PART III

CHAPTER II

EXPERIMENTAL
The synthesis of ligands and their complexes, elemental analysis and various physicochemical techniques adopted for the present investigations are discussed below.

I SYNTHESIS OF LIGANDS

The heterocyclic bases such as pyridine, \( \kappa \)-picoline and quinoline (BDH grade) are available in the laboratory. However, they were purified by distillation.

1. Synthesis of N-substituted thioureas:

The preparation of N-substituted thiourea ligands has been described in chapter II, Part II. For the synthesis of mixed ligand nickel(II) complexes, the following ligands have been employed.

<table>
<thead>
<tr>
<th>Primary ligand</th>
<th>Abbreviation</th>
<th>Secondary Abbreviation</th>
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</thead>
<tbody>
<tr>
<td>1. o-tolythiourea</td>
<td>o-totu</td>
<td>Pyridine (PY)</td>
</tr>
<tr>
<td><img src="image1" alt="o-tolythiourea" /></td>
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<tr>
<td>2. o-ethoxyphenylthiourea</td>
<td>o-etoptu</td>
<td>( \kappa )-Picoline (X-pic)</td>
</tr>
<tr>
<td><img src="image2" alt="o-ethoxyphenylthiourea" /></td>
<td></td>
<td>Quinoline (Q)</td>
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<tr>
<td><img src="image3" alt="o-ethylphenylthiourea" /></td>
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II SYNTHESIS OF COMPLEXES

All the chemicals used were BDH or analar grade.

1. Chloroisothiocyanato dipyridine bis(o-tolylthiourea) nickel(II):

The primary complex, chloroisothiocyanato bis (o-tolylthiourea) nickel(II) was isolated by adopting the procedure as outlined in Part-II, chapter-II. The complex thus obtained (4.846 gm, 0.01 mol) in ethanol was treated with pyridine (1.60 ml, 0.02 mol). The complex was carefully refluxed for about two hours over a hot water bath. Then the reaction mixture was concentrated to a small volume (~8-10 ml) which turned to a gummy mass. This on very long trituration with pet-ether (40-60°C) and cooling for about two hours yields a grey coloured solid. It was washed with pet-ether - alcohol mixture (2:1 v/v) and dried over concentrated sulphuric acid in a desiccator. Yield 3.3 gms. (52%).

2. Bromoisothiocyanato dipyridine bis(o-tolylthiourea) nickel(II):

This complex was isolated by adopting the procedure as discussed above, except that anhydrous nickel bromide was used in place of nickel chloride hexahydrate. (Yield 3.9 gms, 58%).
Other chloro or bromo mixed ligand nickel(II) complexes were synthesised utilizing α-picoline and quinoline by adopting the procedure mentioned above.

In case of α-picoline and quinoline mixed ligand complexes, refluxing was carried out for about four hours and six hours respectively. This, on concentration to a small volume (~8-10 ml) turned into hard gummy mass which was then kept in a freeze (0-10°C) for about 8-10 days when it got solidified. Complexes were washed carefully with pet ether-alcohol mixture (2:1 v/v) and dried over P₂O₅ in desiccator.

III ANALYSIS OF COMPLEXES

The analysis of complexes for nickel, sulphur, halogen, carbon and hydrogen was carried out as dealt in earlier part.

a) Nitrogen Estimation:

For the estimation of nitrogen, Kjeldahl's method was adopted. For the mixed ligand complexes, the digestion in concentrated sulphuric acid was carried out for about 30-40 hours (till the solution became colourless). Afterwards the same procedure as outlined in the chapter-II, part-I was followed.
IV PHYSICOCHEMICAL MEASUREMENTS

a) **Conductivity Measurements:**

The electrical conductivity measurements of the complexes in methanol (1 x 10^{-3} M) were carried out on Elico conductivity bridge type cm-82 having cell constant 0.82.

b) **Magnetic Susceptibility Measurements:**

The magnetic susceptibility determinations of the complexes at room temperature (26°C) were carried out as outlined in Part-I, Chapter-II.

c) **Infrared Spectral Measurements:**

The infrared spectral measurements (4000-600 cm^{-1}) of the ligand and the complexes in nujol mull were made on Perkin Elmer model 397 spectrometer. For a few ligands and complexes, infrared spectra were scanned on Perkin Elmer model 783 spectrophotometer. Far infrared spectral measurements (600-200) cm^{-1} for a few complexes were made on Fourier far IR instrument placing the sample on polythene plates adopting nujol mull technique.

d) **Electronic Spectral Measurements:**

The ultraviolet-visible spectra of the complexes were recorded in the region 300-1500 nm in solid state using nujol mull and also in methanol.
e) **Electron Spin Resonance Spectral Measurements:**

Electron spin resonance spectra of a few complexes were scanned on Varian E-4, X-band spectrophotometer, as described earlier.

f) **Thermal Measurements:**

Thermal measurements in static air were recorded on MOM derivatograph at a heating rate of 10°C per minute. The other experimental details are given in Chapter-II, Part-I.