(a) Brief Review of Previous Work:

The effective electronic configuration of divalent nickel ion is $3d^8$. It forms tetra-, hexa-, and penta-coordinated complexes by use of $3d4s4p^2$, $4sp^3$, $3d4s4p^3$, $4s4p^34d$ and $4s4p^34d^2$ bonding orbitals depending on the electronegativity of the ligand taken and give square planar, tetrahedral, trigonal bipyramidal, square-pyramidal and octahedral geometry. They form paramagnetic and dimagnetic complexes depending on whether the two electrons of the upper $^6g$ orbitals remain free or paired. The compounds reported earlier have been discussed below under different coordination numbers.

**Octahedral Complexes**: The maximum coordination number of Nickel(II) is six. The ground state of Nickel(II) in octahedral coordination is $^3A_2g(t_2g)^6(e_g)^2$. The excited state to which transitions occur are $3T_2g(t_2g)^5(e_g)^3$ and $3T_1g(t_2g)^4(e_g)^4$. Magnetically, octahedral complexes have relatively simple behaviour. In ground state, it has two unpaired electrons, the magnetic moment ranging from 2.9 to 3.4 B.M. depending on the magnitude of the orbital contribution. In some cases like $[\text{NiL}_3]^{2+}$ where $L = o$-phenylene-bis-(dimethyl arsine), exceptions have been recorded, which is dimagnetic in character. It is possible that in an extremely intense ligand field, such as this ligand might give a singlet level originating in a Russell-Saunders state of $d^7$s or $d^7p$ configuration could drop down and becomes the ground state.
A large number of octahedral complexes like Ni(H₂O)₆Cl₂, Ni(en)₃Cl₂, Ni(Bipy)₃Cl₂ and Ni(o-phen)₃Cl₂ are known. The Ni(II) amines are not stable since they lose ammonia easily on standing in air. Some compounds of type [Ni(NH₃)₅X]²⁺ and [Ni(NH₃)₄X₂]²⁺ have been known in solution. In general hexa-coordinated Ni(II) compounds are blue or green in colour. Sometimes it gives pink coloured complex, when Ni(II) atom is strongly coordinated. The stability of Ni(o-phen)²⁺ and Ni(bipy)²⁺ may be associated with the possibilities of same double pi-bonding with the attached groups and this may explain the development of pink colour.

Complexes of type NiL₂X₂ (L = pyridine, substituted pyridine, isoquinoline) have been studied. Nelson and coworkers have discussed the formation of octahedral complexes and pi-accepting properties of metals. They have shown that greater delocalization of pi-electrons and the basicity of a ligand make a better ligand, i.e., isoquinoline is a better ligand than pyridine and quinoline. They have also furnished evidence in support of the M\(^{2+}\)\(\rightarrow\)L pi-bonding from (i) thermodynamic tetrahedral octahedral configuration equilibrium in solid state and (ii) occurrence of certain ligand replacement relations in Nickel(II) and related complexes.

The NiL₂X₂ (L = pyridine, X = Cl⁻, Br⁻) have also been known to form octahedral complexes comprising of bridging halides. When the trans-octahedral structure of NiPy₄X₂ is transformed to a bridged structure of NiL₂X₂, there will be a further distortion as indicated by a greater magnetic moment of 0.1 to 0.3 B.M. over
the value for NiPy₂X₂. Thermal decomposition of NiPy₂Cl₂ at 190°C leads to formation of NiPyCl₂ which also possess a polymeric octahedral structure. Electronic spectra of NiL₂X₂ and bridging NiL₂X₂ (L = Py, beta- and gamma-picoline, isoquinoline, X = Cl⁻, Br⁻, I⁻) complexes have been studied by the above workers.

A thorough study of spectra of Ni(II) complexes with pyridine, symmetrical ethylenediamine etc has been made recently by Rowley and Drago and various ligand field parameters arising out of these tetragonal distortions have been evaluated. They have shown that the spectra fits more with D₄h symmetry than the O₃h symmetry.

Goodgame et al. have prepared complexes of type NiL₂Cl₂ (L = Py, Q), NiL₂Br₂ (L = Py), NiLCl₂ (L = Py, Q, Bzd), NiLBr₂ (L = Py, Q, Bzd) and [Me₄N] [NiCl₂]. The high magnetic moment (3.37 B.M. for NiPy₂Cl₂) and pattern of reflectance spectra lead them to suggest that, the weak ligand field might be enforcing a greater "mixing in" of the 3T₂g excited with the ground state resulting in appreciable spin-orbit coupling. They showed that the octahedral configuration is maintained by NiPy₂Cl₂, NiPyCl₂ and NiCl₃ with increasing amount of distortion.

Nyholm and coworkers isolated a number of substituted pyrazine complexes having octahedral, square-planar and tetrahedral configurations. Back donation has been shown to be considerably more important in pyrazine chemistry than in pyridine chemistry. Imidazole and thiazole complexes of the formula NiL₆X₂ and NiL₄X₂ have been reported by Underhill et al.
In the urea and substituted urea complexes, the bonding has been shown through oxygen and nitrogen atoms. They are all octahedral complexes as confirmed by X-Ray analysis. Thiourea and substituted thiourea appear to form $[\text{NiL}_6]X_2$, $\text{NiL}_4X_2$ and $\text{NiL}_2X_2$ types of complexes. Crystal structure of $\text{Ni(bu)_2Br}_2$ has been studied by X-ray diffraction technique which confirm a distorted octahedral structure. The thiourea groups are all planar and the C-S and C-N distances are not much different from the original thiourea molecule. Octahedral structure of $\text{Ni(bu)_2Cl}_2$ and $\text{Ni(bu)_2(SCN)}_2$ have been established from crystal structure.

Ni(II) complexes of beta-diketonates occur in both polymeric octahedral or square-planar forms depending upon the nature of these ligands. Graddon has generalised that when pK values of beta-diketones are above 14, they form polymeric octahedral structure and an intermediate pK values exhibit intermediate structure, i.e., both square-planar and octahedral forms. In the presence of donor solvents, the polymerization is lifted and a number of mixed ligand complexes are formed and in all these cases the diketone behave as a bidentate ligand. The same behaviour has also been shown in case of beta-diketones having alkyl group at the gamma-positions.

Dey and Sen have isolated complexes of the type $\text{NiL}_2X_2$ ($L = 1,3$-diamino propane-2-ol, $X = \text{SCN}^-$, NCO$^-$). They have reported distorted octahedral geometry for the complex from IR and electronic spectral studies, where the SCN$^-$ and NCO$^-$ groups are S- and O-bonded respectively. Excess Nickel(II) salts reacts with $8$-amino-o-
phenyl quinoline give \( \text{NiLCl}_2, \text{H}_2\text{O} \) which is reported to be octahedral. In the presence of excess ligand \( [\text{NiL}_2\text{X}_2] \) \((\text{X} = \text{Br}^-, \text{NO}_3^-)\) and \( [\text{NiL}_2\text{I}_2] \) were obtained. The iodide complex has a dimeric octahedral configuration and is a \((1:1)\) electrolyte on nitrobenzene whereas, \( \text{NiL}_2\text{X}_2 \) are non-electrolytes with octahedral configuration.

Some complexes of thio- and seleno-semicarbazones of cyclohexanone and benzaldehyde of type \( \text{Ni(NCX)}_2\text{L}_2 \) and \( \text{Ni(NCX)}_2\text{L}_4 \) where \( \text{X} = \text{S}, \text{Se} \) and \( \text{L} = \) thio- and seleno-semicarbazones of cyclohexanone and benzaldehyde have been reported by Vedyanu and his coworkers. The compounds are reported to be octahedral where \( \text{NCS} \) and \( \text{NCSe} \) groups are \( \text{N}\)-bonded and the ligands are bidentate in nature.

Zacharias and his coworkers have reported some Nickel(II) complexes of type \( \text{ML}_2 \) where \( \text{L} = \) triazine-1-oxide. They have suggested a planar as well as pseudo octahedral configuration for the complex. Naguyen and his coworkers have synthesised some hexa-coordinated Nickel(II) chelates from \( \text{N,N-diacytely ethylene diamine and acetyl acetone.} \)

Some six coordinated complexes of Nickel(II) derived from the condensation of glyoxal and biacetyl respectively with 1,3,5-cyclohexane triamine and 1,1,1-tries( amino-methyl ethane) have been reported by Biradar et al. Saha and his coworkers have reported some Nickel(II) complexes of type \( \text{NiL}_2\text{X}_2\text{nH}_2\text{O} \) and \( \text{NiL}_3\text{X}_2\text{nH}_2\text{O} \), where \( \text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{NO}_3^-, \text{SCN}^-, \text{BF}_4^- \) and \( \text{L} = 2\text{-hydrazino-1,6-dimethyl pyrimidine.} \) They have suggested an
octahedral configuration from spectral studies for the complexes except NiL₂Br₂H₂O and NiL₂I₂·2H₂O which were reported to be tetragonal.

Tetrahedral Complexes: Tetrahedral complexes are comparatively less. They are usually blue in colour and occasionally green or yellow in colour. For tetrahedral Nickel(II) complexes visible absorption band at $\sim 15,000 \text{ cm}^{-1}$ is assigned to $3T_1(F) \rightarrow 3T_1(P)$ transition and at $7,000 - 8,000 \text{ cm}^{-1}$ to $3T_1(F) \rightarrow 3A_2$ transition. The former transition having a high molar absorption maxima 200, in comparison to 1 - 10 for octahedral complexes. The development of a green or red colour has been suggested due to charge transfer bands. Tailing into the visible region, appearing mainly in case of coordinated bromide or iodine complexes. The splitting of the visible band is caused by spin orbit coupling which lifts the degeneracy of the $3T_1(P)$ state. The magnetic moment of the tetrahedral complexes ranges between 3.5 - 4.2 B.M. due to two unpaired electrons as against 2.83 B.M. for the spin-only value which do not exceed 3.4 B.M. for octahedral complexes.

Many tetrahedral Nickel(II) complexes with alpha-substituted heterocyclic bases have been isolated. Ligands like alpha-picoline, quinoline and other sterically hindered ligands like 2-methylbenzimidazole and 3-methyl isoquinoline formed tetrahedral complexes of type NiL₂X₂ (X= Cl⁻ or Br⁻). This behaviour, they explain is due to the steric factor which makes space for two
ligands and two anions to be accommodated. But iodide having a much bigger size induces a planar configuration.

A number of simple and mixed anionic complexes have been isolated\(^3\) having tetrahedral configuration \([M]_2[NiCl_4]\) where \(M = Et_4N^+\) or \(Ph_3MeAs^+\) and \(X = Cl^-, Br^-, I^-\) have tetragonal geometry. Goodgame and coworkers\(^4\) have prepared a number of benzimidazole complexes of the type \(ML_2X_2\) and \([Et_4N][MLX_3]\) where \(L =\) benzimidazole, \(X = Br^-.\) They have magnetic moment 3.46 and 3.57 respectively. Similarly complexes of type \(MLX_3\) where \(M = Co, Ni, Cu, X = Cl^-, Br^-, I^-\) and \(L =\) triphenyl phosphine, triphenyl arsine, pyridine, alpha-picoline, and quinoline have been isolated.

Tetrahedral complexes of formula \([Ni(O_3P)_2Cl_2]\), \([Ni(O_3P=O)_2Cl_2]\) and \([Ni(O_3As=O)_2Cl_2]\) are known. The magnetic moment of \([Ni(O_3P)_2Cl_2]\) and \([NiPh_3As]_2[NiCl_4]\) are found to be 2.2 and 0.7 B.M. respectively.

Pret and his coworkers\(^5\) have synthesised complexes of \(Ni(II)\) and \(Co(II)\) taking some 1,4-benzodiazepines as the ligand. They have suggested a pseudo tetrahedral configuration for the complexes. Devoto et al\(^6\) have reported complexes of type \(ML_2X_2\) where \(M = Co(II)\) and \(Ni(II)\), \(L = 3,5\)-diphenyl isooxazole and \(X = Cl^-, Br^-, I^-\), \(SCN^-\). They have suggested a tetrahedral configuration for the complexes.

**Planar Complexes:** Planar complexes of \(Ni(II)\) may be diamagnetic or have two unpaired electrons depending upon whether
the energy of separation between the two uppermost d-orbitals is greater or less than the energy necessary to cause electron pairing. The compounds are usually have yellow, red or brown in colour. From study of large number of such diamagnetic planar complexes it was suggested that a sharp absorption band at 25,000 cm$^{-1}$ with a molar absorption between 3000 - 12,000 cm$^{-1}$ is diagnostic of a square planar arrangement. This uses a set of dsp$^2$ vacant hybrid orbitals for bonding.

Perhaps the first square planar diamagnetic Nickel(II) complex known is bis-(dimethyl glyoximato) Nickel(II). Many yellow 4-substituted pyridine perchlorate complexes Ni(4-X-Py)$_2$(ClO$_4$)$_2$ (X= CH$_3$,NH$_2$) are observed to be square-planar. Some of the pyrazine and substituted pyrazine complexes have also been reported.

Salicylaldimines and substituted salicylaldimines are also square planar coordinated. Bis-(salicylaldiminato)Ni(II) and bis-(N-methyl salicylaldiminato) Ni(II) prepared for the first time by Willis and Mellor. They observed that both diamagnetic solids become partially paramagnetic in chloroform and completely paramagnetic in pyridine. Even in solid state also, the paramagnetism was discovered and controversial reports have been published regarding their structure. Holm et al emphasized an equilibrium of tetrahedral square planar configuration in solution. Graddon supports a paramagnetic square coordination from the electronic spectral data.
Connor and Riley\textsuperscript{55} have reported some ditertiary phosphine complexes of Ni(II) nitrate of composition $[\text{NiL}_2]\text{(NO}_3\text{)}_2$ and suggested a square-planar configuration for the complex. Evgenievich et al.\textsuperscript{56} have studied the complexation behaviour of diphenyl dithiophosphate in presence of alcohol with Nickel(II) and suggested a square planar configuration for the complex. Some aryl thionyl phosphine complexes of Ni(II) have been reported by Donald and his coworkers\textsuperscript{57} to be square-planar. The 2-thionyl substituent is more electron releasing towards phosphorus than the phenyl group when 'P' is coordinated to the metal ion.

Neutral and anionic complexes of quinoxaline 2,3-dithiol of type $[\text{H}_2\text{L}_3\text{Ni}]\text{(X)}_2$ where $L = \text{Cl}^-,\text{Br}^-,\text{ClO}_4^-$ have been synthesized by Rignedoli\textsuperscript{58} et al. They have suggested a square planar configuration, where the ligand is S-S coordinated to metal ion. Nikolaev and his coworkers\textsuperscript{59} have synthesised some complexes of Ni(II) of type $\text{NiL}_2\text{X}_2$ where $L = \text{ClO}_4^-,\text{NO}_3^-$, and $L$ is 'aminoguanidine'.

\textbf{Penta-coordinated complexes:} Much less five coordination complexes of Ni(II) are reported in literature. The formation of a square-planar complex of Ni(II) involving the use of $4d^4s^4p^2$ bond orbitals leaves one $4p$ orbital of Nickel atom vacant. It appears feasible that, this orbital might be used by one more ligand to give a five coordinate complex. This would involve the use of $3d^4s^4p^3$ hybrid orbitals for bonding. So also $4s^4p^3d$ orbitals can be used for the formation of five-coordinate complexes.
Formation of K₃[\text{Ni(CN)}₅] was first studied in this light by spectrophotometry. It has been discovered by Barclay and Nyholm that very strong field ligands with the donor atoms suitably placed occupy such positions in a five-coordinated geometry NiX₂ triarsine (X= Br or I) complexes having square-pyramidal geometry.

The alkyl substituted phosphite complexes exhibit pentacoordination in the presence of coordinated cyanide anions. Diphosphines also play a similar role in the formation of pentacoordinated complexes of Ni(II). Many hybrid ligands have been prepared containing N, O, S, P and As donor atoms and their ability towards complex formation tested by Sacconi and coworkers. Sacconi has also isolated both low and high spin penta-coordinated complexes with trigonal bipyramidal geometry using tetradentate hybrid ligands of tripod-shape. Dyer et al also reported the formation of five coordinate trigonal bipyramidal \([\text{NiXL}]^+\) (L=tris-(o-diphenyl phosphinoethyl phosphine) complexes using the tetradentate ligand.

Cowez et al have prepared high-spin penta-coordinated complexes of Ni(II) with oxime derivatives, quinaldic acid and mero-stelbenediamine and on the basis of X-ray study suggested a square pyramidal structure. Five coordinate Ni(II) complex with bis-(acetamido) thioether derivatives have been prepared.

Five coordinate 2-methyl pyridine adducts of bis-(salicylidenediminato) nickel(II) complexes have been prepared by Lindoy and
Mockles and coworkers have reported some lutidine adducts of Ni(II)-dithiophosphinates and they have suggested the complexes to be penta-coordinated.

Sacconi et al have reported some Nickel(II) complexes of type $[\text{NiSO}_2(OR)L]$ where $R = \text{methyl or ethyl}$, $Y = \text{BF}_4^-$ or $\text{BPh}_4^-$ and $L$ is tris-(2-diphenylphosphinoethyl) phosphine. They have suggested a distorted trigonal bipyramidal structure with the sulphur atom of ethyl sulphato group in an axial position. Penta-coordinated Ni(II) complexes of type $\text{NiL}$ have been synthesised by Boge and his coworkers where $L$ is a pentadentate schiff base $\text{N-N'}$-bis-(2-hydroxy-5-\text{X-phenyl}) phenyl methylene)-1,7-1,7-diamine ($X = \text{Cl or CH}_3$). The adducts of $\text{NiL}$ with heterocyclic nitrogen donor ligands gives six-coordinate complexes.
In this section several tetra- and hexa-coordinated Nickel(II) complexes are reported with oxygen, nitrogen and sulphur donor ligands. They have been classified into four categories for discussion:

(a) Nickel(II) complexes with tridentate ligands.
(b) Nickel(II) complexes with bidentate ligands.
(c) Mixed ligand complexes of Nickel(II) with nitrogen donor ligands.
(d) Some anionic complexes of Nickel(II).

(a) Nickel(II) Complexes with tridentate ligands:

A. Nickel(II) complexes with ethyl acetoacetate semicarbazone and ethyl acetoacetate thiosemicarbazone:

1. (i) Preparation of ethyl acetoacetate semicarbazone - The method of preparation is given in Section 4(b).

(ii) Preparation of the complex: - Nickel(II) complex was prepared by reacting nickel chloride and the ligand in 1:1 ratio in an ethanolic medium and refluxing for about two hrs. over a water-bath. It was then filtered, washed with ethanol followed by ether and dried in vacuo.

2. (i) Preparation of ethyl acetoacetate thiosemicarbazone: - The method of preparation is given in Section 4(b).

(ii) Preparation of the complexes: - Nickel(II) complexes were prepared by reacting nickel chloride and nickel nitrate separately
with ethyl acetoacetate thiosemicarbazone in 1:1 ratio in an ethanolic medium and refluxing for about 2 hours over a water bath. On keeping over night, complexes separated out. These were then filtered, washed with ethanol followed by ether and dried in vacuo.

Analytical, conductance and magnetic susceptibility measurements are given in Table 1 and spectral data in table 2.

Table 1: Analysis, m.p., colour, conductance and magnetic susceptibility data.

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.P. (°C.)</th>
<th>Colour &amp; form</th>
<th>% Nickel Found</th>
<th>% Nickel Calc</th>
<th>% Nitrogen Found</th>
<th>% Nitrogen Calc</th>
<th>( \Delta M ) mhos cm²</th>
<th>( \mu_{\text{eff}} ) B.M.</th>
</tr>
</thead>
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<td>L</td>
<td>129*</td>
<td>White cryst</td>
<td>-</td>
<td>22.25</td>
<td>22.46</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>L'</td>
<td>88</td>
<td>- do-</td>
<td>22</td>
<td>20.21</td>
<td>20.69</td>
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<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \text{NiLCl}_2 )</td>
<td>220*</td>
<td>Green.</td>
<td>17.34</td>
<td>17.58</td>
<td>12.34</td>
<td>12.55</td>
<td>5.6</td>
<td>2.95</td>
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<tr>
<td>( \text{NiL'}\text{Cl}_2 )</td>
<td>225*</td>
<td>- do-</td>
<td>16.71</td>
<td>16.97</td>
<td>11.98</td>
<td>12.14</td>
<td>8.6</td>
<td>3.1</td>
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<tr>
<td>( \text{NiL'}\text{(NO}_3\text{)}_2 )</td>
<td>184</td>
<td>- do-</td>
<td>15.62</td>
<td>15.74</td>
<td>16.91</td>
<td>17.33</td>
<td>10.4</td>
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* decomposition

Table 2: Infrared and electronic spectral data

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<th>Compound</th>
<th>( \nu(C=S) )</th>
<th>( \nu(C=N) )</th>
<th>( \nu(C=0) )</th>
<th>( \nu(N=S) )</th>
<th>( \nu(Ni=0) )</th>
<th>( \nu(Ni-N) )</th>
<th>( \lambda_{\text{max}} (\epsilon) )</th>
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</thead>
<tbody>
<tr>
<td>L</td>
<td>-</td>
<td>1580</td>
<td>1720</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>L'</td>
<td>1090</td>
<td>1585</td>
<td>1724</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \text{NiLCl}_2 )</td>
<td>-</td>
<td>1570</td>
<td>1700</td>
<td>-</td>
<td>450</td>
<td>370</td>
<td>9.0(6), 15.5(8)</td>
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<tr>
<td>( \text{NiL'}\text{Cl}_2 )</td>
<td>1075</td>
<td>1570</td>
<td>1710</td>
<td>260</td>
<td>440</td>
<td>365</td>
<td>9.8(6), 14.7(7), 24.8(14)</td>
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<tr>
<td>( \text{NiL'}\text{(NO}_3\text{)}_2 )</td>
<td>1080</td>
<td>1575</td>
<td>1715</td>
<td>265</td>
<td>450</td>
<td>360</td>
<td>9.5(7), 15(10), 25(17).</td>
</tr>
</tbody>
</table>

L = Ethyl acetoacetate semicarbazone, L' = Ethyl acetoacetate thiosemicarbazone, B = \( \text{H}_2\text{O} \)
B. (i) Preparation of the tridentate ligand (1-cyano-2-o-hydroxy phenylethyl acrylate):

The method of preparation is given in Section-4(b):

(ii) Preparation of the complex: An ethanolic solution of nickel chloride was added to the tridentate ligand in ethanol in 1:2 ratio followed by dropwise addition of liq. ammonia with constant stirring till precipitate is formed. It was then filtered, washed with ethanol followed by ether and dried in vacuo.

Analytical, conductance and magnetic susceptibility data are given in Table-3 and Spectral data in Table-4.

Table-3: Analysis, conductance, m.p. and magnetic susceptibility data

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.P. (°C) &amp; form</th>
<th>Colour</th>
<th>% Nickel Found &amp; Calc</th>
<th>% Nitrogen Found &amp; Calc</th>
<th>λM mhos cm²</th>
<th>/u_{eff} B.M.</th>
</tr>
</thead>
<tbody>
<tr>
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<td>179* Yellow</td>
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<td>-</td>
<td>6.02</td>
<td>6.45</td>
<td>-</td>
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<tr>
<td>[NiL₂]</td>
<td>208* Yellow</td>
<td>179* Yellow</td>
<td>6.02</td>
<td>6.45</td>
<td>5.42</td>
<td>5.76</td>
</tr>
<tr>
<td></td>
<td></td>
<td>cryst.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>amorph</td>
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</tbody>
</table>

* decomposition

Table-4: IR spectral data

<table>
<thead>
<tr>
<th>Compound</th>
<th>υ(C=O)</th>
<th>υ(C=N)</th>
<th>υ(C-O)</th>
<th>υ(Ni-O)</th>
<th>υ(Ni-N)</th>
<th>υ(C=O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LH</td>
<td>1605</td>
<td>2220</td>
<td>1190</td>
<td>-</td>
<td>-</td>
<td>1650</td>
</tr>
<tr>
<td>[NiL₂]</td>
<td>1600</td>
<td>2210</td>
<td>1185</td>
<td>450</td>
<td>360</td>
<td>1645</td>
</tr>
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</table>

LH = 1-Cyano-2-o-hydroxyphenyl ethyl acrylate

(b) Nickel(II) complexes with bidentate ligands:

A. Complexes of Nickel(II) with ethyl methyl ketone thiosemicarbazone:
(i) Preparation of the ligand (Ethyl methyl ketone thiosemi-carbazone):

The method of preparation is given in Section 4(b).

(ii) Preparation of the complexes: Nickel(II) complexes were prepared by reacting Nickel chloride, nickel nitrate, nickel thiocyanate, and nickel perchlorate, with ligand in 1:2 ratio in an ethanolic medium and refluxing for about 6 hours over a water bath. Complexes of nickel chloride and nitrate separated out on refluxing whereas, thiocyanate and perchlorate complexes were obtained by evaporating the solution after refluxing in air. These were filtered under suction, washed with ethanol followed by ether and dried in vacuo.

Analytical, conductance and magnetic susceptibility data are given in Table 5 and spectral data in table 6.

Table 5: Analysis, conductance and magnetic susceptibility data

<table>
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<tr>
<th>Compound</th>
<th>M.P. (°C)</th>
<th>Colour &amp; Form</th>
<th>% Nickel Found</th>
<th>% Nickel Calc.</th>
<th>% Nitrogen Found</th>
<th>% Nitrogen Calc.</th>
<th>% Sulfur Found</th>
<th>% Sulfur Calc.</th>
<th>$\Delta M_{\text{obs}}$ cm$^2$</th>
<th>$\mu_{\text{eff}}$ B.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>110</td>
<td>White cryst.</td>
<td>-</td>
<td>27.9</td>
<td>28.23</td>
<td>21.79</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$[\text{NiL}_2\text{Cl}_2]$</td>
<td>Green Amorph.</td>
<td>13.71</td>
<td>20.15</td>
<td>15.77</td>
<td>12.5</td>
<td>3.2</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>$[\text{NiL}_2\text{NO}_3)_2]$</td>
<td>220 Pink cryst.</td>
<td>12.35</td>
<td>23.48</td>
<td>14.80</td>
<td>12.0</td>
<td>3.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{NiL}_2(\text{NCS})_2]$</td>
<td>198 Green cryst.</td>
<td>12.58</td>
<td>23.45</td>
<td>27.24</td>
<td>12.5</td>
<td>2.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{NiL}_2(\text{ClO}_4)_2]$</td>
<td>185* Blue cryst.</td>
<td>10.78</td>
<td>15.12</td>
<td>11.57</td>
<td>180</td>
<td>2.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* decomposition.
Table 6: IR and electronic spectral data

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\gamma$(C=S)</th>
<th>$\gamma$(C=N)</th>
<th>$\gamma$(N-H)</th>
<th>$\gamma$(Ni-S)</th>
<th>$\gamma$(Ni-N)</th>
<th>$\delta_{max}$ in kK. ($\varepsilon$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>1120</td>
<td>1600</td>
<td></td>
<td>2950</td>
<td>260</td>
<td>360, 9.466, 14.8 (7), 24.6 (14)</td>
</tr>
<tr>
<td>$[\text{NiL}_2\text{Cl}_2]$</td>
<td>1100</td>
<td>-</td>
<td>265</td>
<td>3000</td>
<td>370</td>
<td>9.0 (7), 15 (8), 25.0 (16)</td>
</tr>
<tr>
<td>$[\text{NiL}_2(\text{NO}_3)_2]$</td>
<td>1195</td>
<td>1280, 1400</td>
<td>3250</td>
<td>3000</td>
<td>365</td>
<td>9.5 (7), 14.5 (6), 24.5 (16)</td>
</tr>
<tr>
<td>$[\text{NiL}_2(\text{NCS})_2]$</td>
<td>1105</td>
<td>2060</td>
<td>270</td>
<td>1050-1130</td>
<td>3200</td>
<td>370, 8.1 (30), 15.4 (180)</td>
</tr>
<tr>
<td>$[\text{NiL}_2(\text{ClO}_4)_2]$</td>
<td>1100</td>
<td>1050-1130</td>
<td>270</td>
<td>3200</td>
<td>370</td>
<td>8.1 (30), 15.4 (180)</td>
</tr>
</tbody>
</table>

L = Ethylmethyl ketone thiosemicarbazone

B. Nickel(II) complex with bidentate Schiff base:

(i) Preparation of salicylaldehyde 2,4-dinitrophenyl hydrazone:

The method of preparation is given in Section 4(b).

(ii) Preparation of the complex:

An ethanolic solution of the Schiff base was reacted with an ethanolic solution of Nickel chloride in 2:1 ratio followed by dropwise addition of liq. ammonia. The chelate separated out which was washed with ethanol, followed by ether and dried in vacuo.

Analytical, conductance and magnetic susceptibility data are given in table 7 and IR and electronic spectral data in table 8.

Table 7: Analytical, conductance & magnetic susceptibility data:

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.P. (°C)</th>
<th>Colour &amp; form</th>
<th>$%$ Nickel Found Calc</th>
<th>$%$ Nitrogen Found Calc</th>
<th>$\Delta M$</th>
<th>$\mu_{hos}$</th>
<th>$\mu_{eff}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LH</td>
<td>248</td>
<td>Orange cryst.</td>
<td>-</td>
<td>17.81</td>
<td>18.50</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$[\text{NiL}_2(\text{H}_2\text{O})_2]$</td>
<td>170</td>
<td>Green cryst.</td>
<td>7.97</td>
<td>8.22</td>
<td>17.77</td>
<td>17.95</td>
<td>17 (DMF)</td>
</tr>
</tbody>
</table>
Table 8: IR and electronic spectral data

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\nu(C=N))</th>
<th>(\nu(C-O))</th>
<th>(\nu(Ni-O))</th>
<th>(\nu(Ni-N))</th>
<th>(\nu_{\text{max}} ) in ((\varepsilon)kK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LH</td>
<td>1610</td>
<td>1210</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>([\text{NiL}_2(\text{H}_2\text{O})_2])</td>
<td>1600</td>
<td>1200</td>
<td>445</td>
<td>510</td>
<td>8.8(6), 14.7(10), 25.0(15).</td>
</tr>
</tbody>
</table>

LH = Salicylaldehyde 2,4-dinitrophenyl hydrazone

(c) Mixed ligand complexes of Nickel(II) with nitrogen donor ligands:

A. Mixed ligand complexes of Nickel(II) with anthranilic acid and nitrogen donor ligands:

(i) Preparation of the chelate: Nickel(II) chelate was prepared by reacting an ethanolic solution of 2.36g of nickel chloride with an ethanolic solution of 2.74g of anthranilic acid in 1:2 ratio, followed by dropwise addition of liq.ammonia. The precipitate thus formed filtered under suction, washed with ethanol followed by ether and dried in vacuo.

(ii) Preparation of mixed ligand complexes: Nickel(II) chelate was suspended in ethanol, mixed with nitrogen donor ligand in 1:2 ratio and the mixture refluxed for 30 minutes, when a clear solution was obtained. On cooling, the solution, crystalline compounds separated out. They were filtered, washed with ethanol, ether and dried in vacuo.

Analytical, conductance and magnetic susceptibility data are given in table 9 and IR and electronic spectral data in table 10.
Table 9: Analytical, conductance and magnetic susceptibility data

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.P. (°C)</th>
<th>Colour &amp; form</th>
<th>%Nickel Found</th>
<th>%Nickel Calc</th>
<th>%Nitrogen Found</th>
<th>%Nitrogen Calc</th>
<th>cm²</th>
<th>B.M.</th>
<th>ΔµHgs</th>
<th>µeff</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiL₂(γ-pic)₂</td>
<td>249*</td>
<td>Green crist.</td>
<td>11.41</td>
<td>11.36</td>
<td>12.05</td>
<td>12.15</td>
<td>9.5</td>
<td>2.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiL₂ Py₂</td>
<td>280*</td>
<td>-do-</td>
<td>11.80</td>
<td>12.01</td>
<td>12.48</td>
<td>12.99</td>
<td>8.2</td>
<td>2.95</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiL₂(DEA)₂</td>
<td>270*</td>
<td>-do-</td>
<td>12.40</td>
<td>12.31</td>
<td>13.02</td>
<td>13.18</td>
<td>5.5</td>
<td>3.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* decomposition.

Table 10: IR and electronic spectral data

<table>
<thead>
<tr>
<th>Compound</th>
<th>Asym ν(C-O)</th>
<th>Sym. ν(C-O)</th>
<th>ν(N-H)</th>
<th>ν(Ni-O)</th>
<th>ν(Ni-N)</th>
<th>ν max(ε) in kK.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiL₂(γ-pic)₂</td>
<td>1600</td>
<td>1400</td>
<td>3280</td>
<td>460</td>
<td>510</td>
<td>9.8(6), 14.5(8), 24.6(15).</td>
</tr>
<tr>
<td>NiL₂ Py₂</td>
<td>1600</td>
<td>1400</td>
<td>3280</td>
<td>430</td>
<td>510</td>
<td>10.5(6), 15.8(8), 25.4(16).</td>
</tr>
<tr>
<td>NiL₂(DEA)₂</td>
<td>1600</td>
<td>1400</td>
<td>3280</td>
<td>440</td>
<td>510</td>
<td>10.2(6), 15.0(7), 24.9(15).</td>
</tr>
</tbody>
</table>

γ-pic = 4-methyl pyridine, Py = pyridine, DEA = Diethylamine, LH = anthranilic acid.

B. Adducts of bis-(ethylacetoacetato) nickel(II) with nitrogen donor ligands:
(i) Preparation of the chelate: Nickel(II) chelate was prepared by reacting ethanolic solution of nickel chloride with ethyl acetoacetate in 1:2 proportion followed by dropwise addition of liqr. ammonia with constant stirring. The green coloured compound thus obtained was filtered off, washed with ethanol and dried in vacuo.

(ii) Preparation of the adducts: Nickel (II) chelate thus obtained was mixed with nitrogen donor ligands separately in 1:2 ratio in minimum quantity of ethanol and refluxed for 30 minutes.
On cooling the solution over-night, the crystalline compounds separated out, which were filtered, washed with ethanol and dried in vacuo.

Analytical, conductance and magnetic susceptibility data are given in table 11 and IR data in table 12.

**Table 11: Analytical, conductance and magnetic susceptibility data**

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.P. (°C)</th>
<th>Colour &amp; form</th>
<th>% Nickel Found</th>
<th>% Nitrogen Found</th>
<th>ΔMhos cm²</th>
<th>μeff B.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni(EAA)(α-pic)₂]</td>
<td>180</td>
<td>Green cryst.</td>
<td>11.51</td>
<td>11.63</td>
<td>5.48</td>
<td>5.55</td>
</tr>
<tr>
<td>[Ni(EAA)₂(pic)₂]</td>
<td>110</td>
<td>-do-</td>
<td>11.54</td>
<td>11.63</td>
<td>5.44</td>
<td>5.55</td>
</tr>
<tr>
<td>[Ni(EAA)₂(DMA)₂]</td>
<td>210*</td>
<td>-do-</td>
<td>14.04</td>
<td>14.36</td>
<td>6.64</td>
<td>6.85</td>
</tr>
</tbody>
</table>

* decomposition

**Table 12: Infrared spectral data**

<table>
<thead>
<tr>
<th>Compound</th>
<th>υ(C=O)</th>
<th>υ(C=C)</th>
<th>υ(Ni-O)</th>
<th>υ(Ni-N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EAA</td>
<td>1650</td>
<td>1630</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[Ni(EAA)(α-pic)₂]</td>
<td>1615</td>
<td>1540</td>
<td>450</td>
<td>365</td>
</tr>
<tr>
<td>[Ni(EAA)(β-pic)₂]</td>
<td>1625</td>
<td>1535</td>
<td>450</td>
<td>370</td>
</tr>
<tr>
<td>[Ni(EAA)₂(DMA)₂]</td>
<td>1625</td>
<td>1540</td>
<td>440</td>
<td>370</td>
</tr>
</tbody>
</table>

EAA = Ethyl acetoacetate, α-pic. = 2-methyl pyridine, β-pic. = 4-methyl pyridine, DMA = dimethyl pyridine amine.
C. Adducts of bis-(salicylaldehydato) nickel(II) with nitrogen donor ligands:

(i) Preparation of the chelate: Nickel(II) chelate was prepared by reacting an ethanolic solution of nickel chloride with salicylaldehyde in 1:2 ratio followed by dropwise addition of liq. ammonia. The precipitate was washed with ethanol, ether, and dried in vacuo.

(ii) Nickel(II) chelate thus obtained were refluxed for 30 minutes with nitrogen donor ligands as solvent. On keeping the clear solution over night, crystalline compounds separated out, which were suction filtered, washed with minimum amount of ethanol and dried in vacuo.

Analytical, conductance, etc are given below:

Table 13: Analytical, conductance & magnetic susceptibility data.

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.P. (°C)</th>
<th>Colour &amp; form</th>
<th>% Nickel Found</th>
<th>% Nitrogen Found</th>
<th>Δm</th>
<th>μeff</th>
<th>cm²</th>
<th>B.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni(Sal)₂Q₂]</td>
<td>215</td>
<td>Green cryst</td>
<td>10.24 10.43</td>
<td>4.88 5.01 5.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ni(Sal)₂IQ₂]</td>
<td>208</td>
<td>-do-</td>
<td>10.18 10.43</td>
<td>4.89 5.01 4.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ni(Sal)₂(ω-pic)₂]</td>
<td>185</td>
<td>-do-</td>
<td>11.90 12.06</td>
<td>5.65 5.79 3.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ni(Sal)₂(β-pic)₂]</td>
<td>215*</td>
<td>-do-</td>
<td>11.82 12.06</td>
<td>5.68 5.79 6.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* decomposition

Sal = Anion of salicylaldehyde, Q = quinoline, IQ = Isoquinoline.
ω-pic = 2-methyl pyridine, β-pic = 3-methyl pyridine
(d) Some anionic complexes of Nickel(II) containing nitrogen donor ligands:

(i) Simple complexes of the type $[\text{Ni(DMA)}_2\text{Cl}_2]$ and $[\text{Ni(Qd)}_2\text{Cl}_2]$ were prepared by taking dimethylamine and quinaldine respectively, in 2:1 ratio with nickel chloride in ethanol. The complexes prepared were suction filtered and washed with ethanol.

(ii) Chlorination: Pure and dry chlorine gas was passed slowly through the ethanolic suspension of the above simple complexes till clear solutions were obtained with an exothermic reaction. The solutions were kept over night when crystalline complexes separated out. They were suction, filtered, washed with ethanol, followed by ether and dried in vacuo.

Bromination: To an ethanolic suspension of the above simple complexes liquid bromine was added dropwise with constant stirring till a clear solutions obtained with an exothermic reaction. On keeping over night, crystalline compound separated out. The compound was suction filtered, washed with ethanol followed by ether and dried in vacuo.

Analytical, conductance and magnetic susceptibility data are given in table 14 and IR data in table 15.

Table 14: Analytical, conductance and magnetic susceptibility data

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>% Nickel &amp; form</th>
<th>% Nitrogen</th>
<th>% Chlorine</th>
<th>$\Lambda_{\text{Mg}}$</th>
<th>$\mu_{\text{eff}}$</th>
<th>B.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{DMAH}_2\text{NiCl}]$</td>
<td>Yellow</td>
<td>22.31 22.17 10.32 10.65 54.17 54.05 225 -</td>
<td>criyst.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{QA}_2\text{NiCl}]$</td>
<td>do-</td>
<td>11.51 12.01 5.19 5.72 28.56 29.05 205 -</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{QA}_2\text{NiCl}_2\text{Br}]$</td>
<td>Green</td>
<td>10.34 10.16 4.35 4.84 12.46 12.29 240 3.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* % of Bromine - Found: 27.81, Calc. 27.69
Table 15: Infrared spectral data

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu$(Ni-Cl)</th>
<th>$\nu$(Ni-Br)</th>
<th>$\nu$(N-H)</th>
<th>$\delta$(N-H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{DMAH}]_2[\text{NiCl}_4]$</td>
<td>220</td>
<td>-</td>
<td>3000</td>
<td>1595</td>
</tr>
<tr>
<td>$[\text{QdH}]_2[\text{NiCl}_4]$</td>
<td>225</td>
<td>-</td>
<td>3020</td>
<td>1590</td>
</tr>
<tr>
<td>$[\text{QdH}]_2[\text{NiCl}_2\text{Br}_2]$</td>
<td>225, 210</td>
<td>1590</td>
<td>1590</td>
<td></td>
</tr>
</tbody>
</table>

DMA - Dimethylamine, Qd - Quinaldine
In this section studies have been made on divalent nickel complexes. Nickel(II) has eight 3d electrons and forms a wide variety of complexes and as already indicated the structure of the complex can either be planar, tetrahedral, trigonal bipyramidal, square-pyramidal and octahedral. The magnetic susceptibility and electronic spectral data are used in conjunction with ligand field theory to determine the structure and deviation from regular symmetry with a fair degree of certainty.

Nickel(II) shows a preference for four coordination over six particularly in its covalent complex. Electronegativity of the attached groups is one of the important factors which determine the stereochemistry. Mellor and Craig pointed out that tendency to form tetrahedral complexes increases as the electronegativity of the attached atom increases. Accordingly, they showed that four oxygen donors bonded to Nickel(II) ions induce tetrahedral structures whereas less electronegative nitrogen or sulfur atoms tend to give square arrangement.

The theoretical values for the crystal field stabilization energy are always largest for square planar and smallest for tetrahedral Nickel(II) complexes. The medium field being common for most ligands, octahedral complexes occur more frequently. The structure will be different, therefore in case of strong and weak fields, produced by the approaching ligands. When the ligand field splitting is larger, the electrons are paired in the low laying orbitals but a greater degeneracy in the weak field prevent
such electron pairing and the complex remains paramagnetic. Hence, the magnetic susceptibility measurement will indicate in this case whether the complex is spin-paired or spin-free.

The complexes have been classified into four different types on the basis of ligands used for complexation and a discussion will be followed on these lines.

(a) Nickel(II) complexes with tridentate ligands:

Nickel(II) complexes with ethylacetoacetate semicarbazone and thiosemicarbazone:

The three complexes prepared with the tridentate ligands have the composition $[\text{NiLX}_2\text{B}]$ and $[\text{NiL'}X_2\text{B}]$ where $L =$ ethyl acetoacetate semicarbazone and $L' =$ ethyl acetoacetate thiosemicarbazone, $X =$ Cl$^-$, NO$_2^-$, B = H$_2$O. All the complexes are green in colour, have low melting points and low conductance values in dimethyl formamide medium (table 1) indicating nonelectrolytic nature. Magnetic susceptibility measurements indicate the presence of two unpaired electrons ($\mu_{\text{eff}} \sim 3.0$ B.M) suggesting a high spin octahedral configuration. Ethylacetoacetate semicarbazone and ethyl acetoacetate thiosemicarbazone can function as tridentate ligands. In case of the thiosemicarbazone ligand, the thiocarbonyl sulfur, imino nitrogen atom and carbonyl oxygen are the three principal points of bonding whereas, ethyl acetoacetate semicarbazone uses two carbonyl oxygen atoms and the imino nitrogen atom for coordination to the Nickel(II) ion. $\nu$(C=S) in the free ligand occurs at 1090 cm$^{-1}$ which shifts to lower frequency region.
(\sim 1075 \text{ cm}^{-1})\) in the complexes indicating bonding through the thiocarbonyl sulfur \(\nu (C=\text{N})\) observed \(\sim 1580 \text{ cm}^{-1}\) in the ligands decreases by \(10\) to \(15 \text{ cm}^{-1}\) in the complexes and this shows the coordination of the imino nitrogen atom of the azomethine link to the metal ions. The appearance of a sharp band around \(1720 \text{ cm}^{-1}\) in the free ligands is attributable to \(\nu (C=\text{O})\) vibration. In the complexes, this has been shifted to lower frequency region \(\sim 1700 \text{ cm}^{-1}\) which indirectly supports the bonding of carbonyl oxygen atom to the metal ion. In all the complexes, a broad hump is observed \(\sim 3450 \text{ cm}^{-1}\) region indicating the presence of coordinating water. However, conclusive evidence of bonding obtained by the occurrence of bands \(\sim 260 \text{ cm}^{-1}\), \(\sim 450 \text{ cm}^{-1}\) and \(\sim 370 \text{ cm}^{-1}\) which correspond to \(\nu (\text{Ni-S})\), \(\nu (\text{Ni-O})\) and \(\nu (\text{Ni-N})\) respectively.

In the nitrato complexes \(\nu \, \Sigma 4\) and \(\nu \, \Sigma 1\) bands (NO\(_2\) asymmetric and symmetric stretch) appear \(\sim 1400\) and \(\sim 1270 \text{ cm}^{-1}\) region respectively. The position of \(\nu \, \Sigma 4\) and \(\nu \, \Sigma 1\) and their separation (\(\Delta \nu \)) of \(130 \text{ cm}^{-1}\) suggest the nitrato group to be monodentate.

In the electronic spectra of Nickel(II) complexes three absorption bands \(\sim 9.0(6), 15.5(8)\) and \(25.5(15) \text{ k.K.} \) regions are noticed which correspond to \(3A_{2g} \rightarrow 3T_{2g}\), \(3A_{2g} \rightarrow 3T_{1g}(F)\) and \(3A_{2g} \rightarrow 3T_{1g}(P)\) transitions respectively. Molar absorptivity values and magnetic moment values indicate high-spin octahedral configuration.
Nickel(II) complex with the tridentate chelating ligand (1-cyano-2-o-hydroxyphenyl ethyl acrylate):

The yellowish brown nickel complex has the composition $[\text{NiL}_2]$ where LH is the tridentate ligand derived by the condensation of salicylaldehyde and cyanoacetic ester. $\Delta_M$ value for the complex in acetone solution is 10.5 mhos cm$^{-2}$ indicating non-electrolytic nature of the complex. The magnetic moment study suggests an octahedral configuration to the complex.

The assignment of three principal bands like $\nu$(C=N), $\nu$(C=O) and $\gamma$(C-O) have been made in the Nickel(II) complex. The band at 2200 cm$^{-1}$ in the free ligand which can be attributed to $\nu$(C=N) vibration has been found to decrease by 10 cm$^{-1}$ in the complex. The sharp peak observed at 1605 cm$^{-1}$ in the chelating ligand can be assigned to $\nu$(C=O) vibration. In Nickel(II) complex this band appears at 1600 cm$^{-1}$. The (C-O) vibration which appears at 1190 cm$^{-1}$ in the free ligand has been shifted down to 1185 cm$^{-1}$ in the complex. The resultant decrease of vibrational frequencies in case of Nickel complex shows indirectly the coordination of hydroxyl oxygen, esteric carbonyl oxygen and cyano nitrogen atoms to the nickel(II) ion. Disappearance of $\nu$(O-H) band in the complex, which appears at 3400 cm$^{-1}$ in the ligand has been observed. Further, polarization of $\nu$(C=C) band is observed in the complex which also indirectly supports the coordination of cyano nitrogen and esteric carbonyl oxygen atoms to the nickel ion. Direct evidence of bonding was obtained by the occurrence of $\nu$(Ni-O) and $\nu$(Ni-N) at 450 cm$^{-1}$ and 360 cm$^{-1}$ respectively in the far IR spectra of the complex.
In case of Ni(II) complex absorption bands appear at 8,500(9.5), 13,500(11) and 23,600(19) cm⁻¹ attributable to 3A₂g → 3T₂g, 3A₂g → 3T₁₈(P) and 3A₂g → 3T₁₈(P) transitions respectively. Low molar absorptivity value and magnetic susceptibility data provide evidence for a high spin octahedral geometry for the Nickel(II) complex.

(b) Nickel(II) complexes with bidentate ligands:

Nickel(II) complexes with ethyl methyl ketone thiosemicarbazone:

Four light pink or blue crystalline (also green) complexes of the composition [NiL₂X₂] and [NiL₂] Y₂ have been synthesized, where L = ethylmethyl ketone thiosemicarbazone, X = Cl⁻, NO₃⁻, SCN⁻ and Y = ClO₄⁻. These have low melting points. Acetone solution of the complexes have low molar conductance values (Λ_m in the range of 10 - 15 mhos cm⁻¹) except the perchlorate complex indicating the nonelectrolytic nature. Λ_m for perchlorate complex is 190 mhos cm⁻¹ indicating it to be 1:2 electrolyte. Magnetic moments of Ni(II) complexes indicate a high-spin octahedral configuration except the perchlorate complex which suggest a tetrahedral environment around the Nickel(II) ion.

Thiocyanato complex has two sharp bands at 2060 and 710 cm⁻¹ attributable to υ(C≡N) and υ(C-S) respectively. In the present case an increase of 30 to 40 cm⁻¹ relative to free thiocyanate ion is indicative of N-bonded terminal thiocyanato group. In the nitrato complex υ₄(NO₂ assymetric and υ₁(NO₂ symmetric) bands appear at 1400 and 1280 cm⁻¹ respectively. The position of υ₄ and
\[ \text{[NiL}_2\text{(SCN)}_2] \]

L = Ethyl methylketone thiosemicarbazone

**Fig-13**
and their separation ($\Delta \nu$) of 120 cm$^{-1}$ suggests the nitrato group to be monodentate. In case of perchlorate complex, a broad hump appears in the 1050 to 1130 cm$^{-1}$ region indicative of an ionic perchlorate which is in agreement with the conductance data showing 1:2 electrolytic nature.

Ethyl methyl ketone thiosemicarbazone has four bonding sites, namely the thiocarbonyl sulfur, nitrogen of the amino groups and the imino nitrogen atom. $\nu$(C=S) in the ligand occurs at 1120 cm$^{-1}$ which shifts in the complexes to lower frequency region, i.e. ~1100 cm$^{-1}$ indicating bonding through thiocarbonyl sulfur. $\nu$(C=N) observed at 1600 cm$^{-1}$ in the ligand, remains unaffected in the (F$^{-}$-I$^{3}$) complexes which shows that imino nitrogen atom is not coordinated with the Nickel(II) ion. Broadening and splitting of $\nu$(N-H) which occurs ~2900 - 3250 cm$^{-1}$ in the complexes indicates bonding through the amino nitrogen atom. However, it is difficult to ascertain whether primary or secondary amino nitrogen atom is bonded to the nickel ion. Bonding through nitrogen and sulfur has been further substantiated by observation of $\nu$(M-N) and $\nu$(M-S) ~360 and ~290 cm$^{-1}$ region respectively.

In the electronic spectra of Ni(II) (chloride, nitrate and thiocyanate) complexes, three absorption bands are observed ~9.4(6) 14.8(7) and 24.6(14) $\mu$m regions assignable to $^{3}_{A_{2g}}$ $\rightarrow$ $^{3}_{T_{2g}}$, $^{3}_{A_{2g}}$ $\rightarrow$ $^{3}_{T_{1g}}$(F) and $^{3}_{A_{2g}}$ $\rightarrow$ $^{3}_{T_{1g}}$(P) transition respectively, characteristic of octahedral environment. For the perchlorate complex bands are observed at 15.4(180) and 8.1(30) attributable to $^{1}_{T_{1g}}$(F) $\rightarrow$ $^{1}_{T_{1g}}$(P) and $^{1}_{T_{1g}}$(F) $\rightarrow$ $^{3}_{A_{2g}}$ transitions. Deep blue colour intensity
X-RAY POWDER PHOTOGRAPH OF

\[ \text{Ni(ethylmethyl ketone thiosemicarbazone)}_2\text{Cl}_2 \]

Fig. 14
of the $T_{1g}(P)$ band and high value of magnetic moment provide evidence for tetrahedral geometry of the complex.

Attempts have been made to establish the structure of the compound $[\text{NiL}_2\text{Cl}_2]$ by X-ray powder diffraction method. The powder pattern obtained is shown at Figure-14. The 'd' values of the lines are given below:

- 6.832(s), 5.906(vs), 4.969(vw), 4.322(vw), 3.826(vww+Br),
- 3.427(vs), 3.226(vvs), 2.871(vv), 2.706(w), 2.525(w+Br),
- 2.359(vww), 2.257(vww), 2.139(w), 1.965(w), 1.884(vww), 1.825(w),
- 1.735(vw), 1.603(vww), 1.544(vww), 1.409(vww).

s - sharp, v - very, w - weak, Br - broad.

Presumably the compound belongs to a cubic system with unit cell dimension. $a = b = c = 9.6\text{Å}$.
Nickel(II) complex with bidentate Schiff base (Salicylaldehyde-2,4-dinitrophenyl hydrazone:

The green crystalline Nickel(II) complex of the type $[\text{NiL}_2(\text{H}_2\text{O})_2]$ where LH = bidentate schiff base derived from the reaction of salicylaldehyde with 2,4-dinitrophenyl hydrazine. The complex has low melting point and low conductance value (17 mhos cm$^2$ in D.M.F) indicating nonelectrolytic nature of the complex. Magnetic moment value is indicative of the presence of two unpaired electrons and suggest an octahedral configuration for the complex.

Study of infrared spectra of the schiff base ligand shows three possible bonding sites for coordination with nickel(II) ion, viz., hydroxylic oxygen, imino nitrogen atom and nitrogen of -NH group. In the ligand $\nu(C=N)$ occurs at 1600 cm$^{-1}$ which has shifted to lower frequency region in the complex due to reduction in the electron density in the azomethine link. $\nu(C-O)$ appears at 1210 cm$^{-1}$ in the ligand and a decrease of 10 cm$^{-1}$ in the nickel complex occurred which indirectly shows the bonding through hydroxylic oxygen atom. The sharp band at 3250 cm$^{-1}$ due to $\nu(NH)$ is observed both in the ligand and in the complex and it proves that ligand is not coordinated through secondary nitrogen atom. A medium broad band appears at 3450 cm$^{-1}$ region assignable to $\nu(O-H)$ of coordinated water. The decrease in both $\nu(C-O)$ and $\nu(C=N)$ in the complexes compared to the ligand suggests bonding at these sites. This has been further substantiated by the observation of two bands at 445 cm$^{-1}$ and 510 cm$^{-1}$ assignable to $\nu(Ni-O)$.
and \( (\text{Ni-N}) \) respectively in the far IR spectra of the complex.

Nickel(II) complex exhibits three absorption bands at 8.8(6), 14.7(10) and 25.0(15) k.K. region assignable to \( 3\text{A}_2g \rightarrow 3\text{T}_{2g} \), \( 3\text{A}_2g \rightarrow 3\text{T}_{1g}(\text{F}) \) and \( 3\text{A}_2g \rightarrow 3\text{T}_{1g}(\text{P}) \) transitions respectively characteristic of high spin octahedral configuration.

(c) **Mixed ligand complexes of Nickel(II) with nitrogen donor ligands:**

Mixed ligand complexes of Ni(II) with anthranilic acid and nitrogen donor ligands:

Three light green crystalline complexes of the type \([\text{NiL}_2\text{X}_2]\) where \( \text{LH} = \text{anthranilic acid} \) and \( \text{X} = \text{nitrogen donor ligands like pyridine, gamma-picoline and diethylamine} \) have been prepared. All the three Nickel(II) complexes have fairly low melting points and are soluble in common organic solvents. Acetone solution of the complexes have low molar conductance values (5-10 mhos cm\(^2\)) indicating nonelectrolytic nature of the complexes. Magnetic moment values indicate the presence of two unpaired electrons suggesting a spin-free octahedral configuration.

Carboxylic acids give rise to two absorption bands due to assymetric C-O and symmetric C-O stretching frequencies \( \sim 1650 - 1700 \) and \( \sim 1400 \text{ cm}^{-1} \) region. In anthranilic acid these two frequencies appear at 1660 and 1410 cm\(^{-1}\) respectively. In nickel(II) anthranilate, these two principal bands shift considerably to lower frequency region on complexation indicating bonding of the oxygen atom of the carboxylate group. In the base adducts these two bands shift to higher frequency regions appearing \( \sim 1600 \) and
1400 cm\(^{-1}\) indicating bonding of the nitrogen donor ligands to the metal ion. \(\nu(N-H)\) in anthranilic acid appears at 3280 cm\(^{-1}\) as sharp band. In nickel anthranilate and base adducts N-H stretching frequency appears either as a broad band or is split into several peaks not so sharp as in the parent compound providing indirect evidence of bonding of the amino nitrogen atom to the Nickel(II) ion. Most of the absorption bands due to nitrogen bases have been modified in the complexes indicating their presence as coordinated molecules in the complexes. This has been further substantiated by the observation of \(\nu(Ni-O)\) and \(\nu(Ni-N)\) \(~450\text{cm}^{-1}\) and \(~510\text{cm}^{-1}\) respectively in the far IR spectra giving rise to direct evidence of bonding for the formation of nickel anthranilate and the base-adducts.

In the solution electronic spectra of Nickel(II) complexes three transitions \(~10.5(6), 15.8(8)\) and \(~25.4(16)\) \(\text{cm}^{-1}\) regions are observed assignable to \(3A_{2g} \rightarrow 3T_{2g}, 3A_{2g} \rightarrow 3T_{1g}(F)\) and \(3A_{2g} \rightarrow 3T_{1g}\) (P) transitions respectively. Molar absorptivity values, position of absorption bands and magnetic moment values indicate a high-spin octahedral configuration for the three complexes.

Adducts of bis-(ethylaceto acetato) Ni(II) with nitrogen donor ligands:

Three mixed ligand Nickel(II) complexes of the type \([NiL_2X_2]^-\) have been synthesised where \(LH = \text{ethyl acetoacetate}\) and \(X\) is a nitrogen donor ligand like \(\alpha\)-picoline, \(\gamma\)-picoline and dimethylamine. All the three complexes are green in colour, have low melting points.
$\Delta_M$ values in acetone medium are found to lie between 10 - 15 mhos cm$^2$ indicating non-electrolytic nature of the complexes. Magnetic susceptibility measurements indicate the presence of two unpaired electrons as expected for a high-spin octahedral configuration.

IR spectra provide evidence for the formation of chelate as well as the adducts with nitrogen bases since most of the ligand absorption bands are shifted. $\nu(M-O)$, $\nu(M-N)$ and $\nu(C=O)$, $\nu(C=C)$ for base adducts are recorded in table 12. Other bands of ethyl acetoacetate are not recorded since there is considerable overlapping by the bonded nitrogen bases. IR spectra of keto esters have been previously reported.

In general, there will be considerable electron release resulting in shifting of $M-O$, $C-O$ and $C-C$ bands of chelates to higher frequency region when the nitrogen donor ligand is bonded to the nickel ion, but superimposed on this effect there will be $\sigma$-bonding between the metal and heteroligand atom which results in electron-drain from the ring system shifting the above bands to lower frequency region. So it is difficult to unambiguously predict whether these bands will shift to higher or lower frequency region. But definite and marked shifts in position of the bands indicate the bonding of the hetero ligands to metal ions.

Electronic spectra have been studied in the range of 180 - 1000 nm. Nickel chelate has intense absorption band in the U.V. around 265 nm and it seems quite likely that this band is due to $\pi \rightarrow \pi^*$ transition in the enolate ion rather than a charge transfer transition. Further, the base adducts have absorption bands
in the U.V. region around 220, 270 and 310 nm indicating $E_0$, $E_2$ (the ester) and B bands respectively of the nitrogen base.

Three absorption bands are noticed for Nickel(II) complexes around 940, 620 and 400 nm assignable to $3A_{2g} \rightarrow 3T_{2g}$ ($\nu_1$), $3A_{2g} \rightarrow 3T_{1g}$ ($\nu_2$) and $3A_{2g} \rightarrow 3T_{1g}$ ($\nu_3$) respectively. Hence, the Nickel(II) complexes reported in the present investigation are high-spin octahedral complexes similar to compounds reported earlier.

Adducts of bis-(salicylaldehydato) nickel(II) with nitrogen donor ligands:

Four adducts of the composition $[\text{NiL}_2X_2]$ where LH = salicylaldehyde, and X = quinoline, isoquinoline, $\beta$-picoline and $\alpha$-picoline, have been prepared. The compounds are fairly soluble in common organic solvents like methanol, benzene, chloroform and acetone. Acetone solution of the complexes have very low molar conductance values (3-7 mhos cm$^{-2}$) indicating nonelectrolytic nature. Magnetic susceptibility measurement shows them to be paramagnetic with two unpaired electrons, $\mu_{\text{eff}}$ values being in the range 3.1 to 3.2 B.M.

IR spectra revealed the shifting of the absorption bands due to nitrogen bases in the base adducts. The characteristic band due to the conjugated C=O group of salicylaldehyde is observed at 1665 cm$^{-1}$ which shifts to lower frequency in the metal chelate (1605 cm$^{-1}$). This band shifts to higher frequency around 1620 - 1630 cm$^{-1}$ in the base adducts providing evidence for the bonding of the nitrogen bases to the metal chelate.
Chloroform base solution of nickel complexes exhibit two absorption bands $\approx 13000$ and $25,000$ cm$^{-1}$ having molar absorptivity values 7 and 16 respectively. The third band due to the transition $3A_{2g}(F) \rightarrow 3T_{2g}(F)$ is not observed in the range of the spectrophotometer. Low molar absorptivity values and magnetic moment data indicate that the base adducts are octahedral in configuration.

(d) Anionic Complexes of Nickel(II)

Three anionic Ni(II) complexes have been prepared. They have the composition $[\text{DMAH}]_2 [\text{NiCl}_4]$, $[\text{QdH}]_2 [\text{NiCl}_4]$ and $[\text{QdH}]_2 [\text{NiCl}_2\text{Br}_2]$ where DMAH and QdH are the cations of dimethylamine and quinaldine respectively. First two compounds are yellow crystalline, whereas, the third compound is green in colour. These are soluble in acetone and have high conductance values, $\Lambda_M$ being more than 150 mhos cm$^2$ indicating 2:1 electrolytic nature of the complexes.

IR spectral studies indicate sharp absorption bands in the $\approx 3000$ cm$^{-1}$ region attributable to $\equiv\text{NH}$ stretching frequency. Direct evidence of halogen bonding to nickel ion is obtained by the occurrence $\nu$(Ni-Cl) and $\nu$(Ni-Br) around 220 cm$^{-1}$ and 210 cm$^{-1}$ in the far IR spectra of the complexes. Yellow complexes reported here are diamagnetic whereas the green complex has a high magnetic moment (3.8 B.M) suggesting a tetrahedral environment.

Visible electronic spectral studies of Ni(II) yellow complexes show one absorption band around 19800 and 20000 cm$^{-1}$ and relatively high extinction coefficient value indicative of a square configuration. Diamagnetic nature of the two complexes and (2:1) electrolytic nature from conductance data supports the above
Two bands are observed in case of the green complex at 15200 (180) and 8200(35) attributable to $T_{1g}(F) \rightarrow T_{1g}(P)$ and $T_{1g}(F) \rightarrow A_{2g}$ transitions respectively. The high molar absorptivity value of the first band and the high magnetic moment due to orbital contribution suggests a possible tetrahedral geometry for the complex.
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