PART I

Studies on Nickel(II) bianionic complexes of thiourea in various Metal-Ligand ratio
The first report about the systematic investigation of nickel (II) thiourea complex was made by Yamaguchi et al\(^1\). It was deduced from I.R. spectral studies that thiourea is bonded through 'S' atom to the metal. Yagupsky and Levitus\(^2\) prepared and characterized other octahedral nickel (II) complexes of substituted thioureas. The I.R. spectral data was used to establish the mode of coordination. It is interesting to note that all the complexes were 'S' bonded.

The next pioneering work in this field had been carried out by Swaminathan and Irving\(^3\). They have observed only 'S' coordination in accordance with the results of I.R. spectral analysis which was also confirmed by X-ray crystallography. Further, Olliff\(^4\) had undertaken detailed study of nickel (II) thiourea complexes and categorically stated about the increased importance of charged resonance contribution of the type \(\text{NH}_2^+ : \text{C(S)}\text{H}_2\) and hence an effective shift of the electron pair towards sulphur atom within the thiourea molecule. At this juncture it is appropriate to mention the canonical forms of thiourea as follows

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

He further, recalled the considerable covalent character in
the C-N bond as it is to be expected in the 'S' bonded complexes. Flint and Goodgame\textsuperscript{5} synthesized complexes of the type $\left[\text{Ni(tu)}_6\right]^{2-}(\text{NO}_3)_2$ and $\left[\text{Ni(tu)}_6\right]^{2-}\text{Cl}_2$ (tu = thiourea). From the far infrared spectral analysis, the $\nu_{\text{M-S}}$ vibrations were assigned at 222 cm$^{-1}$ and 270 cm$^{-1}$ respectively for the above mentioned complexes.

Basso et al\textsuperscript{6} have studied the nickel(II) complexes of the type $\left[\text{Ni(tu)}_6\right]^{2-}X_2$ ($X = \text{NO}_3^-, \text{ClO}_4^-, \text{BF}_4^-$) and characterized them as octahedral complexes. It is concluded that the anions in these complexes are outside the coordination sphere.

Thiourea and its derivatives can coordinate to the central metal ion through sulfur or/and nitrogen. Various authors have reported about the synthesis and infrared studies on thiourea complexes of Fe(III), Ni(II), Co(II)\textsuperscript{7} and have concluded that the metal ion is bonded through 'S' of the thiocarbonyl group.

An equilibrium solid phase reaction which includes thiourea (L), Ni(ClO$_4$)$_2 \cdot 6\text{H}_2\text{O}$ and Ni(ClO$_4$)$_2 \cdot 6\text{L}$, was carried out by Goryunov et al\textsuperscript{8}. The I R spectra of Ni(ClO$_4$)$_2 \cdot 6\text{L}$ system indicate Ni — S bonding.

Dash and Ramanrao\textsuperscript{9} converted Co(Py)$_2\text{Cl}_2$ complex into hexacoordinated complex of the formula $\left[\text{Co(tu)}_4\right]X_2X$ ($X = \text{Cl}^-, \text{Br}^- \text{or I}^-$) which was characterized by magnetic
and conductance studies. The same authors\textsuperscript{10} reported high-spin \( \text{penta} \) coordinated Co(II) complexes of the type \( ^{7}\text{Co}(\text{tu})_{3}\text{X}_{2} \). However, Hall et al.\textsuperscript{11} criticized the observations of Dash and Rao and they have subsequently proved from X-ray studies that the complex \( ^{7}\text{Co}(\text{tu})_{3}\text{X}_{2} \) was an equimolar mixture of tetrahedral and octahedral species.

Pseudo-octahedral anionic complexes of Co(II) having the general composition \( R(\text{CoLX}_{2}Y) \) (where \( R = (\text{C}_{5}\text{H}_{5})_{4}\text{N}, (\text{N-C}_{3}\text{H}_{7})_{4}\text{N}, \text{Ph}_{4}\text{P}, \text{Ph}_{4}\text{AS}; L = \text{triphenylphosphine}, X & Y = \text{Cl, Br, or I} \) ) have been isolated and characterized by spectral and magnetic measurements by Jha and coworkers\textsuperscript{12}. The molar conductance values in nitromethane (\( \sim 90\ \text{mho cm}^{2}\ \text{mol}^{-1} \)) fall within the acceptable range for 1:1 electrolytes. The electronic spectra of these complexes correspond to \( C_{3} \) symmetry. The overall feature of spectra is the presence of one band in the visible region (13000 - 16000 cm\(^{-1}\)) and two bands in the near\( \text{I.R.} \), region (4100 - 4600 cm\(^{-1}\)) and (7100 - 8300 cm\(^{-1}\)) respectively.

The thermal behavior of \( \text{MLSO}_{4} \) (\( M = \text{Co, Zn, Cd}; L = \text{thiourea} \)), \( \text{NiL}_{4}\text{SO}_{4}\cdot\text{MeOH} \) and \( \text{Cu}_{2}\text{L}_{4}\text{SO}_{4} \) has been described by Udups\textsuperscript{13} using a mullite and Platinum crucible for a particular complex. The initial temperature of decomposition and total weight loss at the end of the reaction were the same in both the crucibles. But it is interesting to note that there is marked difference in the thermal curves at 400 - 600 °C.
Biader et al. studied the complex formation between cobalt(II) and thiourea in various solvents, such as ethyl acetate (Etac), propanol (PrOH) and propylene carbonate (Pc). The order of the stability of the complexes with respect to these solvents was PrOH > Etac > PrOH. This behaviour has been explained on the basis of solvent properties viz, donicity, acceptor ability and dielectric constant. But the influence of donicity (DN) was the prevailing effect. Further, it was suggested that the species Co(H₂O)₄S²⁺ seems to be formed when solvent is PrOH or Pc, while Co(H₂O)₆²⁺ is formed when solvent is Etac.

The synthesis of Zn(ClO₄)₂tu (tu = thiourea) and its effect on corrosion in acidic and neutral media has been investigated by Molchanov and coworkers. The protective effect of tu and the complex in the H₂SO₄ medium increases with the increase in their concentration. In presence of sulphate, chloride and in a neutral solution, tu complex is more corrosion inhibitor than the Zn(ClO₄)₂ itself.

Bellomo and coworkers investigated the formation and thermodynamic properties of mononuclear mixed ligand complexes of the type Cd(SCN₂H₄)₂(NO₂)₂⁻P and Cd(SCN₂H₄)₂(S₂O₃)²⁻p in aqueous solution. With the aid of potentiometric studies at different temperatures and ionic concentration, the thermodynamic parameters for the above mentioned complexes were evaluated.
The crystal structure of monothiourea cadmium acetate, \( \text{Cd} \left( \text{CH}_3\text{COO}\right)_2 \text{CS}(\text{NH}_2)_2^- \), has been described by Thanmaniwong et al.\(^{17}\). The crystal is orthorhombic with space group \( \text{Pbcn} \), with \( a = 8.047 \) (2), \( b = 14.391 \) (2) and \( c = 8.819 \) (3) \( \text{Å} \); \( d_c = 1.994 \) for \( Z = 4 \). Further, it is shown that the Cd atom is in six-membered coordination with one bidentate and two bridging bidentate - OAC (acetate) group, and two bridging tu groups which make the total symmetry 2. However, the molecular structure involves hydrogen bonding.

Dongre\(^{18}\) has investigated the stability constant of simple and mixed ligand complexes of thiourea (tu) and glutamate (glu) with Cd(II), polarographically in aqueous medium. The complex\(^{18}\) viz \( \text{Cd(tu)} \) (glu)\(^+\), \( \text{Cd(tu)} \) (glu)\(_2^-\) and \( \text{Cd(tu)} \) (glu)\(_2\) were formed at pH 6.8 and 1.0 M NaClO\(_4\) solution.

A precise calorimetric measurement of Cd(II)-tu and Rb(II)-tu system in 1 M NaClO\(_4\) solution was carried out by Banerjee and Vaz\(^{19}\) using a thermistor as the temperature measuring device. The stepwise and overall changes in the thermodynamic characteristics for the above mentioned systems were evaluated.

A system\(^{20}\) of \( \text{Cu}_3(\text{PO}_4)_2 \) tris thiourea water at 40°C has been studied and the resulting compounds were characterized by determining their densities and also by derivatographic studies.
The reaction between CdCl₂ and thiourea (L) in solution was carried out by Krunks et al. The thermal stability of the complex formed was studied to explain the properties of CdS films, obtained by spraying method. It was concluded that CdS forms from neutral solution of CdCl₂ and L through intermediate formation of CdL₂Cl₂ and with its subsequent decomposition.

An interesting study of Cr(O) complex such as Cr(CO)₅L (L = tu) was made by Costamagna et al. by the reaction of Cr(CO)₅THF in the solvent THF (tetrahydrofuran) with the ligand.

Coordination compounds of Li(IV), Zr(IV) and Hf(IV) with thiourea (tu) were prepared and characterized by Konunova and his group. IR spectral studies reveal that the complexes MCl₄L (L = tu) are dimeric with bridging 'Cl' groups. Another complex with composition MCl₄2L also has the structure similar to MCl₄L but the second L is hydrogen bonded.

The crystal and molecular structure of dichloro (thiourea) tin(II) complex has been described by Harrison et al. The complex was isolated from SnCl₂ and thiourea. X-ray studies reveal that the complex is monoclinic with space group P2₁/C, with a 5.951(2), b 13.937(4), c 8.883(3) Å and β 111.13(2)° for Z = 4. Further, it is realized that
the basic unit of the structure is SnCl$_2$ /"Sc(NH$_2$)$_2"$.
(Sn-Cl = 2.492(4), and 2.609(4), Sn - S = 2.704(4)°Å
to valence angle at Sn are 88.0 (1), 90.6(1), 93.5(1°).)

It is concluded that these formula units are tightly bonded into chain through 'Cl' and 'S' bridging, which are, in turn, weakly bonded by interchain 'Cl' bridges into sheets which are reinforced by N-H — Cl hydrogen bonds. However it is interesting to note that additional N-H — Cl hydrogen bond connects adjacent sheets forming a 3-D network.

X-ray crystal structure determination of two tin (II) complexes of thiourea (tu) were made by Donaldson et.al.$^{26}$.
The first complex, diacetatedis(tu) tin(II) (I) is monoclinic space group P2$_1$, with a 11.932(6), b 10.937(5) c 21.919(5)Å
and β 96.5(1)°, dm=1.32, dc = 1.33 for z=2. The second complex, ditin(II) tetrabromo penta (tu) dihydrate (II) is orthorhombic, space group Pnma, with a 27.83(3), b 16.13(4)
and c 6.11(6)Å; dc=2.37. for z=4. In the case of complex (I)
Sn has a square pyramidal geometry and is bonded by two thiourea and two carboxylate groups via 'S' and 'O' atoms respectively. But in complex (II) there are two Sn atoms, both of which have trigonal pyramidal coordination. Further, the above structures are supported by Sn mossbauer spectral data.

The complexing properties of Zr and Hf with thiourea in aqueous solution have been studied by Konunova et al.$^{27}$
however, no conclusions are drawn regarding the structure.

A double well potential model with variable zero point is proposed by Yang et al.\textsuperscript{28} which can give a reasonable explanation to the 5 successive phases of thiourea.

Complexes of the Ag ions with thiourea and methyl thiourea (L) was studied by Khostsyanskii et al.\textsuperscript{29} potentiometrically. The data obtained for silver thiourea complex indicate the formation of \( \text{AgL}_n^+ \) (\( n=1,2,3 \)). Therefore the three possible species stability constants evaluated are \( \text{p}K_1 = 8.2 \), \( \text{p}K_2 = 10.8 \) and \( \text{p}K_3 = 12.95 \) for thiourea complexes and 6.7, 9.2 and 11.3 respectively for methylthiourea complexes.

Fedorov et al.\textsuperscript{30} calorimetrically studied the formation of Bi(III) thiourea complexes in aqueous solution at 25°C containing 1 mol. HClO\(_4\). With the aid of above calorimetric data the heats of formation are evaluated for the Bi(III) thiourea complexes.

Kulenov et al.\textsuperscript{31} investigated the formation of Gold(I) thiourea complexes in aqueous solution. The formation constant for \( \text{AuL}_2^+ \) (\( L = \text{tu} \)) has been evaluated in 0.1 mol HCl solution containing various concentrations of tu at 25°C. The log \( \beta \) values are found to be 21.3.
The adsorption of tu on silver and copper electrode was studied by Fleischmann et al.\textsuperscript{32} utilizing surface enhanced Raman scattering. The results show that the thiourea adsorbed via 'S'. At low pH values, adsorbed tu remains unprotonated, but it is interesting to note that the spectral intensity is increased and additional bands were also observed due to oxyanions.

The solid state preparation of UO$_2$(OAC)$_2$ adducts with thiourea (tu) were attempted directly in a DSC apparatus by Abate et al.\textsuperscript{33} according to the following scheme,

$$UO_2(OAC)_2\cdot 2H_2O(s) + ntu(s) \rightarrow UO_2(OAC)_2\cdot ntu(s) + 2H_2O(g) (n=1 \text{ to } 6).$$

The DSC data was used to evaluate the heat of formation. However, it is surprising to note that at all stoichiometric ratios the same UO$_2$(OAC)$_2$ tu product was obtained. Further, the thermogravimetric (DTG) and IR spectral measurements were carried out. These physicochemical data are found to be in good agreement with the DSC results.

Pashkov et al.\textsuperscript{34} carried out the stability constants studies of silver (I) thiourea complexes potentiometrically. The data obtained at 25°C and 0.1, 0.5 mol ionic strength (of Na$_2$SO$_4$) using silver electrode, indicate the formation of AgL$^+$ and AgL$_2$\textsuperscript{+} (L=tu) complex cations. The stability constants at the ionic strength of 0.1 for the above mentioned two complex ions are found to be $log \beta_1 = 5.55 \pm 0.07$ and $log \beta_2 = 10.54 \pm 0.06$ respectively.
Adi & Murty\textsuperscript{35} have taken up a detailed study on complexation of VO\textsubscript{3}S\textsubscript{4} with thiourea and substituted thioureas. Complexes of the type VO\textsubscript{3}S\textsubscript{4}Ln \( \sum n=4 \), L=thiourea (tu); n=1, L=phenyl thiourea (Ptu), o-chlorophenylthiourea (q) \( \sum n=1 \), VO\textsubscript{3}S\textsubscript{4}(Py)L' \( \sum n=2 \), m=0.5, L'=tu; n=4, m=1, L'=Ptu; n=1, m=0.5, L'=q, benzoylthiourea \( \sum n=1 \) have been synthesized and characterized by IR, electronic, ESR spectra and magnetic susceptibility studies. The effect of electron donor ligands such as pyridine (Py) on VO\textsuperscript{3} and the behaviour of SO\textsubscript{4} as a bidentate chelating group is discussed. Further, the spin orbit coupling (\( \lambda \)) and other parameters, \( g_1 \), \( g_{11} \), \( \lambda_1 \) and \( \lambda_{11} \) are evaluated, from ESR spectral data. The correlation between delocalizing antibonding, the extent of covalence of metal ligand bond and also the criterion for the inverted order of levels \( \sum e_g(2_B^2) > b_2(2_B^2) \) in octahedral complexes are suggested from these parameters. Thiourea complexes of Bi(NO\textsubscript{3})\textsubscript{3} have been studied in detail by Jansen and coworkers\textsuperscript{36}. The X-ray data indicate the complex \( \sum Bi(NO_3) \) \{SC(NH\textsubscript{2})\textsubscript{2}\} \( \sum n=5 \) \( \sum n=7 \) (NO\textsubscript{3})\textsubscript{2}.H\textsubscript{2}O is triclinic space group P1, with a 9.92 (1), b 9.788 (1), c 15.729 (1) \( ^\circ \)A. \( \kappa = 118.55(1), \beta = 92.99(1) \) and \( \gamma = 93.72(1) \) \( ^\circ \); \( d = 2.12(1) \) and \( d = 2.11 \) for \( Z = 2 \). The bond distances determined for Bi -- S and Bi -- O were 2.673(2) \( ^\circ \)A and 2.814(5) \( ^\circ \)A respectively. Further, the same authors have also taken up similar studies for \( \sum Bi(NO_3) \) \{SC(NH\textsubscript{2})\textsubscript{2}\} \( \sum n=7 \) complex which is monoclinic in nature and all the parameters have been evaluated.
Thermogravimetric investigations for Al, Fe, and Mn complexes of urea were made by Lupin and Peters. Thermal decomposition of Al(urea)$_6$(NO$_3$)$_3$, Fe(urea)$_6$(NO$_3$)$_3$, and Mn(urea)$_4$Cl$_2$ has been carried out in air and Argon atmosphere, by simultaneous recording of TG, DTG and DTA curves. The formation of metal oxides from the decomposition of the complexes was identified by X-ray powder diffraction technique. Further, the data is used to propose the stoichiometry of the complexes.

The complexing property of Os with tu has been described by Sereda and Stadnik. Stepwise complexing of Os with thiourea is carried out in presence of extraneous reducing agent. In the case of OsO$_4^-$, hydrazine and EtOH are used but where as in case of hexachloroosmate, SnCl$_2$ is used. The formation constants are calculated and it is realized that the complexation in aqueous media for hexachloro osmate is ~10 times greater than the values for OsO$_4$ in alcoholic media. It is finally concluded that the presence of chloride seems to effect not the stability of the complex but the rate of formation of the complex.

Sauerbrunn and Sandel studied the reaction of Osmium tetroxide with thiourea spectrophotometrically. A red colour complex was formed by the reaction of thiourea with OsO$_4$ in acidic medium which possesses trivalent Os and
has the composition $\left[\text{Os(NH}_2\text{-CS-NH}_2\right]_6^{-7}^{+++}$ in solution. Os in this compound can be reduced to the divalent state with chromous chloride. Further, a yellowish brown mixed Os(II) chlorothiourea can be formed in the presence of more chromous chloride. It is also possible that the intermediate complex ion $\left[\text{OsO}_2(\text{NH}_2\text{-CS-NH}_2\right]_4^{-7}^{+++}$ can be isolated in the slightly soluble, sulfate form. It is shown that in the acidic solution, the red colour complex will form. When Osmium tetroxide reacts with excess of thiourea, the reaction takes place according to the following equation.

$$2 \text{OsO}_4 + 22 \text{NH}_2\text{CSNH}_2 + 6\text{H}^+ \rightarrow 2 \left[\text{Os(NH}_2\text{-CS-NH}_2\right]_6^{-7}^{+++} + 5 \text{SH}_2\text{O}.$$

It is known that if the oxidizing agent is present in acidic media, it converts thiourea into formamidine disulfide; however, the latter can be converted back to thiourea by strong reducing agent.

The mechanism of the formation and kinetics of monothiourea complexes of Pt(II) has been put forward by Kiseleva and his group. The study was carried out polarographically on a dropping mercury electrode. It was shown
that the polarographic reduction of \(\text{Pt}(\text{NH}_3)_2(\text{thio})\text{Cl}_7\text{Cl}\) complexes involves a two electron process with half wave potential 0.58V for 10^-3 M solution. Further a trans - \(\text{Pt}(\text{NH}_3)_2(\text{thio})_2\text{Cl}_7\) isomer was also obtained by the reaction of trans - \(\text{Pt}(\text{NH}_3)_2\text{Cl}_7\) with thiourea.

An aquation kinetics of trans - RhX(dioxime)L \(\text{L} = \text{thiourea, dioxime} = \text{methylglyoximato, 2,}\text{methylglyoximato}\) at 40° and 65°C was studied by Shpakov et al.. It was found that the replacement of Cl^- takes place faster than the Br^- and aquation rate for the dimethylglyoxime complex is 3 to 4 times higher than the methylglyoxime complex.

The complexing ability of praseodymium with some organic ligands like tu with respect to Pr(ClO_4)_3 has been discussed by Ashikhmina et al.. The complex formed was Pr(ClO_4)_3tu.10H_2O which was characterized by IR and thermoanalytical data.

Droyer et al. synthesized and characterized the Astatine compounds containing thiourea. The formation of cationic Astatine compounds with thiourea derivatives and allylthiourea was studied in aqueous medium. The characterization and the determination of carrier free Astatine compounds was made by studying their ionic mobilities in free electrolytes.
The most favourable conditions for the formation of intensely yellow coloured complexes by the reaction of thiourea on tellurium(IV) compounds in perchloric acid solution were studied by Jilek and Vrestal, the two Czechoslovakian chemists in 1952. This is counted as the first available report on the reaction of tellurium compounds with thiourea. Even though a few reports appear on the thermal stability and structure of tellurium-thiourea complexes, they do not speak of the stoichiometry of the complexes.

A ligand displacement reaction between $\left[\text{TcL}_5\text{Cl}_7\right]^{2-}$ (L = thiourea) and the model ligand 1,2-bis(phenylphosphine)ethane (dppe) was studied with the aid of UV-visible absorption spectrophotometer by Muenze and Grossman. A complex ion of the composition $\left[\text{TcCl}_2\text{dppe}\right]^{2-}$ was formed at 1:13 (Tc : dppe ratio) in 0.18 N HCl, and at 0.96 N HCl, $\left[\text{TcCl}_6\right]^{2-}$ was formed. But $\left[\text{TcCl}_2\text{dppe}\right]^{2-}$ was isolated at much higher Tc : dppe ratios. Rout and coworkers were successful in synthesizing a trans-bis-$\left[\text{C}_7\text{H}_6\text{N}_2\text{S}\right]_{2-}$benzimidazolethione-bis thiourea-tellurium(II) chloride isomer having the formula $\left[\text{Tc(CH}_4\text{N}_2\text{S})_2\left(\text{C}_7\text{H}_6\text{N}_2\text{S}\right)_2\right]^{2-}\text{Cl}_2$. X-ray analysis proves that the complex is monoclinic, space group P21/C, with a 6.623(1), b 11.387(3), c 16.085(3) Å and $\alpha = 1.787$ for $Z = 2$. The crystal structure suggests that Te atom lies at the centre of the symmetry, bonded to two thiourea and two benzimidazolethione via 'S' atom in a trans-square planar arrangement.
1$^{25}\text{Te}$ Mossbauer parameters for a number of square-planar Te(II) and octahedral Te(IV) compounds are evaluated by Calogcro et al.\textsuperscript{49} by adopting an improved Foss model. Further, the authors have also reported the analytical data for several compounds not previously reported.

The crystal and molecular structure of tris thiourea tellurium(II) di(Hydrogen difluoride) was studied by Mark\textsuperscript{50}. The complex crystal is monoclinic in nature and crystallizes as dimeric distorted square planar cations, \( \text{Te(tu)}_{3}^{-2}_{2}^{+} \) (tu=thiourea). X-ray studies reveal that Te occupies the inversion centre site and cations are linked by \( N-H.....F \) hydrogen bonding the environment about two \( \text{FHF} \) anion is decidedly asymmetric and therefore the H atoms are not centred between the F atoms.

The complex formation of Tc with thiourea has been discussed by Muenze et al.\textsuperscript{51} with the aid of spectrometric and electromigration techniques. It was deduced that \( \text{TcO}_{4}^{-} \) is reduced by thiourea to Tc(III) in 6N HCl. Three cations viz \( \text{Tc(tu)}_{6}^{-7}_{3}^{+} \), \( \text{Tc(tu)}_{5}\text{Cl}_{2}^{-7}_{2}^{2+} \) and \( \text{Tc(tu)}_{4}\text{Cl}_{2}^{-7}^{2+} \) were characterized by the above mentioned techniques, however, \( \text{Tc(tu)}_{5}\text{Cl}_{2}^{-7}_{2}^{2+} \) was isolated and chemically characterized.

Further, studies on \( \text{Tc(tu)}_{6}^{-7}\text{Cl}_{3}^{-4}\text{H}_{2}^{0} \) (I) are described by Abrams and coworkers\textsuperscript{52}. The crystal is monoclinic possessing a roughly octahedral geometry, Tc being
coordinated by six S atoms of thiourea groups. The Tc - S bonds $2.43(1)$, $2.41 (1)$, $2.440 (1)$ Å are significantly longer than Tc(v)-S bonds reported previously, but the bond length within the thiourea groups are normal. The structure is held together by an extensive hydrogen bonding. Further, the complexes $\text{Tc(SC(NH$_2$)$_2$)$_6$BF$_4$}$, $\text{Tc Cl$_2$ (diphos)$_2$}$-$Cl.2H$_2$O$, $\text{Tc(CN$_2$u-tert)$_6$BF$_6$}$ and $\text{Tc(P(ome)$_3$)$_6$BF$_6$}$ were prepared from parent complex (I) and characterized.

The effect of the central atom on rotational barriers of the restricted C N-rotation and the $^{13}$C NMR spectra of 1,1-diethyl-3-benzoylthio(seleno)urea has been discussed by Kleinpeter et al. $^{53}$ The barriers are found to be dependent on the electrical polarizibility of the metal ion and the Chalcogen atoms X (X=Se,S). It was concluded that the most of the electron attractive metal ion effect is characteristic variation of $^{13}$C chemical shift.

Fermi resonance, hydrogen bonding and hot bands in the I.R spectrum of thiourea has been described by Bala and Ghosh. $^{54}$ A number of anharmonic and coupling constants have been evaluated and a relevant theory for the calculation of intensities and frequencies of resonance bands has been put forward. Appearance of a series of bands in 1660 cm$^{-1}$ region is assigned for hydrogen bonding. The values for anharmonic constants and hydrogen bond stretching frequency are reported with the aid of the hot band analysis.
At this juncture, it is worthwhile to consider the bonding of thiocyanate group either alone or in association with the other anion to the central metal, since the present work entitled the study of bianionic complexes include thiocyanate as one of the anions.

At the outset let us consider the bonding nature of thiocyanate. Potentially ambidentate thiocyanate group offers interesting bonding possibilities. In metal complexes, the thiocyanate ion may coordinate to central metal ion either through nitrogen $\text{M} \equiv \text{NCS}$, or sulphur $\text{M} \equiv \text{SCN}$ or both $\text{M} \equiv \text{NCS} \rightarrow \text{M}$. It can also act as a bridging ligand between two different metal ions.

It is well known that in general, first row transition metals (Cr, Mn, Fe, Co, Ni, Cu, and Zn) coordinate through nitrogen whereas second half of the second and third series metals (Rh, Pd, Ag, Cd, Hg, Ir, Pt, Au and Hg) coordinate through sulphur. However, other factors such as the oxidation state of metal, the nature of other ligands in the complexes and steric considerations also influence the mode of coordination. $\text{M-SCN}$ group is linear or bent while $\text{M-NCS}$ group is always bent. This seems to suggest that the following resonance structures are predominant in each case.

\[
\begin{align*}
\text{M - NCS group} & \quad \text{M - SCN group} \\
\text{M} & \equiv \overset{\text{+}}{\overset{\text{N}}{\text{N}}} \equiv \overset{\text{C}}{\text{C}} \equiv \overset{\text{S}}{\text{S}} \\
\text{M} & \equiv \overset{\text{s}}{\text{S}} \equiv \overset{\text{C}}{\text{C}} \equiv \overset{\text{N}}{\text{N}}
\end{align*}
\]
Mitchell and Williams\textsuperscript{56} have shown that the CN stretching frequency levels are generally low in the M-NCS complexes than in the M-SCN complexes. For the M-NCS bonding, the $\nu_{CN}$ appears to fall in the range 2080 - 2040 cm\textsuperscript{-1}. The corresponding range for M-SCN bonding is 2120-2080 cm\textsuperscript{-1}. The C - S stretching frequency is more useful in distinguishing these two isomers: 780 - 860 cm\textsuperscript{-1} for M - NCS and 690 - 720 cm\textsuperscript{-1} for M - SCN. The NCS bending frequency is also different between two isomers; 450 - 490 cm\textsuperscript{-1} for the M-NCS and 400 - 440 cm\textsuperscript{-1} for M-SCN group.

Double complex salts containing nickel (II) as cation of the type $\left[\text{NiLnJ}\left[\text{Cr(NCS)}_4(\text{NH}_2\text{CSNH}_2)_2\right]_2\right]^2_2$ (L = various mono, bi, tri and tetradeinate amines; n = 1, 2, 3 & 4) were synthesized by Gaur and Kapoor\textsuperscript{57} and characterized by analytical data. From the electrical conductivity studies, it was concluded that the complexes are ionic in nature.

Several bianionic complexes of nickel(II) thiourea have been investigated with the aid of spectral and thermoanalytical techniques by Sramko et.al.\textsuperscript{58,59}. The complex $\left[\text{Ni Br NO}_3(\text{tu})_4\right]^2_2$ is octahedral with thiourea coordinated through 'S'. X-ray structural analysis confirms that the compound contains $\left[\text{Ni}_2(\text{Br}_2)(\text{tu}_3)\right]^{2+}$ cations and NO\textsubscript{3} anions. The initial thermal decomposition temperature of Ni Br(NO\textsubscript{3}) tu\textsubscript{4} is in the range 160-80°C. However, the loss of weight at 300°C is
caused by the release of Cl or Br with a subsequent formation
of NiS and partial decomposition of thioureas.

The linkage isomeric ratios for thiocyanate trans to
various donors have been determined for a series of cobalt-
oximes \( \text{trans-bis(dimethylglyoximato) thiocyanato cobalt(III)} \) utilizing a proton NMR spectrometer by Burmeister and coworkers. The chemical shift of the methyl proton of the dimethylglyoximate group is sensitive to the nature of the axial ligands, the \( \gamma \) values of the S-bonded isomers being 0.1 ppm less than those of the N-bonded isomers in an aromatic solvent such as nitrobenzene. The ratio of sulphur to nitrogen bound species, \( K(S/N) \), is related to the trans influence and the basicity of the trans ligands. The observed order of decreasing trans influence is roughly in the following order:

alkyls \( \gg \) phosphites \( \gg \) pyridines \( \gg \) anilines \( \gg \) phosphines \( \gg \) thioureas, \( K(S/N) \) decreases in reverse order.

Using \(^1\)H NMR, the above authors have shown that the compound \( \text{Co(DH)}{2}(CN)(NCS) \) is an N-bound isomer contrary to the earlier reports by Gaus et al. that it was an S-bound isomer whose conclusions were based upon infrared and integrated absorption data.

The complexes of the composition \( ML_2(SCN)_2 \) (\( M=\text{Co, Ni}; L=\text{thiourea, N-methylthiourea, N,N'-ethyldithiourea} \))
N-ethylthiourea) were studied by Yagupsky et al.\textsuperscript{62}. The location of the metal-ligand bonding and the structure of these complexes were understood with the aid of vibrational and electronic spectra. The thiourea and methylthiourea form octahedral complexes involving polymerization through 'S' atom, whereas ethyl thiourea complex exists both as a blue tetrahedral and also as a brown red octahedral isomer through thiocyanate bridging.

The nature of the thiourea complexes of bivalent transition metal thiocyanates of the type $\sum^\infty_{n=0} M(tu)_2(NCS)_2^{-7n}$ ($M = \text{Co, Ni, Cd}$) has been described by Moharana and Dash\textsuperscript{63}. They showed that the thiourea and thiocyanate are bonded to metal through 'S' and 'N' atoms respectively.

Novel complexes of nickel(II) halides and thiocyanate with thiourea and substituted thioureas have been synthesized by Issleib et al.\textsuperscript{64}. The complexes $\text{NiX}_2(\text{HL}_2)$ (HL = phenyl-thiourea, etc; $X = \text{Br}^-$, $\text{I}^-$, $\text{SCN}^-$) were characterized by electronic spectra.

The reaction of Cis-$\sum^\infty_{n=0} \text{CoL}_2\text{Cl}_2^{-7} \text{ with NO}_2^-$, $\text{SO}_3^{2-}$, $\text{NCS}^-$ and thiourea (tu) in $\text{H}_2\text{O}$ was studied\textsuperscript{65} with the aid of $^{59}\text{Co}$ NMR spectra to establish the mode of coordination of the substituting ligand. It is interesting to see that in case of $\sum^\infty_{n=0} \text{CoL}_2(\text{SO}_3)_2^{-7}$, SCN is 'N' bonded; and in $\sum^\infty_{n=0} \text{CoL}_2(\text{NCS})\text{H}_2\text{O}^{-7}$...
and $\left[\text{CoL}_2(\text{NCS})_2\right]^+$, SCN is 'N' bonded; and in $\left[\text{CoL}_2(\text{NO}_2)\text{OH}\right]^+$, $\left[\text{CoL}_2(\text{ONO})\text{Cl}\right]^+$, NO$_2^-$ is 'N' and 'O' bonded respectively. The results were compared with those for reaction of $\left[\text{Co(en)}_2\text{Cl}_2\right]^-$ with NO$_2^-$. Isotopic exchange rates in case of dithiocyanato bis (thiourea) cobalt(II) complexes using $^{60}$Co were determined in solution containing CoCl$_2$, thiourea, NH$_4$SCN, Me$_2$CO and phenyl acetate at 293.15 or 303.15°K. It was found that Co(II) in Co(thiourea)$_2$ (SCN)$_2$ exchanges with free Co$^{2+}$ in solution. Further, the same authors$^{67}$ have also studied the effect of salt concentration and temperature (293.15, 303.15°K) on $^{60}$Co exchange between bulk solution and CoL$_2$(SCN)$_2$: (L = thiourea). Geometry, lability and magnetic properties of the complex are discussed. Cobalt(III) trans-sulfito-dioxime containing urca and thiourea derivatives has been reported by Syrtsova et al.$^{68}$ Nanazova et al.$^{69}$ have studied the formation of water soluble CdCl$_2$L and CdCl$_2$2L (L=thiourea) complexes.

It is realised from the literature survey that there are very few reports on nickel(II) thiourea bianonic complexes. Hence, attempts are made in our laboratories to synthesis bianionic complexes of nickel(II) and also to illustrate the characteristic features such as metal ligand bonding, covalency and structure with the aid of chemical and physicochemical methods of analysis.