CHAPTER I

INTRODUCTION
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1. A. General:

The coordination chemistry of thiosemicarbazones and their corresponding transition metal complexes have been the subject of many studies[1-5]. Semicarbazone complexes of transition metals have been reported by various workers[6,7] and the transition metal complexes of thiosemicarbazones of aldehydes [aromatic as well as aliphatic], ketons and β – diketones have been amongst the most widely studied coordination compounds during the recent years.

The thiosemicarbazones containing both hard (N) and soft (S) donors[8,9] in position suitable for chelating metal ions, have been shown to act as versatile complexing agents for various metal ions in different oxidation states.

1. B. Chemistry of metal complexes of thiosemicarbazides and thiosemicarbazones:

The ligands having oxygen and / or nitrogen as the donor atoms are widely studied, the interest in sulphur donor chelating agents grown very rapidly and the number of chemical studies in this area has increased to a considerable proportions. Most of the early investigations on these systems were centered around their use as analytical reagents. The interest in complexes of these ligand systems now covers a
full gamut of areas ranging from general considerations of metal sulphur bonding and electron delocalization in transition metal complexes to potential biological activity and practical applications in the fields as diverse as rubber technology and agriculture. Discussion here is restricted only to O, S and N containing ligands, especially thiosemicarbazones.

1. B.1. Structure of thiosemicarbazide and thiosemicarbazone groups:

Thiosemicarbazide can exist[10,11] in the following tautomeric forms I and II.

\[
\begin{align*}
\text{I} & : \quad \text{NH-NH, } \quad H_2N-\text{C} \equiv \text{S} \\
\text{II} & : \quad \text{II} & : \quad \text{N-NH}_2 \\
\end{align*}
\]

It can act as a neutral or as a charged bidentate ligand by loosing a mercapto proton. Metal complexes containing the ligand in the uncharged form have been more extensively studied than those containing the deprotonated form of the ligand.

Thiosemicarbazone can exist[12, 13] in the following tautomeric forms III and IV.

\[
\begin{align*}
\text{III} & : \quad \text{C}=\text{N} \quad \text{N} \equiv \text{C} \quad \text{S} \\
\text{IV} & : \quad \text{C}=\text{N} \quad \text{N} \equiv \text{C} \quad \text{SH} \\
\end{align*}
\]
In the solid state, these thiosemicarbazones exit\[14\] in the thione form III. In the solution, however they are known to tautomerize\[15\] into the thiol form IV. In alkaline solution the structure IV is more favoured \[15\]. When an additional donor site D is incorporated in such ligands, linked to the carboxylic carbon via one or two intervening atoms D such as N, S and / or O tricoordination may takes place as shown in structure V.

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

With this knowledge taken from the literature\[16\], the 4 - acylthiosemicarbazone - 2 - pyrazolin - 5 - ones, can take any \[16,17\]of the following forms VI-IX.

It is known that such ligands in the solid state exists in the thione form VI and VIII. However, in the solution these forms might be in the equilibrium \[17-19\].
1. B.2. **Metal – ligand bond**:

The thiosemicarbazide or the thiosemicarbazone group has a tendency to form coordinate bonds through thio-keto sulphur or thio-enolic sulphur and through nitrogen of the hydrazine nitrogen (incase of thiosemicarbazide), through the azomethine nitrogen (in case of thiosemicarbazone). These coordinating sites for thiosemicarbazides (X, XI), thiosemicarbazones (XII, XIII) are shown in the following structures: X-XIII

![Structures of thiosemicarbazides and thiosemicarbazones](image)

Monodentate behavior of thiosemicarbazide and thiosemicarbazone is also observed in several Ag(I) and Co(III) complexes [20-24].

The ligands such as salicylaldehyde thiosemicarbazone or 4-acylthiosemicarbozone - 2 - pyrazolin - 5 - ones have an additional coordinating
functionality in the proximity of the S-N donating centres. These ligands are found to act as bidentate or tridentate ligands. The possible coordinating sites are shown in the following structures: XIV - XVIII

As bidentate ligand:

These ligands are known to act as neutral tridentate[25-28] as shown in the following structures: XIX, XXIV or as a mono-negatively charged tridentate by losing mercapto proton [25-30] as shown in structures: XX, XXIII or as a mono-negatively charged tridentate by losing phenolic-OH proton
[25,31-33] of salicylaldehyde thiosemicarbazone or 5 - hydroxy proton of 4 - acylthiosemicarbazones 2 - pyrazolin 5 - ones as shown in the structure XXI or doubly negatively charged tridentate by loosing a mercapto proton and aphenolic proton[25,31,32,34] of salicylaldehyde thiosemicarbazone or 5 - hydroxy proton of 4 - acylthiosemicarbazone 2 - pyrazolin -5 - ones as shown in structures:XXII. The bidentate behavior of such ligands is also observed [31-33] as shown in the structures:XIV-XVII.

As Tridentate Ligand:

As Tridentate Ligand:

XXIII XXIV
1. B.3. **Metal Complexes Containing O N S donor-Sequence:**

The sulphur donor ligands thiosemicarbazones have perhaps not received much attention as e.g. dithiophosphates, dithiocarbamates, dithio-\(\beta\)-diketonates etc. [34-42]. The real impetus toward developing the coordination chemistry of these potential ligands is probably due to their pharmacological activitites [43-64]. It is know that the observed activities is due to their metal-complexing ability[65-72].

There were only about eight metal thiosemicarbazone complexes investigated[73] upto 1975. However, the situation has changed substantially, and a number of metal thiosemicarbazone complexes have been reported during last thirty five years. The recent literature survey shows that this general class of compounds exhibits wide range of stereochemistries in complexation with transition metal ions, some of these complexes have been adequately studied.

Ablov and Gerbeleu[25,31,32] have studied the metal complexes formed by salicyladehydethiosemicarbazone (ONSH\(_2\)). This ligand readily loses a proton from the phenolic group and acts
as a singly charged tridentate, coordinating through the oxygen, the imino nitrogen and the thione sulphur atoms. It can also act as a doubly negatively charged tridentate by losing a proton from the mercapto group. The Co(III) complexes \([\text{Co(ONSH)}_2]\text{Cl}\) and \([\text{Co(ONSH)}(\text{ONS})].\text{H}_2\text{O}\), the Cr(III) complexes \([\text{Cr(ONSH)}_2]\text{Cl}\), \([\text{Cr(ONSH)}(\text{ONS})].\text{H}_2\text{O}\) and the Fe(III) complex \(\text{Fe(ONSH)}\text{X}_2.2.5\text{H}_2\text{O}\) \((\text{X} = \text{Cl, Br})\) have been prepared. With Ni(II) it forms green paramagnetic complexes. The mode of coordination of the neutral ligand is tridentate and the compound is formulated as \([\text{Ni(ONSH}_2]\text{Cl})\text{(NO}_3\text{)}\text{2}\) without any supporting evidence. With Cu(II) and Zn(II), the complexes \(\text{CuX(ONSH)}\text{H}_2\text{O}\) \((\text{X} = \text{Cl, HCO}_2\text{)}\) and \(\text{Zn(ONSH)}_2\text{X}_2\) \((\text{X} = \text{Cl, NO}_3\text{)}\) are formed. The Mossbauer spectra of its Fe(III) complexes and of its 5-chloro and 5-bromo derivatives indicate a temperature-dependent transition between high and low spin states[74].

Mossbauer spectral data have been obtained for the Fe(II) and Fe(III) complexes of the thiosemicarbazones of salicylaldehyde and biacetyl monoxime at 80 and 300 \(^0\text{K}\)[75]. In Fe(III) complexes the greater proportion of the iron atoms are in the low-spin state. The Fe(II) complex of the salicylaldehyde
thiosemicarbazone is high-spin but that of biacetylmonoxime thiosemicarbazone is low-spin. With the thiosemicarbazone of diacetylmonoxime (DAOTSC) two types of complexes are formed with Fe(III) viz, Fe (DAOTSC) $X_2$ and the inner complex Fe (DAOTSC-H)$_2$ [76-78].

Ablov and coworkers[79] used Mossbauer spectroscopy to study a number of thiosemicarbazone complexes of both Fe(II) and Fe(III). The inner complexes formed by the tridentate ligands, pyruvic acid thiosemicarbazone (PVATSC) and the thiosemicarbazone of methyl pyruvate[79] (MePVATSC) with Fe(III) are high spin and have isomer shift and quadrupole shift values in the usual range for high spin Fe(III). The donor atom set is $O_2N_2S_2$ for both compounds.

Pyridine - 2 - aldehydethiosemicarbazone (HPAT) forms stable complexes with Fe(II) and Ni(II) in which it behaves as a neutral tridentate ligand. The Fe(II) complexes $[Fe(HPAT)_2]X_2$ ( $X = \text{Cl, Br}$ ) are spin-paired, whereas Ni(II) complexes $[Ni(HPAT)_2]X_2$ ( $X = \text{Cl, NO}_3$ ) are spin free. The ligand can be deprotonated [80] to yield complexes $[M(PAT)_2]$ $[M=\text{Fe(II),Ni(II)}]$and$[\text{Co(PAT)}_2]\text{Cl.3H}_2\text{O}$. Ablov and
Belichuk[80] reacted \([\text{CoCl(DH)}_2\text{.H}_2\text{O}]\) at low temperature with pyridine-2-aldehydethiosemicarbazone (HPAT) to give \([\text{CoCl(DH)}_2(\text{HPAT})]\) and \([\text{Co(DH)}_2(\text{HPAT})_2]\text{Cl}\). On heating, HPAT displaced DH from the inner coordination sphere giving \([\text{Co(PAT)}_2]\).

Ablov et al.[81] synthesised Co(III) complexes of anthraldehydethiosemicarbazone (H-than) and mixed complex with DMG (DH). They found that in \([\text{Co(than)}_2]\text{X.nH}_2\text{O}\) \((X = \text{Cl, Br, I or NCS})\), the ligand (H-than) is tridentate whereas in \([\text{CoCl(DH)}_2(\text{H-than})]\text{.2H}_2\text{O}\) or \([\text{Co(DH)}_2(\text{H-than})]\text{.Cl}_4\text{5H}_2\text{O}\), it is monodentate and coordinate to Co(III) via S.

Ablov et al.[82] have studied the complexes of cobalt with thiosemicarbazone of pyruvic acid amide (LH) and pyruvic acid diethylamide (L'H). The complexes were formulated as \(\text{CoX}_2(\text{LH})_n\text{EtOH}\) \((X = \text{Cl, Br, NO}_3, \frac{1}{2}\text{SO}_4; n = \frac{1}{2} \text{ or } 1)\), \(\text{CoL}_2\text{X'.2H}_2\text{O}\) \((\text{X'} = \text{Cl, Br, NO}_3)\) and \(\text{CoL}_2\text{Z.H}_2\text{O}\) \((Z = \text{Cl, Br, ClO}_4, \text{NO}_3; n = 1, 2, 3 \text{ or } 5)\). The infrared spectral studies have suggested the tridentate nature of both the ligands.

X-ray diffraction studies have been made on coordination compounds of Ni(II) with thio and selenosemicarbazones of salicylaldehyde and
ammonia[83]. In the presence of organic base, NiLQ (L = O-HOC₆H₄CH = NiNHCSNH₂, Q = α, β, γ - picoline, 2,6-lutidine, morpholine), NiL'Q.5H₂O (L' = O-HOC₆H₄CH = NNHCSeNH₂, Q = pyridine . 2,6-lutidine), NiL'Q.H₂O (Q = PhNH₂, picolines) and NiL'Q (Q = morpholine) types of compounds have been obtained. All these compounds are non-electrolyte and diamagnetic.

Ablov et al. [84] studied the complex formation of Ni(II), with thiosemicarbazones of O-aminobenzaldehyde and O-(dimethylamino) benzaldehyde in presence of NH₄OH. The respective products obtained were NiLNH₃ and NiL₂.2H₂O. Ablov and Belichuk[85] synthesized the coordination compounds of Rh(III) with thiosemicarbazone and 4-phenylthiosemicabazone of pyroracemic acid. The compounds were formulated as [Rh(HL)₂]Cl.3H₂O.

Zeientsov et al. [86,87] synthesized and studied magnetic susceptibility of binuclear and trinuclear compounds of Cu(II) with terdentate derivatives of salicylaldehydethisemicarbazone. Ablov and coworkers[88] made thermomagnatic study of Fe(III) complexes with thiosemicabazones of substituted salicylaldehydes. Gerbeleu [89] have
reported V(III) complexes of salicylaldehyde-thiosemicarbazone. The octahedral NH$_4$[V(ONS)$_2$].H$_2$O and [V(ONSH)(ONS)].H$_2$O complexes have been prepared. Ablov and Bologa[90] synthesized the coordination compounds of Rh(III) with salicylaldehydethiosemicarbazone. The compound was formulated as [Rh(ONSH)]Cl.4H$_2$O.

Hovorka and Holzbecher[91] have studied gravimetric determination of Cd(II) using salicylaldehydethiosemicarbazone. The compound was formulated as Cd(ONSH)$_2$. This method is applicable only for sulphate and nitrate salt of Cd(II) and is inapplicable to a solution containing chloride, fluoride or oxalate of Cd(II) in presence of Ca(II), Sr(II), Ba(II) and Mg(II) salts. Revenko and Gerbeleu[92] have prepared several VO(II) complexes of the dibasic ONS donor ligands. The observed sub-normal magnetic moments, was interpreted in favour of dimeric structure.

Adipoin thiosemicarbazone (ONSH) forms the complexes, M(ONSH)$_2$X$_2$.nH$_2$O (M = Co(II), Ni(II), X = Cl, Br or NO$_3$) and [Co(ONS)$_2$].CH$_3$CO$_2$. The involvement of the oxygen atom in coordination is indicated by the fact that cyclohexanone
Thiosemicabazone[93] does not form complexes with Co(III).

Thiosemicabazone of benzoylformic acid behaves as a monobasic acid under acidic conditions and as dibasic acid in alkaline solution. The author[94] reported the dibasic form for the Fe(II), Co(II), Ni(II), Cd(II) and Pb(II) complexes. Gerbeleu et al.[95] measured magnetic susceptibility for the coordination compounds of Cu(II) with thiosemicarbazones of benzoylformic acid and adipoin. Anomalous magnetic properties were attributed to antiferromagnetic interaction in the compounds. The structure of the two six coordinate paramagnetic complexes of Ni(II) with tridentate thiosemicarbazones of isoquinoline-1-carboxaldehyde and pyridine-2-aldehyde have been determined[96,97].

Gerbeleu reported[98] the metal complexes of resacetophenonethiosemicarbazone and also its mixed ligand complexes with DMG. Resacetophenonethiosemicarbazone acts as tridentate ligand using S and N atoms of hydrazone group and O atom of the phenol group in ortho position. In mixed ligand complexes with DMG it acts as a monodentate ligand. Several authors had examined the tridentate
behavior of isatin-3-thiosemicarbazone with various metal ions. The ligand probably terdentate with the ketone oxygen acting as a donor as well as the N and S of the TSC residue. Hovorka et al.[99] studied the colour reactions of various metal salts with 3-thiosemicarbazones of isatin, 1-methylisatin and 1-benzyl isatin. They have prepared metal complexes of above ligands with Hg(II), Pb(II), Ti(IV), Ni(II), Co(II) and Zn(II).

Gerbeleu et al.[100] synthesized the polynuclear complexes of Cu(II) with S-methylthiosemicarbazones of substituted salicylaldehydes (CuL). The complexes were characterized by magnetic and infrared data. The ligand is tridentate and the complexes are polymeric. Simonova et al.[101] have studied the Fe(III) complexes of 5-Alkylisothiosemicarbazone of substituted salicylaldelydes. The complexes were formulated as FeLCl and [FeL]_2O.

Gerbeleu and his coworkers[102] showed that alkylation of the thiocarbonyl sulphur of thiosemicarbazone derivatives induces not only complexation through the terminal amino group but also functions as a monoacidic ligand. In the presence of
various metal salts these ligands are capable of condensing at the terminal amino nitrogen atom through another aldehyde or ketone to yield quadridentate ligands. Using such template reactions Gerbeleu and Zhovmir[103] claimed to isolate thiosemicarbazone complexes without sulphur coordination.

Gerbeleu et al.[104] described iron(II) complexes of various alkylthiosemicarbazones of the type (FeL₂X₂).nH₂O (where L = the uncharged thiosemicarbazone derivative of acetone, ethyl methyl ketone, cyclopentanone, or cyclohexanone; X = Cl or Br; and n = 0, 1, 2). The cryomagnetic measurements and Mossbauer parameters led these workers to suggest a pentacoordinated high-spin iron(II) configuration for these compounds. In the further study Campbell et al.[105] suggested that room temperature magnetic moments and features of diffuse reflectance spectra of this and other related alkylthiosemicarbazones are indeed compatible with either a five-coordinate or a distorted octahedral geometry. Based on characteristic isomer shift values and the absence of halogendependent bands in the far-IR region, these authors have concluded that the iron(II) high-spin species in these compounds are in a tetragonally distorted octahedral environment with very weakly-
coordinated halides. They found sufficiently large splittings for these complexes.

West et al.[106] prepared and characterized copper(I) and copper(II) complexes of the thiosemicarbazone derivatives of anisaldehyde (ATSHZ), p-Tolualdehyde (TTSZH), Vanilline (VTSZH) and Fluorencene (FTSZH) by IR, Raman electronic spectral studies and by magnetic measurements. They reported the following polymeric structure:(XXV) for [Cu(TTSZ)]_n, [Cu(ATSZ)]_n and [Cu(VTSZ)]_n.nH_2O and dimeric 4 - coordinated copper(I) (structure:XXVI) for [Cu(VTSZ)Cl]_2.H_2O and [Cu(VTSZ)(CH_3COO)]_2 and dimeric 5-coordinated copper(II) (structure: XXVII) for [Cu(FTSZ)_2]_2.2H_2O.

XXV

\[
\text{N} \quad \text{S} \quad \text{Cu} \quad \text{S} \quad \text{N}
\]

XXVI

\[
\text{N} \quad \text{S} \quad \text{X} \quad \text{Cu} \quad \text{S} \quad \text{X} \quad \text{N}
\]

XXVII

\[
\text{N} \quad \text{S} \quad \text{Cu} \quad \text{N} \quad \text{S}
\]
Isatin - 3 - thiosemicarbazone complexes with Co(II), Ni(II), Cu(II), Zn(II), Hg (II) and Pd(II) were synthesized and evaluated for their antimicrobial activity against 7 pathogenic bacteria and 4 - fungi by Konstantinovic et al. [107]. They reported that the complexes have an enhanced activity compared to ligand due to involvement of transition metal during coordination.

The following online structural reports for 1H-Indole - 3 - Carbaldehyde thiosemicarbazone have been made by Rizal et al.[108].

![XXVIII](image)

Zhang et al.[109] synthesized and characterized two new copper thiosemicarbazone complexes with ONNS quadridentate system and were evaluated for anticancer activity on cisplatin resistant neuroblastoma cells. The substituted copper 8-hydroxyquinoline- 2-Carboxaldehyde-4, 4 dimethyl-3-thiosemicarbazide [CuHQDMTS] exhibited stronger cell growth inhibition activity than the unsubstituted copper 8-hydroxyquinoline 2-carboxaldehyde thiosemicarbazide complexes. They selected copper
thiosemicarbazone complexes because copper ions are physiologically trace elements in human bodies.

R = H, CuHQTS
R' = CH₃, CuHQDMTS

Zeng et al. [110] has synthesized and characterized new zinc bromide complex of a Schiff-base ligand derived from thiosemicarbazide and 4-methoxylphenyldehye, which shows Ca. 13 times better SHG efficiency than urea. The Schiff-base ligand is coordinated to the Zn(II) via the monodentate mercapto sulphur atom.

Li and Zhao et al. [111] reported the quantum chemical calculation studies on 4-phenyl-1-(1-phenylethylidene) thiosemicarbazide. They reported that the sulfur atom and all of the nitrogen atoms have bigger negative charges and they are the potential sites to react with metallic ions, which make the title compound a multidentate ligand. They also reported that coordination ability of sulfur atom...
and nitrogen atom of the C = N double bond increases with the increase of polarity of solvent.

Leovac et al. [112] studied the supramolecular arrangement in the complexes of 5-methyl isothiosemicarbazide. Due to non-covalent intermolecular interaction between the complex [Ni(ITSC)₂(NO₃)₂] and [Ni(ITSC)₂(H₂O)₂] (tere).₂H₂O tend to associate into the characteristic 2D-block are separated by 5-methyl moieties (ITSC = S-methylthiosemicarbazide, tere = terpthalate anion). In the case of latter complex are the terpthalate anions are located between the 5-methyl-groups, which transform the 2D into 3D supramolecular structure.

Baghlaf et al. [113] synthesized complexes containing the schiff-base ligand 1-acetyl ferrocene thiosemicarbazone. Nishant et al. [114] prepared new polymeric resin ligand by the condensation of thiosemicarbazides with formaldehyde in the presence of acidic medium. The polymeric ligand and its polymer metal complexes were characterized by elemental analysis, TGA, FT-IR, ¹³C-NMR and ¹H-NMR, UV-visible and EPR studies. They also reported the antibacterial activities of all synthesized polymer against B. substilis, S. aureus (gram-positive) and E.
Coli. They reported that these compound shows excellent activities against bacteria using the shaking flask-method.

Synthesis, magnetic and spectral studies of Chromium(III), Manganese(III), Iron(III) and Cobalt(III), complexes of thiosemicarbazones derived from benzil α-monoxime and unsubstituted/substituted thiosemicarbazides as biological agent have been made by Sharma and Srivastava [115].

Beraldo et al. [116] carried out studies on Nickel(II), Copper(I) and Copper(II) complexes with bidenate heterocyclic thiosemicarbazones of 3-and 4-formyl pyridine (H₃FPT and H₄FPT) & 3-and 4-acetyl pyridine (H₃APT and H₄APT).
Synthesis, physicochemical and voltammetric characterization of high spin octahedral Iron(III) complexes with pyridoxal semi, thiosemi and S-methylisothiosemicarbazones has been reported by Jevtovic et al. [117].

Agarwal et al. [118] have synthesized a novel series of Schiff-bases by condensation of 4-aminoantipyrine and various aromatic aldehydes followed by reaction with thiosemicarbazide. They reported the magnetospectral, antibacterial and antifungal properties of the copper(II) complexes of the following thiosemicarbazones.

![Chemical Structure](image)
West et al. [119] reported the review article on structural studies of 2,6-diacetyl and 2,6-diformylpridine bis(thiosemicarbazones). They reported the 7-coordinated complexes of iron(II), indium(III), tin(IV), bismuth(III) with the bis(thiosemicarbazones) ligands. They proposed binuclear complexes for zinc(II) with bis(thiosemicarbazone) moieties. Copper(II) complexes having general composition CuL₂X₂ [where X = Cl⁻, Br⁻, NO₃⁻, I⁻, SO₄²⁻, L = p-methyl acetophenone thiosemicarbazone] have been prepared and characterized by Chandra et al. [120].

Casas et al. [121] reported the reactions of thiosemicarbazones derived from β-ketoamides and β-ketoesters with Zn(II) and Cd(II) acetates and discovered the unreported zinc complex with a
dideprotenated ligand. The use of a thiosemicarbazone as a chromogen reagent for the spectrophotometric determination of indium(II) has been reported by Herrador et al. [122]. They studied the nature of the complex and the effect of interferences.

Leovac et al. [123] synthesized the mixed ligand octahedral cobalt(III) complexes with the following salicyladehyde semi-(H₂L¹), thiosemi-(H₂L²) and S-methyliso thiosemicabazone (H₂L³).

\[ XXXIV \]

\[ \text{XXXIV} \]

\[ X = O \ [H₂L¹] \quad \text{and} \quad = S \ [H₂L²] \]

\[ XXXV \]

\[ \text{XXXV} \]

Agarwal et al. [124] proposed the following structure for the oxovanadium(IV) complexes of 4[N-(4'-nitrobenzalidene)amino] antipyninethiosemicarbazone [4'-NO₂ BAAPTS] and 4 [N-(furan -2'-aldimine)amino] antipyrine thiosemicarbazone
[FFAAPTS] with general composition
VOX₂L[X = Cl, Br, I, NO₃ or NCS] and VO(CIO₄)₂ (L)
H₂O [L = 4'-NO₂ BAAPTS or FFAAPTS].

\[
\begin{align*}
XXXVI & \quad \begin{array}{c}
\begin{array}{c}
\text{N} \\
\text{S} \\
\text{N}
\end{array} \\
\text{V} = \text{O}
\end{array} \\
\text{X}
\end{align*}
\quad \text{and} \quad
\begin{align*}
XXXVII & \quad \begin{array}{c}
\begin{array}{c}
\text{N} \\
\text{S} \\
\text{N}
\end{array} \\
\text{V} = \text{O}
\end{array} \\
\text{OH}_2
\end{align*}
\]

Leovac et al. [125] reported the crystal and molecular structure of [2,6-diacetyl pyridine bis (S-methylisothiosemicarbazonato)] diazide-iron(III) of the formula [Fe(HL)(NO₃)₂]. The two novel oxovanadium(IV) complexes of 2-acetylpyridine-S-methylidithiocarbazate [acpy-mdtch] and 2-acetylpyridine-4 phenylthiosemicarbazate (acpy-Pttsc) have been synthesized and characterized by Koo et al. [126].

The thermodynamic stability constants and thermodynamic parameters have been calculated by Akgemci and Atalay [127] for Cu(II), Co(II), Zn(II) and Cd(II) complexes with 9-ethyl-3-carbazole carboxaldehyde-4-phenyl-3-thiosemicarbazone. New palladium(II) complexes with 3,5-diacyl 1,2,4-triazole
bis(thiosemicarbazone) \( (H_2L^2) \), 2,6-diacetylpypridine bis(thiosemicarbazone) \( (H_2L^3) \) and benzyl bis(thiosemicarbazone) \( (H_2L^4) \) namely \([\text{Pd} \ (H_2L^2) \text{Cl}_2]\) (1), \([\text{Pd} \ (H_2L^3) \text{Cl}_2]\) (2) and \([\text{Pd}L^4]\) (3) were synthesized and characterized by Souza et al.[128]. They claimed that this is the first report on a single crystal structure of a bis(thiosemicarbazone) palladium(II) complex. They have also tested cytotoxic activity of this compound.

Synthesis and Characterization of bis (cyclopentadienyl) titanium(IV) derivatives with 2,6-diacetylpypridine-bis-(S-alkyl isothiosemicarbazones)
and their reactions with β-diketones was reported by Sengupta et al. [129].

X-ray crystal structure of cytotoxic planar Ni(II) complexes of N,N-dimethyl 2-acetylpyridine thiosemicarbazone was reported by Padhye et al. [130]. They confirmed that rigid planar structure provided by the thiosemicarbazone moiety was probably responsible for the stability and biological activity.

Bindu and Kurup [131] have synthesized and characterized base adducts of iron(III) and cobalt(III) complexes containing salicylaldehyde N(4)-phenylthiosemicarbazone and heterocyclic base(s). Beraldo et al. [132] synthesized and characterized Nickel(II), Copper(I) and Copper(II) complexes of thiosemicarbazones derived from 3-and 4-formylpyridine and 3-and 4-acetylpyridine.

Roy and Basu [133] separated gold and silver using a chelating resin namely thiosemicarbazide incorporated Amberlite IRC-50. Transition metal complexes containing a bidentate N, S donor ligand i.e. cis-3,7-dimethyl-2,6-octadienthiosemicarbazone have been synthesized and characterized [134] by elemental analysis, molar
conductance, magnetic susceptibility measurements and various spectral studies.

Beraldo et al. [135] have synthesised three new copper complexes of general formula [Cu(HL)Cl₂], where HL = N(4)-ortho, N(4)-meta and N(4)-paratoluoyl-2-benzoylpyridine thiosemicarbazones. The studied compounds have also been tested for their antifungal activity against *Candida albicans*. Complexes of ruthenium(III), rhodium(III) and irridium(III) with ligands bearing 2,6-diacetyl pyridine bis (S-alkylisothiosemicarbazones) have been reported by Sharma and Srivastava [136].

Bera and Saha [137] have reported the electrochemical behaviour of series of copper(II) complexes of pyrazolylthiosemicarbazones and 5-alkyl / aryl dithiocarbazates under quasi-reversible one electron reduction in the range of -0.370 V to -0.480 V versus SCE.

Mn(II), Co(II), Ni(II) and Cu(II) complexes with thiosemicarbazone derived from 2-acetyl thiophene have been reported by Chandra and Kumar [138].
Prasad and Reddy [139] has used 1-phenyl-1,2-propanedione-2-oxime thiosemicarbazone as a spectrophotometric reagent for the determination of Cu(II) and Ni(II). Spectrophotometric determination of nickel(II) with 2-hydroxy-3-methoxybenzaldehyde thiosemicarbazone was made by Reddy et al. [140].

Synthesis, characterisation and coordination properties of 5-methyl-3-formylpyrazone N-benzylthiosemicarbazone have been reported by Bera and Saha [141]. Joshi et al. [142] reported the synthesis of new thiosemicarbazide 1,2,4-triazoles heterocycles bearing thiophene nucleus. Synthesis and structural evaluation of transition metal complexes of thiosemicarbazone and semicarbazone derived from pyrrole-2-carboxaldehyde has been made by Chandra and Kumar [143].

Amine exchange reactions of bis (isonitroso-β-ketoimino) nickel(II) complexes with polyamines and thiosemicarbazide have been reported [144]. Thakur et al. [145] reported the Oxotitanium complexes of ortho-substituted benzalidene thiosemicarbazones. Balasubramanian and Chinnasamy [146] reported the catalytic activities of triphenylphosphine /
triphenylarsine complexes of ruthenium(II) with mono basic bidentate thiosemicarbazones. Kumar et al. [147] have made physico-chemical and spectral studies of nickel(II) complexes of 2-substituted benzaldehyde semicarbazones and thiosemicarbazones.

Some new palladium(II) complexes of S-methyl, S-benzyl-β-N-(5-methylpyrazole-3-yl) methylene dithiocarbazate and 5 - methyl - 3 - formylpyrazole 3-pyrrolidinyl, N-benzylthiosemicarbazone have been synthesized and characterized by P. Bera [148]. Spectroscopic and biochemical studies of chromium(III) and manganese(II) complexes with p-vanillin containing thiosemicarbazone and semicarbazone ligands were reported [149]. Oxo technetium (V) complexes with a novel class of tridentate thiosemicarbazide ligands were prepared and synthesized [150]. The author reported that this is the first examples of Oxo technetium(V) complexes with N, S chelate-bonded thiosemicarbazones.
The synthetic, spectroscopic and biological studies of sixteen ring substituted 4-phenyl thiosemicarbazones and 4-nitrophenyl thiosemicarbazones of anisaldehyde, 4-chloro benzaldehyde, 4-fluorobenzaldehyde and vanillin with ruthenium(III) and rhodium(III) chlorides were reported by Srivastava et al. [151].

Research article on synthesis, structure, electrochemistry and spectral characterization of bis-isatin thiosemicarbazone metal complexes and their antitumour activity against *E. A. Carcinoma* in Swiss Albino mice was reported by Sathisha et al. [152]. The representative structure of the ligand is as follow.

![Chemical structure](image)

Using slow evaporation technique semiorganic single crystal of thiosemicarbazide cadmium chloride and mercury ions doped
thiosemicarbazide cadmium choride were synthesized and discussed in details by Linet et al. [153]. Rhenium(V) coordination compounds with pyroracemic acid and phenylglycoxylic acid thiosemicarbazones for various metal-to-ligand ratio in 1-7 M hydrohalic acids were reported by Kaloev and Turieva [154]. Syntheses and crystal structure of an organometallic thiosemicarbazones and an organometallic enehydrazides were studied by Shi et al. [155].

New lead(II) complexes with N, S-ligands including a lead pyrazolonate with unusual packing, the flexibility was reported by Casas et al. [156]. Syntheses, characterization and vitro antiamoebic activity of new Pd(II) complexes with 1-N-substituted thiocarbamoyl - 3 , 5-diphenyl-2-pyrazolin derivatives was reported by Budakoti et al. [157].

Reddy et al. [158] describe the selective and sensitive extractive spectrophotometric determination of micro amounts of palladium(II) in spiked samples, using a new reagent N-ethyl-3- carbazole carbaxaldehyde thiosemicarbazone. Konstantinovic et al. [159] prepared and characterized the isatin-β-thiosemicarbazone complexes of Co(II), Ni(II), Cu(II), Zn(II), Hg(II) and Pd(II). They also reported the
thermal stability of the complexes. Labisbal et al. [160] made structural studies of pyrazineformamide N,4-methylthiosemi-carbazone and its zinc(II) and cadmium(II) complexes. A. Gautam et al. [161] reported the synthesis, spectroscopic and antimicrobial studies on bivalent complexes of bis(thiosemicarbazone) type ligand.

Fan et al. [162] reported the two different structure for (E)-1-(2-pyridylmethylene) thiosemicarbazone units for In(III) complex.

\[
\begin{align*}
\text{InCl}_3 & + \text{In(III) complex} \\
\end{align*}
\]

A series of streptocide-, sulfacyl-, norsulfazole-, ethazole-, sulfadimezinc-, and sulfapyridazine-, containing copper(II) and nickel(II) salicylidenethiosemicarbazidates and salicylidene-4-phenilthiosemicarbazidates possessing high antimicrobial activity has been reported by Gulya et al. [163]

Synthesis, spectral characterization and eukaryotic DNA degradation of thiosemicarbazones and their platinum(IV) complexes were reported by Al-
Hazmi et al. [164]. Novel cyclopalladated and coordination palladium and platinum complexes derived from $\alpha$-diphenylethanedione bis(thiosemicarbazones) has been reported by Matesanz and Souza [165]. They have also reported structural studies and cytotoxic activity against human $A - 2780$ and $A - 2780$ cis $R$ carcinoma cell lines.

N-ethyl-3-carbazolecarboxaldehyde-3-thiosemicarbazone was proposed as a new sensitive reagent for the extractive spectrophotometric determination of zin(II) by Reddy et al. [166]. Crystal structure of Bis [1 - (2 - hydroxyethyl) -4, 10-diazapyrazolo fluoren - 5(1H) - one thiosemicarbazonato]zinc(II) dimethylformamide trisolvate monohydrate was reported by Che[167]. $^1$H, $^{13}$C and $^{51}$V NMR spectroscopic and single crystal studies for three oxovanadium(IV) and three cis-dioxovanadium(V) complexes with thiosemicarbazones has been made by Deflon et al. [168]. Schiff base complexes of Cu(II), Co(II) and Ni(II) with two coumarin-3-yl-thiosemicarbazone derivatives (1E) - 1 - [1-(2-oxo-2H-chromen-3-yl) ethilidene] thiosemicarbazide were reported [169].
Synthesis, characterization, crystal structures in vitro and in vivo antitumor activity of palladium(II) and zinc(II) complexes with 2-formyl and 2-acetylpyridine N-(4)-1-(2-pyridyl)-piperazinylthiosemicarbazone were reported by Demertzi et al. [170]. Payraz et al. [171] reported the synthesis, crystal structure and biological activity of 1-(1H-benzoimidazol-2-yl) ethanone thiosemicarbazone and its cobalt complex. They have also investigated the free radical scavenging activity of the compound against 1, 1-diphenyl-2-picrylhydrazilhydrate.

Arguelles et al. [172] reported the complexes of 2-acetyl-y-butyrolactone and 2-furancarbaldehydethiosemicarbazones. Anilkumar and Chandra [173] synthesized octahedral Co(II) and Ni(II) complexes with thiosemicarbazone and semicarbazone derived from pyrole-2-carboxaldehyde. They proposed the tetragonal geometry for Cu(II) complex with the above ligand. Four molybdenum(VI) thiosemicarbazonato complexes have been synthesized and characterized by Seena and Kurup [174]. They prepared dinuclear complexes [(MoO$_2$L$_1$)$_2$] and [(MoO$_2$L$_2$)$_2$], by the reaction of [(MoO$_2$(acac)$_2$] with 2-hydroxyacetophenone N(4)-cyclohexyl (H$_2$L$_1$) and
N(4)-phenyl \([H_2L^2]\) thiosemicarbazone in the alcoholic medium.

White et al. [175] prepared zinc and copper bis(thiosemicarbazonato) complexes containing more than one metal centre with a view to examine their application for molecular imaging. They reported that zinc complexes are fluorescent with excitation and emission at relatively long wavelengths. Beraldo et al. [176] have synthesized 4-nitroacetophenone-derived thiosemicarbazones and their copper(II) complexes with significant \textit{in vitro} antitrypanosomal activity.

Tarasconi et al. [177] reported that compounds of Cu(I) stabilized in its reduced state by two triphenylphosphines, in which 4-fluro benzaldehydethiosemicarbazone and N-methyl thiosemicarbazone act as a chelating agent through their sulfur and iminonitrogen. Reaction of 3-indole carboxaldehyde with aminothiocarbonylhydrazine form 3- indole carboxaldehyde thiosemicarbazones [178]. These thiosemicarbazones form the following complexes with palladium(II).
Warren et al. [179] designed M(II) bis(thiosemicarbazonato) complexes for fluorescence imaging, where M = Ni(II), Cu(I) and Zn(II). A report on pentadentate thiosemicarbazones as a versatile chelating system has been made by Bermejo et al. [180]. They have checked the influence of different factors such as experimental procedure, size of metal, structure of ligand and metal oxidation state on the final structure of the complex. Zhao et al. [181] synthesized 1-(rhodamine B) lactum-thiosemicarbazide as a chemo sensor for copper ion.

The four complexes of iron and cobalt with pentadentate ligands, 2,6-diacetylpyridinebis(thiosemicarbazone) and 2,6-diacetylpyridinebis
(phenylthiosemicarbazones) were synthesized and characterized by Eichhorn et al. [182]. The report on structure and metal type effects on cure kinetics of DGEBA with benzol bisthiosemicarbazone complexes has been made [183]. The study on the redox behaviour of substituted thiosemicarbazones and the influence of these substitutions in the thiosemicarbazone moiety on the redox properties has been made [184].

Synthesis and antimicrobial studies of some new 3-[phenyldiazenyl] benzaldehyde N-phenyl thiosemicarbazones have been made by Halve et al. [185]. Franco et al. [186] reported the synthesis and x-ray structural study of novel Ni(II) complexes with pyridoxal-semicarbazone and pyridoxalthiosemicarbazone. Synthesis, characterisation and antibacterial activities of polyurea-containing thiosemicarbazide-metal complexes were reported by Hasnain et al. [187].

Tosi et al. [188] examined the ligand behaviour of pyridoxalthiosemicarbazone in series of metal complexes of formula M (H₂L) X₂, M (HL) X and ML [M = Co, Ni or Zn, X = NO₃ or CH₃CO₂]. Desiraju et al. [189] have made topological analysis of hydrogen bond in 1-formyl-3-thiosemicarbazide. A new
semiorganic non-linear optical thiosemicabazide cadmium chloride monohydrate has been synthesised by Yayavel et al. [190] and grow the transparent single crystal by slow cooling and slow evaporation method.

Hameed et al. [191] reported the synthesis of biologically active heterocyclic compounds (R) -1-(4-bromobenzoyl)-4-(1-phenyl propyl) thiosemicabazide. Cycloplatination of thiosemicarbazones derived from furane was reported by Adrio et al. [192]. They also reported the crystal and molecular structure of [{pt[OC$_2$H$_4$] C (Me) = NN = C(S) NHEt}]$_2$ {µ - Ph$_2$P(CH$_2$)$_2$PPh$_2$}. Interaction of organolead (IV) derivatives with formyl and acetylferrocene thiosemicarbazones was studied by Touced et al. [193]. The trans octahedral geometry of the complexes were reported on the basis of x-ray crystallography. Pundir and Chandra [194] have made spectral studies on cobalt(II) complexes of 12-membered macrocyclic ligands having thiosemicarbazone moieties. Tuceda et al. [195] have synthesised the diphenyllead(IV) complexes with alkylglyoxylatethiosemicarbazones. They studied the structure of the complexes by x-ray diffraction, by $^1$H and $^{13}$C NMR spectra.
The thiosemicarbazide formaldehyde polymer metal complexes with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) were reported [196]. The polychelates act as new anti-bacterial agent. Chen et al. [197] have synthesized 1-(3,5-Dimethoxybenzoyl) - 4 - (2-methoxy-phenyl) thiosemicabazide, a important intermediate for the synthesis of biologically active heterocyclic compounds.

Red, diamagnetic square planer nickel(II) complexes with pyridoxalthiosemicarbazone was synthesized by Franco et al. [198]. Gulea et al. [199] reported the crystal structure of copper sulfate and thiocynate complexes with 5-bromo and 5-nitrosalicyaldehyde thiosemicarbazones. Structural and spectral studies on nickel(II) complexes with N(4), N(4)-(butane-1,4-diyl) thiosemicarbazones have been made by Manoj and Kurup [200]. Antibacterial and antifungal activity of some transition metal complexes of thiosemicarbazone schiff base derived from N^4 - (7 Chloraquinolin-4'-ylamino) thiosemicarbazide have been reported by Abou Melha [201].

Template synthesis and investigation of some 3d-element coordination compounds with
tetradentate ligands derived from alkylated thiosemicarbazides have been reported by Cocu [202]. A novel and simple fluorescence enhancement method for selectivity sensing iodide was proposed, it is based on metal complex formation between mercuric(II)ion with fluorophore(p-((dimethyl amino)benzylidene) thiosemicarbazide and with anion in aqueous solution have been reported by Zheng et al. [203]. Clera et al. [204] described the synthesis and characterization of compounds (Ru 1 - Ru 12) of the type [Ru(S)$_2$(K)], where S = 1,10-phenanthroline/2,2'-bipyridine and K = itsz, MeO-btsz, 4-Cl-btsz, 2-F-btsz, and hfc [itsz = isatin-3-thiosemicarbazone, MeO-btsz = 1-(4'-methoxy-benzyl)-thiosemicarbazone, hfc = 2-{[3-chloro-4-fluorophenylimino]methyl}phenol, 4-Cl-btsz = 1-(4'-chlorobenzyl)-thiosemicarbazone, 2-Cl-btsz = 1-(2'-chlorobenzyl)-thiosemicarbazone, 2-F-btsz = 1-(2'-fluorobenzyl)-thiosemicarbazone)]. They measured anticancer activity against transplantable murine tumor cell line E. A. Carcinoma. Leovac et al. [205] have synthesized nickel(II)complex with 1,3-diphenylpyrazole - 4-carboxaldehydethiosemicarbazone and reported the unusually deformed coordination geometry.
A series of 1-(1-arylethylidene) thiosemicarbazide compounds and their analogues were synthesized and characterized by $^1$H-NMR, and by mass spectra. They[206] reported that the synthesized compound show tyrosinase inhibitory activities. Sharma and Srivastava reported the synthesis, magnetic and spectral studies of chromium(III), manganese(III), iron(III) and cobalt(III) complexes of thiosemicarbazones derived from benzil α-monoxime and unsubstituted/substituted thiosemicarbazides as biological agents [207].

Synthesis and structural investigation of mono and polynuclear copper complexes of 4-ethyl-1-(pyridine-2-yl) thiosemicarbazide have been reported by Hasssnien et al.[208]. Sethuraman and Kannan [209] synthesized Ruthenium(II) carbonyl complexes of dehydroaceticacid thiosemicarabazide. They proposed the distorted octahedral geometry for the complexes by single crystal x-ray diffraction study. Li. Jia et al. [210] synthesised the following planar (thiocyanato - N) bis (thiosemicarbazide - S) copper(I) complex.
A new semiorganic non-linear optical thiosemicarbazide cadmium chloride monohydrate single crystal was prepared [211] by slow cooling and slow evaporation methods. Martinez et al. [212] and reported the following distorted square planar cis-bis(thiosemicarbazide – N S) palladium(II)dinitrate complex.

\[
\begin{array}{c}
\text{NH}_2 \\
\text{NH}_2 \\
\text{Pd} \\
\text{NH}_2 \\
\text{NH}_2
\end{array}
\]

\[\text{2NO}_3^-
\]

Calatayud et al. [213] prepared the crystal \([\text{Cd}(\text{LMe}_2\text{H}_4)(\text{NO}_3)_2], \quad [\text{Cd}(\text{LMe}_2\text{H}_4)(\text{NO}_3)_2(\text{H}_2\text{O})]\]
\text{NO}_3\cdot\text{H}_2\text{O}, where \text{LMe}_2\text{H}_4 = \text{benzilbis (4-methyl-3-thiosemicarbazone)}. This novel cadmium crystal posses the two cadmium atoms with different coordination numbers 7 and 8. They established the structure of
complexes by mass, $^{13}\text{C}$ and $^{113}\text{CdCp}$ / MAS-NMR spectroscopy. Sunil et al. [214] reported the six new Co(II) and Co(III) complexes of di-2-pyridyl ketone N(4)-cyclo hexyl thiosemicarbazone and of di-2-pyridylketone N(4)-phenyl thiosemicarbazone. Zn(II) complex with 1-S-methyl carbodithionate-4-substituted thiosemicarbazide have been prepared and characterized by Ahmed [215]. A new series of cobalt(II) and nickel(II) complexes, $[\text{M(Ligand)}(\text{H}_2\text{O})_2(\text{Y})]$ [$\text{M} = \text{Co(II)}$ or $\text{Ni(II)}$, $\text{Y} = \text{Cl}^-$, $\text{Br}^-$ or $\text{NO}_3^-$] containing the Schiff base semicarbazone and thiosemicarbazone formed from 4-hydroxycoumarin-3-carbaldehyde have been reported by Abou-Melha [216]. Costanzo et al. [217] reported the crystal structure of human orginase 1-thiosemicarbazide complex.

The coordination behaviour of phthaloylbis(thiosemicarbazide) towards VO(II), Co(II), Cu(II), Zn(II) and UO$_2$(II) ions has been investigated by Abou Hussen et al. [218]. The reports on the syntheses and the characterization of 12 ferric complexes with pyridoxalthiosemicarbazone have been made by Floquet et al. [219]. They highlighted the richness of the coordination chemistry by using this ligand. They prepared the wide family of ferric compounds with charge varying from +3 or -1.
Fan et al. [220] proposed the following structure of dichloro(ethanol-O){(E)-1-[1-(2-pyridyl)ethylidene] thiosemicarbazonato - 3N, N', S} indium(III) complex.

\[
\text{XXXVII}
\]

Di - μ - thiosemicarbazide \(^4\)S : S [bis(thiosemicarbazide-S)copper(I)] diiodide compound \([\text{Cu}_2\{\text{SC(NH}_2\text{)}\text{NH NH}_2\}\}_6\]I\(_2\), was prepared by Li et al. [221]. They reported that each Cu\(^1\) ion is coordinated by four S atoms of the ligand in the complex. El-Asmy et al. [222] reported the spectral, thermal, electrochemical and analytical studies on Cd(II) and Hg(II) thiosemicarbazone complexes. Chandra and Tyagi [223] reported the synthesis, spectral and antifungal studies of the following bidentate ligands with the Ni(II), Pd(II) and Pt(II) metal ions.
A series of \( \text{1-}(\text{5 substituted-2-oxoindolin-3-ylidene})\)-\( \text{4-}(\text{substituted-pyridin-2-yl}) \) thiosemicarbazide derivatives were synthesized and characterized by Vaidhylingam et al. [224]. Two water soluble mixed ligand \([\text{Pd(bpy)(dahmp)}]\text{Cl} \) and \([\text{Ag(bpy)(Hdahmp)}]\text{NO}_3 \) complexes were synthesized and characterized by Mostafa and Bardria [225], where dahmp and Hdahmp are deprotonated monoanion and protonated neutral 4,6-diamino-5-hydroxy-2-mercaptopyrimidine.

Synthesis, spectroscopy, thermal behaviour and X-ray crystal structure of lead(II) complexes derived from S-methyl / benzylthiocarbazates have been reported by Bera et al. [226]. They reported the tricapped trigonal prismatic arrangement with steriochemically inactive lone pair on central lead(II). The reactions of \( \text{N,N-substituted thiosemicarbazides with copper salts and either copper(II)} \)
thiosemicarbazide complexes, 1,3,4-thiadiazonium salts or 1,3,5-thiadiazoles have been investigated by Dilworth et al. [227].

Synthesis, spectral studies and invitro antibacterial activity of steroidal thiosemicarbazone and their palladium(II) complexes have been made by Khan and Yusuf [228]. Nishat et al. [229] prepared new antibacterial polychelates of thiosemicarbazide formaldehyde resin with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) metal ions. Dimethylsulfoxide ruthenium(II) complexes of thiosemicarbazones and semicarbazones were reported [230].

Quiroga et al. [231] described the isolation of an intermediate in the platination of p - nitroacetophenone 4 – Methylthiosemicarbazone, it has a potential application as an antitumor drug. The molecular parameters such as the highest occupied molecular orbital energy ($E_{HOMO}$), lowest unoccupied molecular orbital energy ($E_{LUMO}$), the energy gap between $E_{HOMO}$ and $E_{LUMO}$, dipolemoment and charges on the atoms of 5 – fluoro – isatin – 3 - (N - benzylthiosemicarbazone) as monomer were studied by Sagdine et al. [232].
Bingol et al. [233] synthesized and characterized new copper(II) and nickel(II) complexes of 4-morpholinoacetophenone thiosemicarbazone. Renjusha and Kurup [234] reported the structural and spectral studies on manganese(II) complexes of di-2-pyridyl ketone N(4)-methyl and N(4)-ethyl thiosemicarbazone. A new series of first-row transition metal complexes with 1-acetylpyridinium chloride-4-benzoylthiosemicarbazone have been prepared and characterized by El. Ayaam et al. [235]. Jin and Cheng [236] reported that the reaction of 4-salicyloylthiosemicarbazide [H₃St] with FeCl₃·6H₂O in methanol solution, it gave novel 18- metallocrown-6 [Fe(st)(H₂O)₆]·21H₂O. They also reported that the ring of the metallocrown was consisted of six interlink [Fe-N-N] as repeated unit. Chandra et al. [237] synthesized and characterized Ni(II) and Cu(II) complexes of general composition [ML₂X₂] (where L = 2-pyridine carboxaldehyde thiosemicarbazone, M = Ni(II) and Cu(II), X = Cl⁻, NO₃⁻, and ½ SO₄²⁻).

A novel and simple fluorescence enhancement method for selectivity sensing iodine on metal complex formation between mercuric(II) ion with fluorophore (p-(dimethylamino)benzylidene) thiosemi-
carbazide and with anion in aqueous solution was proposed by Lin et al. [238].

1. C. Present Work

With the recognition of the fact that many functionally important biomolecules contain S–N donor site in suitable positions and the discovery of antibacterial, antiviral and antitumor properties of various thiosemicarbazides, thiosemicarbazones and their metal complexes[239], interest in the study of the chemical, biochemical and stuructural aspect of these compounds and their derivatives is growing. The biological activity is, in general, believed to originate from metal complexing[240] and reductive[241] capacitit.

The survey of literature cited above shows that chelating properties of thiosemicarbazones having ONS donor sequence have been well established. The chemistry of 2,4-dihydro-3H-pyrazol-3-ones have assumed considerable importance because of their practical use as potential laser materials[242,243] and also as NMR shift reagents[244-248]. Several investigations regarding the synthesis and characterizations of the metal complexes derived from
different derivatives of 4-subsituted-2,4-dihydro-3H-pyrazol-3-ones have also been made[249-265].

But to the best of our knowledge no work has been reported on the synthesis and complexation studies of following heterocyclic thiosemicarbazone ligands.

I. 4 - Benzoylthiosemicarbazone - 2, 4 dihydro - 5 - methyl - 2 [4′-nitrophenyl] - 3H - pyrazol -3-ones. i.e. 4 - Benzoylthiosemicarbazone - 3 - methyl - 1 - [4′ - nitrophenyl] - 2 - pyrozin - 5 - one [B₄MNPO].

II. 4 - Acetylthiosemicarbazone - 2, 4 dihydro - 5 - methyl - 2 [4′-nitrophenyl] - 3H - pyrazol - 3 -one. i.e. 4 - Acetylthiosemicarbazone - 3 - methyl - 1 - [4′ - nitrophenyl] - 2 - pyrozin - 5 - one [A₄MNPO].

III. 4 - Propionylthiosemicarbazone - 2, 4 dihydro - 5 - methyl - 2 [4′-nitrophenyl] - 3H - pyrazol - 3 -one. i.e. 4 - Propionylthiosemicarbazone - 3 - methyl - 1 - [4′ - nitrophenyl] - 2 - pyrozin - 5 - one [P₄MNPO].

IV. 4 - p - Toluylthiosemicarbazone - 2, 4 dihydro - 5 - methyl - 2 [4′-nitrophenyl] - 3H - pyrazol - 3 -ones.
i.e. 4 - p - Toluythiosemicarbazone - 3 - methyl - 1 - [4' - nitrophynyl] - 2 - pyrozolin - 5 - one [TtMNPO].

It is therefore thought worthwhile to study structure and properties of VO(II), Cr(III), Mn(II), Fe(II), Fe(III), Co(II), Ni(II) and Cu(II) and Zn(II) complexes with the heterocyclic thiosemicarbazone ligand I-IV.

These metal complexes were characterized by colour, elemental analyses, conductivity measurements, spectral studies, thermal analyses. The electronic spectral and magnetic studies have been made to assign the probable structure to the complexes. $^{13}$C-NMR and mass spectra of ligands (I-IV) studied in the present work are also recorded.

The results of these investigations are presented in four chapters as outlined below:

Chapter II describes the synthesis and characterization of the heterocyclic thiosemicarbazone ligands I-IV.

Chapter III contains brief descriptions of physico-chemical methods used in the present work.
Chapter IV describes the results of the physico-chemical studies made on the metal complexes. The results of the study are analyzed with a view to correlate structure with various properties. This chapter also describes the thermal decomposition study of the metal complexes.

Chapter V describes the studies on antimicrobial activities of the thiosemicarbazone ligands and their metal complexes.
REFERENCES


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