Chapter 3

Experimental
This chapter includes the synthesis of Co(II), Ni(II), Cu(II) and Zn(II) complexes of Schiff bases derived from nucleophilic addition of 4-amino-3-mercapto-6-methyl-5-oxo-1,2,4-triazine, 4-amino-3-mercapto-5-oxo-1,2,4-triazine, 4-amino-5-mercapto-3-methyl-1,2,4-triazole, 4-amino-3-ethyl-5-mercapto-1,2,4-triazole to different aldehydes. The starting material for the preparation of triazines and triazoles was thiocarbohydrazide [204]. Triazines and triazoles were prepared by the reported methods. 4-amino-3-mercapto-5-oxo-1,2,4-triazine (AMOT) and 4-amino-3-mercapto-6-methyl-5-oxo-1,2,4-triazine (AMMOT) were prepared by refluxing thiocarbohydrazide with glyoxylic acid [73] and pyruvic acid respectively [72]. 4-amino-5-mercapto-3-methyl-s-triazole (AMMT) and 4-amino-3-ethyl-5-mercapto-s-triazole (AEMT) were prepared by refluxing thiocarbohydrazide with glacial acetic acid and propionic acid respectively [205, 206]. All the triazines and triazoles were recrystallized by using water. 1,3-diphenyl-1$H$-pyrazole-4-carboxaldehyde and 3-(4-nitrophenyl)-1-phenyl-1$H$-pyrazole-4-carboxaldehyde were prepared by reported literature methods [207]. Different ligands were then synthesized by condensation of the respective triazines/triazoles with various aldehydes.

3.1 Synthesis of Schiff bases

3.1.1 Schiff bases derived from 4-amino-3-mercapto-6-methyl-5-oxo-1,2,4-triazine with 3-bromo-4-hydroxy-5-methoxybenzaldehyde, 2-chloro-6-fluorobenzaldehyde and 3-(4-nitrophenyl)-1-phenyl-1$H$-pyrazole-4-carboxaldehyde.

4-[(3-bromo-4-hydroxy-5-methoxybenzylidene)-amino]-3-mercapto-6-methyl-5-oxo-1,2,4-triazine ($HL^a$)

To a solution of 4-amino-3-mercapto-6-methyl-5-oxo-1,2,4-triazine (1.030 g, 6.49 mmol) in 10 ml of absolute alcohol, a solution of 3-bromo-4-hydroxy-5-methoxybenzaldehyde (1.5 g, 6.49 mmol) in 10 ml of absolute alcohol was added and the reaction mixture was heated under reflux for six hours. The yellowish colored product obtained was filtered, washed several times with cold ethanol, dried and then recrystallized from absolute alcohol.

Yellow; Yield: 81%; m.p. 228-230°C.

4-[(2-chloro-6-fluorobenzylidene)-amino]-3-mercapto-6-methyl-5-oxo-1,2,4-triazine ($HL^b$)

A solution of 4-amino-3-mercapto-6-methyl-5-oxo-1,2,4-triazine (1.00 g, 6.32 mmol) was added to hot solution of 2-chloro-6-fluorobenzaldehyde (1.003 g, 6.32 mmol) in
absolute alcohol and the reaction mixture was refluxed for four hours. The product formed was filtered off, washed with cold ethanol, dried and then recrystallized from absolute alcohol.

Creamish White; Yield 71%; m.p. 222-224°C.

4-[(3-(4-nitrophenyl)-1-phenyl-1H-pyrazol-4-ylmethylene)-amino]-3-mercapto-6-methyl-5-oxo-1,2,4-triazine (HL1c)

A solution of 4-amino-3-mercapto-6-methyl-5-oxo-1,2,4-triazine (1.0g, 6.32 mmol) in absolute alcohol was added to a solution of 3-(4-nitrophenyl)-1-phenyl-1H-pyrazol-4-carboxaldehyde (1.85 g, 6.32 mmol) in absolute alcohol. The reaction mixture was then refluxed for nine hours. The solution was cooled at room temperature and the volume was reduced on a rotary evaporator. The precipitated product was filtered off, washed with cold ethanol and then recrystallized from the same solvent.

Light yellow; Yield 77%; m.p. 244-246°C.

3.1.2 Schiff bases derived from 4-amino-3-mercapto-5-oxo-1,2,4-triazine with 4-cyanobenzaldehyde, 2,4-dichlorobenzaldehyde and 1,3-diphenyl-1H-pyrazole-4-carboxaldehyde

4-[(4-cyanobenzylidene)-amino]-3-mercapto-5-oxo-1,2,4-triazine (HL2a)

1.0 g (6.94 mmol) of 4-amino-3-mercapto-5-oxo-1,2,4-triazine was taken in 20 ml of absolute alcohol. To this, solution of 0.91 g (6.94 mmol) of 4-cyanobenzaldehyde in 20 ml of absolute alcohol was added and refluxed for six hours. The solution was cooled at room temperature and then reduced the volume on a rotary evaporator. The product formed was filtered off, washed with cold ethanol and then recrystallized from absolute alcohol.

Creamish White; Yield 81%; m.p. 238-240°C.

4-(2,4-dichlorobenzylidene)-amino]-3-mercapto-5-oxo-1,2,4-triazine (HL2b)

To a solution of 4-amino-3-mercapto-5-oxo-1,2,4-triazine (1.0 g, 6.94 mmol) in absolute alcohol was added a solution of 2,4-dichlorobenzaldehyde (1.21 g, 6.94 mmol) in absolute alcohol and refluxed for four hours. The volume of the solution was reduced on a rotary evaporator and the product formed was filtered off, washed with ice cold ethanol and recrystallized.

Light Yellow; Yield 84%; m.p. 232-234°C.
4-[(1,3-diphenyl-1H-pyrazol-4-ylmethylene)-amino]-3-mercapto-5-oxo-1,2,4-triazine (HL_{2c})

A solution of 4-amino-3-mercapto-5-oxo-1,2,4-triazine (1.0 g, 6.94 mmol) in absolute alcohol was added to a solution of 1,3-diphenyl-1H-pyrazol-4-carboxaldehyde (1.72g, 6.94 mmol) in absolute alcohol and refluxed for eight hours. The reaction mixture was then cooled at room temperature and reduced the volume of the solution on a rotary evaporator. The yellowish product formed was filtered off, washed with ice cold ethanol and then recrystallized from absolute alcohol.

Yellow; Yield 79%; m.p. 240-242°C.

3.1.3 Schiff bases derived from 4-amino-5-mercapto-3-methyl-1,2,4-triazole and 4-amino-3-ethyl-5-mercapto-1,2,4-triazole with 3-methyl-thiophene-2-aldehyde

4-[(3-methylthiophene-2-ylmethylene)-amino]-5-mercapto-3-methyl-1,2,4-triazole (HL_{3a})

The Schiff base, 4-[(3-methylthiophene-2-ylmethylene)-amino]-5-mercapto-3-methyl-1,2,4-triazole, was synthesized by refluxing a mixture of 3-methylthiophene-2-aldehyde (0.97 g, 7.69 mmol) with 4-amino-5-mercapto-3-methyl-1,2,4-triazole (1.0 g, 7.69 mmol) for 4h using absolute alcohol as a solvent. The reaction mixture was kept overnight at room temperature and the creamish colored product thus formed was filtered off and recrystallized from the same solvent.

Creamish White; Yield 84%; m.p. 210°C.

4-[(3-methylthiophene-2-ylmethylene)-amino]-3-ethyl-5-mercapto-1,2,4-triazole (HL_{3b})

A solution of 3-methylthiophene-2-aldehyde (0.87 g, 6.94 mmol) in 10 ml of absolute alcohol was added to hot solution of 4-amino-3-ethyl-5-mercapto-1,2,4-triazole (1.0 g, 6.94 mmol). The reaction mixture was refluxed for 5h and then kept overnight at room temperature. The solid product formed was filtered, washed with cold ethanol and recrystallized.

Light orange; Yield 83%; m.p. 212-214°C.

3.2 Synthesis of Metal complexes

3.2.1 Metal complexes of Schiff bases derived from 4-amino-3-mercapto-6-methyl-5-oxo-1,2,4-triazine with 3-bromo-4-hydroxy-5-methoxybenzaldehyde, 2-chloro-6-fluorobenzaldehyde and 3-(4-nitrophenyl)-1-phenyl-1H-pyrazole-4-carboxaldehyde

Metal complexes of 4-[(3-bromo-4-hydroxy-5-methoxybenzylidene)-amino]-3-mercapto-6-methyl-5-oxo-1,2,4-triazine (HL_{1a})
**Experimental**

**Metal complexes of HL\textsuperscript{1a} (1:1)**

The 1:1 metal complexes were synthesized by mixing hot ethanolic solutions of the HL\textsuperscript{1a} (0.20 g, 0.54 mmol) to the hot ethanolic solutions of acetates of Co(II) (0.134 g, 0.54 mmol), Ni(II) (0.134 g, 0.54 mmol), Cu(II) (0.107 g, 0.54 mmol) and Zn(II) (0.118 g, 0.54 mmol). The precipitates formed immediately were filtered off, washed successively with warm water, ethanol, acetone and finally dried on water bath.

Co(L\textsuperscript{1a})(OAc).3H\textsubscript{2}O: Brown; Yield: 82%, Ni(L\textsuperscript{1a})(OAc).3H\textsubscript{2}O: Green; Yield: 83%, Cu(L\textsuperscript{1a})(OAc).H\textsubscript{2}O: Brown; Yield: 80%, Zn(L\textsuperscript{1a})(OAc).3H\textsubscript{2}O: Yellow; Yield: 79%

**Metal complexes of HL\textsuperscript{1a} (1:2)**

For the synthesis of 1:2 metal chelates, hot ethanolic solutions of acetates of Co(II) (0.134 g, 0.54 mmol), Ni(II) (0.134 g, 0.54 mmol), Cu(II) (0.107 g, 0.54 mmol) and Zn(II) (0.118 g, 1.08 mmol) were added to the hot ethanolic solutions of the HL\textsuperscript{1a} (0.40 g, 1.08 mmol). The resulting metal complexes were filtered, washed with warm water, ethanol to remove unreacted ligand or metal acetates and finally with acetone and dried on water bath.

Co(L\textsuperscript{1a})\textsubscript{2}.2H\textsubscript{2}O: Light Brown; Yield: 81%, Ni(L\textsuperscript{1a})\textsubscript{2}.2H\textsubscript{2}O: Green; Yield: 84%, Cu(L\textsuperscript{1a})\textsubscript{2}.2H\textsubscript{2}O: Dark Brown; Yield: 79%, Zn(L\textsuperscript{1a})\textsubscript{2}.2H\textsubscript{2}O: Yellow; Yield: 78%

**Metal complexes of 4-\{2-chloro-6-fluorobenzylidene\}-amino]-3-mercapto-6-methyl-5-oxo-1,2,4-triazine (HL\textsuperscript{1b})**

**Metal complexes of HL\textsuperscript{1b} (1:1)**

To the hot ethanolic solutions of the HL\textsuperscript{1b} (0.20 g, 0.67 mmol) were added hot ethanolic solutions of acetates of Co(II) (0.166 g, 0.67 mmol), Ni(II) (0.166 g, 0.67 mmol), Cu(II) (0.08 g, 0.67 mmol) and Zn(II) (0.147 g, 0.67 mmol). The resulting metal complexes were filtered, washed with warm water, ethanol to remove unreacted ligand or metal acetates and finally with acetone and dried on water bath.

Co(L\textsuperscript{1b})(OAc).3H\textsubscript{2}O: Brown; Yield: 85%, Ni(L\textsuperscript{1b})(OAc).3H\textsubscript{2}O: Green; Yield: 86%, Cu(L\textsuperscript{1b})(OAc).H\textsubscript{2}O: Green; Yield: 81%, Zn(L\textsuperscript{1b})(OAc).3H\textsubscript{2}O: Yellow; Yield: 80%

**Metal complexes of HL\textsuperscript{1b} (1:2)**

The 1:2 metal complexes were synthesized by treating hot ethanolic solutions of acetates of Co(II) (0.166 g, 0.67 mmol), Ni(II) (0.166 g, 0.67 mmol), Cu(II) (0.08 g, 0.67 mmol) and Zn(II) (0.147 g, 0.67 mmol) with the hot ethanolic solutions of the
HL\textsuperscript{1b} (0.40 g, 1.34 mmol). The precipitates formed were filtered off, washed with warm water followed by ethanol, acetone and finally dried on water bath.

Co(L\textsuperscript{1b})\textsubscript{2}.2H\textsubscript{2}O: Brown; Yield: 84%, Ni(L\textsuperscript{1b})\textsubscript{2}.2H\textsubscript{2}O: Light green; Yield: 83%, Cu(L\textsuperscript{1b})\textsubscript{2}.2H\textsubscript{2}O: Dark green; Yield: 82%, Zn(L\textsuperscript{1b})\textsubscript{2}.2H\textsubscript{2}O: Yellow; Yield: 81%

Metal complexes of 4-[(3-(4-nitrophenyl)-1-phenyl-1H-pyrazol-4-ylmethylene)-amino]-3-mercapto-6-methyl-5-oxo-1,2,4-triazine (HL\textsuperscript{1c})

Metal complexes of HL\textsuperscript{1c} (1:1)
The hot ethanolic solutions of acetates of Co(II) (0.12 g, 0.46 mmol), Ni(II) (0.12 g, 0.46 mmol), Cu(II) (0.09 g, 0.46 mmol) and Zn(II) (0.11 g, 0.46 mmol) were treated with the hot ethanolic solutions of 0.2 g (0.46 mmol) of HL\textsuperscript{1c}. The metal complexes precipitated out immediately were filtered off, washed with warm water, ethanol and acetone and finally dried.

Co(L\textsuperscript{1c})(OAc).3H\textsubscript{2}O: Grey; Yield: 80%, Ni(L\textsuperscript{1c})(OAc).3H\textsubscript{2}O: Green; Yield: 79%, Cu(L\textsuperscript{1c})(OAc).H\textsubscript{2}O: Yellow; Yield: 84%, Zn(L\textsuperscript{1c})(OAc).3H\textsubscript{2}O: Yellow; Yield: 83%

Metal complexes of HL\textsuperscript{1c} (1:2)
To the hot ethanolic solution of acetates of Co(II) (0.12 g, 0.46 mmol), Ni(II) (0.12 g, 0.46 mmol), Cu(II) (0.09 g, 0.46 mmol) and Zn(II) (0.11 g, 0.46 mmol) were added the hot ethanolic solutions of HL\textsuperscript{1c} (0.4 g, 0.92 mmol). The precipitates formed immediately were filtered, washed with warm water, ethanol followed by acetone and dried.

Co(L\textsuperscript{1c})\textsubscript{2}.2H\textsubscript{2}O: Grey; Yield: 81%, Ni(L\textsuperscript{1c})\textsubscript{2}.2H\textsubscript{2}O: Yellowish Green; Yield: 78%, Cu(L\textsuperscript{1c})\textsubscript{2}.2H\textsubscript{2}O: Yellowish Brown; Yield: 85%, Zn(L\textsuperscript{1c})\textsubscript{2}.2H\textsubscript{2}O: Yellow; Yield: 81%

3.2.2 Metal complexes of Schiff bases derived from 4-amino-3-mercapto-5-oxo-1,2,4-triazine with 4-cyanobenzaldehyde, 2,4-dichlorobenzaldehyde and 1,3-diphenyl-1H-pyrazole-4-carboxaldehyde

Metal complexes of 4-[(4-cyanobenzylidene)-amino]-3-mercapto-5-oxo-1,2,4-triazine (HL\textsuperscript{2a})

Metal complexes of HL\textsuperscript{2a} (1:1)
The solutions of 0.20 g (0.78 mmol) of HL\textsuperscript{2a} dissolved in 10 ml of ethanol were added to hot ethanolic solutions of acetates of Co(II) (0.194 g, 0.78 mmol), Ni(II) (0.193 g, 0.78 mmol), Cu(II) (0.155 g, 0.78 mmol) and Zn(II) (0.171 g, 0.78 mmol) with constant
Experimental

stirring. The precipitated complexes were filtered, washed with warm water, ethanol followed by acetone and dried on water bath.

Co(L²a)(OAc).3H₂O: Brown; Yield: 83%, Ni(L²a)(OAc).3H₂O: Green; Yield: 86%, Cu(L²a)(OAc).H₂O: Yellow; Yield: 80%, Zn(L²a)(OAc).3H₂O: Yellow; Yield: 78%

**Metal complexes of HL²a (1:2)**

The hot ethanolic solutions of acetates of Co(II) (0.194 g, 0.78 mmol), Ni(II) (0.193 g, 0.78 mmol), Cu(II) (0.155 g, 0.78 mmol) and Zn(II) (0.171 g, 0.78 mmol) were added to the hot ethanolic solutions of HL²a (0.40 g, 1.56 mmol). The precipitates formed immediately were filtered off, washed with warm water, ethanol and acetone and finally dried on water bath.

Co(L²a)₂.2H₂O: Brown; Yield: 84%, Ni(L²a)₂.2H₂O: Dark Green; Yield: 85%, Cu(L²a)₂.2H₂O: Yellowish Brown; Yield: 81%, Zn(L²a)₂.2H₂O: Yellow; Yield: 79%

**Metal complexes of 4-[(2,4-dichlorobenzylidene)-amino]-3-mercapto-5-oxo-1,2,4-triazine (HL²b)**

**Metal complexes of HL²b (1:1)**

The solutions of 0.20 g (0.66 mmol) of HL²b dissolved in ethanol were added to hot ethanolic solutions of Co(II) acetate (0.17 g, 0.66 mmol), Ni(II) acetate(0.17 g, 0.66 mmol), Cu(II) acetate (0.13 g, 0.66 mmol) and Zn(II) acetate (0.15 g, 0.66 mmol) respectively. The corresponding solid complexes were filtered, washed several times with warm water, followed by ethanol and acetone and finally dried on water bath.


**Metal complexes of HL²b (1:2)**

The hot ethanolic solutions of Co(II) acetate (0.17 g, 0.66 mmol), Ni(II) acetate (0.17 g, 0.66 mmol), Cu(II) acetate (0.13 g, 0.66 mmol) and Zn(II) acetate (0.15 g, 0.66 mmol) were added to the hot ethanolic solutions of the HL²b (0.40 g, 1.32 mmol) with continuous stirring. The precipitates formed immediately were filtered off, washed with warm water, ethanol followed by acetone and dried.

Co(L²b)₂.2H₂O: Brown; Yield: 83%, Ni(L²b)₂.2H₂O: Dark Green; Yield: 84%, Cu(L²b)₂.2H₂O: Light Brown; Yield: 84%, Zn(L²b)₂.2H₂O: Yellow; Yield: 79%

**Metal complexes of 4-[(1,3-diphenyl-1H-pyrazol-4-ylmethylene)-amino]-3-mercapto-5-oxo-1,2,4-triazine (HL²c)**
Metal complexes of HL\textsuperscript{2c} (1:1)
The metal complexes were synthesized by treating hot ethanolic solutions of acetates of Co(II) (0.13 g, 0.53 mmol), Ni(II) (0.13 g, 0.53 mmol), Cu(II) (0.11 g, 0.53 mmol) and Zn(II) (0.11 g, 0.53 mmol) with solutions of 0.20 g (0.53 mmol) of the HL\textsuperscript{2c}. The precipitates formed immediately were filtered off, washed with warm water, ethanol and acetone and finally dried.
Co(L\textsuperscript{2c})(OAc).3H\textsubscript{2}O: Grey; Yield: 81%, Ni(L\textsuperscript{2c})(OAc).3H\textsubscript{2}O: Green; Yield: 81%, Cu(L\textsuperscript{2c})(OAc).H\textsubscript{2}O: Brown; Yield: 77%, Zn(L\textsuperscript{2c})(OAc).3H\textsubscript{2}O: Yellow; Yield: 80%

Metal complexes of HL\textsuperscript{2c} (1:2)
The hot ethanolic solutions of acetates of Co(II) (0.13 g, 0.53 mmol), Ni(II) (0.13 g, 0.53 mmol), Cu(II) (0.11 g, 0.53 mmol) and Zn(II) (0.11 g, 0.53 mmol) were added to the hot ethanolic solutions of HL\textsuperscript{2c} (0.40 g, 1.06 mmol). The precipitates formed immediately were filtered, washed with warm water, ethanol followed by acetone and dried.
Co(L\textsuperscript{2c})\textsubscript{2}.2H\textsubscript{2}O: Grey; Yield: 84%, Ni(L\textsuperscript{2c})\textsubscript{2}.2H\textsubscript{2}O: Green Yellow; Yield: 83%, Cu(L\textsuperscript{2c})\textsubscript{2}.2H\textsubscript{2}O: Brown; Yield: 79%, Zn(L\textsuperscript{2c})\textsubscript{2}.2H\textsubscript{2}O: Yellow; Yield: 82%

3.2.3 Metal complexes of Schiff bases derived from 4-amino-5-mercapto-3-methyl-1,2,4-triazole and 4-amino-3-ethyl-5-mercapto-1,2,4-triazole with 3-methylthiophene-2-aldehyde

Metal complexes of 4-[(3-methylthiophene-2-ylmethylene)-amino]-5-mercapto-3-methyl-1,2,4-triazole (HL\textsuperscript{3a})

Metal complexes HL\textsuperscript{3a} (1:1)
The solid complexes were prepared by mixing hot ethanolic solutions (20 mL) of the HL\textsuperscript{3a} (0.2 g, 0.84 mmol) with ethanolic solutions (20 mL) of acetates of Co(II) (0.21 g, 0.84 mmol), Ni(II) (0.21 g, 0.84 mmol), Cu(II) (0.17 g, 0.84 mmol) and Zn(II) (0.18 g, 0.84 mmol). The precipitates formed immediately were filtered, washed thoroughly with warm water, ethanol to remove unreacted metal acetates or ligands and finally with acetone and dried on water bath.
Co(L\textsuperscript{3a})(OAc).3H\textsubscript{2}O: Grey; Yield: 84%, Ni(L\textsuperscript{3a})(OAc).3H\textsubscript{2}O: Light Green; Yield: 86%, Cu(L\textsuperscript{3a})(OAc).H\textsubscript{2}O: Green; Yield: 82%, Zn(L\textsuperscript{3a})(OAc).3H\textsubscript{2}O: Creamish; Yield: 83%
Experimental

Metal complexes HL$^{3a}$ (1:2)
Warm aqueous ethanolic solutions (20 mL) of acetates of Co(II) (0.21 g, 0.84 mmol), Ni(II) (0.21 g, 0.84 mmol), Cu(II) (0.17 g, 0.84 mmol) and Zn(II) (0.18 g, 0.84 mmol) were added slowly to the ethanolic solutions of the HL$^{3a}$ (0.4, 1.68 mmol). The complexes precipitated immediately were filtered and purified by washing thoroughly with water, ethanol and finally with acetone and dried on water bath.

Co(L$^{3a}$)$_2$.2H$_2$O: Grey; Yield: 85%, Ni(L$^{3a}$)$_2$.2H$_2$O: Light Green; Yield: 84%, Cu(L$^{3a}$)$_2$.2H$_2$O: Yellowish Green; Yield: 81%, Zn(L$^{3a}$)$_2$.2H$_2$O: Creamish; Yield: 83%

Metal complexes of 4-[(3-methylthiophene-2-ylmethylene)-amino]-3-ethyl-5-mercapto-1,2,4-triazole (HL$^{3b}$)

Metal complexes of HL$^{3b}$ (1:1)
Metal acetates of Co(II) (0.19 g, 0.79 mmol), Ni(II) (0.19 g, 0.79 mmol), Cu(II) (0.16 g, 0.79 mmol) and Zn(II) (0.17 g, 0.79 mmol) dissolved separately in 20 mL of ethanol, were treated with the hot ethanolic solutions of HL$^{3b}$ (0.2 g, 0.79 mmol). The precipitates formed were filtered and purified by washing thoroughly with warm water, ethanol and finally with acetone and dried.

Co(L$^{3b}$)(OAc).3H$_2$O: Grey; Yield: 81%, Ni(L$^{3b}$)(OAc).3H$_2$O: Green; Yield: 82%, Cu(L$^{3b}$)(OAc).H$_2$O: Yellow; Yield: 84%, Zn(L$^{3b}$)(OAc).3H$_2$O: Creamish; Yield: 82%

Metal complexes of HL$^{3b}$ (1:2)
The hot ethanolic solutions (20 mL) of HL$^{3b}$ (0.4 g, 1.58 mmol) were slowly added to the ethanolic solutions (15 mL) of acetates of Co(II) (0.19 g, 0.79 mmol), Ni(II) (0.19 g, 0.79 mmol), Cu(II) (0.16 g, 0.79 mmol) and Zn(II) (0.17 g, 0.79 mmol), which resulted in the immediate precipitation of metal derivatives. The products formed were filtered and washed thoroughly with warm water, ethanol to remove unreacted metal acetates or ligands and finally with acetone and dried on water bath.

Co(L$^{3b}$)$_2$.2H$_2$O: Grey; Yield: 80%, Ni(L$^{3b}$)$_2$.2H$_2$O: Light Green; Yield: 83%, Cu(L$^{3b}$)$_2$.2H$_2$O: Yellowish Green; Yield: 85%, Zn(L$^{3b}$)$_2$.2H$_2$O: Yellow; Yield: 83%