CHAPTER - 3
CHAPTER - III

SYNTHESIS ELEMENTAL ANALYSIS
AND MICROBIAL STUDIES

Introduction

As indicated in chapter 1, four novel ligands were synthesized and their elemental analysis was carried out, nine others were used to prepare complexes with Ni (II), Cu (II) and Co (II) with 3,3'-dipyridine and 4, 7, -dimethyl -1, 10 phenanthroline which were then subjected to elemental analysis. The following lines describe the nature of reagents used and the procedures followed for the syntheses, elemental analysis and microbial studies.

3.1 Synthesis of ligands

All the reagents used were of analytical purity grade. The four new ligands were synthesized by following the usual practice of preparing azomethines by the condensation of a primary amine with an active carbon. It is known\(^1\) that Schiff's bases are formed via carbinolamine as intermediate, which, on loss of a water molecule, yield the desired base. The process for the synthesis of the four ligands is described in the following sub-sections.

3.1.1 Synthesis of 2 - hydroxy benzalidine anthranilic and (HBAA)

6.9 g (0.05 mole) of anthranilic acid was dissolved in minimum amount of ethanol and mixed with a 5.32 ml (0.05mole) of salicylaldehyde in 25 ml
ethanolic solution. The mixed solution was refluxed over a water bath for one hour. It was allowed to stand overnight. Orange red crystals were obtained. The crystals were filtered off and washed with water several times. After final washing with ethanol, the crystals were dried.

3.1.2 Synthesis of 2-hydroxybenzalidine – 2-amino phenol (HBAT)

Ethanolic solution of (0.05 mole) of aminophenol in ethanol and (.05 mole) of anthranilic acid also in ethanol were mixed together, and refluxed on a water bath for over one hour. Dark yellow crystals so obtained were filtered and washed with alcohol and some ether. They were finally recrystallised from ethanol.

3.1.3 Synthesis of diphenylamine –2, 2-dicarboxylic acid (DPDA)

0.05 mole of each anthranilic and o-chlorobenzoic acid respectively were taken in a flask fitted with a condenser. Water was added to make the solution aqueous and the solution was neutralized with potassium carbonate. The mixture so obtained was refluxed on a water bath for about five hours. Animal charcoal was added to decolorize the solution and the contents boiled and filtered under suction. The filtrate was acidified with dilute hydrochloric acid and then allowed to cool. A solid was precipitated. It was filtered, washed and recrystallised from alcohol.
3.1.4 Synthesis of 2,2'-dithiosalicylic acid (DTSA)

10g of thiosalicylic acid was suspended in water and reacted with 2g of copper sulphate solution acidified with 2 ml g 4 N hydrochloric acid while stirring the mixture for about an hour gave a crystalline precipitate. After filtration, the crystals were recrystallised from 95% acetone.

3.2 Synthesis of ternary complexes

The complexes were synthesized by the method due to Walton et al\textsuperscript{2,3} and Musumeci et al\textsuperscript{4,7} Thus, one of the following two procedures was followed for the purpose. For purposes of calculation of 2x10\textsuperscript{-3} moles of ligands, metal salts etc., the molecular weight of the substance was divided by 5000 and the value taken in grams.

Procedure I

The equimolar (2x10\textsuperscript{-3}M) amounts of the two ligands (one acidic and other neutral base) were dissolved separately in aqueous / alcoholic / acetonic solutions and were mixed together while stirred briskly. The metal acetate in the same molar proportion (2x10\textsuperscript{-3}M) dissolved in ethanol was the added slowly with constant stirring and shaking. One was careful to maintain the pH between 5 and 6 by addition of alcoholic ammonia solution.

The mixed well stirred solution was heated on a water bath for about an hour and then cooled. A precipitate separated, the solution was filtered and the precipitate washed with distilled water / benzene / acetone / ether and dried in a vacuum dessicator over fused CaCl\textsubscript{2} / P\textsubscript{4}O\textsubscript{10}. 
Procedure II

A solution of the acid was prepared in ethanol and mixed with on aqueous solution of metal acetate in the pre-determined proportion to get a metal (II) dicarboxylate solution. It was subjected to evaporation until minute crystals separated. After washing the crystals with a mixture of 50% ethanol – diethylether, they were dried in vacuum over anhydrous aluminum chloride at the room temperature

The aqueous acetonic solution of the simple complex (metal (II) – dicarboxylate) was added to the equimolar solution of the other ligand i.e. the base in alcohol. The complex was precipitated. It was washed with a 50% solution of acetone in water, benzene and acetone in the order stated and then dried at the room temperature under reduced pressure.

3.2.01 Synthesis of M (dipy.) TDPA complexes

A solution of 0.0122g dipyridine in 25 ml ethanol was added to 25 ml g ethanolic solution of 0.3564 g TDPA with brisk stirring. Procedure I was followed. To this solution an alcoholic solution of metal acetate [0.3993g of Cu (II) acetate monohydrate / 0.4980 g of Co (II) acetate tetrahydrate or 0.4976 g Ni (II) acetate tetrahydrate was slowly added attended by constant stirring by means of a magnetic stirrer. The precipitate was digested over a water bath, filtered under suction and washed with water, acetone, benzene alcohol and ether in the order stated. It was finally dried in vacuum over P₄O₁₀.
3.2.02 Synthesis of M (dipy) HBAA complexes

Procedure I was found suitable for the preparation of this complex. 0.3122g of 3,3'-dipyridine in alcohol, 0.4820g of HBAA also in alcoholic solution, and equimolar anions (2x10^{-3}M) of the metal acetate were mixed together accompanied by constant stirring. The pH of the solution was maintained between 5.0 and 6.0 by addition of alcoholic ammonia. The precipitate was digested over a water bath, filtered washed with 1:1 water acetone mixture, alcohol, benzene and then with ether. The washed precipitate was dried over P_4O_{10} in vacuum dessicator.

3.2.03 Synthesis M(dipy.) DTSA complexes

0.61 28g of DTSA in 25ml alcohol and 0.3122g of 3,3' – dipyridine also in alcohol were mixed together with constant stirring. Equimolar amounts of respective metal acetate solution with pH in the range of 5.0 to 6.0 was mixed with constant stirring. The precipitate, so obtained was digested on a water bath, filtered and washed with water, acetone, and benzene and then ether. It was dried in a vacuum dessicator at over phosphorus pentoxide.

3.2.04 Synthesis of M(dipy) TDAA complexes

Procedure II was followed in this case. A solution of TDAA (0.3002g) in alcohol was added to equimolar solution (2x10^{-3}M) of 0.3992 g Cu (II) acetate monohydrate / 0.4976g of Ni (II) acetate tetra hydrate / 0.4980 g Co (II) acetate tetra hydrate to get the corresponding metal dicarboxylate. The solution was evaporated to separate the minute crystals. These were filtered, washed with alcohol and ether and dried over P_4O_{10} in a vacuum dessicator. The boiling
suspension of the crystals was mixed with \(2 \times 10^{-3}\)M solution of 3,3'-dipyridine. The precipitate obtained was filtered, washed and dried as usual over \(\text{P}_2\text{O}_{10}\) at the room temperature.

3.2.05 Synthesis of M – (dipy) MBA complexes

As per procedure I, 0.3082g of MBA in 25 ml acetone and to 0.5122 of 3,3 dipyridine in 25 ml of ethanol were mixed together with constant stirring keeping the pH in the range of 5.0 – 6.0. An aqueous acetonic (1:1) solution (2.0 \(\times 10^{-3}\) M) of the corresponding metal acetate hydrate was added while still stirring the solution. The precipitate so obtained was digested an a water bath, filtered, washed with water, acetone benzene alcohol and ether in the stated order and then dried in vacuum over fused \(\text{CaCl}_2\) at the room temperature.

3.2.06 Synthesis of M- (dipy) DTPA complexes

Procedure II was found suitable for the preparation of these ternary complexes. 0.3122 g of 3,3'-dipyridine was added to a warm solution of dithiopropionates prepared by mixing equimolar amounts of metal acetate and DTPA in alcohol. The procedure was accompanied by constant stirring. The colored precipitate was washed as usual with water, acetone, alcohol, benzene and then with ether. It was washed under suction over fused calcium chloride in a vacuum desiccator.

3.2.07 Synthesis of M- (dipy.) DNSA complexes

Following procedure I, 0.4920 g of DNSA in ethanol and 0.3122g of dipyridine also in ethanol were mixed together with constant stirring. The pH of
the solutions was maintained in the range of 5.0 and 6.0 by ethanolic ammonia. The corresponding metal (II) acetate solution in ethanol was added slowly with constant stirring. A parrot green Cu (II) complex, dark yellow Co (II) complex and green Ni (II) complex precipitate obtained was washed successively with different solvents and dried under reduced pressure in a vacuum dessicator.

3.2.08 Synthesis Of M- (dipy) DBSA complexes

Here again the procedure I was found advantageous. 0.5918 g of DBSA and 0.3122 g of 3,3'-dipyridine in ethanolic solutions were mixed vigorously with equimolar amount the metal acetate (2x10^{-3}) in ethanol solution. The pH was not allowed go out of 5.0 to 6.0 range. The precipitate was digested on water bath. filtered, washed as usual, with a number of solvents. The greenish yellow [copper ternary complex], yellow [Co (II) ternary complex] and green [Ni (II) ternary complex] was dried under suction over P_{4}O_{10} in a vacuum dessicator.

3.2.09 Synthesis of M- (dipy) (HNA) complexes

0.3762 of HNA dissolved in minimum volume of acetone was mixed with 0.3122 g 3.3'-dipyridine in alcohol. The pH was brought in the range of 5.0 and 6.0 sand 2x10^{-3} M of the metal was added. Coloured precipitate obtained was digested on a water bath, filtered, washed with water, acetone, benzene and finally with ether. The crystals were then dried at the room temperature under reduced pressure in a vacuum dessicator over P_{4}O_{10}.

3.2.10 Synthesis of M-(dipy) DPDC complexes

Following procedure II, 0.5140 g of DPDC in alcohol 0.3992 g of Cu (II) acetate monohydrate / 0.4976 g Ni (II) acetate monohydrate also in alcohol were
mixed together, heated on a water bath for evaporation. Crystals of metal dicarboxylate separated. To the suspension of dicarboxylate, 2x10^{-3} M solution of 3,3'-dipyridine (0.3122 g) in alcohol was added to get the crystalline precipitate. It was filtered, washed successively with water, acetone and ether. It was dried in a vacuum dissicator over P_{4}O_{10} at the room temperature.

3.2.11 Synthesis of M-(dipy) HBAT complexes

0.4580 g of HBAT was dissolved in alcohol and the pH range of the solution was brought in the range of 5 and 6 by adding ethonolic ammonia. To this solution, 2x10^{-3} Moles of the metal acetate as well as 3,3'-dipyridine were added. Brick red / black / dark brown precipitate was obtained respectively the precipitate was filtered and washed with benzene, alcohol and then ether. The precipitate was finally dried in a vacuum dessicator under reduced pressure over P_{4}O_{10}.

3.2.12 Synthesis of M-(dipy) PDA complexes

2x10^{-3} dicarboxylate of the three metals prepared as per procedure II were separately dissolved in alcohol and treated with 0.3122 g of 3,3'-dipyridine while maintaining the pH in the range of 5 and 6. The solution was washed, stirred and filtered. The filtrate, on evaporation, yielded blue / blue green / pink crystal for Cu (II) / Ni (II) / Co (II) ternary complex respectively. The crystals were washed successively with water, dried under reduced pressure in a vacuum dessicator.

3.2.13 Synthesis of Cu-dipy IMDA complex

Sodium salt of IMDA (0.2662 g), 0.3122 g of 3,3'-dipyridine and 0.3992 g of Cu (II) acetate monohydrate were mixed together in alcohol. Deep blue
crystals were obtained. They were digested on a water bath, filtered, washed with water acetone, benzene and then with ether. The crystals were dried over \( \text{P}_4\text{O}_{10} \) under reduced pressure in a vacuum dessicator.

3.2.14 Synthesis of Copper (Phen) DTPA complex

0.4202 g of DTPA in ethanol, phenanthroline (Phen) in acetone and the resultant solution was mixed with 0.3992 g of (all concentrations 2x10\(^{-3}\) m) of Cu (II) acetate monohydrate while keeping the pH between 5.0 and 6.0. A green precipitate was obtained. It was digested on a water bath, cooled, filtered and washed with water, alcohol, acetone, benzene and then ether. It was dried in a vacuum dessicator at the room temperature and reduced pressure over anhydrous CaCl\(_2\).

3.2.15 Synthesis of M-(phen) HBAA complexes

Procedure I was followed. 0.4820 g of HBAA in alcohol, 0.4164 g of (phen) in acetone and alcoholic solution of 2.0x10\(^{-3}\) mole of metal acetate in alcoholic solution were mixed gradually accompanied by constant stirring while maintaining the pH between 5 and 6. The precipitate, brown in each case, was digested on a water bath, washed, with solvents as in 3.3.14 and finally dried.

3.2.16 Synthesis of M (phen) DTSA complexes

2x10\(^{-3}\) moles of DTSA in alcohol and (phen) in acetone were mixed together with constant stirring. Metal acetate (2x10\(^{-3}\) moles) in alcohol was added which keeping the pH between 5 and 6. Light green/violet precipitate obtained
for Cu (II)/ Ni (II) / Co (II) ternary complexes was digested on a water bath cooled, filtered and washed and dried as in 3.2.14

3.2.17 Synthesis of M- (phen.) MBA complexes

0.3028 g of MBA, m ethanol and 0.4164 g of 4,7-dimethyl-1. 10-phenanthroline were mixed with constant stirring. Maintaining the pH between 5 and 6, 0.3992 g of Cu (II) acetate monohydrate/0.4980 g of Co (II) acetate monohydrate /0.4976 g of Ni (II) acetate tetrahydrate was added slowly to the mixed ligand solution. A yellow/ dark yellow/ light green precipitate was obtained for Cu (II)/Co (II)/Ni (II) ternary complex. It was digested on a water bath, cooled, filtered, washed with water, alcohol, acetone and then ether. It was dried over anhydrous CaCl₂ in a vacuum dissipator under reduced pressure.

3.2.18 Preparation of M- (phen) DNSA complexes

2x10⁻³ moles of DNSA in alcohol solution and (phen) in acetone solution were mixed together accompanied by constant stirring. The pH was kept between 5 and 6 and equimolar concentration of the corresponding metal acetate was added gradually. The precipitate obtained was digested over a water bath, cooled, filtered and washed and dried as in sub-section 3.2.17.

3.2.19 Preparation for M- (phen.) DBSA complexes

0.4164g of 4,7- dimethyl-1, 10- phenanthroline (phen) in acetone and equimolar amount of 3,5- dibromosalicylic acid (DBSA) in alcohol were mixed together gradually accompanied by constant stirring. Alcohol i.e. ammonia was added to maintain pH between 5 and 6 and on ethanolic solution of 2.0x10⁻³
moles of the metal acetate was added again with constant stirring. Light green/pink/green crystalline precipitate was obtained for Cu (II)/ Co (II)/ Ni (II)/ ternary complex. The precipitate was digested washed and dried as sub-section 3.2.17.

3.2.20 Synthesis of M-(phen) HBAT complexes

Procedure II was followed. 0.002 moles of HBAT and equimolar amount of metal acetate were mixed in minimum volume of ethanol. The solution was stirred vigorously and cooled in a water bath. The crystals of metal HBAT salt were obtained. The crystals were separated, dissolved in alcohol and 0.002 moles (0.4164 g) of (phen) in ethanol was added with constant stirring.

The precipitate obtained was digested over a water bath, cooled, filtered and washed with water, alcohol and then ether. It was dried over P₄O₁₀ in a vacuum dissipator.

3.2.21 Synthesis of M- PDA complexes

Procedure II was followed and 0.002 moles of metal acetate and PDA were dissolved in ethanol separately. The solutions of (phen) and PDA were mixed and stirred thoroughly keeping the pH of the ligand mixture solution between 5 and 6. The metal acetate solution was added with constant stirring. Blue/Pink/ light green precipitate was obtained for Cu (II)/ Co (II)/ Ni (II) ternary complex. The precipitate was digested on a water bath cooled, filtered, washed with water alcohol, acetone and ether in succession and dried as in earlier sub-sections
3.3 Elemental analysis and molecular formula

The purity of the ligands synthesized and the ternary of the complexes of Cu (II), Ni (II) and Co (II) established by TLC and chemical analysis. The molecular formula, in each case, was derived from elemental analysis, TGA and molecular weight determination. The samples were analyzed for C, H, and N by micro analytical technique at the Regional Sophisticated Instrumentation Centre, CDRI, Lucknow, Department of Chemistry, IIT New Delhi and NPL, New Delhi. Tredwells standard method was used for determination of sulphur content in ligands and complexes. Cu (II), Ni (II) and Co (II) content of the complex was determined by gravimetric method as cuprous thiocyanate, Ni-dimethyl glyoximate and Co-dithiocyanate respectively as described by Vogel in his authoritative texts.

The molecular weights of ternary metal complexes were determined by Rast method and cryoscopic method in DMSO using the following relationship.

\[
M = \frac{100X W_2X K_f}{W_1 X \Delta T}
\]

Where

- \(M\) = Molecular weight of the compound
- \(W_1\) = Weight of the solvent
- \(W_2\) = Weight of the compound (solute) whose \(M\) is to be found out.
- \(\Delta T\) = Depression in freezing point (in °K)
- \(K_f\) = Molal depression constant for DMSO = 4.07
The results of elemental analysis legends have been presented in table 3.01 while their physical measurements appear in table 3.02.

Table 3.03 – 3.08 carry the data obtained for ternary complexes of Cu (II), Co(II) and Ni (II). The conductivity measurement, in each case, was carried out on a Toshniwal digital conductivity meter (L01.10A) with a dip type cell at 29 ± 20°C m 10-3 M solution of DMF on DMSA.

3.5 Microbial studies

3.5.1 Introduction

The action of organic compounds used as ligands and their ternary complexes with Cu (II), Co (II) and Ni (II) has been investigated.

In terms of microbial studies, any substances capable of arresting the multiplication of pathogens are called ‘static’ while those capable of killing them are called ‘cidal’. In fact, in general, most if not all, ‘static’ substances become ‘cidal’ if concentration and/or time of exposure to substance is enhanced.

On the formation of neutral complexes such as those prepared during the present investigations, the microbial activity of the ligand appears to register an increase probably due to the greater liposolubility of the complex. Presumably, the presence of metal ion facilitates the migration of ligand across the cell membranes. If not, the metal itself must possess toxic characteristics. In the latter case, the coordinated ligand acts as a carrier across the membranes.

A number of chelates \(^{10-14}\) of metals such as copper, cobalt, nickel, iron, manganese, magnesium, zinc and gold are found in the biological systems. N,
**TABLE – 3.01**

ELEMENT ANALYSIS RESULTS OF SYNTHESIZED ORGANIC LIGANDS.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>% Analysis founds/(Calculated)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>HBAA</td>
<td>78.03 / (77.36)</td>
</tr>
<tr>
<td>HBAT</td>
<td>67.01 / (68.12)</td>
</tr>
<tr>
<td>DPDC</td>
<td>64.78 / (65.37)</td>
</tr>
<tr>
<td>DTSA</td>
<td>55.09 / (54.84)</td>
</tr>
</tbody>
</table>

**TABLE – 3.02**

PHYSICAL MEASUREMENTS OF SYNTHESIZED ORGANIC LIGANDS.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Colour</th>
<th>Melting Point °C</th>
<th>Soluble in formula</th>
<th>Molecular</th>
<th>Molecular Weight Found (Calculated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HBAA</td>
<td>Orange-red</td>
<td>196°C</td>
<td>Et &amp; DMF</td>
<td>C_{14}H_{11}NO_{3}</td>
<td>225 / (217)</td>
</tr>
<tr>
<td>HBAT</td>
<td>Dark yellow</td>
<td>135°C</td>
<td>Ac, M, Et &amp; DMF</td>
<td>C_{13}H_{11}NSO</td>
<td>235 / (229)</td>
</tr>
<tr>
<td>DPDC</td>
<td>White</td>
<td>148°C</td>
<td>A, Ac, Et &amp; Gl</td>
<td>C_{14}H_{11}NO_{4}</td>
<td>253 / (257)</td>
</tr>
<tr>
<td>DTSA</td>
<td>White</td>
<td>287°C</td>
<td>M, Et, Ac, Gl, DMF &amp; DMSO</td>
<td>C_{14}H_{10}N_{2}O_{4}</td>
<td>310 / (306)</td>
</tr>
</tbody>
</table>

(Et- Ethanol, Ac – Acetone, Et– Ether, Gl – propylene glycol, M – Methanol, DMF – dimethyl formamide, DMSO – Dimethy sulfoxide)
<table>
<thead>
<tr>
<th>Compounds</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
<th>Cu</th>
</tr>
</thead>
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<tr>
<td>Cu (dipy.) TDPA.H_2O</td>
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<td>4.35</td>
<td>6.92</td>
<td>7.92</td>
<td>15.25</td>
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<tr>
<td>Cu (dipy.) MBA</td>
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<td>3.23</td>
<td>7.60</td>
<td>8.71</td>
<td>16.98</td>
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<td>Cu (dipy.) TDAA.H_2O</td>
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<td>3.63</td>
<td>7.37</td>
<td>8.40</td>
<td>16.36</td>
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<tr>
<td>Cu (dipy.) DTSA</td>
<td>55.06</td>
<td>3.05</td>
<td>5.42</td>
<td>12.01</td>
<td>12.04</td>
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<td>15.67</td>
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<td>Cu (dipy.) HBAA.H_2O</td>
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<td>3.99</td>
<td>8.92</td>
<td>-</td>
<td>13.23</td>
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<td>4.09</td>
<td>8.97</td>
<td>6.89</td>
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<td>45.65</td>
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<td>12.40</td>
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<td>14.29</td>
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<td>Cu (dipy.) DBSA</td>
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<td>2.01</td>
<td>5.63</td>
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<td>12.28</td>
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<tr>
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<td>7.02</td>
<td>-</td>
<td>15.75</td>
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<td>12.93</td>
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<td>3.75</td>
<td>6.72</td>
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<td>15.02</td>
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<tr>
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<td>58.42</td>
<td>3.42</td>
<td>5.01</td>
<td>11.18</td>
<td>10.92</td>
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<tr>
<td>Cu (phen.) DTPA</td>
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<td>4.10</td>
<td>5.92</td>
<td>13.21</td>
<td>13.30</td>
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<tr>
<td>Cu (phen.) PDA.H_2O</td>
<td>55.30</td>
<td>3.81</td>
<td>9.20</td>
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<td>14.01</td>
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<tr>
<td>Cu (phen.) HBAA.H_2O</td>
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<td>4.25</td>
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<td>11.99</td>
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<td>5.92</td>
<td>10.52</td>
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<tr>
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<td>2.92</td>
<td>11.19</td>
<td>-</td>
<td>12.69</td>
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<tr>
<td>Cu (phen.) DBSA</td>
<td>44.42</td>
<td>2.39</td>
<td>4.87</td>
<td>-</td>
<td>11.19</td>
</tr>
<tr>
<td>Compounds</td>
<td>Colour</td>
<td>Decomposition Temp. (°C)</td>
<td>Solution in</td>
<td>Molar Conductance (Ohm⁻¹ Cm² mol⁻¹)</td>
<td>Molecular Formula</td>
</tr>
<tr>
<td>------------------</td>
<td>-------------------</td>
<td>--------------------------</td>
<td>---------------------</td>
<td>-------------------------------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>Cu (dipy.) TDPA.H₂O</td>
<td>Blue</td>
<td>206</td>
<td>Gl, DMF &amp; DMSO</td>
<td>18.55</td>
<td>Cu (C₁₈H₁₈O₄N₂S)</td>
</tr>
<tr>
<td>Cu (dipy.) MBA</td>
<td>Grey</td>
<td>345</td>
<td>M &amp; DMF</td>
<td>18.89</td>
<td>Cu (C₁₇H₁₂O₃N₂S)</td>
</tr>
<tr>
<td>Cu (dipy.) TDAA.H₂O</td>
<td>Light green</td>
<td>210</td>
<td>M, Gl, DMF &amp; DMSO</td>
<td>13.45</td>
<td>Cu (C₂₄H₁₄O₂N₂S)</td>
</tr>
<tr>
<td>Cu (dipy.) DTSA</td>
<td>Green</td>
<td>289</td>
<td>Gl, DMF 7 DMSO</td>
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<td>Cu (C₁₈H₁₆O₄N₂S₂)</td>
</tr>
<tr>
<td>Cu (dipy.) DTPA</td>
<td>Light blue</td>
<td>205</td>
<td>M, Gl, DMF &amp; DMSO</td>
<td>18.38</td>
<td>Cu (C₁₇H₁₃O₄N₃S)</td>
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<tr>
<td>Cu (dipy.) PDA.H₂O</td>
<td>Blue</td>
<td>260</td>
<td>M, Gl, DMF &amp; DMSO</td>
<td>18.80</td>
<td>Cu (C₁₇H₁₃O₅N₃)</td>
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<td>Cu (dipy.) HBAA.H₂O</td>
<td>Light green</td>
<td>321</td>
<td>DMF &amp; DMSO</td>
<td>19.31</td>
<td>Cu (C₂₃H₁₂O₂N₃S)</td>
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<td>Cu (dipy.) HBAT.H₂O</td>
<td>Brick red</td>
<td>271</td>
<td>M, Gl, DMF &amp; DMSO</td>
<td>11.62</td>
<td>Cu (C₁₇H₁₀O₃N₄)</td>
</tr>
<tr>
<td>Cu (dipy.) DNA  S</td>
<td>Parrot green</td>
<td>269</td>
<td>M, Gl, DMF &amp; DMSO</td>
<td>12.10</td>
<td>Cu (C₁₇H₁₀O₃N₄Br₂)</td>
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<tr>
<td>Cu (dipy.) DBSA</td>
<td>Greenish yellow</td>
<td>249</td>
<td>M, Gl, DMF &amp; DMSO</td>
<td>19.64</td>
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<td>M, Gl, DMF &amp; DMSO</td>
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<td>Cu (dipy.) IMDA.H₂O</td>
<td>Indigo blue</td>
<td>189</td>
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<td>Cu (C₂₄H₁₈O₃N₃S)</td>
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<td>Cu (dipy.) DPDC.H₂O</td>
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<td>242</td>
<td>M</td>
<td>7.35</td>
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<td>M, DMF, DMSO, &amp; b</td>
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<td>Cu (C₂₁H₁₄O₃N₄Br₂)</td>
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<tr>
<td>Compounds</td>
<td>C</td>
<td>H</td>
<td>N</td>
<td>S</td>
<td>Co</td>
</tr>
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<td>---------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
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<tr>
<td>Co (dipy.) TDPA.H₂O</td>
<td>46.80 / (46.92)</td>
<td>4.25 / (4.44)</td>
<td>6.90 / (6.86)</td>
<td>7.68 / (7.83)</td>
<td>14.32 / (14.40)</td>
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<tr>
<td>Co (dipy.) MBA</td>
<td>55.62 / (55.56)</td>
<td>3.27 / (3.30)</td>
<td>7.72 / (7.64)</td>
<td>8.77 / (8.73)</td>
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</tr>
<tr>
<td>Co (dipy.) TDAA.H₂O</td>
<td>49.90 / (49.87)</td>
<td>4.32 / (4.20)</td>
<td>6.57 / (6.46)</td>
<td>7.42 / (7.39)</td>
<td>13.53 / (13.61)</td>
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<tr>
<td>Co (dipy.) DTSA</td>
<td>55.42 / (55.46)</td>
<td>3.17 / (3.11)</td>
<td>5.42 / (5.41)</td>
<td>12.25 / (12.35)</td>
<td>11.42 / (11.35)</td>
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<tr>
<td>Co (dipy.) DTPA</td>
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<td>4.01 / (3.82)</td>
<td>6.58 / (6.63)</td>
<td>15.20 / (15.15)</td>
<td>13.83 / (13.92)</td>
</tr>
<tr>
<td>Co (dipy.) PDA.H₂O</td>
<td>51.25 / (51.23)</td>
<td>3.27 / (3.30)</td>
<td>10.62 / (10.58)</td>
<td>-</td>
<td>14.69 / (14.80)</td>
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<tr>
<td>Co (dipy.) HBAA.H₂O</td>
<td>70.06 / (60.99)</td>
<td>3.99 / (4.06)</td>
<td>8.82 / (8.92)</td>
<td>-</td>
<td>12.58 / (12.48)</td>
</tr>
<tr>
<td>Co (dipy.) HBAT.H₂O</td>
<td>63.30 / (63.26)</td>
<td>4.45 / (4.54)</td>
<td>8.40 / (8.20)</td>
<td>6.12 / (6.25)</td>
<td>11.47 / (11.51)</td>
</tr>
<tr>
<td>Co (dipy.) DNSA</td>
<td>46.14 / (46.26)</td>
<td>2.17 / (2.29)</td>
<td>12.75 / (12.73)</td>
<td>-</td>
<td>13.25 / (13.36)</td>
</tr>
<tr>
<td>Co (dipy.) DBSA</td>
<td>40.01 / (40.08)</td>
<td>2.20 / (1.98)</td>
<td>5.48 / (5.52)</td>
<td>-</td>
<td>11.45 / (11.58)</td>
</tr>
<tr>
<td>Co (dipy.) HNA</td>
<td>62.69 / (62.82)</td>
<td>3.48 / (3.52)</td>
<td>7.12 / (7.00)</td>
<td>-</td>
<td>14.57 / (14.69)</td>
</tr>
<tr>
<td>Co (phen.) HBA₂H₂O</td>
<td>59.01 / (60.11)</td>
<td>3.72 / (3.85)</td>
<td>6.90 / (6.70)</td>
<td>7.59 / (7.65)</td>
<td>14.21 / (14.06)</td>
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<tr>
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<td>4.99 / (4.91)</td>
<td>11.10 / (11.12)</td>
<td>10.27 / (10.31)</td>
</tr>
<tr>
<td>Co (phen.) PDAXH₂O</td>
<td>56.01 / (55.97)</td>
<td>3.78 / (3.85)</td>
<td>9.20 / (9.35)</td>
<td>-</td>
<td>13.00 / (13.09)</td>
</tr>
<tr>
<td>Co (phen.) HBAAH₂O</td>
<td>64.00 / (64.09)</td>
<td>4.48 / (3.54)</td>
<td>8.12 / (8.03)</td>
<td>-</td>
<td>11.29 / (11.24)</td>
</tr>
<tr>
<td>Co (phen.) HBAT.XH₂O</td>
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<td>6.02 / (3.81)</td>
<td>10.75 / (10.73)</td>
<td>8.02 / (8.17)</td>
<td>14.99 / (15.02)</td>
</tr>
<tr>
<td>Co (phen.) DNSAXH₂O</td>
<td>51.89 / (51.09)</td>
<td>2.78 / (4.43)</td>
<td>11.45 / (11.38)</td>
<td>-</td>
<td>11.75 / (11.95)</td>
</tr>
<tr>
<td>Co (phen.) DBSXH₂O</td>
<td>44.83 / (44.92)</td>
<td>2.48 / (5.92)</td>
<td>4.91 / (5.00)</td>
<td>-</td>
<td>10.65 / (10.50)</td>
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</table>
### Table - 3.06

**Physical Measurements of Cobalt (II) Complexes.**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Colour</th>
<th>Decomposition Temp. (°C)</th>
<th>Solution in</th>
<th>Molar Conductance (Ohm⁻¹ Cm² mol⁻¹)</th>
<th>Molecular Formula</th>
<th>Molecular weight Found / Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co (dipy.) TDPA H₂O</td>
<td>Pink</td>
<td>222</td>
<td>D, DMSO &amp; B</td>
<td>5.71</td>
<td>Co (C₁₆H₁₆O₅N₂S)</td>
<td>415 / (408)</td>
</tr>
<tr>
<td>Co (dipy.) MBA</td>
<td>Light pink</td>
<td>278</td>
<td>DMF, DMSO, m &amp; B</td>
<td>16.22</td>
<td>Co (C₁₇H₁₂O₅N₂S)</td>
<td>376 / (367)</td>
</tr>
<tr>
<td>Co (dipy.) TDAA·H₂O</td>
<td>Pink</td>
<td>195</td>
<td>M, DMF &amp; B</td>
<td>38.63</td>
<td>Co (C₁₄H₁₄O₅N₂S)</td>
<td>374 / (380)</td>
</tr>
<tr>
<td>Co (dipy.) DTSA</td>
<td>Violet</td>
<td>301</td>
<td>M, DMF, DMSO &amp; B</td>
<td>4.70</td>
<td>Co (C₂₄H₁₆O₄N₂S₂)</td>
<td>502 / (519)</td>
</tr>
<tr>
<td>Co (dipy.) DTPA</td>
<td>Pink</td>
<td>275</td>
<td>DMF &amp; DMSO</td>
<td>38.99</td>
<td>Co (C₁₆H₁₆O₄N₂S₂)</td>
<td>432 / (423)</td>
</tr>
<tr>
<td>Co (dipy.) PDA·H₂O</td>
<td>Light pink</td>
<td>284</td>
<td>M, G, DMF, DMSO &amp; B</td>
<td>13.15</td>
<td>Co (C₁₁H₁₃O₅N₃)</td>
<td>389 / (398)</td>
</tr>
<tr>
<td>Co (dipy.) HBAA·H₂O</td>
<td>Light yellow</td>
<td>279</td>
<td>M, G, DMF &amp; DMSO</td>
<td>23.58</td>
<td>Co (C₂₄H₁₉O₄N₃)</td>
<td>465 / (472)</td>
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<tr>
<td>Co (dipy.) HBAT·H₂O</td>
<td>Black</td>
<td>291</td>
<td>M, G, DMF, DMSO &amp; B</td>
<td>18.60</td>
<td>Co (C₂₃H₁₉O₂N₃S)</td>
<td>462 / (458)</td>
</tr>
<tr>
<td>Co (dipy.) DNSA</td>
<td>Dark yellow</td>
<td>214</td>
<td>M, G, DMF &amp; DMSO</td>
<td>5.10</td>
<td>Co (C₁₇H₁₆O₃N₂Br₂)</td>
<td>451 / (441)</td>
</tr>
<tr>
<td>Co (dipy.) DBSA</td>
<td>Yellow</td>
<td>275</td>
<td>M, G, DMF &amp; DMSO</td>
<td>17.72</td>
<td>Co (C₁₇H₁₆O₃N₂)</td>
<td>490 / (509)</td>
</tr>
<tr>
<td>Co (dipy.) HNA</td>
<td>Brown</td>
<td>300</td>
<td>G, DMF &amp; DMSO</td>
<td>6.20</td>
<td>Co (C₂₁H₁₄O₃N₂)</td>
<td>405 / (401)</td>
</tr>
<tr>
<td>Co (phen.) HBA·2H₂O</td>
<td>Dark yellow</td>
<td>305</td>
<td>M, G, DMF &amp; DMSO</td>
<td>7.40</td>
<td>Co (C₂₄H₂₀O₄N₂S)</td>
<td>440 / (453)</td>
</tr>
<tr>
<td>Co (phen.) DTSA</td>
<td>Violet</td>
<td>220</td>
<td>G, DMF, DMSO &amp; D</td>
<td>7.60</td>
<td>Co (C₂₈H₂₄O₄N₂S₂)</td>
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</tr>
<tr>
<td>Co (phen.) PDA·H₂O</td>
<td>Pink</td>
<td>300</td>
<td>M, G, DMF, DMSO &amp; D</td>
<td>9.82</td>
<td>Co (C₂₁H₁₇O₅N₃)</td>
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</tr>
<tr>
<td>Co (phen.) HBAA·H₂O</td>
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<td>311</td>
<td>M, G, DMF, DMSO &amp; D</td>
<td>6.67</td>
<td>Co (C₂₈H₂₄O₄N₃S)</td>
<td>514 / (524)</td>
</tr>
<tr>
<td>Co (phen.) HBAT·H₂O</td>
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<td>M, G, DMF, DMSO,D &amp; B</td>
<td>6.70</td>
<td>Co (C₂₂H₂₂O₃N₃S)</td>
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<tr>
<td>Co (phen.) DNSA·2H₂O</td>
<td>Orange</td>
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<td>M, G, DMF, DMSO,D &amp; B</td>
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<td>Co (C₂₁H₁₈O₅N₃)</td>
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</tr>
<tr>
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<td>Co (C₂₁H₁₆O₄N₂Br₂)</td>
<td>586 / (595)</td>
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### TABLE – 3.07

ELEMENTAL ANALYSIS OF NICKEL (II) COMPLEXES.

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<th>H</th>
<th>N</th>
<th>S</th>
<th>Ni</th>
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<td>4.22</td>
<td>6.92</td>
<td>7.62</td>
<td>14.12</td>
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<td>7.52</td>
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<td>4.32</td>
<td>6.57</td>
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<td>3.01</td>
<td>5.42</td>
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<td>11.12</td>
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<tr>
<td>Ni (dipy.) DTPA</td>
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<td>3.75</td>
<td>6.58</td>
<td>15.01</td>
<td>13.83</td>
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<tr>
<td>Ni (dipy.) PDA. H₂O</td>
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<td>3.25</td>
<td>10.62</td>
<td>-</td>
<td>14.56</td>
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<td>3.99</td>
<td>8.82</td>
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<td>12.23</td>
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<td>8.40</td>
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<td>12.75</td>
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<td>13.01</td>
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<td>2.47</td>
<td>5.11</td>
<td>-</td>
<td>10.23</td>
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<tr>
<td>Compounds</td>
<td>Colour</td>
<td>Decomposition Temp. (°C)</td>
<td>Solution in</td>
<td>Molar Conductance (Ohm⁻¹ Cm² mol⁻¹)</td>
<td>Molecular Formula</td>
</tr>
<tr>
<td>-------------------</td>
<td>-----------------</td>
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</tr>
<tr>
<td>Ni (dipy ) TDPA H₂O</td>
<td>Sky blue</td>
<td>199</td>
<td>M + B 7 DMF + DMSO</td>
<td>5.71</td>
<td>Ni (C₁₉H₁₈O₅N₂S)</td>
</tr>
<tr>
<td>Ni (dipy ) MBA</td>
<td>Grey</td>
<td>245</td>
<td>DMF, m + B</td>
<td>2.93</td>
<td>Ni (C₁₁H₁₂O₂N₂S)</td>
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<tr>
<td>Ni (dipy ) TDAA H₂O</td>
<td>Blush white</td>
<td>252</td>
<td>M, Gl, DMF, DMSO &amp; D</td>
<td>6.55</td>
<td>Ni (C₁₄H₁₄O₅N₃S)</td>
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<tr>
<td>Ni (dipy ) DTSA</td>
<td>Light blue</td>
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<td>M &amp; B + m</td>
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<td>Ni (C₂₄H₁₅O₄N₂S₂)</td>
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<tr>
<td>Ni (dipy ) DTPA</td>
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<td>217</td>
<td>M, DMF, D &amp; B + m</td>
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<tr>
<td>Ni (dipy ) PDA H₂O</td>
<td>Yellowish-green</td>
<td>295</td>
<td>M, Gl, DMF, DMSO, D&amp;B</td>
<td>12.92</td>
<td>Ni (C₁₇H₁₃O₃N₃)</td>
</tr>
<tr>
<td>Ni (dipy ) HBAA H₂O</td>
<td>Brown</td>
<td>298</td>
<td>M, Gl, DMF, DMSO &amp; D</td>
<td>6.62</td>
<td>Ni (C₂₉H₁₉O₃N₃)</td>
</tr>
<tr>
<td>Ni (dipy ) HBAT H₂O</td>
<td>Dark brown</td>
<td>278</td>
<td>M, Gl, DMF, &amp; DMSO</td>
<td>5.74</td>
<td>Ni (C₂₃H₁₉O₂N₃S)</td>
</tr>
<tr>
<td>Ni (dipy ) DNSA</td>
<td>Parrot green</td>
<td>257</td>
<td>Gl, DMF, DMSO &amp; D</td>
<td>16.35</td>
<td>Ni (C₁₇H₁₀O₇N₄)</td>
</tr>
<tr>
<td>Ni (dipy ) DBSA</td>
<td>Green</td>
<td>295</td>
<td>M, Gl, DMF &amp; DMSO</td>
<td>13.01</td>
<td>Ni (C₁₇H₁₀O₃N₂Br₂)</td>
</tr>
<tr>
<td>Ni (dipy ) HNA</td>
<td>Yellowish-green</td>
<td>208</td>
<td>Gl, DMF &amp; DMSO</td>
<td>12.60</td>
<td>Ni (C₂₁H₁₄O₃N₂)</td>
</tr>
<tr>
<td>Ni (dipy ) DPDC H₂O</td>
<td>Grey</td>
<td>220</td>
<td>DMF, D</td>
<td>11.70</td>
<td>Ni (C₂₃H₁₉O₃N₃)</td>
</tr>
<tr>
<td>Ni (phen ) MBA</td>
<td>Light green</td>
<td>271</td>
<td>M, Gl, DMF, DMSO &amp; D</td>
<td>12.42</td>
<td>Ni (C₂₈H₂₀O₄N₂S₂)</td>
</tr>
<tr>
<td>Ni (phen ) DTSA</td>
<td>Light green</td>
<td>238</td>
<td>M, Gl, DMF, DMSO &amp; D</td>
<td>11.20</td>
<td>Ni (C₂₉H₂₃O₃N₃)</td>
</tr>
<tr>
<td>Ni (phen ) PDA H₂O</td>
<td>Light green</td>
<td>300</td>
<td>M, Gl, DMF, DMSO &amp; D</td>
<td>11.10</td>
<td>Ni (C₂₃H₁₆O₂N₂S₂)</td>
</tr>
<tr>
<td>Ni (phen ) HBAA H₂O</td>
<td>Dark brown</td>
<td>242</td>
<td>M, Gl, DMF, DMSO &amp; D</td>
<td>6.30</td>
<td>Ni (C₂₉H₂₃O₃N₃)</td>
</tr>
<tr>
<td>Ni (phen ) HBAT H₂O</td>
<td>Brown</td>
<td>287</td>
<td>M, Gl, DMF, DMSO, D &amp; B</td>
<td>8.86</td>
<td>Ni (C₂₃H₁₄O₃N₄)</td>
</tr>
<tr>
<td>Ni (phen ) DNSA</td>
<td>Canary-yellow</td>
<td>290</td>
<td>M, Gl, DMF, DMSO &amp; D</td>
<td>47.02</td>
<td>Ni (C₂₃H₁₉O₃N₂Br₂)</td>
</tr>
<tr>
<td>Ni (phen ) DBSA H₂O</td>
<td>Green</td>
<td>215</td>
<td>M, DMF, &amp; DMSO</td>
<td>33.46</td>
<td>Ni (C₂₉H₁₄O₃N₂)</td>
</tr>
</tbody>
</table>
O and S containing metal chelates have been used a bactericide while those of gold with sulpho drugs have been investigated\textsuperscript{15} for the same purpose. A number of other studies\textsuperscript{17-21} detail the bacteriocidal and fungicidal properties of certain organic compounds and metal chelates.

Metal complexes of phenanthroline, bipyridine and tetrapyridine have also been investigated\textsuperscript{22-25} for their biological activity. These complexes exhibit a marked ability to inhibit proliferation of gram +ve and gram -ve bacteria. In these complexes, the ligand are strongly bonded to the metal ions. That means the complex should remain undissociated. Change of metal in the complex cation \(\text{MB}^{n+}\) where B is a ligand such as bipyridine or tetrapyridine and M = Fe /Rm/ Os, Co, Zn, In has not effect on its biological activity but if, for example, bipyridine is replaced by ethylenediamine, there is a measurable change in biological action. We might, therefore, surmise that the complex as a whole and not a fragment is participating. Thus, the mode of action must be physical and any chemical change is ruled out.

According to Albert\textsuperscript{25} the antifungal and antibacterial activity of 8-hydroxyquinoline complexes may be attributed to the presence of coordination centers for metal-ligand chelate linkage.

Metal specific antibacterial and antifungal activity has been supported by a number of workers\textsuperscript{26-29}.

The microbial activity of schiff’s bases is also well studied\textsuperscript{30-31} Similarly, ligands and their complexes have been effective for, anti-carcinogenic, anaesthetic, anti-convulsant, anti-tubercular action\textsuperscript{32-34} and anti-microbial.
The greater activity of metal chelates of thiosemicarbazones compared to ligands only has been reported. The rate of penetration of the ligand complexes on the ligand alone to the microbe has been found to be directly proportional to the lipid solubility of the former. In addition, it has been postulated that there is linear relationship between microbial activity and lipophilic character of the biocidal agent.

McCallan and Wilcoxon and Somers have studied the fungitoxicity in vitro of some inorganic ions.

The vapours of elementary sulphur from sulphur chelates has been held responsible for fungicidal action of the latter. The vapours diffuse in to the spores or mycelia of the fungus owing to their solubility in the constituents, probably lipids, of the cells.

The natural course of hydrogenation/dehydrogenation reaction is disturbed due formation of H₂S.

It is this H₂S which affects the spores and vitality of the fungus. Fe, Cu, Mn, and Zn present in enzymes also bind with sulphur. Consequently the metabolism, as a whole, of the fungi is disorganized and affected.

The comparative study of toxicity of Cu-oxine salicylate and substituted salicylate ternary complex has been carried out by Anjaneyuler and coworkers. It has been theorized that the Cu-ternary complex dissociates to a binary copper-oxine complex which exhibits its toxicity towards fungi by combining and blocking metal binding sites in enzymes.
On the other hand, Block\textsuperscript{46} has postulated that the neutral chelates break up to free oxine which attaches to metal prosthetic group of the enzyme.

Studies\textsuperscript{46-47} have also taken place to investigate the effect of synthesized complex of heterocyclic N and S containing ligands.

The present investigations also cover the study of microbial action of newly synthesized compounds and a number of metal chelates of the aforementioned type on selected bacteria.

**Experimental**

The nutrient solution at pH between 6.5-7.0 was prepared by dissolving 1.5 g of sodium nitrate, 0.5 g of dipotassium hydrogen phosphate, 0.25 g of potassium chloride and 15 g of sucrose in 500 ml of distilled water. 50 ml this solution was taken in different conical flasks and 0.35 g of agar agar (7\%) was added to each one of them. The culture media thus prepared was sterilized for about 15 minutes at 15 lbs pressure and 121\textdegree{}C in an autoclave by moist heat sterilization method \textsuperscript{48}.

25 mg of ligand or ternary complex dissolved in propylene glycol or DMF or DMSO formed the test solution.

**Screening for BIOCIDAL ACTION**

Food poisoned technique i.e. agar diffusion method or serial dilution method was used for the purpose.
5ml of sample solution was thoroughly shaken with warm culture medium at 40 °C to make up the volume to 50 ml. The resultant solution was transferred to two different clean petri-dishes containing a little soil. The petri-dishes were inoculated in an inoculation chamber having ultra violet lamp under aseptic conditions 48-50. Blank observations were made to neglect the effect of environment.

All the petri-dishes were placed in an incubator to 32 °C. A 48-hour period was fixed for observation on growth of bacteria in petri-dishes. This period for fungi was kept at 7 days.

All the substances were screened at 500 ppm concentration for which 25g the substances was dissolved in 50 ml of the culture medium.

**Determination of Minimum Inhibitory Concentration (MIC) values**

After establishing the microbial activity of the species at 500 ppm, it was considered worthwhile to study their action at lower concentrations to work out the MIC values.

The procedure is similar to that followed for 500 ppm described in the subsection 3.5.3. A stock solution of was prepared by dissolving 50 mg of the ligand / chelate in 10 ml of propylene glycol or DMF. Test solutions corresponding to 100, 200, 300, 400 ppm were prepared by mixing 1, 2, 3 and 4 ml respectively of the stock solution in hot culture medium at 40 ± 1 °C and the volume made up to 50 ml in each case.
The specific fungus or bacteria was introduced by the loop of a platinum wire in the petri-dishes for the above set of concentrations. One was careful to sterilize the platinum loop by heating it in an oxidizing flame before use for inoculation of fungus bacteria. The growth of bacteria and fungus was observed for 48-hours and 7 days respectively. The lowest concentration at which the fungi / bacteria was not detectible was identified.

**Fungi and Bacteria tested**

The ligand and complexes were subjected to biological activity on the following fungi and bacteria:

**Fungi:**

(i) *Aspergillus sydowii* Blue

(ii) *Aspergillus flavus* Yellow green

(iii) *Aspergillus niger* Black

(iv) *Aspergillus fumigativ* Dark green

(v) *Aspergillus nidulanse* Green reverse violet

(vi) *Aspergillus terreus* Brown

**Bacteria:**

(i) *Staphylococcus aurous* Gram + ve

(ii) *Escherichia coli* Gram - ve
References


4. S. Musumea And A Seminara Z Anorg Alleg Chem. 433, 297 (1977)


17. R.S. Verma And S.A. Imam, Ind. J. Microbial., 13, 45 (1973)


41. S.E.A. Mecallan And F. Wilcoxon, Contrib. Boyce. Thompson Inst. 6. 479 (1934)


49. F.M. Price And K.E. Sanford, Tissue Culture Ano In Animal, 2, 379 (1976).