CHAPTER-1

1.1 INTRODUCTION

The progress in the studies on the coordination was very rapid not only because of the utility and economic importance of metal chemistry but also for the intrinsic interest in many of the coordination compounds and the intellectual challenge of the structural problems to be solved. Even today the majority of the contributions in field of Inorganic Chemistry deal with the studies on various aspects of the coordination compounds of metals.

It is indeed difficult to establish with absolute the origin of research in this area of chemistry. It is often ascribed to C.Tessart[1], who in 1798 isolated CoCl₃·6NH₃, that we know now [Co(NH₃)₆]Cl₃. Subsequent developments were associated with G.Magnus, W.C.Zeise, T.Graham, C.E.Claus, C.W.Blomstrand and S.M.Jørgensen. Translations of selected papers dating from 1828, with detailed comments by G.B.Kaufmann are available in 'Classics in Coordination Chemistry'[2] Parts I and II. Modern coordination chemistry dates to Alfred Werner. Werner’s theory was interpreted in terms of electronic theory of valence by Lowry[3] and Sidgwick[4]. The classical or Werner complexes are now regarded as electron pair donor-acceptor adducts where donors are ligands and metal ions forming complexes are acceptors. However a large number of non-classical complexes where π-acceptors or π-acids act as ligands are well recognized. Designing a ligand is an important part in the synthesis of
coordination compounds. Choice of a ligand for the formation of a complex of a metal or a class of metals is not empirical or arbitrary one. Thermodynamic stability of a metal complex depends upon metal-donor bond energy which is predominantly enthalpy effect. The metal-donor bond energy depends upon the nature of the donor atoms and nature of the metal ions.

Donor atoms are classified as ‘hard’ or ‘soft’[5] according as they are non-polarizable and polarizable respectively. Hard bases are characterized by strong proton basicity whereas soft bases contain highly polarizable atoms and have negligible proton basicity. For bases in which the coordinating atom is from group 15, 16 and 17, the atoms nitrogen, oxygen and fluorine are the hardest in each group. These hard bases usually form stable complexes with class ‘a’ metal ions[6] (hard acids) which are characterised by small size, high positive oxidation state and no easily distorted outer electron. Class ‘b’ (soft acid) behaviour of metal ions is associated with a low or zero oxidation state; large size and easily distorted outer electrons. They usually form stable complexes with ligands containing donor atoms other than the members of first period of group 15, 16 and 17 of the periodic table.

For hard acids the order of stability of complexes is as follows:

F > Cl > Br > I
O >> S > Se > Te
N >> P > As > Sb

whereas for soft acids the order of stability is
F < Cl < Br < I
O << S ~ Se ~ Te
N << P > As > Sb

So in general hard acids prefer to associate with hard bases and soft acids prefer soft bases.

In addition stability of the complexes also depends upon the chelate effect [7] and macrocyclic effect [8]. These two effects are predominantly entropy effect.

Ligands having nitrogen as site for coordination has more versatile characteristics. It can be considered as a 'border line' base in the hard-soft concept. As it is of smaller size and high electron density, can coordinate with 'hard acid' metal ions e.g. beryllium(II), calcium(II), chromium(III), iron(III) etc. On the other hand the lone pair of electron on nitrogen has considerable extent of polarisability. On the other hand the transition metal ions with nearly filled d- orbital viz. nickel(II), palladium(II), platinum(II) etc. have high deformability. These facts lead to greater interpenetration of orbitals of ligand and metal ions. As a result nitrogen also has high affinity towards 'soft' transition metal ions. So we can conclude nitrogen can coordinate with metal ion of both class 'a' and class 'b'.

Therefore it is evident that ligand with donor site nitrogen would prefer hard or border line metal ions. Again as sulphur contains low lying vacant 3d orbital of suitable energy, metal to ligand back donation is possible from transition metal ions having
filled or almost filled d-orbital to sulphur containing ligands. That is why sulphur as donor atom would prefer bonding to 'soft' or class 'b' metal ions. So a bidentate or multidentate ligand containing nitrogen and sulphur would bind to almost all transition metal ions. Therefore such ligands would have a versatile coordinating behaviour to transition metals.

From above discussion it is clear that ligands containing both sulphur and nitrogen as possible site for coordination are of high interest and study worthy. Another point of interest for sulphur containing ligand is that sulphur can act as bridging ligand and polymeric complex may be formed through bridging by such sulphur center. Example of such polymeric complex formation will be discussed in later part of this chapter.

1.2 DIFFERENT COMPLEXES HAVING NITROGEN AND SULPHUR AS COORDINATION SITES:-

Thio urea (NH₂-CS-NH₂) may be considered as diamide of thio carbonic acid and it has the following structure with sulphur and two nitrogen atoms as possible site for coordination:-

\[
\begin{array}{c}
\text{S} \\
\text{H₂N} \quad \text{C} \quad \text{NH₂}
\end{array}
\]
Thio urea has almost equal contribution of the three following forms:-

\[
\begin{align*}
&\text{NH}_2 \quad /M_2 \quad /\text{NH}_2 \\
&\text{NH}_2 \\
&\text{S} \quad \text{C} \\
&\text{NH}_2 \\
&\text{S} \quad \text{C} \\
&\text{NH}_2
\end{align*}
\]

So it has the potentiality to form bonds through sulphur and even nitrogen, though the basicity of the nitrogen atom is extremely low [9]. Different complexes of interest were prepared using thiourea and its derivatives as ligand. Such complexes had shown antitumour, antiviral, bacteriostatic and antioxidative activities[10,11]. M.Nardelli et. al. prepared and characterized a number of complexes viz. Pb(tu)\(_2\)Cl\(_2\)[12], Ni(tu)\(_2\)(NCS)\(_2\)[13] etc using X-Ray crystallography and other techniques. The X-ray crystallographic study of Ni(tu)\(_4\)Cl\(_2\)[14] showed the presence of two formula units in the tetragonal unit cell of the compound and each nickel atom is surrounded by four thiourea and two chlorine atoms to form a distorted octahedron. Infrared spectral study[15] of Pt(tu)\(_2\)Cl\(_2\), Pt(tu)\(_4\)Cl\(_2\), Pd(tu)\(_4\)Cl\(_2\), Zn(tu)\(_2\)Cl\(_2\) and Ni(tu)\(_2\)Cl\(_2\) complexes conclusively proved that the band at 730 cm\(^{-1}\) was due to C-S stretching. Although in the same communication the band at \(~1100\) cm\(^{-1}\) was also proposed to be due to C-S stretching, K.Swaminathan et.al [9] argued that the second band did not undergo any change in intensity due to complexation so it should not be a C-S stretching band.

The complexes Ni(tu)\(_6\)(ClO\(_4\))\(_2\), Ni(tu)\(_6\)(NO\(_3\))\(_2\), Ni(tu)\(_6\)(Br)\(_2\), Ni(tu)\(_4\)(Cl)\(_2\), Ni(tu)\(_4\)(Br)\(_2\), Ni(tu)\(_2\)(NCS)\(_2\) were also prepared and studied by infrared spectroscopy [16]. It was found that bands at 1400 cm\(^{-1}\), 1100 cm\(^{-1}\) and that at 700 cm\(^{-1}\) shifted due to coordination. These observations also suggest considerable covalent character of the nickel-sulphur bond.
T.J. Lane et al. [17] prepared some transition metal complexes of methyl thiourea. From their infrared spectra they proposed that zinc(II) and cadmium(II) complexes were coordinated through sulphur atom but interestingly platinum(II), palladium(II) and copper(I) had been coordinated through nitrogen centre. In another approach [18] cobalt(II) and nickel(II) complexes of N-allyl thiourea were prepared. The complexes were characterized by measuring electrical conductance, magnetic susceptibility, infrared and electronic spectra and were found to be octahedral with coordination through nitrogen atom of the thiourea derivative. A complex of nickel, Ni(tu)$_2$(NCS)$_2$ was found to be polymeric and thiourea occupied the bridging position through sulphur [19, 20].

K. Angela et al. [21, 22] prepared cobalt(II), nickel(II), palladium(II), zinc(II), cadmium(II), iron(II) and copper(II) complexes with 3-N-dibenzofuryl thiourea as ligand and they had characterized the compounds on the basis of elemental analysis, molar conductance, magnetic moment, molecular mass determination and ultraviolet and infrared spectroscopic studies. In all the cases the ligands behaved as bidentate chelating agent with sulphur and nitrogen as coordination sites and the prepared complexes showed prominent antibacterial activity.

J.P. Barbier et al. synthesized cobalt, nickel and copper complexes using N-disubstituted N'-ethoxy carbonyl thiourea [23] as ligand. They reported the nickel complex to have square planar geometry as found from magnetic and nuclear magnetic resonance data.
Preparation and characterization of similar complexes were also done using \(N,N\) disubstituted \(N'\)-benzoyl thiourea as ligand\([24,25]\).

Recently crystal structures of silver cyanide complexes of thiourea and its derivative had been reported by F.B.Stocker et.al.\([26]\). They prepared complexes using thiourea, 1-methyl-2-thiourea, 1,3-dimethyl-2-thiourea; 1,1,3,3-tetramethyl thiourea and \(N,N'\) ethylene thiourea as ligands and found all the structures as either one or two dimensional polymeric arrays held together by bridging sulphur and cyano groups.

Copper(II), nickel(II) and cobalt(II) complexes with \(N,N\)-diphenyl-\(N'\)-(4-phenyl benzoyl) thiourea, \(N,N\)-diphenyl-\(N'\)-(4-chlorol benzoyl) thiourea, \(N,N\)-di-\(n\)-propyl-\(N'\)-(4-chlorol benzoyl) thiourea were prepared and characterized using elemental analysis, infrared, nmr, mass spectrometry and X-ray crystallography by H.Arslan et.al.\([27]\). In all the cases the ligands coordinated in bidentate manner yielding \(cis\) \(ML_2\) type of complexes. The complexes were established to have a distorted tetrahedral geometry from their nmr spectral and X-ray crystallographic data.

A.T.Kabbani et.al.\([28]\) recently reported some cobalt(II), nickel(II) and copper(II) complexes of thiourea derivatives i.e. \(N\)-[(benzoyl-amino) thioxomethyl]-amino acid, where amino acids are phenylalanine, cysteine, alanine, histidine and serine. The complexes were characterized by uv-visible, infrared and nmr spectroscopy. They reported bidentate coordination of the ligand through the carboxylate group of amino acid.
Recently K.Ambujam et.al[29] in their course of study on new semiorganic nonlinear optical (NLO) materials, had chosen thiourea due to its large dipole moment and extensive network of hydrogen bonds. Single green crystals of Ni(tu)\textsubscript{4}Cl\textsubscript{2} were grown on silica gel and characterized by X-ray diffraction, uv-visible spectroscopy, photoconductivity and dielectric studies along with thermo gravimetric analysis. X-ray diffraction study had shown that the crystals contained body centered tetrahedral symmetry, with hexa coordinating molecular structure. FTIR spectroscopy revealed that the ligand was coordinated through sulphur atoms. The uv-vis spectrum established the transmission range to be 300 nm to 2500 nm, with a sharp absorption peak at the red end of the visible region. This absorption band was responsible for the colour of the crystal. The mechanical strength of the crystal was determined by Vicker hardness test. Hardness value was found to increase with load. The sample decomposed completely between 200°C to 542°C. The onset of decomposition was found to be 237°C. Dielectric constants were studied with respect to applied frequency at room temperature. C value was 76 at 750Hz but decreased to 35 at 5 M Hz. i.e high value at low frequency and vice versa. The value of dipole moment was 10.53 D. This also showed similar variation. The compound showed negative photo conductivity and that might be due to reduction in number of charge carriers in presence of radiation. Optical property indicated that it should behave as an active material for the harmonic generation of lasers.

Thiourea derivatives and their complexes had shown antifungal and antiyeast activities. J.J.Criado et.al. prepared a number of such thiourea derivatives. The chloride and ethyl
ester morpholine thiourea derivative and their nickel(II) complexes[30] showed antifungal activities against the major pathogens responsible for crop damage. Similarly nickel(II) and platinum(II) complexes of benzoyl thiourea[31] had shown antifungal activity and they were active against major plant pathogens like *Botrytic cinerea*, *Colletotrichum fangariae*, *Fusarium oxysporum* and *Phoma betae*. N-Benzoyl-N' alkyl thiourea and their nickel(II), cobalt(III) and platinum(II) complexes[32] were active against fungus *Penicillium digitatum* and yeast *Sacchanomjaes cerevisiae*.

From the above discussion it is clear that thiourea and its derivatives can coordinate with metal ions in various ways and their complexes have prominent antibacterial and antifungal activities.

Thioamide(-CS-NH$_2$) has the following structure:-

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

Different transition metal complexes with thioamides or substituted thioamides as ligands had been synthesized and characterized. Complexes of nickel(II) and palladium(II) with thiobenzamide as ligand were synthesized by A.A.Aarts et.al. The electronic and vibrational spectra of the prepared complexes showed *cis* square planar complex formation by palladium(II) while nickel(II) formed *trans* octahedral complex [33]. They also reported preparation and characterization of some Au(I) complexes with thioacetamide, thiobenzamide, N,N-dimethyl thioformamide and N,N-dimethyl thioacetamide[34] ligands.
S.D. Robinson and A. Sahajpal [35] prepared and characterized some complexes of ruthenium and osmium using N-alkyl and N-aryl thioformamide (RN \text{---} CH \text{---} S) as ligand. They prepared metal complexes of that ligand with composition MXL(CO)(PPh_3)_2 [where M=Ru, Os and L=( RNCH \text{---} S) and X=Cl, Br & OCOCF_3]. They also reported ruthenium complex of composition RuL_2(PPh_3)_2. Structure and stereochemistry of the complexes were established by infrared, ^1H nmr and ^31P nmr spectroscopy.

Recently trans-(di N,N-diethyl-(2-phenyl diazenyl) thioformamide complexes of nickel, copper, palladium and platinum [36] had been crystallized and structures were determined at low temperature. All the complexes were found to be M(N_2S_2) type. The crystals of nickel and copper complexes belonged to tetragonal system and the central atom was found to have tetrahedral structure. On the other hand crystals of palladium and platinum belonged to monoclinic system and had a distorted square planar geometry.

N-[Bis(isoproxy) thiophosphoryl] thiobenzamide and N-[Bis(isoproxy) thiophosphoryl] N' phenyl thiourea had been used to synthesize and characterize silver and gold complexes [37]. L.V. Sudha et al prepared copper(II), zinc(II) and cadmium(II) complexes with N-(2-pyridyl) thioacetamide and N-(2-pyridyl) thiobenzamide as ligands. The compounds were characterized by infrared, ^13C and ^1H nmr spectroscopy [38].
Voltammetric study for composition and stability of copper(I) complexes with thioacetamide (taa) as ligand were done by H.M. Jeng et al. with the help of square wave voltammetry using fast pulse technique [39]. They found the complexes of the composition CuI(taa) and CuI(taa)2 were stable at pH < 1 i.e. at highly acidic medium.

Recently some mixed ligand complexes were prepared with the composition trans-[CoIII(acacen)2(ta)2]ClO4 and trans-[CoIII(ba)2en(ta)2]PF6 where H2acacen = bis(acetylacetone) ethylene diimine and H2(ba)2en = bis(benzoyl acetone) ethylene diimine, ta = thioacetamide [40]. The complexes were characterized by elemental analyses, infrared, uv-visible, nmr and x-ray spectroscopy. Thioacetamide ligands were found to be coordinated through sulphur centre in axial position of the distorted octahedral geometry.

Crystal structure of bis-(thioacetamide)nickel(II) thiocyanate was reported by M. Nardelli et al. [41] where coordination around nickel was octahedral, two sulphur atoms of two thioacetamide and two sulphur and two nitrogen atom from four different NCS groups acted as donor sites. The interesting observation was NCS group acts as bridging ligand forming polymeric structure. The structure was similar to that of Ni(tu)2(NCS)2 [19, 20].

Crystal structure of the nickel(II) complex of pyridine-2,6 dithiocarbomethylamide was described by Alois Lopitsch et al. [42] where nickel atom had been surrounded by
square bipyramidal coordination of four thioamide sulphur atoms and two pyridine nitrogen atoms.

Recently 2,2' bipyridine-6-carbothioamide complex of nickel(II) was synthesized and characterized [43] and the complex was found to be coordinated by NNS donor sites of the ligand.

Copper complexe using thioamide and carbonyl as ligand [44] had been synthesized by Chmutova et.al. and they described the structure on the basis of spectroscopic methods as well as by quantum mechanical model. Using dithiooxamide as ligand the composition of the compound was found to be metal: ligand 1:2 with $N_2S_2$ as coordinating core. On the other hand $S_4$ coordination was observed with the complexes where dithiomalonamide was used as ligand.

Thiosemicarbazide (tscH) can have following two structures:

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

So it can act as neutral ligand as per first structure or it can lose the thiol proton to behave as mononegative bidentate ligand.
Structure of thiosemicarbazone can be represented as:-

\[
\begin{array}{c}
\text{S} \\
\text{—NH—C—NH—}
\end{array}
\]

In solution thiosemicarbazone probably also exists in thiol form along with the above mentioned thione form,

\[
\begin{array}{c}
\text{S—H} \\
\text{—NH—C—N—N—C—}
\end{array}
\]

So they can also behave both like neutral bidentate and charged bidentate ligand depending upon preparative conditions. Furthermore it is interesting that it is possible to isolate complexes having both tautomeric forms of the ligand. A neutral chelate of cobalt with molecular formula \([\text{Co(Hnqtsc)(nqsc)\cdot H}_2\text{O}\]) had been prepared \([\text{H}_2\text{nqts}=2\text{-hydroxy-1,4-napthaquinone-1- thiosemicarbazone}]\) and according to magnetic and spectral data the compound appeared to contain both tautomers of the ligand.

Thiosemicarbazides and thiosemicarbazones are of great biological importance due to their antifungal, antibacterial\([45]\) and antitumor\([46]\) action. 1-Acyl-4-aryl-thiosemicarbazides\([47]\) showed tuberculostatic activity and different transition metal complexes with these ligands were prepared to exploit such biological activities.

Thiosemicarbazides, thiosemicarbazones and their corresponding transition metal complexes had been studied in detail and reviewed adequately by Livingstone\([48]\), Akbar ali & Livingstone\([49]\), Campbell\([50]\) and Subhas Padhye & G.B.Kauffman\([51]\).
So the following discussion will be confined about such complexes which have been reported since 1980 onwards.

Copper(II), cobalt(II), nickel(II) and mercury(II) complexes of 1,4-diphenyl thiosemicarbazide (dptsc) had been reported[52]. The composition of these complexes were found as [Cu(Hdptsc)X·H₂O] nH₂O where X= Cl, Br or CH₃COO; n=0 or 1; [M((Hdptsc)₂ yH₂O] where M= Co⁺Ⅱ, or Ni⁺Ⅱ, y=0 or 1; [Hg(dptsc)Cl₂] 2H₂O and [Cu(dptsc)₂SO₄] H₂O. The stereochemistry of the complexes were studied with the help of magnetic and electronic measurements. The anomalous magnetic moments observed had been explained. Infrared spectral studies had been used to determine the bonding sites in the complexes.

The preparation and properties of a series of transition metal complexes M(spts) nH₂O (M=Co(II), Ni(II), Cu(II), Zn(II) and Cd(II), spts is the deprotonated form of 1-succinyl bis(4-phenyl-thiosemicarbazide) i.e H₂spsts and n=0-2] were reported[53]. Analytical, spectral (electronic, infrared and nmr), conductometric and magnetic data showed that the cobalt(II) and copper(II) complexes had tetrahedral and octahedral structures respectively whereas the nickel(II) complex had a mixed stereochemistry of tetrahedral and square planar isomers. The ligand behaved as a dibasic quadridentate {NSSN} donor. The stiochiometry and stability constants of cobalt(II), nickel(II) and copper(II) complexes were determined spectrophotometrically. The electrical properties were also investigated and activation energies were calculated. The values obtained for cobalt(II),
nickel(II) and copper(II) complexes were similar to that of narrow band semiconductor materials.

Ligational, corrosion inhibition and antimicrobial properties of 4-phenyl-1-benzenesulfonyl-3-thiosemicarbazide \([\text{pbst}]\) with complexes of the type \([\text{Co(pbst)(OAc)}(\text{H}_2\text{O})_2], [\text{Co(pbst)}_2\text{H}_2\text{O}], [\text{Ni(pbst)(OAc)}]_2\text{H}_2\text{O}, \text{M(pbst)}_2\) where \(\text{M} = \text{nickel and zinc}; [\text{Cu(pbst)}(\text{H}_2\text{O})_2]\) were described[54]. The complexes were characterized by elemental analyses, molar conductivity measurements, nmr, infrared and reflectance spectral studies and by magnetic moment measurements. The infrared spectra showed that the ligand behaved as mononegative, bidentate, coordinating via NH and C-S groups. Thioenolisation had been confirmed by pH titration of Hpbst and its metal complexes against 0.01 M NaOH solution. The antibacterial and antifungal activities of the ligand and corresponding complexes were studied. It was observed that the ligand possessed greater anti microbial activities than its complexes. The corrosion inhibitory property was studied on aluminium in \(\text{CCl}_3\text{COOH}\) using Hpbst by weight loss and corrosion potential measurements. It was found that the effectiveness depends upon its concentration.

Chelating behavior of substituted 1-benzoyl-4-phenyl thiosemicarbazide[55] were explored by complex formation of the ligand(LH) with cobalt, nickel, copper, zinc and cadmium. The reaction products were studied by elemental analyses, molar conductivity, magnetic susceptibility measurements, reflectance and infrared spectral studies. The infrared spectra showed that LH coordinated via nitrogen and sulphur or
via nitrogen and oxygen. The $ML_2$, $n\text{H}_2\text{O}$ ($M=\text{Cu, Ni; } n=0-2$) complexes had square planar stereochemistry whereas $\text{CoL}_2$ had octahedral and tetrahedral structures. The influence of substitution in the benzene ring on the stereochemistry was studied.

The ligand 1,4-dibenzoyl-3-thiosemicarbazide (dbtsc)[56] formed complexes of the type $[M(\text{Hdbtsc})(\text{SCN})]$ ($M=\text{Mn(II), Co(II) and Zn(II)}$), $[M(\text{Hdbtsc})(\text{SCN})(\text{H}_2\text{O})]$ ($M=\text{Ni(II), Cu(II)}$) $[M(\text{Hdbtsc})\text{Cl}]$ ($M=\text{Co(II), Ni(II), Cu(II) and Zn(II)}$) $[\text{Mn(dbtsc)}\text{Cl}_2]$. They had been characterized by elemental analyses, magnetic susceptibility measurements, uv-vis, infrared, $^1\text{H}$ and $^{13}\text{C}$ nmr and FAB mass spectral data. Room temperature esr spectra of the manganese(II) and copper(II) complexes showed characteristics of tetrahedral and square planar complexes respectively. The ligand and its soluble complexes were screened against several bacteria, fungi and tumour cell lines. It was found that all thiocyanato and chloro complexes inhibited the growth of *Pseudomonas flauracences*. Copper complexes exhibited excellent antifungal activity against *Aspergillus flavus* and *Aspergillus niger*. The ligand exhibited better antitumour activity than copper(II) complexes against Jurket and Daltons Lymphoma cell lines.

Complexes of N-substituted thiosemicarbazide with ruthenium(II)-2,2'-bipyridyl were prepared and characterized by infrared, uv-vis and $^1\text{H}$ nmr spectroscopy in addition to their elemental analyses[57]. The complexes were tested for anti cancer activity against *Ehrlich Ascites Carcinoma*. Their effects on the hematological profile of the tumour hosts had also been studied. The complexes were found to possess antibacterial activity against both Gram +ve and Gram –ve stains of bacteria.
Bis(thiosemicarbazide) nickel(II) dicarboxylate and the substitution products with different hydrogen bonding groups in the complex had been used for structural manipulation to explore the supramolecular structures of bis(thiosemicarbazidato) nickel(II) i.e. neutral complexes[58]. The carboxylate group can act as a base and a neutral complex can be generated. The crystal structures of different substituted products showed that only thioamide hydrogen atom was responsible for hydrogen bond formation.

Recently a new class of platinum blues have been isolated and characterized[59]. This blue complexes of platinum(II) have the composition of PtL₂ where LH= 1-phenyl thiosemicarbazide, 4- phenyl thiosemicarbazide, 1,4-diphenyl thiosemicarbazide and 4-(2-pyridyl)- thiosemicarbazide. Electronic spectra of all the complexes showed a metal to ligand charge transfer band in the 650 to 750 nm region in different solvents. Infrared spectra indicated bonding through sulphur and nitrogen while ¹H nmr spectra suggested bonding through hydrazinic nitrogen atom.

Thiosemicarbazide reacts with butane 2,3-dione oxime to give a schiff base product via the selective reaction of hydrazine nitrogen atom. Ligating property of the ligand with palladium(II) was investigated[60]. It was found that palladium(II) was bound in a trimodal, cis arrangement to oxime nitrogen, hydrazine nitrogen and sulphur atom. Crystal structure revealed that oxime thiosemicarbazide had reacted with PdCl₂(PhCN)₂ presumably via the elimination of HCl ,in the thiol rather than thione form. The hydrogen bonding interaction of the oxime hydrogen that caused the ligand to be a
dimer in the solid state was lost on complexation with palladium(II) giving the complex a monomeric structure.

Pd(DMSO)$_2$Cl$_2$ was taken as starting material to prepare complexes of the composition PdL$_2$Cl$_2$ where L is nitrogen, sulphur donor ligands derived from S-methyl dithiocarbazate, S-benzyl dithiocarbazate, and thiosemicarbazide[61]. The complexes had been characterized by elemental analyses, infrared, electronic spectra, nmr and thermogravimetry. Based on the above experiments the ligands were found to coordinate via thione sulphur and azomethine nitrogen atom. The antiamoebic action of the complexes was also evaluated against *Entamoeba histolytica* (strain HK-9).

Red green crystals of [Ni(tscH)$_2$]$^{+2}$[tere]$^{2-}$ were isolated by mixing equimolar aqueous solution of [Ni(tscH)$_2$]NO$_3$ and disodium salt of terephthalic acid[62]. It was found that the ligand molecules had been coordinated by thione sulphur and terminal NH$_2$ group of the ligand. The complex formed polymeric chain by hydrogen bond through the dicarboxylate anion as :-

![Diagram of complex structure]
Redox behavior of bis(2,2'-bipy)-ruthenium(II) complexes containing thiosemicarbazide ligands were reported[63]. The prepared complexes were of two types. In \([\text{Ru(bipy)}_2\{N-S\}]^{2+}\) type of complexes the 4-aryl thiosemicarbazide ligand chelated in the keto form through hydrazinic nitrogen and thione sulphur. On the other hand in \([\text{Ru(bipy)}_2\{N-S\}]^{+}\), the thiosemicarbazide moiety remained chelated to ruthenium(II) through hydrazinic nitrogen and deprotonated thiolato sulphur atom.

Kinetics of interaction of thiosemicarbazide with cis-\([\text{Ru(bipy)}_2(\text{H}_2\text{O})_2]\)^{2+} was studied[64] spectrophotometrically at pH 4.8. It was concluded that the reaction proceeded via outer sphere association complex formation followed by two slow consecutive steps. The first step was conversion of the complex into inner sphere complex whereas second step was the entrance of thiosemicarbazide molecule in the coordination zone of the ruthenium(II). In each step an aqua ligand was displaced. The equilibrium constant for outer sphere complex formation had been evaluated together with rate constant.

Bis(1,10 phenanthroline)ruthenium(II) or Bis(2,2' bipy)ruthenium(II) complexes with benzoin thiosemicarbazide ligand was tested in-vivo for anticancer activity against transplantable murine tumour cell line, Ehrlich's Ascitic Carcinoma (EAC)[65]. It was observed that the complexes increased life span of the EAC-bearing mice, decreased their tumour size and viable ascitic cell count. Clinical tests showed improved Hb, RBC and WBC counts. It was also observed that ruthenium(II) complexes protected red blood cells from 2,2' azo-bis(2 methyl propionamidine) dihydrochloride (AAPH).
induced hemolysis. Inhibitory effect was found to be dose-dependent at a concentration range of 20-120 µg/ml.

Reaction of Ru(bipy)Cl₄ with different thiosemicarbazides(L) in methanol produced Ru(L)(bipy)Cl₂ type of complex where the ligand had been coordinated in the thione form[66]. The complexes were characterized by elemental analyses, magnetic moment measurement and spectroscopic techniques. The redox behavior was studied by cyclic voltammetry.

Nickel(II) and palladium(II) were found to form complexes with thiosemicarbazide(tsc), 1-phenyl thiosemicarbazide(1-ptsc) and 4-phenyl thiosemicarbazide(4-ptsc) with composition MLCl₂ and ML₂Cl₂. Electronic spectra of them suggested distorted octahedral symmetry for Ni(tsc)Cl₂, Ni(tsc)₂Cl₂, Ni(4-ptsc)Cl₂, Ni(4-ptsc)₂Cl₂ where as the complex Ni(1-ptsc)₂Cl₂ was weakly paramagnetic suggesting square planar geometry[67].

Structure of Ni(CN)₂(tsc).H₂O was elucidated by X-Ray diffraction study[68]. It was found that the compound has square planar geometry with two adjacent cyano carbon atoms. Nitrogen and sulphur atoms from thiosemicarbazide ligand were linked to the nickel(II). Ni-S distance was 2.169Å and that for Ni-N was 1.923 Å. Water molecule did not enter the inner coordination sphere, but was hydrogen bonded to the ligand units of the complex and seemed to play a very important role in the crystal structure.
Crystal structure[69] of diaqua bis (1,1,4-trimethyl thiosemicarbazide) nickel(II) dinitrate revealed a distorted octahedral geometry around nickel atom. The two water molecules occupied the axial positions of that geometry. Thiosemicarbazide NH group and water remained in hydrogen bonded form with nitrate anion.

Reaction of aromatic thiosemicarbazides with palladium(II) cation produced complexes with composition Pd(H₂L)Cl₂, Pd(HL)₂ and Pd(L). Infrared spectra showed that the ligand behaved as neutral, mononegative or binegative species. It was found that the ligand coordinated in a bidentate or bridging tetra dentate way[70].

Ruthenium and palladium complexes of 1-phenylacetyl -4- phenyl-3- thiosemicarbazide (H₂papts) and 1-phenoxyacetyl -4- phenyl - 3 -thiosemicarbazide (H₂pxapts) were characterized by infrared, electronic and ¹H nmr spectra, conductometric titration and thermal analyses[71]. Composition of the complexes were found to be Ru(HL)₂(H₂O)₂ and Pd(Hpapts)(bipy)+. The Ru complexes were efficient catalyst for oxidation of primary alcohol to aldehyde and acid, secondary alcohol to ketone and aryl halide to aldehydes and acids in presence of NaIO₄ as cooxidant.

Complexes of thiophene-2-carboxaldehyde thiosemicarbazon with ruthenium(III), rhodium(III), iridium(III) and platinum(IV) were octahedral in structure[72]. Analytical data suggested formation of three types of complex M(HL)₂Xₙ, ML₃ and [PtL₃]Cl (X= Cl,Br or 1/2SO₄, n= 3 for Ru, Rh and Ir, n =4 for Pt). Complexes of rhodium(III), platinum(IV) and iridium(II) were diamagnetic whereas that of ruthenium had magnetic
moment in the range of 1.75-1.80 BM at room temperature. Molar conductance measurements in 10^{-3} M MeOH solution at 25^\circ C showed that the complexes of general formula M(HL)\textsubscript{2}X\textsubscript{3}, M(HL)\textsubscript{2}X\textsubscript{4} and ML\textsubscript{3} were 1:1, 1:2 and non electrolytes respectively. Molar conductivity and spectroscopic (uv and infrared) data suggested that the compounds had octahedral structure.

2-Acetyl pyridine thiosemicarbazone can act as a tridentate ligand[73]. Its ligating property was explored for palladium(II) complexes with neutral(LH) and deprotonated ligand(L). [Pd(HL)\textsubscript{2}]X\textsubscript{2} and PdL\textsubscript{2} (where X=Cl, Br) type of complexes were studied by elemental analyses, conductivity measurement and spectroscopic studies. Crystal structure of PdLBr showed that the complex had a square planar geometry with NNS donor sites, and a planar tricyclic ligating system had been formed. The protonation constants of the ligand were also determined spectrophotometrically.

Interestingly thiosemicarbazones could also behave as bridging ligand. The X-ray crystal structure of palladium(II) complex of 2-hydroxyacetophenone N(4)-ethylthiosemicarbazone showed it to be an approximately symmetric, triangular, trinuclear complex with bridging thiosemicarbazonato sulphur atoms[74]. The three bridging ligands had same formal charge and bonding pattern. The species could be formed from the monomer on dissolution in dimethyl formamide or directly from LiPdCl\textsubscript{4} and thiosemicarbazone in methanol ammonia solution.
Similarly 2-hydroxy-4-methoxyacetophenone N(4)-dimethylthiosemicarbazone (4MeOAp4Me2) also formed triangular trinuclear complex with palladium(II). The X-ray crystallographic structure determination of [Pd(4MeOAp4Me2)]3.DMSO showed it to contain a chair type hexagon of alternating palladium and sulphur atoms with the shape of a molecular bowl[75].

Binuclear nickel(II) complexes of N(4) substituted thiosemicarbazones had also been reported[70]. They were found to contain phenoxide bridges.

A series of ruthenium(II) complexes of the NNS donor ligands, methyl 2-pyridyl ketone 4-(4-tolyl)thiosemicarbazone (HL) had been synthesized[76] using RuCl3.xH2O and Ru(PPh3)3Cl2. Chemical and electrochemical studies had been carried out. Structures of two of the prepared complexes were confirmed by single crystal X-Ray diffraction. The thione form of the ligand was coordinated to the ruthenium atom through the pyridine nitrogen, imine nitrogen and the thione sulphur atom. The existence of a new unstable ligand methyl(2-pyridyl)-methylenimine (mpi) was confirmed from crystal structure study. The complex [Ru(HL)(PPh3)(mpi)]Cl2 produced through reductive cleavage of the hydrazinic N-N bond of the thiosemicarbazone ligand.

Nickel(II), copper(I) and copper(II) complexes of thiosemicarbazone derived from 3- and 4-formyl pyridine and from 3- and 4- acetyl pyridine had been characterized [78] on the basis of micro analyses, molar conductivity, magnetic moment measurements and infrared, nmr spectral data. 3- and 4- formyl pyridine coordinated nickel(II) as M:L=
1:2 with one protonated and one deprotonated ligand with composition \([M(LH)L]ClO_4^-\). Tetrahedral geometry was suggested with the first ligand while the second one formed square planar structure. Octahedral nickel(II) complexes of composition \([Ni(LH)_2L]ClO_4^-\) were formed with the ligands 3- and 4- acetyl pyridine thiosemicarbazone. Here also two ligands were neutral while the third was anionic.

Neutral 2-acetyl pyridine-(2-methyl thiosemicarbazone), 2-acetyl pyridine-(4-methyl thiosemicarbazone), 2-acetyl pyridine-(4-phenyl thiosemicarbazone) were used to prepare complexes of the type \(M(HL)_2Cl_2\) \([M= palladium and platinum]\) and \(M(HL)_2Cl_3\) \([M= ruthenium, rhodium and Iridium]\). It was found for palladium(II) and platinum(II) the ligands behaved as neutral bidentate, whereas for ruthenium(III), rhodium(III) and iridium(III) they were neutral tridentate. These results were based on elemental analyses, molar conductivity, magnetic moment measurements and infrared, uv-vis, raman and \(^1H, ^{13}C\) nmr spectral data\[79\]. Various ligand field and nephelauxetic parameters had also been calculated. The ligands and their platinum metal-group complexes were found to exhibit potent cytotoxic activity against Ehrlich ascites tumour cells in vitro.

Ten mixed ligand thiosemicarbazone complexes of composition \([M(bipy)_2(bztsc-R)]ClO_4\) \([M= Ru, Os, bipy = 2,2' bipyridine, Hbztsc-R= benzaldehyde thiosemicarbazone]\) and two complexes of composition \([M(bipy)_2(acts)e)]ClO_4\) where \(Hacts= acitone thiosemicarbazone\) were shown to be diamagnetic\[80\]. They all showed several intense metal to ligand charge transfer (MLCT) band in visible region.
of electronic spectra in acetonitrile solvent. Structure of [Ru(bipy)$_2$(bztsc-NO$_2$)]ClO$_4$ and [Ru(bipy)$_2$(actsc)]ClO$_4$ had been determined by X-ray crystallography. Benzaldehyde thiosemicarbazone exist in thione form with phenyl group trans to hydrazinic nitrogen atom. It was found to coordinate to the metal through hydrazinic nitrogen and sulphur forming four membered chelate rings. On the other hand ‘actsc’ coordinated through imine nitrogen and sulphur forming five membered chelate rings. The difference in coordination modes of two types of ligands appeared to result from the difference in steric bulk. In acetonitrile solution they all showed reversible M(II)-M(III) oxidation in the range 0.18 v and 0.58 v vs SCE followed by irreversible oxidation in the range 1.11 v to 1.60 v vs SCE. Two successive one electron reductions of the coordinated bipyridine were also observed in the range -1.53 volt to -1.96 volt vs SCE.

Isatin-β-thiosemicarbazone(H$_2$L) complexes of manganese, iron, cobalt, nickel, copper and zinc were studied[81]. X-ray structure of [Ni(HL)$_2$]EtOH and [Ni(HL)$_2$.2DMF revealed distorted octahedral coordination with monodeprotonated ligand that behaved as ONS terdentate. Biological studies carried out in vitro on human leukaemic cell lines U937. The result showed that the free ligand and copper(II) complex were more active in the inhibition of cell proliferation than the nickel(II) complex. No compound was able to induce apoptosis.

Reaction of ring substituted 4-phenyl thiosemicarbazones of salicylaldehyde and o-hydroxyacetophenone(LH) with [Ru(PPh$_3$)$_3$]Cl$_2$ in refluxing MeOH produced
[Ru(PPh3)2 (LH)]Cl where the ligand acted as monoanionic tridentate ONS donor. The ligands coordinated to ruthenium(II) through deprotonated phenolic oxygen, thione sulphur and azomethine nitrogen[82].

Thiosemicarbazone derivative of vitamin K3 were synthesized to form complexes with manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) [83]. The complexes were studied by uv-visible, infrared spectroscopy and thermal analyses. They exhibited strong inhibitory action against Gram(+) staphylococcus aureus and Gram(-) Hay bacillus, E.Coli. The antibacterial activity of the complexes was stronger than that of the ligand.

Reaction of 4-formylantipyrine with thiosemicarbazide, N(3)-methyl thiosemicarbazide and N(3)-ethyl thiosemicarbazide produced the expected thiosemicarbazones. The reactions of them with K2PdCl4 produced Pd{N-S}2 complexes with coordination through the imine nitrogen and thiolate sulphur of anionic thiosemicarbazone moiety[84]. Such results were based on spectral studies i.e. infrared, uv-vis, 1H and 13C nmr spectroscopy and electrochemical techniques. Crystal structure of one of the complexes showed trans arrangement of the two bidentate ligands.

Mixed ligand complexes of thiosemicarbazone derived from thiophen-2-carboxaldehyde and cyclooctadiene with ruthenium(II)[85] showed significant antiamoebic property and they were more effective than metrodinazole against HK-9 strain of Entamoeba histolytica in vitro. Similar thiosemicarbazone complexes of
ruthenium(II) and palladium(II) were prepared where thiosemicarbazone derived from 5-nitrophen-2-carboxaldehyde and cycloalkyl amino thiocarboxyl hydrazines were used as ligands. According to spectral studies the ligands behaved as bidentate, coordinating through thionic sulphur atom and azomethine nitrogen. Microdilution method was used for assessment of antiamoebic activity against HK-9 strain of *Entamoeba histolytica*. Enhancement of such activity was resulted by introducing palladium(II) and ruthenium(II) in thiosemicarbazone moiety[86].

The next higher homologue of thiosemicarbazide is thiocarbohydrazide (tch), having the following structure:

\[
\text{S} \quad \text{H}_2\text{N}---\text{C}---\text{NH}---\text{NH}_2
\]

It can also react in the thiocarbohydrazide form. Many metal complexes were prepared and studied to learn whether coordination to metal ions still occurs through sulphur atom or whether available nitrogen atoms are taken for coordination to form a coordination sheath consisting of only nitrogen atoms. Buu-Hoi Ng.Ph., Loc and Xuong reported thiocarbohydrazide as an analytical reagent [87] to form characteristic precipitate with a number of cations.

It was reported to form complexes of the type \( \text{M(tch)}_2\text{Cl}_2 \) [where \( \text{M=Co(II), Zn(II), Cd(II), Hg(II), Pd(II)} \) and \( \text{M(tch)}_3\text{Cl}_2 \) [where \( \text{M=Cu(II) and Ni(II)} \) [88]. The complexes were studied using infrared, electronic spectral data and magnetic moment
measurements. According to infrared studies the modes of coordination for zinc(II), cadmium(II), mercury(II), cobalt(II), nickel(II) and copper(II) complexes were:

![Complex structure](image)

Electronic spectra of the complexes of iron(II), cobalt(II) and nickel(II) complexes suggested distorted octahedral arrangement and room temperature magnetic moment values were in accordance with that observation.

Complexes of N-substituted thiocarbohydrazide R-NHNHCSNHNH₂ [R = acetyl, benzoyl, nicotinyl, 2-chlorobenzoyl, 2-hydroxybenzoyl] with nickel(II) had also been investigated[89]. Three types of complexes Ni₄L₂Cl₂, NiLCl₂₄H₂O and NiL₂ had been prepared. Electronic spectra in the solid state and in solution, magnetic moments, and infrared spectra were used to assign their structures. The ligand field parameters Δq, B' and β were calculated. The parameters indicated that the complexes of the class Ni₄L₂Cl₂ were pseudotetrahedral, the ligand acting as monodentate and coordinating through sulphur atom. The NiLCl₂₄H₂O type complexes were polymeric, distorted octahedral involving bridging halogen atoms, as well as a bridging ligand molecule. The ligands in these cases were bidentate, the coordination occurring through sulphur and the end nitrogen atom. The neutral chelates were paramagnetic and polymeric sulphur bridged structures had been assigned to them.
Cobalt(II), nickel(II) and copper(II) complexes of diphenyl thiocarbohydrazide with composition ML(H₂O)₂ were synthesized and studied using infrared and diffuse reflection electronic spectroscopy, magnetic moment, conductivity and DTA studies[90]. Metals were shown to coordinate to the dinegative ligand through nitrogen and sulphur centers. The copper complex was found to be a dimer.

The reaction of nickel(II) acetate with 1,5 thiocarbohydrazones(HL) produced neutral bis chelate NiL₂. Reaction of NiCl₂ however resulted in partial hydrolysis of the dihydrazones to give Ni(RCH=NNCSNH₂)₂Cl₂ chelate complexes. Deprotonation of these chelates with pyridine gave neutral chelate Ni(RCH=NN=CSNH₂)₂. The copper(II) salts were readily reduced by hydrazone ligands to Cu(I) chelates of the type CuL, Cu(HL)Cl and Cu₂(HL)Cl₂[91].

Condensation reaction of 1,1′ diacetyl ferrocene with thiocarbohydrazide formed bis-(1,1′-disubstituted ferrocenyl) thiocarbohydrazone[92,93]. This compound acted as ligand for coordination with cobalt(II), nickel(II), copper(II) and zinc(II). The compounds were characterized by physical, spectral and analytical methods. Antibacterial effect were screened against E.coli, Bacillus subtillis, Staphylococcus aureus, Pseudomonas aeruginosa and Salmonella typhi. Antifungal effect studied against Trichophyton longifuses, Candida albicans, Aspergillus flavus, Microsporum canis, Fusarium solani and Candida glabrata. All the compounds showed good activity as antibacterial and antifungal agents. Such activity increased in most of the cases on complexation with metal ions.
Ligands obtained on condensation of N,N'-thiocarbohydrazide with 2-hydroxy acetophenone or 5-chloro-salicylaldehyde reacted with chromium(III), manganese(II), iron(III), cobalt(II), nickel(II), copper(II) and zinc(II) to form a variety of mono nuclear or binuclear complexes[94]. In such complexes the ligands were in mono, bi and/or tri deprotonated form. Bonding sites were found to be azomethine nitrogen, phenolic oxygen and thiol sulphur atoms. The complexes were tetrahedral or octahedral in nature. Preliminary antimicrobial screenings had shown them to be active.

The ligand bis(hydroxy iso nitroso benzoyl acetone) thiocarbohydrazone, had been synthesized by the interaction of thiocarbohydrazide with isonitroso benzyl acetone in 1:2 molar proportion in MeOH. Its complexes with ruthenium(III), rhodium(III), palladium(II) and platinum(II) were prepared and characterized by elemental analyses, magnetic susceptibility, conductance measurement, infrared and $^1$H nmr spectral data and by thermal analyses[95].

Bis(diacetylmonoxime) thiocarbohydrazone (H$_2$dmnt) had been obtained as the condensation product of diacetylmonoxime and thiocarbohydrazide[96]. The prepared ligand was characterized by elemental analyses, infrared and $^1$H nmr. It was found to be a strong chelating agent and its coordinating property was studied towards vanadyl, cobalt(II), nickel(II), copper(II) and platinum(IV). Different experimental data revealed formation of mono nuclear complexes with cobalt(II) and platinum(IV) and binuclear for the rest. The ligand bound in the deprotonated form through oxime, hydrazone nitrogen as well as the thiol or thione sulphur forming five or six membered ring. All
the complexes exhibited an octahedral geometry but the copper(II) complex showed a square pyramidal geometry. The ligand showed another interesting characteristic, yellow coloration in acidic media changed to reddish brown in basic media. This property gave the ligand the ability to serve as an analytical indicator for weak acid-base titrations.

A series of mono and binuclear complexes of the type Na₂[M{(3fsa)₂-TCH}(H₂O)ₙ] mH₂O and [M₂{(3fsa)₂-TCH}(H₂O)ₙ] mH₂O had been synthesized where (3fsaH₂)₂-TCH was a Schiff base derived from 3-formyl salicylic acid and thiocarbohydrazide, n,m= 0,1,2; [M= Co(II),Ni(II) and Cu(II)]. Characterizations were done on the basis of elemental analyses, thermal analyses, molar conductivity, magnetic moment measurement, infrared and uv-visible spectral studies[97]. It was found that the mono nuclear copper(II) and nickel(II) complexes were square planar, whereas that of cobalt(II) was tetragonal pyramidal with water molecules at epical position. Subnormal magnetic moment value for binuclear nickel(II) complex was observed. The fungi toxicities of the complexes against some fungal pathogens had been studied.

Template reaction of condensation of benzil and thiocarbohydrazide in presence of divalent metal salts in methanolic medium produced a series of complexes of the type [M(tml)X₂] [tml is the tetra dentate macro cyclic ligand, M= Co(II), Ni(II), Cu(II), Zn(II) and X= Cl, CH₃COO⁻, NO₃⁻]. The complexes had been characterized with the help of elemental analyses, molecular weight determination, molar conductivity, magnetic moment measurement, nmr, infrared and uv-visible spectral studies.
Electronic spectra along with magnetic moment data suggested six coordinated octahedral geometry for these complexes. Low values of molar conductance indicated the complexes as non electrolyte. Biological activity of the metal complexes was tested in vitro against a number of pathogenic bacteria[98].

Thiohydrazides have the following keto or enol structure:

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

So it also contains two nitrogen atoms and a sulphur atom as possible site for coordination. Structurally they are similar with thiosemicarbazide(tsc-H) but number four nitrogen is absent here. This group of ligand had been taken to coordinate a number of transition metal ions to study whether absence of number four nitrogen atom had any effect on the structure and properties of such complexes.

A potential tetradentate ligand N-benzoyl-N'-thiobenzohydrazide (H₂btbh) and N-salicyl- N'-thiobenzohydrazide (H₂sbth) had been coordinated with cobalt(II), nickel(II) and zinc(II)[99]. The prepared complexes were characterized on the basis of elemental analyses, magnetic moment measurement, nmr, infrared and uv-visible spectral studies. Ligands and complexes were screened towards a number of bacteria.

Complexes of N-nicotinoyl-N'-2-furanthiocarbohydrazide(H₃N-fth) with vanadyl, manganese(II), iron(II/III), cobalt(II), nickel(II), copper(II) and zinc(II) were
characterized by elemental analyses, magnetic moment measurement, nmr, infrared and uv-visible spectral studies along with esr and FAB Mass spectrometry[100]. Room temperature esr of vanadyl and iron(III) complexes yielded $g$ values characteristic of octahedral complexes. The complexes were electrically insulating at room temperature however conductivity increased from 333 to 383 k, with a band gap of 0.46 to 0.77 eV. This indicated that the complexes had semi conducting behavior. The ligand and its complexes had been screened against several bacteria and fungi.

Reaction of isonicotinic acid hydrazide and carboxymethyl dithiobenzoate produced N-isonicotinoyl-N'-thiobenzoyl hydrazine(Hintb) which form the following complexes $M$(Hintb)$_2$Cl$_2$,$[M$=Co(II),Ni(II) and Zn((II)]; Cu(Hintb)Cl$_2$; $M$(Hintb)$_2$(CH$_3$COO)$_2$,$[M$=Co(II),Ni(II)]; [Cu(intb)(CH$_3$COO)] and Zn(intb)$_2$. They were characterized by physicochemical methods. Room temperature ESR spectra of Cu(Hintb)Cl$_2$ and [Cu(intb)(CH$_3$COO)] showed characteristic of monomeric and dimeric species respectively. Ligand and the complexes were screened against a number of fungi and bacteria[101].

N-salicyloyl-N'-p-hydroxy thiobenzohydrazide(H$_2$stbh) and N-benzoyl-N'-thiobenzohydrazide(H$_2$btbh) and their cobalt(II), nickel(II), copper(II) and zinc(II) complexes were characterized on the basis of physicochemical studies[102]. Infrared and nmr studies suggested dibasic tetradentate behaviour of the ligands bonding through thiolato sulphur, enolic oxygen and two hydrazinic nitrogens in a polymeric fashion. Electronic spectra indicated [Ni(stbh)(H$_2$O)$_2$] and [Co(stbh)(H$_2$O)] to be
distorted octahedral while Cu(btbh) has square planar geometry. In vitro anti tumour results of the ligand and complexes on P-815 (murine mastocytoma) and L-929 (murine fibro blast) indicated that these compounds showed significant inhibition of 3H-thymidine and 3H-uridine incorporation in DNA and RNA respectively in these tumour cells at dose levels of 1, 2.5 and 5 μg/cm³. Such study showed Cu(btbh) had significant dose dependent inhibitory effect on DNA synthesis. In vivo administration of Cu(btbh) and [Ni(stbh)(H₂O)₂] resulted into prolongation of life span of Dalton’s Lymphoma (DL) bearing mice.

A series of monometallic palladium(II) complexes with thiosemicarbazones and thiobenzoylhydrazones were synthesized and characterized by spectroscopic methods[103]. The crystal structure of chloro(phenyl-2-pyridyl ketone thiosemicarbazonato) palladium(II) and chloro(phenyl-2-pyridyl ketone thiobenzoylhydrazonato) palladium(II) were also determined. The ligands behaved as N,N,S donor, monoanionic, coordinating through thiolato sulphur, imine nitrogen and pyridyl nitrogen atom. The structure of the complex was found to be:-

![Complex Structure](image)

The palladium(II) ion had been coordinated in square planar geometry with two adjacent five membered rings. Catalytic activity of the complexes in homogeneous
hydrogenation of phenyl acetylene was tested with reference to the chemoselectivity from a triple bond to a double bond. A high chemoselectivity was observed with the chloro complex. A catalytic cycle may also be suggested for such hydrogenation reaction.

1.3 SCOPE OF PRESENT RESEARCH :-

From above discussion it is clear that various transition metals can form complexes with chelating ligands having sulphur and nitrogen as possible site for coordination. They have been synthesized and studied in great detail. But ligating property of simple thiohydrazides with general formula R-CS-NH-NH₂ has not been explored in large extent till date. Jensen and Pedersen first synthesized theses thiohydrazides and noticed the formation of coloured precipitate with a few first transition series transition metal ions[104] Such ligands have already been used as analytical reagent for determination of ruthenium, rhenium, osmium, platinum etc[105,106]. Recently platinum complexes with these group of ligands along with that of thiosemicarbazide derivatives had been isolated and characterized[107].

The aim of present research is to isolate different thiohydrazide complexes of nickel(II), palladium(II), ruthenium(II) and osmium(VI), to study their structure and characteristics by means of spectroscopic techniques and screen them whether they have any potential use as drugs. During this work thiobenzhydrazide (Htbh), ortho-hydroxy
thiobenzhydrazide (o-Hhtbh), furan-2-thiohydrazide (Hfth) and thiophen-2-thiohydrazide (Htth) have been chosen as ligands.

Such ligands have –CS-NH-NH$_2$ group available for coordination as thiosemicarbazide but number four nitrogen atom is absent here. Along with thiobenzhydrazide (Htbh), ortho-hydroxy thiobenzhydrazide (o-Hhtbh) has also been taken as a coordinating ligand to examine whether the –OH group at ortho position has any influence on coordination or not. Furan-2-thiohydrazide (Hfth) and thiophen-2-thiohydrazide (Htth) has been taken to study the participation of hetero atoms of aromatic ring in coordination process.

So our study includes synthesis and characterization of the complexes of thiohydrazide ligands viz. thiobenzhydrazide (Htbh), ortho-hydroxythiobenzhydrazide (o-Hhtbh), furan-2-thiohydrazide (Hfth) and thiophen-2-thiohydrazide (Htth) with nickel(II), palladium(II), ruthenium(II) and osmium(VI). Biological activity of the prepared complexes has also been studied to examine their potential use as drugs.
References:

42. C. Kratky, J. Schurz, E. Gagliardi & A. Lopitsch, Monatshefte fur Chemie/Chemical Monthly, 112, No.6, June, 1981


60 K.V.Katti, P.R.Singh & C.L.Barnes, J.Chem.Soc(Dalton Trans) 2153,1993


64 A.Mukherjee(Goswami) &K.De, Trans.Met.Chem, 30(6),677,2005


40
88 G.R.Burns, Inorganic Chemistry, 7, 277,1968