CHAPTER VIII

DIPYRIDINE/QUINOLINE-BIS-SALICYLALDEHYDE- AND
BIS-(PYRIDYL-2- AND 3-) SALICYLALDEHYDINATION NICKEL(II).
CHAPTER - VIII

DIPYRIDINE/QUINOLINE-BIS-SALICYLALDEHYDATE- AND
BIS-(PYRIDYL-2- AND 3-) SALICYLALDIMINONICKEL(II)*

Abstract:

DIAQUO-BIS-SALICYLALDEHYDONICKEL(II) reacts with
heterocyclic amines (L = pyridine, β-picoline, 2-, 3- and 4-
aminopyridines and quinoline) to form diamino-bis-salicylalde-
hydonicelk(II). The compounds have been characterised as
nonelectrolytic and octahedral complexes of the type [Ni(Sal)₂L₂].

Ni(II) forms complexes with schiff-bases, prepared
from 2- and 3-aminopyridines and salicylaldehyde, to produce com-
pounds of types [Ni(Sal.L')₂·H₂O]ₙ (Sal.L' = schiff-base from
salicylaldehyde and 2-aminopyridine) and [Ni(Sal.L'')₂]ₙ (Sal.L'' =
schiff-base from salicylaldehyde and 2-aminopyridine). They are
characterised as polymeric octahedral complexes involving
ligand bridges.

Introduction:

Reports have been made in the literature of some Ni(II)
complexes involving salicylaldehydes and their adducts.¹,² The
trans-octahedral adducts of bis-salicylaldehydonickel(II) with
water and pyridine (isolated in solid state) and with β-picoline
(in solution) have been studied. The cis-octahedral geometry has
been observed with o-phenanthroline adducts.¹,² Various types of

The present work was aimed at getting some more compounds, physical data and making generalisation of some of the properties observed. This part of the thesis describes the preparation, magnetic and spectral properties of pyridine, substituted pyridine and quinoline adducts of salicylaldehyde-nickel(II) complex and the schiff-base complexes of the same metal prepared from salicylaldehyde and 2- and 3-aminopyridines. Literature survey shows that such complexes have not hitherto been studied in solid state excepting dipyridine-bis-salicylaldehydatenickel(II).

**Experimental:**

**A. Chemicals and Solvents**

All chemicals used were of pure grade and the solvents were used after necessary purification.

Methanol, ethanol and acetone solvents were purified as described earlier. Solvent ether was used without further purification.

All the ligands were of extra pure grade and were used without further purification.

**B. Synthesis**

1. Preparation of $[\text{Ni(Sal)}_2 L_2]$ compounds.

$[\text{Ni(Sal)}_2 (\text{H}_2\text{O})_2]$ was dissolved in minimum quantity of warm ethanol and was mixed with stoichiometric quantity of the amine (dissolved in ethanol). The mixture was refluxed for 30 minutes.
Compounds containing pyridine, β-picoline and quinoline were obtained by slow evaporation of the solution under vacuum. The 2-aminopyridine derivative appeared rather quickly whereas those with 3- and 4-aminopyridines separated on slow evaporation as beautiful crystals. The compounds were washed with minimum benzene and dried in vacuo.

Compounds containing 4-aminopyridine gave beautiful emerald-green crystalline solid immediately but changed to yellowish-green micro-crystalline compound when removed from the mother-liquor. Attempts to prepare the derivatives having α-picoline and 2-methyl quinoline failed to give any solid complex containing the amine. Only a gummy product was obtained on evaporation.

(ii) Preparation of schiff-base complexes of nickel(II) derived from salicylaldehyde and aminopyridines

\[
\text{[Ni(Sal.L')_2NCO]}_n \text{and [Ni(Sal.L")_2]}_n \text{compounds.}
\]

Stoichiometric amount of salicylaldehyde and the aminopyridines were refluxed together for about an hour. The resulting viscous liquid was added to ethanolic solution of anhydrous nickel chloride and the mixture was refluxed for about an hour. The resulting solid was filtered, washed with ethanol and ether and then dried in vacuo.

C. Physical measurements -

The analytical, melting point and molar conductance (from acetone) data were obtained in the manner as in chapter III and have been recorded in Table VIII.1. The magnetic moments obtained from solid specimens have been recorded in Table VIII.2. The \( [\text{Ni(Sal)_2.L_2}] \) type compounds are soluble in most
organic solvents. The \([\text{Ni(Sal.L}_1')_2\text{H}_2\text{O}]_n\) compound is only slightly soluble in acetone, methanol etc. whereas the \([\text{Ni(Sal.L}_3')_2\text{H}_2\text{O}]_n\) compound is almost insoluble in all common organic solvents.

Infra-red spectra were not drawn in far infra-red region. Electronic spectra of \([\text{Ni(Sal.L}_1')_2\text{H}_2\text{O}]_n\) and \([\text{Ni(Sal.L}_3')_2\text{H}_2\text{O}]_n\) could not be taken in methanol or any other solvent due to lack of solubility. Spectra in methanol and nujol mull of \([\text{Ni(Sal.gL}_2]_n\) compounds have bands almost in same positions. Table VIII.5 reports the band positions in nujol mull only. For electronic spectra, a UNICAM SP 500 spectrophotometer was used.

Results and Discussion:

(1) \([\text{Ni(Sal.gL}_2]_n\) Compounds.

As already described these compounds were isolated by mixing the amines to the \([\text{Ni(Sal.gL}_2(N\text{H}_2\text{O}]_2\) compounds. Excepting the diaquo- and dipyridine derivatives the rest of the compounds are new. In all the cases the adducts formed were of 1:2 type: \([\text{Ni(Sal.gL}_2\) . Analytical data given in Table-VIII.1 suggests \([\text{Ni(Sal.gL}_2\) compounds to be quite pure except the pyridine adduct. The failure of isolation of \(\chi\)-picoline adducts may be due to higher synergic factors and that of the \(\chi\)-picoline and 2-methylquinoline adduct may be due to steric hindrance from orthomethyl groups. As already described \(\chi\)-aminopyridine adduct is initially formed as emerald green, crystalline, unstable compound which changes to a more stable form after separation from mother-liquor. The unstable intermediate could not be identified, but the stable end product has the composition of a diamine adduct.

The compounds are soluble in most organic solvents.
All the compounds isolated have molar conductivities of \(21.6 \text{mhos} \times \text{cm}^2 \text{ mole}^{-1}\) at room temperature in acetone (table VIII.1) which are normal for nonelectrolytes.

**Magnetic Moment**

The T.I.P. corrected magnetic moments of the compounds are found to be within 3.10 - 3.18 BM, comparable to the octahedral complexes of \(d^8\) high spin configuration.\(^5\) The approximate g-factor calculated to be within 2.19 - 2.25 are also consistent with \(d^8\)-octahedral configuration.\(^6,7\) The spin orbit coupling constant \((\zeta)\) lies within 175 - 253 cm\(^{-1}\) as against free-ion value \((\zeta_0)\) of 324 cm\(^{-1}\). Consequently the covalency parameter \((\sqrt{\cdot})\) remains within 0.54 - 0.80.\(^6,7\)

\[
\mu_{\text{eff}} = g \frac{S(S+1)}{2}
\]

\[
g = 2 \left(1 - \frac{4\pi}{10\Delta q}\right)
\]

\[
\sqrt{\cdot} = \frac{\zeta}{\zeta_0}, \text{ where } (\zeta_0 = 324 \text{ cm}^{-1})
\]

Infra-red spectra of complexes have been given in Table VIII.3 where assignments of some important modes of vibrations are noted. The disappearance of \(\nu \text{(O-H)}\) band due to water molecules at 3460 cm\(^{-1}\) of the starting material, [Ni(Sal)\(_2\)H\(_2\)O\(_2\)], the appearance of modified vibrations of the ligands and the general decrease in the \(\nu \text{(C=O)}\) from 1540 cm\(^{-1}\) in the starting material to \(\sim 1512 \text{ cm}^{-1}\) confirm definite formation of adducts. The amine \(\nu \text{(N-H)}\), stretching vibrations\(^8\) at \(\sim 3300 \text{ cm}^{-1}\) remain almost unaltered in aminopyridine adducts, indicating their non-involvement in bonding to the metal. The phenolic C-O stretching vibrations\(^8,9\) in the adducts
generally occur at lower positions compared to the starting diaqua-
disalicylaldehyde-dinickel(II) complex (1940 cm\(^{-1}\)).

The pKa (LH\(^+\)) values of the hetero ligands (L) are found
to have a somewhat linear relationship with \(\nu(C=O)\) vibrations in
the adducts, [Ni(Sal)\(_2\).L\(_2\)] (Figure VIII-5). Similar observation is
not found with the phenolic (C-O) vibration. This suggests that
there is an almost linear relationship between the electron donor
property/basicity of the hetero ligand and the carbonyl bond-order
of the salicylaldehyde moiety which is otherwise related to the
bond strength of the covalent carbonyl oxygen-metal bond. pKa of
\(\beta\)-diketones have also been reported to have linear relationship
with \(\nu(M-O)\) in the \(\beta\)-diketonato complexes. A
A correlation of
pKa (LH\(^+\)) with \(\nu(C=O)\) can therefore be well-explained considering
the electronic charge accumulation over the ligated metal ion.
The amount of participation of the \(\sigma\)- and \(\pi\) characters of the
hetero ligands is difficult to evaluate until more number of lig-
ands are studied with specific donor properties.

Electronic spectral bands and other related parameters
have been presented in Table VII.-5. They show a number of absor-
pptions which are difficult to explain completely. The general pat-
tern of bands, however, is quite explainable under an octahedral
field. The band occurring at \(\sim 10,000\) cm\(^{-1}\) is termed as \(\nu_1(\equiv 10\beta\delta)\)
as explained in the analogous adducts in acetylacetonatonicke(II).
This may therefore be assigned to \(2\Delta g \rightarrow 3\Gamma_{2g}\). Another band appe-
s at \(\sim 16,000\) cm\(^{-1}\). In a strong donor system under \(\sigma_h\) symmetry
the \(\nu_2/\nu_1\) ratio becomes \(\sim 1.6\). Hence the 16,000 cm\(^{-1}\) band may be
taken to be the \(\nu_2\) band with \(2\Delta g \rightarrow 3\Gamma_{15}(F)\) transition. The \(\nu_3\)
bands were calculated using theoretical procedures.
The Racah and Naphelauxetic parameters have been calculated as in earlier chapters. These parameters indicate large covalency to be present in the molecules. The bands observed at ~ 13,000 cm\(^{-1}\) are either weak or shoulders which may be assigned to a spin forbidden triplet-singlet transition \((^3A_g \rightarrow ^1E_g)\). The intense bands occurring within 22,830–25,000 cm\(^{-1}\) may be charge transfer bands which possibly envelope \(\gamma_3\) absorptions.

(ii) \(\text{[Ni(Sal-L')_2H_2O]}_n\) and \(\text{[Ni(Sal-L")_2]}_m\) Compounds.

The Schiff-base complexes were obtained from methanol in 1:2 (Ni: Schiff-base) ratio. The Schiff-base formed out of salicyaldehyde and 2-aminopyridine results in a mono-aquo complex with nickel(II) instead of a diaquo one. The analytical data and the spectral evidence suggest that these Schiff-base complexes are of two types. The compound prepared using 2-aminopyridine has a coordinated water molecule, \(\text{[Ni(Sal-L')_2H_2O]}_n\), and that from 3-aminopyridine has no water molecule \(\text{[Ni(Sal-L")_2]}_m\).

The analytical data of the compounds have been given in Table VIII.1 and the spectral evidences in Tables VIII.3 and 5.

The latter compound is insoluble, but the molar conductance of the former could be taken in acetone in very dilute solution and found to be 18.5 mhos cm\(^2\) mole\(^{-1}\) indicating the compound to be a nonelectrolyte.

Absence of \(\gamma\) (N–H) vibrations in both the compounds confirms Schiff-base formation. In the aquo-bis-(pyridyl-2)-salicylaldiminatonicke(II), a broad band is observed at 3450 cm\(^{-1}\) showing the presence of co-ordinated water molecules. In case of bis-((pyridyl-3)-salicylaldiminatonicke(II)), such band
is absent. The Schiff-base formation and complexation has been substantiated by the appearance of $\nu(C=\equiv N)$ vibration $^{3,11}$ mixed with $\gamma(C=C)$ vibration at $\approx 1600 \text{ cm}^{-1}$ and the absence of bands at $\approx 1520 \text{ cm}^{-1}$ for $\gamma(C=0)$.

The greater insolubility of the Schiff-base complexes in common solvents suggests possibility of polymeric structure. On this postulation from the evidence of the presence of coordinated water molecule in the 2-aminopyridine derivative and the absence of the same in 2-aminopyridine derivative, structures VIII.1a and 2a may be suggested for them.

Further evidence to this suggestion comes from the positions of the phenolic $\gamma(C=O)$ bands. Such bands in the adducts, [Ni(Sal)$_2$L$_2$], and the Schiff-base complex, derived from 2-aminopyridine, are more or less at the same position indicating a strain of almost equal amount in the salicylidene nucleus. A large decrease by 62 cm$^{-1}$ in the Schiff-base complex derived from 2-aminopyridine is probably caused by the greater polymerisation and stronger strain in the crowded complex geometry. Unfortunately, our attempts to determine the molecular weights by Rast's method did not give any reproducible result.

The electronic spectra have the bands in the positions expected from octahedral d$^3$ complexes of nickel(II). In the Schiff-base complex from 2-aminopyridine, the bands at 10,300 cm$^{-1}$ was designated as $\gamma_1$, 16,660 cm$^{-1}$ as $\gamma_2$ and the band at 29,020 cm$^{-1}$ as $\gamma_3$. $\gamma_2/\gamma_1$ values (~1.61) confirm its octahedral geometry. In the case of the Schiff-base complex derived from 2-aminopyridine, a band is observed at 16,000 cm$^{-1}$ which may be taken as $\gamma_2$ in an octahedral
As assigned for other compounds, the bands at $\sim$14,000 cm$^{-1}$ may be spin forbidden ones ($^{3}A_{2g} \rightarrow ^{1}E_g$) and the split bands at $\sim$ 23,000 cm$^{-1}$ of higher intensity may be of charge transfer origin. The extra bands at $\sim$ 25,000 cm$^{-1}$ are perhaps due to the charge transfer involving the presence of azomethine groups.

The Racah (B) and the nephelauxetic parameters ($\beta^{35}$) have been given in Table VIII.5, which show large covalency in the metal-ligand bond.

**Magnetic Moment**

The observed magnetic moments of the compounds are
consistent with high spin $d^2$-octahedral configuration (Table VIII.2). Other magnetic parameters have values similar to those for $[\text{Ni(Sal)}_2\text{L}_2]$ type compounds.

From the foregoing discussions, all the complexes studied may be concluded to be of distorted octahedral type, the distortion being more in $[\text{Ni(Sal.3-Am.Py)}]$ (Structure VIII.2a). In the aquo-bis-(pyridyl-2)-salicylaldiminonickel (II), the co-ordination number is six with an environment of $\text{N}_3\text{O}_3$ donor system where the third oxygen and third nitrogen atoms are taken from the water molecule and the pyridyl nitrogen of an adjacent complex molecule respectively. On the other hand bis-(pyridyl-3)-salicylaldiminonickel(II) is a continuous chain molecule having co-ordination sphere of $\text{N}_4\text{O}_2$, involving two pyridine (of two adjacent complex molecules) and two azomethine nitrogens. Such a complex is expected to have a marked degree of distortion in the octahedral geometry and to be insoluble in most organic solvents, as observed.
Table VIII.1

Colour, form, melting point, analytical and molar conductance data of Ni(II) complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>Form</th>
<th>M.P. (°C)</th>
<th>% Ni</th>
<th>% H₂O</th>
<th>Λ M mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni(Sal)₂(Py)₂]</td>
<td>Yellowish green</td>
<td>Crystalline</td>
<td>125</td>
<td>12.1</td>
<td>-</td>
<td>2.6</td>
</tr>
<tr>
<td>[Ni(Sal)₂(β-Pic)₂]</td>
<td>Light-brown</td>
<td>-do-</td>
<td>177</td>
<td>12.0</td>
<td>-</td>
<td>2.4</td>
</tr>
<tr>
<td>[Ni(Sal)₂(C₅H₄NO₂)₂]</td>
<td>Yellowish Micro-green</td>
<td>crystalline</td>
<td>200d</td>
<td>12.0</td>
<td>-</td>
<td>21.6</td>
</tr>
<tr>
<td>[Ni(Sal)₂(2-Am.Py)₂]</td>
<td>-do-</td>
<td>-do-</td>
<td>174</td>
<td>12.0</td>
<td>-</td>
<td>6.2</td>
</tr>
<tr>
<td>[Ni(Sal)₂(3-Am.Py)₂]</td>
<td>-do-</td>
<td>-do-</td>
<td>200d</td>
<td>12.0</td>
<td>-</td>
<td>2.9</td>
</tr>
<tr>
<td>[Ni(Sal)₂(4-Am.Py)₂]</td>
<td>-do-</td>
<td>-do-</td>
<td>220d</td>
<td>12.0</td>
<td>-</td>
<td>3.4</td>
</tr>
<tr>
<td>[Ni(Sal-2-Am.Py)₂H₂O]</td>
<td>Green</td>
<td>Crystalline</td>
<td>235d</td>
<td>12.3</td>
<td>3.7</td>
<td>18.5</td>
</tr>
<tr>
<td>[Ni(Sal-2-Am.Py)₂]</td>
<td>Yellow</td>
<td>Amorphous</td>
<td>210d</td>
<td>12.7</td>
<td>-</td>
<td>a</td>
</tr>
</tbody>
</table>

a = Insoluble
Table VIII.2

Magnetic susceptibility, T.I.P. corrected magnetic moment, g-factor, spin orbit coupling constant (λ) and covalency parameters (¥) of Ni(II) complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \chi \times 10^6 ) (CGS Unit)</th>
<th>( N \lambda \times 10^6 ) (CGS Unit)</th>
<th>( \mu_{\text{eff}} ) (B.M.)</th>
<th>( g )</th>
<th>( \lambda ) (cm(^{-1}))</th>
<th>¥</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Ni(Sal)}_2\text{Py}_2^-])</td>
<td>4177</td>
<td>209</td>
<td>3.11</td>
<td>2.199</td>
<td>255</td>
<td>0.69</td>
</tr>
<tr>
<td>([\text{Ni(Sal)}_2(\alpha\text{-pic})_2^-])</td>
<td>4363</td>
<td>215</td>
<td>3.13</td>
<td>2.248</td>
<td>258</td>
<td>0.80</td>
</tr>
<tr>
<td>([\text{Ni(Sal)}_2\text{Cl}_2^-])</td>
<td>4363</td>
<td>214</td>
<td>3.13</td>
<td>2.248</td>
<td>256</td>
<td>0.79</td>
</tr>
<tr>
<td>([\text{Ni(Sal)}_2(2\text{-am-Py})_2^-])</td>
<td>4152</td>
<td>209</td>
<td>3.10</td>
<td>2.194</td>
<td>250</td>
<td>0.72</td>
</tr>
<tr>
<td>([\text{Ni(Sal)}_2(3\text{-am-Py})_2^-])</td>
<td>4231</td>
<td>209</td>
<td>3.13</td>
<td>2.214</td>
<td>175</td>
<td>0.54</td>
</tr>
<tr>
<td>([\text{Ni(Sal)}_2(4\text{-am-Py})_2^-])</td>
<td>4161</td>
<td>210</td>
<td>3.10</td>
<td>2.194</td>
<td>250</td>
<td>0.72</td>
</tr>
<tr>
<td>([\text{Ni(Sal-2-am-Py}_2\text{H}_2\text{O})_n^-])</td>
<td>4339</td>
<td>216</td>
<td>3.19</td>
<td>2.256</td>
<td>258</td>
<td>0.80</td>
</tr>
<tr>
<td>([\text{Ni(Sal-3-am-Py}_2\text{H}_2\text{O})_n^-])</td>
<td>4177</td>
<td>208</td>
<td>3.11</td>
<td>2.199</td>
<td>225</td>
<td>0.69</td>
</tr>
</tbody>
</table>
### Table-VIII.3

Important infra-red spectral bands with assignments of Ni(II) complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>3460 br</th>
<th>-</th>
<th>-</th>
<th>-</th>
<th>-</th>
<th>-</th>
<th>3450 br</th>
<th>-</th>
<th>((\text{C-H}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Ni(Sal)}_2]_2)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3260 w</td>
<td>3270 m</td>
<td>3300 m</td>
</tr>
<tr>
<td>([\text{Ni(Sal)}_2]_2)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3300 m</td>
<td>3300 w</td>
<td>3330 m</td>
</tr>
<tr>
<td>([\text{Ni(Sal)}_2]_2)</td>
<td>1650 s</td>
<td>1625 s</td>
<td>1625 s</td>
<td>1617 s, br</td>
<td>1632 s</td>
<td>1630 vs</td>
<td>1635 vs</td>
<td>1630 vs</td>
<td>1625 s</td>
</tr>
<tr>
<td>([\text{Ni(Sal)}_2]_2)</td>
<td>1617 m</td>
<td>1600 s</td>
<td>1595 s</td>
<td>1600 sh</td>
<td>1580 m</td>
<td>1585 s</td>
<td>1575 m</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>([\text{Ni(Sal)}_2]_2)</td>
<td>1540 vs</td>
<td>1513 m</td>
<td>1515 m</td>
<td>1510 m</td>
<td>1510 m</td>
<td>1510 m, br</td>
<td>1511 m</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>([\text{Ni(Sal)}_2]_2)</td>
<td>1340 s</td>
<td>1337 m</td>
<td>1335 m</td>
<td>1315 m</td>
<td>1322 m</td>
<td>1300 m, br</td>
<td>1330 sh</td>
<td>1320 m</td>
<td>1278 m</td>
</tr>
</tbody>
</table>

- **Phe-nolic**
Table VIII.4

The pKa [LH+] of hetero ligands and \( \gamma \) (C=O) bands of the corresponding [Ni(Sal)\( \text{L}_2 \)] compounds.

<table>
<thead>
<tr>
<th>Hetero-ligand</th>
<th>pKa LH⁺</th>
<th>( \gamma ) (C=O) in cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>14</td>
<td>1540</td>
</tr>
<tr>
<td>Quinoline</td>
<td>4.89</td>
<td>1510</td>
</tr>
<tr>
<td>Pyridine</td>
<td>5.21</td>
<td>1513</td>
</tr>
<tr>
<td>( \beta )-Picoline</td>
<td>5.67</td>
<td>1515</td>
</tr>
<tr>
<td>2-Aminopyridine</td>
<td>6.36</td>
<td>1520</td>
</tr>
<tr>
<td>3-Aminopyridine</td>
<td>9.1</td>
<td>1520</td>
</tr>
<tr>
<td>4-Aminopyridine</td>
<td>9.12</td>
<td>1521</td>
</tr>
</tbody>
</table>
Table - VIII-5
Electronic spectral data of Ni(II) compounds (Bands expressed in cm⁻¹ unit).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$\gamma_3^a$</th>
<th>$\gamma_2$</th>
<th>$3A_2g \rightarrow E_g$</th>
<th>$\gamma_1^b$</th>
<th>$\gamma_2/\gamma_1^b$</th>
<th>$\beta_c$</th>
<th>$\beta_{35}^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ni}(\text{Sal})_2(\text{H}_2\text{O})_2]$</td>
<td>23,500</td>
<td>15,520</td>
<td>13,880</td>
<td>&lt;9,900</td>
<td>1.57</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{Ni}(\text{Sal})_2(\text{Py})_2]$</td>
<td>23,030</td>
<td>24,100</td>
<td>16,660</td>
<td>13,330</td>
<td>10,300</td>
<td>1.60</td>
<td>937.5</td>
</tr>
<tr>
<td>$[\text{Ni}(\text{Sal})_2(\text{L-Pic})_2]$</td>
<td>23,960</td>
<td>24,150</td>
<td>16,560</td>
<td>13,810</td>
<td>10,250</td>
<td>1.61</td>
<td>978.0</td>
</tr>
<tr>
<td>$[\text{Ni}(\text{Sal})_2(\text{Q})_2]$</td>
<td>24,840</td>
<td>24,150</td>
<td>16,560</td>
<td>13,810</td>
<td>&lt;9,900</td>
<td>&gt;1.63</td>
<td></td>
</tr>
<tr>
<td>$[\text{Ni}(\text{Sal})_2(2-\text{Am-Py})_2]$</td>
<td>23,130</td>
<td>24,300</td>
<td>16,130</td>
<td>13,290</td>
<td>10,000</td>
<td>1.61</td>
<td>958.3</td>
</tr>
<tr>
<td>$[\text{Ni}(\text{Sal})_2(2-\text{Am-Py})_2]$</td>
<td>23,290</td>
<td>24,330</td>
<td>16,230</td>
<td>10,030</td>
<td>1.61</td>
<td>958.3</td>
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<tr>
<td>$[\text{Ni}(\text{Sal})_2(4-\text{Am-Py})_2]$</td>
<td>23,110</td>
<td>23,810</td>
<td>16,730</td>
<td>13,570</td>
<td>10,320</td>
<td>1.61</td>
<td>983.7</td>
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<tr>
<td>$[\text{Ni}(\text{Sal}-2-\text{Am-Py})_2\cdot\text{H}_2\text{O}]_n$</td>
<td>25,000</td>
<td>23,810</td>
<td>16,800</td>
<td>13,830</td>
<td>&lt;9,900</td>
<td>&gt;1.62</td>
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<tr>
<td>$[\text{Ni}(\text{Sal}-2-\text{Am-Py})_2]_n$</td>
<td>23,020</td>
<td>24,660</td>
<td>16,660</td>
<td>13,500</td>
<td>10,300</td>
<td>1.61</td>
<td>987.5</td>
</tr>
</tbody>
</table>

- $\gamma_3^a$ - calculated value
- $\gamma_2^b$ - $\gamma_1^b = 100\gamma_d$
- $\beta_{35}^c$ - $\beta_0 = 1040$ cm⁻¹ (ref. 12)
- $\beta_c$ - value taken from ref. 2
References

Infrared spectra (4000-2000 cm$^{-1}$) of (a) $\text{Ni(Sal)}(2-\text{NH}_2\text{Py})$, (b) $\text{Ni(Sal)}(3-\text{NH}_2\text{Py})_2$, and (c) $\text{Ni(Sal)}(4-\text{NH}_2\text{Py})_2$ in nujol mull showing $\nu$(N-H) and $\gamma$(O-H) absorptions.
Fig. VIII.2 - Infrared spectra (4000-2000 cm$^{-1}$) of (a) $[\text{Ni(Sal.$L''$)}_2]_{\text{n}}$ ($L''$ = 3-NH$_2$Py) and (b) $[\text{Ni(Sal.$L'$)}_2\cdot\text{H}_2\text{O}]_{\text{n}}$ ($L'$ = 2-NH$_2$Py) in nujol mull indicating schiff-base formation.
Fig. VII.3 - Electronic spectra (300-1000 nm) of (I) \( \text{[Ni(Sal)_2(H_2O)_2]} \)
(II) \( \text{[Ni(Sal)_2(Py)_2]} \), (III) \( \text{[Ni(Sal)_2(β-pic)_2]} \), (IV) \( \text{[Ni(Sal)_2(q)]_2} \)
(V) \( \text{[Ni(Sal)_2(2-NH_2Py)_2]} \), (VI) \( \text{[Ni(Sal)_2(3-NH_2Py)_2]} \) and (VII) \( \text{[Ni(Sal)_2(4-NH_2Py)_2]} \) from nujol film.
Electronic spectra (300-1000 nm) of (IX) Ni(Sal L)2*H2O (L = 2-NH2Py) and (X) Ni(Sal L) (L = 3-NH2Py) from "nujol film."
Fig. VIII.5 - $pK_a \left[ LH^+ \right]$ vs. (C=O) vibration (in the $\left[ Ni(Sal)_2L_2 \right]$ complex) showing the approximate linear relationship for ligands (1) $H_2O$, (2) Py, (3) -pic, (4) Q, (5) 2-NH$_2$Py, (6) 3-NH$_2$Py, (7) 4-NH$_2$Py.