biological interest. Despite, they have been utilized as single source material for the preparation of metal sulphide nano-particles. By elegant choice of dithiocarbamate ligands and transition metal ions, monometallic or polymetallic dithiocarbamate complexes can be prepared.

On the other hand, Schiff bases (also known as imine or azomethine) is a nitrogen analogue of an aldehyde or ketone in which the carbonyl group ($C=O$) has been replaced by an imine or azomethine ($N=C$) group ($RCH=NR'$, where R, R', R'' are alkyl and (or) aryl substituent. Schiff bases are capable of forming complexes with a number of metal ions which can exhibit unusual coordination, high thermodynamic stability and kinetic inertness. The coordination geometry of these complexes depends upon the electronic nature and size of the metal ions, repulsions between non-bonded atoms in different ligand arms, and the inherent stiffness due to the presence of aromatic rings, etc. These ligands form an important system in asymmetric catalysis and their transition metal complexes can often mimic biological sites. They are therefore of great interest as enzyme models. Especially, their six-coordinated complexes can display a variety of structural and magnetic properties. The azomethine functional group is reportedly responsible for antimicrobial activity, which can be altered depending upon the type of substituent present on the aromatic rings.

Taking into account the above mentioned aspects, the work presented in this thesis is based on the synthesis, spectral characterization, unambiguous crystal

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structure determination, investigation of optical properties of some monometallic transition/ non-transition metal complexes derived from dithiocarbamate and *N*, *O*-Schiff base ligands. The simple and straightforward methodologies have been employed in the synthesis of these complexes. The thesis is divided into six chapters **Chapter 1** covers a systematic literature review on 1,1-dithiocarbamate and *N*, *O*-Schiff base ligand systems and their versatile coordination chemistry with transition and non-transition metals in a variety of stoichiometries and properties. The objectives of the present investigation are also described in this background.

Chapter 2 is dedicated to the use of some novel ligand precursors such as *N*-methyl-(1-naphthyl)-*N*-methylferrocenyl amine (**L**¹), *N*-methyl-(2-pyridyl)-*N*-methylferrocenyl amine (**L**²) and *N*-furfuryl-*N*-methylferrocenyl amine (**L**³) in the development of a series of monometallic bis-dithiocarbamate complexes of Co(II), Ni(II), Cu(II) and Zn(II) bearing ferrocenyl moiety. The ligand precursors **L**¹-**L**³ have been prepared and well characterized by microanalysis and NMR technique. The required dithiocarbamate ligands have been prepared *in situ* by the reaction of ligand precursors **L**¹-**L**³ with CS₂ under a basic reaction condition which on further reaction with various transition metal ions yielded monometallic bis-dithiocarbamate complexes.

Chapter 3 is divided into two parts chapter 3A and chapter 3B. Chapter 3A comprises of the synthesis and characterization of new 3-aminocoumarin based monometallic dithiocarbamate complexes whereas chapter 3B comprises of the synthesis and characterization of new *N*-(2-arylmethylideneamino)ethyl piperazine based monometallic dithiocarbamate complexes bearing functionalized ligand backbone. The 3-aminocoumarin and *N*-(2-arylmethylideneamino)-ethyl piperazine have been prepared by following a modified literature procedure.

Chapter 4 includes the synthesis of a series of secondary amine precursors such as 2-(cyclohexylamino)-3-chloro-1,4-naphthoquinone (1), 2-(benzylamino)-3-chloro-1,4-naphthoquinone (2), 2-(furfurylamino)-3-chloro-1,4-naphthoquinone (3), 2-(2-pyridylmethylamino)-3-chloro-1,4-naphthoquinone (4), 2-(3-pyridylmethylamino)-3-chloro-1,4-naphthoquinone (5), 2-(*n*-butylamino)-3-chloro-1,4-naphthoquinone (6) and 2-(benzylamino)-1,4-naphthoquinone (7) for the development of monometallic

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bis-dithiocarbamate complexes bearing naphthoquinone. This chapter is also divided into two parts.

Chapter 4A is devoted to the synthesis and characterization of a number of secondary amine precursors which are listed above. The analysis of crystal packing patterns suggests that the manipulation in the various *N*-substituents greatly affects the conformations of the molecules and thereby the kind of non-conventional intermolecular interactions such as C-H...O, C-H...pi, N-H...O etc which ultimately affects the crystal packing patterns in the solid state as illustrated in the following figure.

Chapter 4B deals with the use of secondary amines precursors **7** *i.e* 2-chloro-3-{2-(piperazinyl)ethyl}-amino-1, 4-naphthoquinone (**7**) in the preparation of some monometallic bis-dithiocarbamate complexes. The corresponding dithiocarbamate ligand has been prepared *in situ* by the reaction with CS₂ in triethylamine solvent which on interaction with various transition/non-transition metal ions such as Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) yielded a series of monometallic dithiocarbamate complexes.

Chapter 5 deals with synthesis of some monometallic Bis-*N,O,O*-tridentate Schiff base and complexes bearing coumarin. *N,O,O*-tridentate Schiff base ligands. The Bis-*N,O,O*-tridentate schiff base ligands 3-[(2-hydroxyphenylmethylideneamino) coumarin (**L**¹) and 3-[(2-hydroxy-1-naphthylmethylideneamino)coumarin (**L**²) have been efficiently synthesized by the reaction of 3-amiocoumarin and *o*-hydroxy benzaldehyde or *o*-hydroxy naphthaldehyde and characterized spectroscopically. The ligands **L**¹ and **L**² have been used successfully to generate corresponding monometallic Bis-*N,O,O*-tridentate schiff base metal complexes.

All the compounds have been thoroughly characterized by microanalysis, relevant spectroscopy *viz.* MS, IR, ¹H, ¹³C NMR, EPR, UV-visible, Fluorescence spectroscopic methods and thermo gravimetric techniques. The unambiguous structures of representative compounds have been determined by means of single crystal X-ray diffraction study. The electrochemical and antimicrobial properties of a majority of the compounds have been investigated.