Chapter II

EXPERIMENTAL
i). CHEMICALS USED:

The following chemicals were used in preparing the Schiff bases.

**Monoamines:**

- Aniline
- p-Toluidine
- p-Chloro-aniline
- p-Anisidine
- o-Ami-no-phenol

These were obtained from:

- B.D.H. Reagent.
- Riedel grade.
- Reagent grade.
- Fluka grade.

**Diamines:**

- Ethylene-diamine
- p-Phenylenediamine
- m-Phenylenediamine.
- Benzidine
- p,p'-Diaimino-diphenyl-amine.

These were obtained from:

- Riedel grade.
- Fluka grade.
- Fluka grade.
- Reagent grade.
- Reagent grade.

**p-p'-Diamino-diphenyl-sulphide** was prepared as follows:

A hot solution of 72.5 gms. of SnCl₂·2H₂O in 80 ml. of 12N HCl was added immediately to a hot solution of 14 gms. of **p,p'-dinitro-diphenyl-sulphide** in 150 ml. of glacial
acetic acid. After few minutes the solution was evaporated to dryness in vacuum. The residue was dissolved in water and 50% alkali was added. The precipitated base was filtered, washed with alkali, then with water and dried. The crude p,p'-diamino-diphenylsulphide was recrystallised from ethanol water mixture, m.p. found 104-105°C.

Thiosemicarbazide used in preparing thiosemicarbazones was of Fluka grade.

### Aldehydes:

- **Vanillin**
  - Fluka grade
- **Salicylaldehyde**
  - Bush Reagent.

The substituted salicylaldehydes were prepared by Duff's method (1), they were:

- 3-Methyl salicylaldehyde,
- 4-Methyl salicylaldehyde,
- 5-Methyl salicylaldehyde,
- 5-Chloro salicylaldehyde.

The phenols used in preparing the above aldehydes were:

- o-Cresol
  - Reagent grade.
m-Cresol                   Reagent grade
p-Cresol                   - do -
p-Chloro-phenol            - do -

PROCEDURE:

A mixture of 300 gms. of glycerol and 70 gms. of boric acid was heated in a 2 litre beaker with stirring until the temperature reached 165°. An intimate mixture of 50 gms. of the phenol and 50 gms. of hexamethylenetetramine was prepared by grinding the material together thoroughly. The mixture was then added with vigorous stirring to the glycerol-glyceroboric acid solution previously cooled to 150°. The reactants were stirred for 20 minutes during which the temperature was maintained between 150-165° by heating or cooling as necessary. Finally the reaction mixture was allowed to cool to 115° and was then acidified with a mixture of 50 ml. of concentrated sulfuric acid and 150 ml. water. The acidified reaction mixture was then steam distilled. It was heated to about 110-120° while steam was being passed through it.

5-Methyl salicylaldehyde and 5-chloro salicylaldehyde were obtained as solids whereas 3-methyl salicylaldehyde and 4-methyl salicylaldehyde were liquids and obtained by
extracting the steam distillate with ether and drying over anhydrous sodium sulphate.

Acetylacetone was used in preparing a few Schiff bases and was a BDH reagent.

The solvent used for the preparation of the Schiff bases was ethyl alcohol. It was distilled before use.

The reagents used in preparing the benzimidazoles were as follows:

- o-Phenylene diamine
- Formic acid
- Acetic acid
- Propionic acid
- Lactic acid
- Salicylic acid
- Mendelic acid
- Nicotinic acid
- Anthranilic acid

For these reagents, Fluka grade and Reagent grade were used.

ii). **PURIFICATION OF THE SOLVENTS:**

The solvents used were methyl alcohol, ethyl alcohol, acetone, ether and ethyl acetate.
**ABSOLUTE METHYL ALCOHOL:**

Absolute methyl alcohol was prepared from the usual methyl alcohol by treatment with magnesium activated by iodine (2).

Five grams of dry magnesium turnings and 0.5 gm. of resublimed iodine were placed in a 2 litre round bottomed flask fitted with a double surface reflux condenser. 50-75 ml. of methyl alcohol was added through the condenser and the mixture was warmed until the iodine disappeared. If a vigorous evolution of hydrogen did not take place, a further 0.5 gm. of iodine was added and the mixture was heated until all the magnesium was converted into the methoxide. 900 ml. of the methyl alcohol was then added, and the mixture boiled for 30 minutes under reflux. The product was then distilled with exclusion of moisture.

**ACETONE:**

Commercial acetone was purified as follows:

Acetone was refluxed with successive small quantities of potassium permanganate until the violet colour persists. It was then dried with anhydrous potassium carbonate, filtered from the desiccant and distilled. Ethyl acetate,
ether and ethyl alcohol were distilled before use.

iii). PREPARATION OF VARIOUS SCHIFF BASES:

(a). Schiff bases from monoamines:

Equimolar proportions of the aldehyde and monoamines in ethyl alcohol were refluxed for an hour. On cooling, the Schiff bases separated out. They were filtered, and recrystallised from ethyl alcohol and dried in vacuum over fused calcium chloride.

(b). Schiff bases from diamines:

The aldehyde (0.02 mole) and diamine (0.01 mole) in ethyl alcohol were refluxed for an hour. The reaction mixture was then allowed to cool when the Schiff bases separated out. It was then filtered and recrystallised with ethyl alcohol. Finally the Schiff base was dried in vacuum over fused calcium chloride.

(c). Thiosemicarbazones:

Aldehyde (0.01 mole) and thiosemicarbazide (0.01 mole) in methyl alcohol were refluxed for 2-3 hours. On cooling the Schiff base separated out. It was then filtered, recrystallised with ethyl alcohol and dried in vacuum over
fused calcium chloride.

iv). **PREPARATION OF BENZIMIDAZOLES:**

Benzimidazole.
2-Methyl benzimidazole.
2-Ethyl benzimidazole.
2-(<hydroxyethyl) benzimidazole.

These benzimidazoles were prepared according to the following method (3).

\[ \text{o-Phenylene diamine (0.02 mole), the requisite acid (0.03 mole), and 20 c.c. of 4N hydrochloric acid were boiled for 30-40 minutes under reflux. On neutralisation of the filtered solution with ammonia the benzimidazoles separated out.} \]

Benzimidazoles and 2-methyl benzimidazole were recrystallised from water whereas 2-(<hydroxyethyl) benzimidazole was recrystallised from 50% alcohol.

The following procedure was followed in preparing 2-phenyl benzimidazole and 2-(<hydroxy benzyl) benzimidazole.

Equimolar proportions of \text{o-phenylene diamine and the}
carboxylic acid were mixed with a sufficient quantity of polyphosphoric acid (for 0.2 mole quantity of the carboxylic acid about 10-20 parts by weight of polyphosphoric acid were used) to give a stirrable paste. The mixture was heated slowly to 250° and the resulting solution stirred at 250° (± 3°) for 4 hours, permitted to cool at about 100°C and poured in a thin stream into a large volume of rapidly stirred ice cold water. The insoluble residue was collected by filtration, washed with a small amount of water, and reslurried in an excess of 10% sodium carbonate solution. The alkaline slurry was filtered and the product washed thoroughly with water and dried at 60°. The crude product was recrystallised from alcohol.

In preparing 2-(β-pyridyl) benzimidazole and 2-(o-amino phenyl) benzimidazole, the reaction was carried out as above, except that the product which was soluble in acidic medium was treated with 50% NaOH solution until the slurry was alkaline. During the basification ice was added as required to prevent an excessive rise in temperature, but the mixture was not cooled sufficiently to cause the precipitation of inorganic salts. The crude product was collected by filtration, washed free of alkali and inorganic salts, dried and recrystallised with alcohol.
In the case of 2-(o-hydroxyphenyl)benzimidazole, the reaction was carried out as followed for 2-phenyl benzimidazole, except that isolation was accomplished by extracting the product from the carbonate washed residue with successive portions of boiling ethyl alcohol. After treatment of the combined alcoholic extracts with a small amount of activated charcoal, the boiling filtrate was treated with hot water until crystallisation was imminent. The product was recrystallised from the solution upon cooling and was collected by filtration.

vi). PREPARATION OF ANHYDROUS ZIRCONYL CHLORIDE:

Zirconyl chloride octahydrate used in preparing the complexes under study and anhydrous zirconyl chloride, was of Fluka grade.

Anhydrous zirconyl chloride was prepared according to the method mentioned by Moeller (5).

To 20 gms. of finely ground zirconyl chloride octahydrate in a round bottomed flask was added 50 ml. of freshly distilled thionyl chloride at room temperature when evolution of sulfur dioxide and hydrogen chloride took place. After the bubbling stopped, the flask was equipped with a
reflux condenser, and the slurry was refluxed for 1 to 2 hours. The condenser was then arranged for distillation, and the excess thionyl chloride was removed under reduced pressure. The flask containing the product was transferred immediately to a vacuum desiccator containing potassium hydroxide and stored for about 12 hours to remove the remaining thionyl chloride.

vi). PREPARATION OF THE COMPLEXES:

Complexes of zirconyl chloride with Schiff bases:

Schiff base complexes of zirconium were prepared by condensing zirconyl chloride octahydrate and the Schiff bases in methanol for 2-3 hours and cooling when the complexes separated.

In some cases where anhydrous zirconyl chloride was used, the reactions were carried out in dry acetone.

Complexes of zirconyl chloride with benzimidazoles:

Anhydrous zirconyl chloride in acetone was added to the benzimidazole in the same solvent and heated for a short time to give the complex.
vii). **ELEMENTAL ANALYSIS:**

**Estimation of Zirconium:**

Zirconium in the complexes was estimated gravimetrically as ZrO₂ as follows:

About 0.1 to 0.2 gms. of the complex was accurately weighed into a 250 ml. beaker. It was decomposed with concentrated nitric acid, cooled and diluted to 150 ml. with water. Zirconium was then precipitated as the hydroxide by adding ammonia till the solution was strongly alkaline. The precipitate was digested on a water bath for 30 minutes and filtered through Whatman 41 filter paper and washed with water several times. When the washing was complete, the filter paper along with the precipitate was placed in a previously weighed silica crucible and ignited for an hour. The residue was then weighed as ZrO₂.

**Estimation of chloride (6):**

Chloride in the complexes was estimated gravimetrically as AgCl.

About 0.1 to 0.2 gms. of the complex was weighed accurately into a 250 ml. beaker. 150 ml. of water was then added and heated over a sand bath for half an hour.
Then 15-20 ml. of ammonia solution was added and heating was continued for some time. The solution was then cooled and filtered. The filtrate was collected and acidified with concentrated nitric acid and 20-25 ml. of 1% silver nitrate was added to it with constant stirring. The precipitate was allowed to settle and tested for complete precipitation. The suspension was then heated nearly to boiling, stirring at the same time. This was continued until the precipitate coagulated and the supernatant liquid was clear. The beaker was then set in the dark for 1-2 hours before filtration. It was then filtered through a previously weighed sintered crucible. The precipitate was washed free of silver nitrate with 0.01 to 0.2N nitric acid. The crucible was then dried at 130-150°C for an hour, and then cooled and weighed as AgCl. The percentage of chloride in the complexes was then calculated.

**Estimation of nitrogen:**

Nitrogen in the complexes was estimated by Kjeldahl method.
Estimation of Sulphur:

1. **Wet Process:**

   A known amount of the complex was heated at 100°C in a kjeldahl flask with 20 ml. of conc. HNO₃ until the material got dissolved. Then 5 ml. of HClO₄ (of 72% strength) of the sample was added to it and the heating continued for 24 hours. After this the temperature was raised to remove all nitric acid and digestion of the residue was continued with HClO₄ till a clear solution was obtained. The flask was cooled, the contents filtered, and sulfate determined as BaSO₄.

2. **Dry Process:**

   A weighed amount of the complex was transferred onto a thin layer of Eskula's salt (mixture containing anhydrous Na₂CO₃ and MgO in 1:2 proportions by weight) in a 50 ml. nickel crucible and covered with 6 gm. of the salt. The contents were heated on a low flame for about half an hour and then the temperature was raised (600-650°C) and heated for about an hour to oxidise sulphur to sulphate. Cooled, and the cold mass was extracted with hot water and sulphate was determined as BaSO₄.
Electrical Conductivity:

The molar conductivity of a solution was obtained from the following relation:

\[
\Lambda_M = \frac{1000 \times \text{Cell constant} \times \text{specific Conductance}}{	ext{Molar concentration}}.
\]

The conductivity measurements were made using an Elico CM-82 conductivity bridge provided with a dip-type conductivity cell having platinised platinum electrodes. The cell constant was determined by measuring the resistances of aqueous KCl solutions, the specific conductivities of which were known accurately from the literature (7). The value of cell constant was found to be 0.829 cm⁻¹. For measuring the conductivities of the solutions of the complexes under investigation, the solutions of 10⁻³M concentration were employed.

The observed molar conductivities of the complexes were interpreted in terms of type of the electrolyte with the help of the values known in the literature.

The values are given in Table 1.
### TABLE 1

**Molar Conductance in various solvents.**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Type of the Electrolyte</th>
<th>Molar Conductance (ohm(^{-1}) cm(^2) mole(^{-1}))</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMF</td>
<td>1:1</td>
<td>85</td>
<td>8, 9</td>
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<tr>
<td></td>
<td>1:2</td>
<td>140-170</td>
<td>10, 11</td>
</tr>
<tr>
<td></td>
<td>1:3</td>
<td>200-260</td>
<td>10, 12</td>
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<tr>
<td>DMSO</td>
<td>1:1</td>
<td>37-43</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>70-80</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>1:3</td>
<td>110</td>
<td>15, 16</td>
</tr>
<tr>
<td>Methanol</td>
<td>1:1</td>
<td>100</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>160-220</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>1:3</td>
<td>290-350</td>
<td>18</td>
</tr>
</tbody>
</table>
INFRARED SPECTRA:

The infrared spectra of the complexes and the ligands in nujol mull were recorded on Perkin-Elmer infracord spectrometer or Beckman IR-20 Spectrophotometer or Carlzeiss U.R.-10 Spectrophotometer.

ULTRA-VIOLET SPECTRA:

The Ultra-violet spectra of the complexes and the ligands were measured with a Hilger UVEPLK, H-700, using quartz cells. The weighed samples were dissolved in the solvent employed and the solutions were diluted to the required strength. All the measurements were carried out at room temperature.
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