

## SUMMARY AND CONCLUSION

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The increasing interest in thiosemicarbazones that has arisen in recent decades has to a large extent been prompted by their broad therapeutic activity. The thiosemicarbazones of aromatic aldehydes and ketones have been shown to possess a diverse range of biological activities including anticancer, antitumor, antibacterial, antiviral, antimalarial and antifungal properties owing to their property to diffuse through the semipermeable membrane of the cell lines. Metal complexes of thiosemicarbazones often display enhanced activities when compared to the uncomplexed thiosemicarbazones. The enhanced effect may be attributed to the increased lipophilicity of the metal complexes compared to the ligand alone. The presence of coordination sites in the complexes enhances their activity. It is observed that biological activity depends on the parent aldehyde or ketone and increases remarkably when bulky groups are present at N<sup>4</sup> position.

Thiosemicarbazones are thiourea derivatives and are prepared by the condensation of thiosemicarbazides with aldehydes or ketones in acidic medium. They are represented by the general formula  $R^1R^2C=N-NH-C(S)-NH_2$ . They generally exist in the thioamido form in the solid state but in solution, they tend to exist as an equilibrium mixture of thioamido and thioiminol forms. The thioamido-thioiminol equilibrium depends on the pH of the medium used for reaction. Thiosemicarbazones can bind to a metal center in the neutral or the anionic forms.

Thiosemicarbazones have emerged as an important class of ligands over a period of time, for a variety of reasons, such as variable donor properties, structural diversity and biological applications. In order to pursue the interesting coordinating properties of thiosemicarbazones, complexes with different types of ligand environments are essential. So in the present work we chose two different ONS donor thiosemicarbazones as principal ligands. Introduction of heterocyclic bases like 1,10-phenanthroline, 2,2'-bipyridine, 4,4'-dimethyl-2,2'-bipyridine and 5,5'-dimethyl-2,2'-bipyridine, the classical N,N donor ligands leads to the syntheses of mixed ligand complexes which can cause different bonding, spectral properties and geometries in coordination compounds.

We have synthesized the following two new ligands using 5-bromo-3-methoxysalicylaldehyde, N(4)-phenylthiosemicarbazide and N(4)-cyclohexylthiosemicarbazide.

- 5-Bromo-3-methoxysalicylaldehyde-N(4)-phenylthiosemicarbazone
- 5-Bromo-3-methoxysalicylaldehyde-N(4)-cyclohexylthiosemicarbazone

The thesis is divided into eight chapters.

### *Chapter 1*

Chapter 1 involves a brief prologue to thiosemicarbazones and their metal complexes, bonding and coordination strategy of thiosemicarbazones and their various applications. The objectives of the present work and the various physicochemical methods adopted for the characterization of the thiosemicarbazones and their complexes are also discussed in this chapter.

## Chapter 2

Chapter 2 describes the syntheses of two new aldehyde based ONS donor thiosemicarbazones and their characterization by elemental analyses, mass, FTIR, UV-vis and <sup>1</sup>H NMR spectral studies. X-ray quality single crystals of these two ligands were grown and their molecular structures were established by single crystal X-ray diffraction studies.

The thiosemicarbazones synthesized are

- 5-Bromo-3-methoxysalicylaldehyde-N(4)-phenylthiosemicarbazone
- 5-Bromo-3-methoxysalicylaldehyde-N(4)-cyclohexylthiosemicarbazone

## Chapter 3

This chapter discusses the syntheses and characterization of two oxidovanadium(IV) complexes with one of the thiosemicarbazones. They are mononuclear complexes with heterocyclic bases 1,10-phenanthroline and 2,2'-bipyridine as coligands. Both the complexes are characterized by various techniques such as elemental analyses, molar conductivity studies, magnetic susceptibility measurements, FTIR, UV-vis and EPR spectral studies. The observed molar conductivity values in 10<sup>-3</sup> M DMF solution confirm that both the complexes are non-electrolytic in nature. Magnetic susceptibility measurements clearly indicate that the two complexes are paramagnetic in nature with vanadium in +4 oxidation state. In both the complexes, thiosemicarbazones are coordinated to the metal centre in the thioiminolate form and act as dideprotonated tridentate ligands. In the EPR spectra, *g* values are found to be less than the free electron value and in DMF at 77 K, they displayed well resolved axial anisotropy with two sets

of eight line pattern with  $g_{\parallel} < g_{\perp}$  and  $A_{\parallel} > A_{\perp}$  relationship characteristic of an axially compressed  $d_{xy}^1$  configuration.

#### *Chapter 4*

Chapter 4 deals with the syntheses and characterization of five nickel complexes of the thiosemicarbazones by CHNS analyses, conductivity and magnetic susceptibility measurements, infrared and electronic spectral studies. All the complexes are found to be non-electrolytic in nature. The five-coordinate complexes are found to be paramagnetic with two unpaired electrons. In all of them, thiosemicarbazone moiety coordinates to the metal in the thioiminolate form as evidenced from the infrared spectra.

#### *Chapter 5*

This chapter describes the syntheses and characterization of ten copper(II) complexes. The characterization techniques include elemental analyses, molar conductivity studies, magnetic susceptibility measurements, FTIR, UV-vis and EPR spectral studies and single crystal X-ray diffraction studies. Heterocyclic bases like 1,10-phenanthroline, 2,2'-bipyridine, 4,4'-dimethyl-2,2'-bipyridine and 5,5'-dimethyl-2,2'-bipyridine were used as coligands. In all the complexes, thiosemicarbazone exists in thioiminolate form and coordinates to the metal through azomethine nitrogen, thioiminolate sulfur and phenolate oxygen. The molar conductivity values obtained for all the complexes confirmed their non-electrolytic nature. The magnetic susceptibility measurements reveal that all the complexes are paramagnetic and for mononuclear complexes the effective magnetic moment values are found to be close to the spin only

value which corresponds to a single unpaired electron. The low magnetic moment values for two complexes may be due to considerable antiferromagnetic interaction between the metal centers. EPR spectra in polycrystalline state at 298 K show that some of the compounds are isotropic, some are axial and others are rhombic in nature. In DMF at 77 K, some complexes are found to be axial with hyperfine lines in the parallel and perpendicular regions. Superhyperfine splittings give clear evidence for the coordination of azomethine nitrogen and that of heterocyclic bases to the metal. 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. The complexes in which  $g_{\parallel} > g_{\perp} > 2.0023$  suggest a distorted square pyramidal structure and rules out the possibility of a trigonal bipyramidal structure which would be expected to have  $g_{\parallel} < g_{\perp}$ . We could isolate X-ray quality single crystals for two of the complexes by the slow evaporation of their mother liquors. They exhibit distorted square pyramidal geometry with O, N and S atoms of the principal ligand and one of the N atoms from the heterocyclic base occupying the square plane and the other N atom of base occupying the axial position. Intra and intermolecular hydrogen bonds facilitate packing in the crystal lattice. C-H $\cdots$  $\pi$  and  $\pi\cdots\pi$  interactions are also present.

### *Chapter 6*

Chapter 6 explains the syntheses and characterization of eight zinc complexes of the thiosemicarbazones by CHNS analyses, conductivity and magnetic susceptibility measurements, infrared and electronic spectral studies. The observed molar conductivity values in  $10^{-3}$  M DMF solution confirm that all the complexes are non-electrolytes. The tridentate

character of the thiosemicarbazones is inferred from IR spectra. The structure of one of the complexes has been resolved using single crystal X-ray diffraction studies. The crystal structure revealed a monoclinic space group  $P2_1$ . The compound adopts a distorted square pyramidal geometry with an  $N_2OS$  core as the base. The secondary amine group of the Schiff base dianion forms a hydrogen bond to the O atom of the dimethylformamide solvent. In the crystal, the phenyl ring of one of the two Schiff base anions is disordered over two positions in a 1:1 ratio. The crystal is found to be a racemic twin.

### *Chapter 7*

Eight cadmium complexes have been synthesized and physico-chemically characterized by CHNS analyses, conductivity and magnetic susceptibility measurements, infrared and electronic spectral studies. Heterocyclic bases like 1,10-phenanthroline, 2,2'-bipyridine, 4,4'-dimethyl-2,2'-bipyridine and 5,5'-dimethyl-2,2'-bipyridine act as coligands. The molar conductivity measurements in DMF ( $10^{-3}$  M) indicate that all the complexes are non-electrolytes. The IR spectral studies show that the thiosemicarbazones coordinate in thioiminolate form in all the complexes and act as dideprotonated tridentate ligands.

### *Chapter 8*

Chapter 8 includes the synthesis, crystal structure and spectral characterization of a dioxidomolybdenum(VI) complex of 5-bromo-3-methoxysalicylaldehyde-N(4)-phenylthiosemicarbazone. The characterization techniques include elemental analyses, magnetic susceptibility measurements, FTIR and UV-vis spectral studies. The compound is

diamagnetic in nature. The molecular structure of this complex was established by single crystal X-ray diffraction study. The coordination geometry around molybdenum is distorted octahedral in which the ligand coordinates to the metal in a tridentate manner forming five membered and six membered metallocycles involving the  $\text{MoO}_2^{2+}$  moiety. Oxygen, nitrogen and sulfur atoms of the ligand and one of the terminal oxo atom occupy the equatorial positions of the complex. The axial positions are occupied by the other terminal oxygen and oxygen atom of the solvent N,N-dimethylformamide.

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