CHAPTER - 3
SYNTHESIS OF MIXED LIGAND COMPLEXES
Chapter-3: SYNTHESIS OF MIXED LIGAND COMPLEXES

3.1 Synthesis of diaqua complexes

3.1.1 Preparation of N,N’-bis(2-hydroxyacetophenone)ethylenediamine diaqua nickel(II) Ni(OAcPh-en)·(H₂O)₂

Prepare 0.01 M nickel chloride hexahydrate in alcohol-water mixture (1:1) and 0.01 M N,N’-bis(2-hydroxyacetophenone)ethylenediamine in alcohol-water mixture (1:1). Mix the two solutions and adjust the pH of the solution about 6.5 to 7.0 pH by adding dilute NH₃. Reflux the solution for 1 hour. Pale green and thick precipitate settled at the bottom. The obtained precipitates were quickly filtered and washed well with water, alcohol and ether. Precipitates were dried in air.

Yield: 75 % Melting point: 235 °C

The following diaqua complexes were prepared by above procedure.

1) Mn(OAcPh-en)·(H₂O)₂
   N,N’-bis(2-hydroxyacetophenone)ethylenediaminediaquamanganese(II)
2) Fe(OAcPh-en)·(H₂O)₂
   N,N’-bis(2-hydroxyacetophenone)ethylenediaminediaquaferrous(II)
3) Co(OAcPh-en)·(H₂O)₂
   N,N’-bis(2-hydroxyacetophenone)ethylenediaminediaquacobalt(II)
4) Cu(OAcPh-en)·(H₂O)₂
   N,N’-bis(2-hydroxyacetophenone)ethylenediaminediaaquacopper(II)
5) Zn(OAcPh-en)·(H₂O)₂
   N,N’-bis(2-hydroxyacetophenone)ethylenediaminediaquazinc(II)
6) Mn(OAcPh-opd)·(H₂O)₂
   N,N’-bis(2-hydroxyacetophenone)o-phenylenediaminediaqua manganese(II)
7) Fe(OAcPh-opd)·(H₂O)₂
   N,N’-bis(2-hydroxyacetophenone)o-phenylenediaminediaquaferrous(II)
8) Co(OAcPh-opd)·(H₂O)₂
N,N’-bis(2-hydroxyacetophenone)-o-phenyldiaminediaquacobalt(II)

9) Ni(OAcPh-opd)·(H₂O)₂

N,N’-bis(2-hydroxyacetophenone)-o-phenyldiaminediaquinickel(II)

10) Cu(OAcPh-opd)·(H₂O)₂

N,N’-bis(2-hydroxyacetophenone)-o-phenyldiaminediaquacopper(II)

11) Zn(OAcPh-opd)·(H₂O)₂

N,N’-bis(2-hydroxyacetophenone)-o-phenyldiaminediaquazinc(II)

3.1.2 Preparation of N,N’-bis(2-hydroxynaphthaldehyde)ethylenediamine diaquanickel(II) Ni(ONap-en)·(H₂O)₂

Prepare 0.01 M nickel chloride hexahydrate in alcohol-water mixture (1:1) and 0.01 M N,N’-bis(2-hydroxynaphthaldehyde)ethylenediamine in alcohol-water mixture (1:1). Mix the two solutions and adjust the pH of the solution about 6.5 to 7.0 pH by adding dilute NH₃. Reflux the solution for 1 hour. Pale green and thick precipitate settled at the bottom. The obtained precipitates were quickly filtered and washed well with water, alcohol and ether. Precipitates were dried in air.

Yield: 82 % Melting point: 228 °C

The following diaqua complexes were prepared by above procedure.

1) Mn(ONap-en)·(H₂O)₂

N,N’-bis(2-hydroxynaphthaldehyde)ethylenediaminediaquamanganese(II)

2) Fe(ONap-en)·(H₂O)₂

N,N’-bis(2-hydroxynaphthaldehyde)ethylenediaminediaquaferrous(II)

3) Co(ONap-en)·(H₂O)₂

N,N’-bis(2-hydroxynaphthaldehyde)ethylenediaminediaquacobalt(II)

4) Cu(ONap-en)·(H₂O)₂

N,N’-bis(2-hydroxynaphthaldehyde)ethylenediaminediaquacopper(II)

5) Zn(ONap-en)·(H₂O)₂

N,N’-bis(2-hydroxynaphthaldehyde)ethylenediaminediaquazinc(II)

6) Fe(ONap-opd)·(H₂O)₂
3.2 Synthesis of Mixed-ligand complexes

3.2.1 Preparation of $\text{N,N'-bis(2-hydroxynaphthaldehyde)ethylenediamine bis(4-methoxybenzylidene)ethylenediaminenickel(II)}$ $[\text{Ni(ONap-en)(MeBen-en)}] \cdot \text{H}_2\text{O}$

The preparation of $[\text{Ni(ONap-en)(MeBen-en)}] \cdot \text{H}_2\text{O}$ was carried out by refluxing an ethanoic solution (250ml) of $\text{N,N'-bis(2-hydroxynaphthaldehyde)ethylenediaminediaquaferrous(II)}$ (0.01M) with Neutral bi dentate ligand bis(4-methoxybenzylidene) ethylenediamine (0.01M) for one hour. The solution was then concentrated and cooled in air to overnight. The formed crystals were collected and recrystallized. Finally the crystals were dried in air.

Yield: 77.13 % Melting point: 262 °C

The following Mixed-ligand complexes were prepared by above procedure.

1) $\text{N,N'-bis(2-hydroxynaphthaldehyde)ethylenediaminebis(4-methoxy benzylidene)ethylenediaminemanganese(II)}$ $[\text{Mn(ONap-en)(MeBen-en)}] \cdot \text{H}_2\text{O}$

2) $\text{N,N'-bis(2-hydroxynaphthaldehyde)ethylenediaminebis(4-methoxy benzylidene)ethylenediamineferrous(II)}$ $[\text{Fe(ONap-en)(MeBen-en)}] \cdot \text{H}_2\text{O}$

3) $\text{N,N'-bis(2-hydroxynaphthaldehyde)ethylenediaminebis(4-methoxy benzylidene)ethylenediaminecobalt(II)}$ $[\text{Co(ONap-en)(MeBen-en)}] \cdot \text{H}_2\text{O}$

4) $\text{N,N'-bis(2-hydroxynaphthaldehyde)ethylenediaminebis(4-methoxy benzylidene)ethylenediaminecopper(II)}$
3.2.2 Preparation of N,N’-bis(2-hydroxyacetophenone)ethylenediamine bis(4-methoxybenzylidene) ethylenediaminincopper(II) 
\[
[\text{Cu(ONap-en)(MeBen-en)}]\cdot\text{H}_2\text{O}
\]

5) N,N’-bis(2-hydroxynaphthaldehyde)ethylenediaminebis(4-methoxy benzylidene)ethylenediaminezinc(II) 
\[
[\text{Zn(ONap-en)(MeBen-en)}]\cdot\text{H}_2\text{O}
\]

6) N,N’-bis(2-hydroxynaphthaldehyde)ethylenediaminebis(4-methoxy benzylidene)o-phenylenediamineferrous(II) 
\[
[\text{Fe(ONap-en)(MeBen-opd)}]\cdot\text{H}_2\text{O}
\]

7) N,N’-bis(2-hydroxynaphthaldehyde)ethylenediaminebis(4-methoxy benzylidene)o-phenylenediamineferrous(II) 
\[
[\text{Fe(ONap-en)(MeBen-opd)}]\cdot\text{H}_2\text{O}
\]

8) N,N’-bis(2-hydroxynaphthaldehyde)ethylenediaminebis(4-methoxy benzylidene)o-phenylenediamineferrous(II) 
\[
[\text{Cu(ONap-en)(MeBen-opd)}]\cdot\text{H}_2\text{O}
\]

3.2.2 Preparation of N,N’-bis(2-hydroxyacetophenone)ethylenediamine bis(4-methoxybenzylidene) ethylenediamminecopper(II) 
\[
[\text{Ni(OAcPh-en)(MeBen-en)}]\cdot\text{H}_2\text{O}
\]

The preparation of [Ni(OAcPh-en)(MeBen-en)]·H₂O was carried out by refluxing an ethanoic solution (250ml) of N,N’-bis(2-hydroxyacetophenone) ethylenediaminediaqua nickle(II) (0.01M) with Neutral bi dentate ligand bis(4-methoxybenzylidene) ethylenediamine (0.01M) for one hour. The solution was then concentrated and cooled in air to overnight. The formed crystals were collected and recrystallized. Finally the crystals were dried in air.

Yield: 79.40 % Melting point: 282 °C

The following Mixed-ligand complexes were prepared by above procedure.

1) N,N’-bis(2-hydroxyacetophenone)ethylenediaminebis(4-methoxy benzylidene)ethylenediaminemanganese(II) 
\[
[\text{Mn(OAcPh-en)(MeBen-en)}]\cdot\text{H}_2\text{O}
\]

2) N,N’-bis(2-hydroxyacetophenone)ethylenediaminebis(4-methoxy benzylidene)ethylenediamineferrous(II) 
\[
[\text{Fe(OAcPh-en)(MeBen-en)}]\cdot\text{H}_2\text{O}
\]
3) N,N’-bis(2-hydroxyacetophenone)ethylenediaminebis(4-methoxy benzylidene)ethylenediaminecobalt(II)  
\[\text{Co(OAcPh-en)(MeBen-en)}\cdot\text{H}_2\text{O}\]

4) N,N’-bis(2-hydroxyacetophenone)ethylenediaminebis(4-methoxy benzylidene)ethylenediaminecopper(II)  
\[\text{Cu(OAcPh-en)(MeBen-en)}\cdot\text{H}_2\text{O}\]

5) N,N’-bis(2-hydroxyacetophenone)ethylenediaminebis(4-methoxy benzylidene)ethylenediaminezinc(II)  
\[\text{Zn(OAcPh-en)(MeBen-en)}\cdot\text{H}_2\text{O}\]

6) N,N’-bis(2-hydroxyacetophenone)ethylenediaminebis(4-methoxy benzylidene)phenolinediaminecobalt(II)  
\[\text{Mn(OAcPh-en)(MeBen-opd)}\cdot\text{H}_2\text{O}\]

7) N,N’-bis(2-hydroxyacetophenone)ethylenediaminebis(4-methoxy benzylidene)phenolinediaminecobalt(II)  
\[\text{Co(OAcPh-en)(MeBen-opd)}\cdot\text{H}_2\text{O}\]

8) N,N’-bis(2-hydroxyacetophenone)ethylenediaminebis(4-methoxy benzylidene)phenolinediaminecobalt(II)  
\[\text{Ni(OAcPh-en)(MeBen-opd)}\cdot\text{H}_2\text{O}\]

9) N,N’-bis(2-hydroxyacetophenone)ethylenediaminebis(4-methoxy benzylidene)phenolinediaminecobalt(II)  
\[\text{Cu(OAcPh-en)(MeBen-opd)}\cdot\text{H}_2\text{O}\]

10) N,N’-bis(2-hydroxyacetophenone)ethylenediaminebis(4-methoxy benzylidene)phenolinediaminecobalt(II)  
\[\text{Zn(OAcPh-en)(MeBen-opd)}\cdot\text{H}_2\text{O}\]

11) N,N’-bis(2-hydroxyacetophenone)ethylenediaminebis(4-methoxy benzylidene)phenolinediaminecobalt(II)  
\[\text{Mn(OAcPh-en)(Ben-en)}\cdot\text{H}_2\text{O}\]
13) N,N'-bis(2-hydroxyacetophenone)ethylenediaminebis(benzylidene)ethylenediamineferrous(II) 
   [Fe(OAcPh-en)(Ben-en)]·H₂O

14) N,N'-bis(2-hydroxyacetophenone)ethylenediaminebis(benzylidene)ethylenediaminecobalt(II) 
   [Co(OAcPh-en)(Ben-en)]·H₂O

15) N,N'-bis(2-hydroxyacetophenone)ethylenediaminebis(benzylidene)ethylenediaminenickel(II) 
   [Ni(OAcPh-en)(Ben-en)]·H₂O

16) N,N'-bis(2-hydroxyacetophenone)ethylenediaminebis(benzylidene)ethylenediaminecopper(II) 
   [Cu(OAcPh-en)(Ben-en)]·H₂O

17) N,N'-bis(2-hydroxyacetophenone)ethylenediaminebis(benzylidene)ethylenediaminezinc(II) 
   [Zn(OAcPh-en)(Ben-en)]·H₂O

18) N,N'-bis(2-hydroxyacetophenone)ethylenediaminebis(benzylidene)o-phenylenediaminecobalt(II) 
   [Mn(OAcPh-en)(Ben-opd)]·H₂O

19) N,N'-bis(2-hydroxyacetophenone)ethylenediaminebis(benzylidene)o-phenylenediamineferrous(II) 
   [Fe(OAcPh-en)(Ben-opd)]·H₂O

20) N,N'-bis(2-hydroxyacetophenone)ethylenediaminebis(benzylidene)o-phenylenediaminecobalt(II) 
   [Co(OAcPh-en)(Ben-opd)]·H₂O

21) N,N'-bis(2-hydroxyacetophenone)ethylenediaminebis(benzylidene)o-phenylenediaminenickel(II) 
   [Ni(OAcPh-en)(Ben-opd)]·H₂O

22) N,N'-bis(2-hydroxyacetophenone)ethylenediaminebis(benzylidene)o-phenylenediaminecopper(II) 
   [Cu(OAcPh-en)(Ben-opd)]·H₂O
23) N,N’-bis(2-hydroxyacetophenone)ethylenediaminebis(benzylidene)o-phenylenediaminezinc(II)
   [Zn(OAcPh-en)(Ben-opd)]·H₂O

3.2.3 Preparation of N,N’-bis(2-hydroxyacetophenone)o-phenylenediamine bis(4-methoxybenzylidene)o-phenylenediaminenickel(II)
   [Ni(OAcPh-opd)(MeBen-opd)]·H₂O

The preparation of [Ni(OAcPh-opd)(MeBen-opd)]·H₂O was carried out by refluxing an ethanoic solution (250ml) of N,N’-bis(2-hydroxyacetophenone)o-phenylenediamine diaquanickel(II) (0.01M) with Neutral bi dentate ligand bis(4-methoxybenzylidene)o-phenylenediamine (0.01M) for one hour. The solution was then concentrated and cooled in air to overnight. The formed crystals were collected and recrystallized. Finally the crystals were dried in air. Yield: 76.20 %, Melting point: 240 °C

The following Mixed-ligand complexes were prepared by above procedure.

1) N,N’-bis(2-hydroxyacetophenone)o-phenylenediaminebis(4-methoxy benzylidene)o-phenylenediaminemanganese(II)
   [Mn(OAcPh-opd)(MeBen-opd)]·H₂O
2) N,N’-bis(2-hydroxyacetophenone)o-phenylenediaminebis(4-methoxy benzylidene)o-phenylenediamineferrous(II)
   [Fe(OAcPh-opd)(MeBen-opd)]·H₂O
3) N,N’-bis(2-hydroxyacetophenone)o-phenylenediaminebis(4-methoxy benzylidene)o-phenylenediaminecobalt(II)
   [Co(OAcPh-opd)(MeBen-opd)]·H₂O
4) N,N’-bis(2-hydroxyacetophenone)o-phenylenediaminebis(4-methoxy benzylidene)o-phenylenediaminecopper(II)
   [Cu(OAcPh-opd)(MeBen-opd)]·H₂O
5) N,N’-bis(2-hydroxyacetophenone)o-phenylenediaminebis(4-methoxy benzylidene)o-phenylenediaminezinc(II)
   [Zn(OAcPh-opd)(MeBen-opd)]·H₂O
3.2.4 Preparation of N,N’-bis(2-hydroxynaphthaldehyde) o-phenyline diaminebis(4-methoxybenzylidene) ethylenediaminenickel(II) 

\[ \text{Ni(O\text{Nap-opd})(Me\text{Ben-en})} \cdot \text{H}_2\text{O} \]

The preparation of \[ \text{Ni(O\text{Nap-opd})(Me\text{Ben-en})} \cdot \text{H}_2\text{O} \] was carried out by refluxing an ethanoic solution (250ml) of N,N’-bis(2-hydroxynaphthaldehyde) o-phenylinediaminediaquanickel(II) (0.01M) with Neutral bidentate ligand bis(4-methoxybenzylidene)ethylenediamine (0.01M) for one hour. The solution was then concentrated and cooled in air to overnight. The formed crystals were collected and recrystallized. Finally the crystals were dried in air.

Yield: 72.30%, Melting point: >360 °C

The following Mixed-ligand complexes were prepared by above procedure.

1) N,N’-bis(2-hydroxynaphthaldehyde) o-phenylinediamine bis(4-methoxy benzylidene) ethylenediaminemanganese(II)

\[ \text{[Mn(O\text{Nap-opd})(Me\text{Ben-en})]} \cdot \text{H}_2\text{O} \]

2) N,N’-bis(2-hydroxynaphthaldehyde) o-phenylinediamine bis(4-methoxy benzylidene) ethylenediamineferrous(II)

\[ \text{[Fe(O\text{Nap-opd})(Me\text{Ben-en})]} \cdot \text{H}_2\text{O} \]

3) N,N’-bis(2-hydroxynaphthaldehyde) o-phenylinediamine bis(4-methoxy benzylidene) ethylenediaminecobalt(II)

\[ \text{[Co(O\text{Nap-opd})(Me\text{Ben-en})]} \cdot \text{H}_2\text{O} \]

4) N,N’-bis(2-hydroxynaphthaldehyde) o-phenylinediamine bis(4-methoxy benzylidene) ethylenediaminecopper(II)

\[ \text{[Cu(O\text{Nap-opd})(Me\text{Ben-en})]} \cdot \text{H}_2\text{O} \]

5) N,N’-bis(2-hydroxynaphthaldehyde) o-phenylinediamine bis(4-methoxy benzylidene) ethylenediaminezinc(II)

\[ \text{[Zn(O\text{Nap-opd})(Me\text{Ben-en})]} \cdot \text{H}_2\text{O} \]

6) N,N’-bis(2-hydroxynaphthaldehyde) o-phenylinediamine bis(4-methoxy benzylidene) o-phenylinediaminemanganese(II)

\[ \text{[Mn(O\text{Nap-opd})(Me\text{Ben-opd})]} \cdot \text{H}_2\text{O} \]

7) N,N’-bis(2-hydroxynaphthaldehyde) o-phenylinediamine bis(4-methoxy benzylidene) o-phenylinediamineferrous(II)
[Fe(ONap-opd)(MeBen-opd)]·H₂O
8) N,N’-bis(2-hydroxynaphthaldehyde)o-phenylenediaminebis(4-methoxy benzylidene)o-phenylenediaminecobalt(II)
[Co(ONap-opd)(MeBen-opd)]·H₂O
9) N,N’-bis(2-hydroxynaphthaldehyde)o-phenylenediaminebis(4-methoxy benzylidene)o-phenylenediaminenickel(II)
[Ni(ONap-opd)(MeBen-opd)]·H₂O
10) N,N’-bis(2-hydroxynaphthaldehyde)o-phenylenediaminebis(4-methoxy benzylidene)o-phenylenediaminecopper(II)
[Cu(ONap-opd)(MeBen-opd)]·H₂O
11) N,N’-bis(2-hydroxynaphthaldehyde)o-phenylenediaminebis(4-methoxy benzylidene)o-phenylenediaminezinc(II)
[Zn(ONap-opd)(MeBen-opd)]·H₂O
12) N,N’-bis(2-hydroxynaphthaldehyde)o-phenylenediaminebis (benzylidene)ethylenediaminemanganese(II)
[Mn(ONap-opd)(Ben-en)]·H₂O
13) N,N’-bis(2-hydroxynaphthaldehyde)o-phenylenediaminebis (benzylidene)ethylenediamineferrous(II)
[Fe(ONap-opd)(Ben-en)]·H₂O
14) N,N’-bis(2-hydroxynaphthaldehyde)o-phenylenediaminebis (benzylidene)ethylenediaminecobalt(II)
[Co(ONap-opd)(Ben-en)]·H₂O
15) N,N’-bis(2-hydroxynaphthaldehyde)o-phenylenediaminebis (benzylidene)ethylenediaminenickel(II)
[Ni(ONap-opd)(Ben-en)]·H₂O
16) N,N’-bis(2-hydroxynaphthaldehyde)o-phenylenediaminebis (benzylidene)ethylenediaminecopper(II)
[Cu(ONap-opd)(Ben-en)]·H₂O
17) N,N’-bis(2-hydroxynaphthaldehyde)o-phenylenediaminebis (benzylidene)ethylenediaminezinc(II)
[Zn(ONap-opd)(Ben-en)]·H₂O
Chapter 3

3.3 General properties of the all complexes

All the complexes were found to be crystalline, stable in atmosphere and insoluble in water but soluble in organic solvent like methanol, ethanol and dimethylformamide.