CHAPTER 4

4.1 Introduction

Sulfur compounds are very promising in coordination chemistry due to their pharmaceutical properties. They are interesting due to their ability to form stable chelates with the essential metal ions in which the fungus needs ions in its metabolism. Transition metal complexes of some thiosemicarbazones possess some degree of cytotoxic activity. Thiosemicarbazones and their metal complexes have evoked considerable interest because of their biological activities, such as antitumor, antiviral, anticancer, antifungal, antibacterial, and antimalarial.

4.2 Experimental

4.2.1 Preparation of ligands

a) Acetylcyclohexanethiosemicarbazone (ACTSC):
An equimolar amount of Cyclohexylmethylketone (0.01 M) and thiosemicarbazide(0.01M) were dissolved in 20 ml aqueous methanol. The resulting mixture was reflux for 24 hours in the Presence of catalytic amount of gl.acetic acid. The progress of the reaction and purity of the products were monitored by TLC. After completion of the reaction, reaction mixture was poured into crushed ice. The separated product was filtered wash with cold water, several times and dried at room temperature.

\[ \text{Thiosemicarbazide} + \text{Acetylcyclohexane} \xrightarrow{\text{Reflux CH}_3\text{COOH}} \text{Acetylcyclohexane thiosemicarbazone} \]

Scheme-4.1

b) 3-methylbutanalthiosemicarbazone (MBTSC):
An equimolar amount of 3-methylbutaraldehyde (0.01 M) and thiosemicarbazide (0.01M) were dissolved in 20 ml aqueous methanol. The resulting mixture was reflux for 24 hours in the Presence of catalytic amount of gl.acetic acid. The progress of the reaction and purity of the products were monitored by TLC. After completion of the reaction, reaction mixture was poured into crushed ice. The separated product was filtered wash with cold water, several times and dried at room temperature.
c) **4-Bromothiophene-2-carbaldehydethiosemicarbazone (BTTSC):**

An equimolar amount of 4-Bromothiophene-2-carbaldehyde (0.01 M) and thiosemicarbazide (0.01M) were dissolved in 20 ml aqueous methanol. The resulting mixture was reflux for 24 hours in the Presence of catalytic amount of gl.acetic acid. The progress of the reaction and purity of the products were monitored by TLC. After completion of the reaction, reaction mixture was poured into crushed ice. The separated product was filtered wash with cold water, several times and dried at room temperature.

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{H} \\
\text{S} & \quad \text{N} \\
\text{H} & \quad \text{NH}_2
\end{align*}
\]

Scheme-4.2

4.2.3 Preparation of metal complexes

a) **Metal complexes of Acetylcyclohexane thiosemicarbazone (ACTSC):**

The metal complexes of acetylcyclohexane thiosemicarbazone were prepared by refluxing an ethanolic solution of the ligand (0.3mg, 2mmol) and respective metal salt solution (0.15, 1mmol). The reaction mixture was refluxed for 2 hours. Then maintain pH of the reaction mixture for complexation dilute ammonium hydroxide solution was added. It was filtered, washed with ethanol and dried in vaccum.

\[
\begin{align*}
\text{MX}_2.\text{nH}_2\text{O} + 2\text{HL} & \quad \overset{4\text{hr, methanol, Reflux}}{\rightarrow} \quad [\text{M(\text{HL})}_2.2\text{H}_2\text{O}] + 2\text{HX} \\
\text{(M= Co, Ni, Zn, Cd, Hg, Cu, Fe, X= Cl, HL} & \quad \overset{4\text{hr, methanol, Reflux}}{\rightarrow} \quad [\text{M(\text{HL})}_2.2\text{H}_2\text{O}] + 2\text{HX}
\end{align*}
\]

Scheme- 4.4

b) **Metal complexes of 3-Methylbutanal thiosemicarbazone (MBTSC):**

The metal complexes of 3-Methylbutanal thiosemicarbazone were prepared by refluxing an ethanolic solution of the ligand (0.3mg, 2mmol) and respective metal salt solution (0.15, 1mmol). The reaction mixture was refluxed for 2 hours. Then maintain...
pH of the reaction mixture for complexation dilute ammonium hydroxide solution was added. It was filtered, washed with ethanol and dried in vacum.

\[ \text{MX}_2\cdot n\text{H}_2\text{O} + 2\text{HL}^2 \xrightarrow{4\text{hr, methanol, Reflux}} \text{ammonia} \rightarrow [\text{M} (\text{HL}^2)_2\cdot 2\text{H}_2\text{O}] + 2\text{HX} \]

(M= Co, Ni, Zn, Cd, Hg, Cu, Fe, X= Cl, \(\text{HL}^2=\text{MBTSC}\))

**Scheme- 4.5**

c) **Metal complexes of 4-Bromothiophene-2-carbaldehyde thiosemicarbazone (BTTSC):**

The metal complexes of 4-Bromothiophene-2-carbaldehyde thiosemicarbazone were prepared by refluxing an ethanolic solution of the ligand (0.3mg, 2mmol) and respective metal salt solution (0.15, 1mmol). The reaction mixture was refluxed for 2 hours. Then maintain pH of the reaction mixture for complexation dilute ammonium hydroxide solution was added. It was filtered, washed with ethanol and dried in vacum.

\[ \text{MX}_2\cdot n\text{H}_2\text{O} + 2\text{HL}^3 \xrightarrow{4\text{hr, methanol, Reflux}} \text{ammonia} \rightarrow [\text{M} (\text{HL}^3)_2\cdot 2\text{H}_2\text{O}] + 2\text{HX} \]

(M= Co, Ni, Zn, Cd, Hg, Cu, Fe, X= Cl, \(\text{HL}^3=\text{MBTSC}\))

**Scheme- 4.6**