PART III

Studies on Nickel (II) bianionic Complexes derived from Mixed Ligands.
PART III

CHAPTER I

INTRODUCTION
Several authors have studied the thermal decomposition of pyridine thiocyanate mixed ligand complexes. Their investigations arrived however at contradictory conclusions. But a critical study of the thermal decomposition, the isolation of decomposition products and their structural investigations, magnetic susceptibility measurements, IR, UV spectral studies of $M(FY)_4(NCS)_2$ and $M(FY)_2(NCS)_2$ (where $M=Mn(II), Co(II), Ni(II))$ were made by Liptay et al. This is believed to be the first report on the isolation of the intermediate product of thermal decomposition reaction. The bivalent transition metals are precipitated by pyridine and thiocyanate ions from their aqueous solution in the form of mixed complex of the composition $M(FY)_4(NCS)_2$ or $M(FY)_2(NCS)_2$. They showed that Mn(II), Co(II), Ni(II) complexes contain four pyridine ligands while the Cd(II) and Cu(II) and Zn(II) complexes have only two. Further, they concluded that the derivatives of these complexes possess octahedral polynuclear structure (I).
kinetics and enthalpy changes in the decomposition of Ni(NCS)$_2$($3$-$R$-pyridine)$_4$ complexes ($R$=ethyl, Cl, Br, CN, NH$_2$) were reported by Horvath and his group. Isothermal TG and DSC measurements were used to study the effect of the pyridine substitution ($3$-$R$) on the kinetics and enthalpy changes in the thermal decomposition of Ni(NCS)$_2$($3$-$R$-py)$4$ complexes. It is interesting to see that they found activation energy ($E$) of the interface advance decreased with the increase in the volume of the substituent, allowing the assumption of a dissociative activation mechanism in the thermal decomposition reaction. Further, a relationship between $E$ and $\Delta H$ and the occurrence of the kinetic compensation effect in $A = f (E)$ is described.

A derivatographic study of thermal decomposition of Co(PY)$_4$(NCX)$_2$ ($X$ = O, S, Se) was carried out by Zsako et al. It is shown that in the first two decomposition stages, four pyridine molecules are released. The Co(NCS)$_2$ is relatively stable intermediate while others immediately undergo further decomposition reaction.

\[
\begin{align*}
\text{Co (NCO)}_2 & \longrightarrow \text{Co(CN)}_2 \longrightarrow \text{Co}_3\text{O}_4 \\
\text{Co(NCO)}_2 & \longrightarrow \text{Co(CN)$_2$ + O}_2 \\
3\text{Co(CN)}_2 + 11\text{O}_2 & \longrightarrow \text{Co}_3\text{O}_4 + 6\text{CO}_2 + 6\text{NO} \\
\text{Co(NCS)}_2 & \longrightarrow \text{Co}_2\text{(SeO)}_3 \longrightarrow \text{Co}_3\text{O}_4
\end{align*}
\]

However, Co(NCS)$_3$ at higher temperature, gives a mixture of
sulphate and oxide. They have derived the kinetic parameters and pointed out that these parameters depend upon the working conditions. Thermal decomposition of CuL₂(NCS)₂, where L = NH₃, pyridine and its methyl and halo derivatives were investigated by Kabesova and his group⁴. The initial decomposition temperature is 70-80°C and 100-110°C for 2-substituted pyridine and other complexes respectively. Further, the authors have grouped the ligands according to scheme of decomposition exhibited by them.

Majumdar et al⁵ have carried out the extraction and spectrophotometric determinations of Co(II) with substituted pyridines and thiocyanates. Co(II) forms complex with α-picoline, β-picoline, γ-picoline, 2,4,6-collidine in the presence of thiocyanate. The complexes are readily extractable into ethylacetate. They have also proposed a quick and simple method for determining cobalt (in microgram amount) in the presence of Fe and Cu. Further, solvent extraction and spectrophotometric determination of Pd(II) as pyridine/α-picoline/β-picoline/γ-picoline/4,6-collidine thiocyanate; and extractive gravimetric determination of Ni(II) as pyridine/β-picoline/γ-picoline thiocyanate have been reported by the same group of workers⁶. They have pointed out that Ni(II) does not form complex in the presence of thiocyanate when the methyl group is in 2-position of the pyridine ring. So α-picoline and 2,4,6-collidine can be
used for the separation of Ni(II) from Co(II), Cu(II) and Cd(II). Preparation and characterization of a series of compounds of the type $\left[\text{Ce(Phen)}_4\right]_2\left[\text{Cr(NCS)}_4(L)\right]_2$ and $\left[\text{Ce(Phen)}_4\right]_2\left[\text{Cr(NCS)}_4(L')\right]_2$, where $L =$ ammonia, aniline, p-toluidine, urea, thiourea and $L' = 1,10$-phenanthroline(Phen), 2,2' bipyridyl (bipy), have been made by Pandey and his group. They have pointed out that the bonding in parent isothiocyanate chromium complex is unaffected by the presence of cerium complex moiety. Significant negative shift in asymmetric and symmetric NH stretching in the spectra of aniline and p-toluidine, indicate the presence of coordinated bases. Similarly a remarkable shift of C=O and C=S stretching frequencies in the spectra of urea and thiourea confirm their presence inside the coordination sphere. Conductivity measurements in DMF indicate 1:4 electrolytic nature of these complexes. Complexes of the type $\left[\text{Ni(H}_2\text{tsc})_2\right]_2\left(\text{NO}_3\right)_2$, $\text{Na(tsc)}X$, ($X = H_2O, NH_3$, pyridine or aniline), $\text{Cu(Htsc)}\text{Cl}$ and $\left[\text{Zn(H}_2\text{tsc})_2\right]_2\text{Cl}_2$, ($H_2\text{tsc}$=salicyl dehyde thiosemicarbazone) have been studied with the aid of magnetic and spectral data by Ablov et al.
The structure I is proposed and it is concluded that metal is in tetrahedral environment.

Structural, electronic spectral and magnetic studies on transition metal thiocyanates were carried out by Dockum et al.\textsuperscript{9} Mn(bpy) (NCS)\textsubscript{2} and Co(bpy)(NCS)\textsubscript{2} \((\text{bpy}) = 2,2'\text{-bipyridine})\ were isolated by thermolytic decomposition of the corresponding bis(bipyridine) complex, M(bpy)\textsubscript{2}(NCS)\textsubscript{2}. IR, UV, ESR and X-ray patterns indicate that complexes are zigzag chain polymers with stepwise metal thiocyanate bridging, metal being in an octahedral geometry. Variable temperature \((1.5-303^\circ\text{K})\) magnetic susceptibility measurements indicate a broad maxima centred at \(-18^\circ\text{K}\) for Mn(bpy)(NCS)\textsubscript{2} and at \(T < 1.5^\circ\text{K}\) for Co(bpy) (NCS)\textsubscript{2}. A rapid decrease in the moment for each compound shows antiferromagnetic exchange in the polymer chain. Such exchange is proposed to be stepwise in nature. Further, with the use of Heisenberg Dirac-Von Vlock dipolar coupling model, the exchange energy \('J'\) was estimated and found to be \(-2.5\ \text{cm}^{-1}\) for Mn(bpy)(NCS)\textsubscript{2}. Stability constants of thiocyanate complexes of tris(2,2'bipyridyl)-Ni(II) in aqueous solution is studied by Pyartman et al.\textsuperscript{10}. The solvolysis of \(\underset{\text{n}}{\text{Ni}}(\text{bipy})_3\text{SCN}_2\), at \(25^\circ\text{C}\) at ionic strength \(0.1 - 0.75\mu\text{M NaF-NaSCN mixed solution decreases first and then increases as the concentration of SCN}^-\) increases. The stability constants and composition of \(\underset{\text{n}}{\text{Ni}}(\text{bipy})_3\text{SCN}_2^-\text{n} \ (n=1-4)\) complexes were calculated.
Further, the distribution of outer sphere complexes is discussed as a function of SCN\textsuperscript{−} concentration. Dutta and Benerjee\textsuperscript{11} have studied the Cu(II) mixed ligand complexes with salicyldehydethiosemicarbazone and heterocyclic bases (2,2′-bipyridyl, and 1,10-phenanthroline). The IR spectral data indicate that thiosemicarbazone ligands are attached to Cu(II) ion in the following form

\[ X^*_{\text{M}} - X = \text{H, Cl, Br or 5,6 benzo} \]

The electronic spectral band positions for these complexes in pyridine or chloroform are consistent with a six coordinate \( \text{CuN}_3\text{O}_2\text{S}_3^\text{−} \) (bridging 'O') or \( \text{CuN}_3\text{OS}_2^\text{−} \) (bridging 'S') chromophore resulting through polymerization. It is obvious to note that the heterocyclic bases coordinate through ring 'N'. Cobalt(II) azido and thiocyanate complexes of the composition \( \text{CoL}_n\text{X}_2 \) (\( \text{L}=4-\text{R substituted pyridine, R}=\text{H, Cl, Br, Me, Et, NH}_2, \text{CN, CHO, COMe, CO}_2\text{Me, CO}_2\text{Et,} \), \( n=2,4, \text{X}=\text{N}_3, \text{SCN}_7 \) are prepared\textsuperscript{12} and characterized by IR, electronic and magnetic measurements. Studies show that in \( \text{CoL}_2\text{X}_2 \), the
cobalt ion is in octahedral environment in which thiocyanate and azido groups are bridged.

\[ N_3 = \overline{\overline{N=\overline{N}N}} \leftrightarrow \overline{\overline{N=\overline{N}N}} \leftrightarrow \overline{\overline{N=\overline{N}N}} \]
Gohar has reported the metal pseudohalide complexes with some pyridine derivatives having end to end bridging. The complexes of the type CuL$_n$(N$_3$)$_2$ (L = 3- and 4-CHO; 3- and 4-Ac; 2-, 3-and 4-CO$_2$Me; 2,3-and 4-CO$_2$Et and 4-CN derivatives of pyridine; n = 1,2) and CuL$_2$(NCS) (L = 4-CHO, 4-Ac, 4-CO$_2$Et, 4-CO$_2$Me derivatives of pyridine) were prepared and characterized with the aid of spectral and magnetic data. The studies reveal that all ligands are bidentate but azido group is bidentate, bridging through end 'N' atoms. CuL$_2$(NCS) possesses bridging thiocyanate group and each copper atom has a distorted tetrahedral environment.

Mixed ligand anionic complexes of Cd(II) having the composition $[M]_2[CaCl_4L]_2$, $[M]_2[CaCl_4L']_2$, $[M]_2[CaCl_4L''_2]$ and $[M]_2[CaCl_4L''']_2$, where M=monomethyl ammonium cation, L = pyridine, 3-picoline, 4-picoline, quinoline, 4-aminopyridine, piperidine or thioache; L' = 3-picoline, quinaldine or 2,6-lutidine; L''=ethylenediamine, o-phenylenediamine, 1,10-phenanthroline or 2,2'-bipyridine; L''' = oxine or piperidylthiocarbamate, have been synthesised by Mahapatra et al. From the analysis, conductance and spectral studies it was concluded that the compounds of first and third categories are octahedral in configuration. The compounds of second category are presumed to be penta coordinated because of the mono-adduct formation favoured by sterically hindered nitrogen donor ligands like 3-picoline, quinaldine and 2,6-lutidine. The compounds of the fourth category are also penta coordinated as revealed from IR studies.
Cobalt and copper mixed ligand complexes are synthesised and characterized by the same group\textsuperscript{15}. The complexes of the general formula \((\text{MeNH}_3)_2 \text{MCl}_4 L_2\) (I), \((\text{MeNH}_3)_2 \text{MCl}_4 L'\) (II) and \((\text{MeNH}_3)_2 \text{MCl}_3 L''\) (III) where \(L = \beta\text{-picoline, } H_2O, N_2H_4; L' = \alpha\text{-picoline, } \alpha\text{-phenylenediamine, propylenediamine, } 8\text{-hydroxyquinoline;} L'' = \text{quinaldine, thiourea, piperidyl/Morphoyldithiocarbamate} \) were isolated and studied by chemical and physical methods. Studies reveal that complexes of the first category are either octahedral or distorted octahedral, those of second category are penta-\((L' = \alpha\text{-picoline)}\) and hexa coordinated, \((L' = \alpha\text{-phenylenediamine, propylenediamine)}\). Third category complexes are tetra \((L'' = \text{thiourea, quinaldine)}\) and penta coordinated, \((L'' = \text{piperidyl/Morphoyldithiocarbamate)}\). Das\textsuperscript{16} have isolated the complexes of the type \(\text{M(acac)} - (O_2CCCCL_3)\) and \(\text{M(acac)} (O_2CCCCL_3) L_2\) (Hacac = acetylace-tone; \(L = \alpha\text{-picoline, imidazole, } 2\text{-picoline-N-oxide, thiourea, M = Cu, Na). Thermal, spectral and magnetic properties of these complexes were studied. IR spectra reveal the presence of bidentate acac and Cl\textsubscript{3}CO\textsubscript{2} group in all the complexes. TG studies show that as the temperature increases, the mixed ligand complexes start decomposing with the loss of neutral donor ligands, followed by Cl\textsubscript{3}CO\textsubscript{2} and acac in definite steps to form finally MO at 600 - 670°C. They have proposed that nickel complex \(\text{Ni(acac)} (O_2CCCCL_3) L_2\) possess an octahedral structure.
Dave etal. have prepared the adducts of NiLL',
\((\text{H}_2\text{L} = \text{thiosemicarbazone of } 2,\text{-OH-5-R-C}_6\text{H}_3\text{C(O)CH}_2\text{R'})\)
\((R = \text{Cl, Me}, R' = \text{H, Me}; L' = \chi, \beta, \gamma\text{-picoline, piperidine, morpholine, 2,2'-bipyridyl, 1,10-phenanthroline})\). The complexes have been characterized by usual physicochemical methods. It is concluded that the adducts of bidentate bases are insoluble and are polymeric while the monodentate bases are soluble and have square planar geometry. The authors of the same school have also prepared the complexes of the type CuLL' ('\text{H}_2\text{L} = \text{thiosemicarbazone of } 2,\text{-OH-5-R-C}_6\text{H}_3\text{C(O)R'})
\((R=\text{Cl, Me}; R'=\text{Me, Et}, L'=\text{py, } \chi, \beta, \gamma\text{-picoline, piperidine, morpholine, 2,2'-bipyridyl, 1,10-phenanthroline})\). The complexes were characterized by conventional techniques. It is shown that complexes are polymeric with weak antiferromagnetic exchange between Cu(II) ions. Calu etal have reported thermal analysis data of \(\text{K}_3\text{-Cr(NCS)}_6\text{-}\gamma\text{H}_2\text{O}\) and \(\text{LH}_2\text{-Cr(NCS)}_4\text{-}\gamma\text{H}_2\text{O}\), where \(L=\text{NH}_3\), pyridine, \(\gamma\text{-picoline, 2-methylquinoline, 0.5(2, 2'-bipyridine)}\). The TG, DTG and DTA curves show the common behaviour (SCN ligand decomposition) as well specific behaviour for each complex due to \(L\). They have pointed out that the thermal decomposition of these complexes gets complicated due to the presence of the basic ligands \((L)\). Some weak bases with low boiling points are easily eliminated which determines thermal behaviour of the complexes. A general mechanism of thermal decomposition is
advanced involving dehydration and decomposition for both LH+ and $\text{Cr(NCS)}_4L_2^-$. The mechanism of decomposition was confirmed from the determination of activation energies by different processes.

The thermal decomposition of $\text{Ni(NCS)}_2L_3\cdot H_2O$ ($L$=pyridine-N-oxide), $\text{Ni(NCS)}_2L^1_3$ ($L^1$=2-methylpyridine-N-oxide), and $\text{Ni(NCS)}_2L^2_2\cdot$EtOH. ($L^2$=3-methyl-pyridine-N-oxide) and $\text{Ni(NCS)}_2L^3_2\cdot H_2O$ ($L^3$=4-methyl pyridine-N-oxide) complexes have been reported. On heating, the bound solvent molecules evolve first and then the decomposition of heterocyclic ligands begins. The spectral and magnetic data indicate a pseudo-octahedral configuration of the starting complex, $\text{Ni(NCS)}_2L^2_3$, $\text{Ni(NCS)}_2L^2_2$ and $\text{Ni(NCS)}_2L^3_2$. For $\text{Ni(NCS)}_2L^4_3\cdot xH_2O$ ($L^4$=L, $x=0, 1$; $L=L^1$, $x=0$) a dimeric structure is proposed, while, for $\text{Ni(NCS)}_2L^5_2\cdot 7H_2O\cdot$EtOH ($L^5=L^2$ and $L^3$, $x=0, 1$) a polymeric structure is assigned.

Arora and Sankhla have studied the mixed ligand complexes of bis(ethylacetacetoacetato) Copper(II) with thiourea and substituted thioureas. $\text{CuL}_2(H_2O)_2$ in CHCl$_3$ on treatment with Q (Q=thiourea, allylthiourea, N,N'-diphenyl thiourea, methylthiourea and benzoyl thiourea) gives $\text{CuL}_2Q_2$. These complexes were characterized by IR, electronic and magnetic data. The studies reveal that spin free complexes have a distorted octahedral structure in which thiourea is $S$-bonded.
The authors of the same school have also conducted very similar studies for NiQ2I<2 system and reported that the complexes are octahedral (3.02-3.27 B.M.) on the basis of calculations of crystal field parameters.

Ali et al. have prepared the ligand acetylacetone bis(thiourea) (L) by the condensation of thiourea and acetylacetone in methanol. This ligand was employed in the synthesis of the complexes having the composition ML2Cl2 (M=Pd, Cu, Cd, UO2), M1Cl4 (M1=Pt, Ir) M2LCl3H2O (M2=Rh, Ru), HgL2Cl2 and [MnLCl2]2-. IR, electronic, magnetic and DTA data support for the ligand (L) coordination through two amino groups in all the complexes, except Mn complex in which ligand is tetradentate and bounded via azomethine 'N' and 'N' atoms of amino groups giving a dimeric structure to the complexes. Electrical conductivity data indicate 1:1 and 1:2 electrolytic nature for Ir and Mn complexes while all other complexes are non-conducting.

Kinetic parameters of pyridine substitution by outer sphere anion were derived from the thermogravimetric analysis of Co(en)2(PY)Br2 and Co(en)2(PY)BrBr2 by using Coats - Redfern (1964) method.

The influence of sample weight and of heating rate were studied and statistical analysis of the results indicate
that activation energy $E$ decreases in the order $\text{Br} > \text{I}$. It is interesting to note that activation energy ($E$) and pre-exponential factor values show a tendency to decrease with increasing sample weight and heating rate.

Padhy et al. have taken up the studies on mixed ligand complexes. They isolated the complexes, $\text{CoL}_2^1\text{L}_2^1\text{ClO}_4^1$ ($\text{L}^1=\text{N-allylthiourea, L=morpholine}$) and $\text{CoL}_2^2\text{L}_2^2\text{ClO}_4^2$ ($\text{L}^2=1,10$ phenanthroline) and characterized them by usual chemical and physical methods. The ligands $\text{L}$ and $\text{L}^1$ coordinate via nitrogen in case of (I), while in (II), $\text{L}$ ligates through oxygen, but $\text{L}^2$ is bonded through both nitrogen atoms in case of (II). They have proposed a pentacoordinated structure for these complexes.

Mixed ligand complexes of $\text{Co(II)}$, $\text{Ni(II)}$, $\text{Cu(II)}$ and $\text{Zn}$ salts with o-hydroxy propiophenone and quinoline were studied by Roy and his group. The complexes of the type $\text{ML}_2\text{L}'\text{X}$ ($\text{M=above said metal ions, HL=2-hydroxy propiophenone; L'=quinoline, X=Cl, Br, NO}_3$), $\text{ML}_2\text{L}'\text{L}'$ ($\text{M=Co, Ni}$) and $\text{ML}_2\text{L}'$ ($\text{M=Cu, Zn}$) were isolated and characterized by conventional techniques. The complexes $\text{ML}_2\text{L}'\text{X}$ were obtained from 1:1:1 mixture of metal salts, HL and $\text{L}'$ in absolute ethanol and adjusting the pH to 7. The $\text{ML}_2\text{L}'\text{L}'$ were prepared in two steps by treating metal acetates with ethanolic HL in 1:2
ratio followed by treatment of isolated metal chelate in ethanolic solution with quinoline in 1:2 ratio. IR spectra reveal the bonding by 'O' of carbonyl and hydroxyl groups which is further supported by appearance of \( v_{\text{M-O}} \) band at 440-460 cm\(^{-1}\). Coordination of quinoline via 'N' and 'Cl' is also proved from IR and far IR studies. Ni(II) monochelate complexes are diamagnetic and show one absorption band at 16.5 kK presumably indicating a square planar configuration in cases of NiL Cl Q and NiL(NO\(_3\))Q (Q=Quinoline), whereas NiL\(_2\)Q\(_2\) bis chelate gives three absorption bands at 9.5, 13.8, 24.4 kK, which are attributed to

\[
\begin{align*}
3^T_{2g}(F) & \leftrightarrow 3^A_{2g}', \\
3^T_{1g}(F) & \leftrightarrow 3^A_{2g}', \\
3^T_{1g}(P) & \leftrightarrow 3^A_{2g}'
\end{align*}
\]

transition respectively. These studies coupled with magnetic moment (3.1 B.M.) data suggest octahedral geometry of Ni(II) ion in the complexes.

Kukushkin and coworkers\(^{27}\) have prepared the histhiourea cationic complexes, Cis-\(\text{PtL}_2\text{Q}_2\text{Cl}_2\), Cis-\(\text{PtL}_2\text{(FY)}_2\text{Cl}_2\) and \(\text{PtL}_2\text{Q}_2\text{Cl}_2\) (where L=thiocura, pyridine, \(\beta\)-picoline, imidazole; \(\text{L}^1\) = methyl thiourea, \(\text{Q}^1\) = tetra methyl ethyl diamine) from \(\text{PtL}_4\text{Cl}_2^{2+}\) or \(\text{PtL}_4\text{Cl}_2^{2+}\). All the complexes are characterized by conventional techniques.

CuLQ (\(\text{H}_2\text{L} = \text{salicylidene-glycine (I)}, -\alpha\)-alanino, -\(\beta\)-alanine, -phenylalanine, -valine(II); Q = ethyleneuroa, 2-chlorophenyl thiourea) were prepared and characterized\(^{28}\)
by magnetic and spectral studies. The authors have pointed out that the stability of these complexes is related to the presence of a tridentate Schiff-base. Mixed ligand complexes of Cr(III), Co(II), Cu(II) and Zn(II) with p-diethylaminoanil of phenylglyoxal and either thiourea or NH$_3$ ligand were isolated$^{29}$ as binary mixtures of isomers and separated on TLC. The isomers are identified by correlation of their $R_f$ values and spectral parameters.

In our school of research, studies on mixed ligand complexes have been carried out by Kokatnur et al.$^{30}$ The complexes of the type $M$($acac$)$_2$(N-bz-$N'$-tu)$_2$ ($M$=Ni(II) and Co(II); $acac$=acetylacetone; N-bz-$N'$-tu=N-benzoyl-$N'$, substituted thioureas) were synthesised and characterized by analytical and spectral studies. Conductivity measurements show low $A\lambda M$ values (4-32 mho cm$^{-2}$ mol$^{-1}$) indicating non-electrolytic nature of the complexes. Infrared spectral studies prove the bonding of acetylacetone via both oxygen atoms and that of N-benzoyl-$N'$ substituted thiourea through 'S' to central metal ion. The following structure was proposed tentatively with the aid of electronic and magnetic studies.

\[ L = \text{N-benzoyl-$N'$ substituted thioureas.} \]
Further work on mixed ligand complexes at our school of research has been carried out by Tembe. The complexes of type \( \text{Ni(acac)}_2(N\text{-bz-}N'\text{-tu})_2 \) \( \text{N-bz-}N'\text{-tu=}\text{N-bz-}N'\text{-2,5 diEtoptu, N-bz-}N'\text{2,5diMeoptu, N-bz-}N'\text{-}(\text{OH})\text{etu and } \text{N-bz-}N'\text{-Furftu} \) were synthesised and characterized by analytical and spectral studies. The molar conductivity values in DMSO (1.5-4.5 mho cm\(^2\) mol\(^{-1}\)) account for non-electrolytic nature of complexes. Coordination of ligand (thioureas) through 'S' was revealed from IR spectra, except the complex derived from \( \text{N-bz-}N'\text{-}(\text{OH})\text{etu} \) where bonding is through nitrogen. The participation of oxygen of nickelacetylacetonate and sulphur of thioureas in complexes is ascertained from the \( \nu_{M-O} \) and \( \nu_{M-S} \) bands appearing in the region 435-444 cm\(^{-1}\) and 360-390 cm\(^{-1}\) respectively. The solid state electronic spectra of the complexes exhibit three bands at 8368-10000 cm\(^{-1}\) (\( \nu_1 \)), 16666-17391 cm\(^{-1}\) (\( \nu_2 \)) and 22727-26316 cm\(^{-1}\) (\( \nu_3 \)). Except for the second band (\( \nu_2 \)), all the bands are generally weak in intensity which is characteristic of octahedral nature of \( \text{Ni(II)} \) complexes. Further, the magnetic susceptibility values (2.86-3.42 B.M.) support the nature of bonding adduced from IR spectral data.

The work on mixed ligand complexes at our school of research was carried out with Ni/Co acetylacetonate and substituted thioureas. The up-to-date literature survey, described in the earlier paragraphs show no reports on substituted thioureas with heterocyclic bases in presence of anions. The lack of literature, bonding nature of thioureas in presence of heterocyclic bases and cations, prompted us to undertake this present work.