CHAPTER 3

EXPERIMENTAL

3.1 Chemicals

All solvents and reagents were commercially available and used as obtained without further purification unless otherwise stated.

3.2 Spectroscopic Analysis

3.2.1 ^{1}H and ^{13}C NMR Spectroscopic Analysis

^{1}H and ^{13}C NMR spectra were carried out using a Lambda JEOL 400 MHz FT-NMR and ECA 400 MHz FT-NMR Spectrometer using deuterated $CHCl_3$ as solvent for the ligands. Chemical shifts are reported in ppm on δ scale, and the coupling constant is given in Hz.

3.2.2 Infrared Spectroscopic Analysis

The IR absorption spectra of all samples were recorded on Shimadzu 1600 and Perkin Elmer RX1 spectrophotometers. The IR absorption spectra of liquid samples were measured on a KBr cell while the solid samples were dispersed in KBr salt and pressed into thin pellets before measurement. The IR frequency range of interest was 4000 cm^{-1} to 400 cm^{-1}.

3.2.3 Gas Chromatography – Mass Spectroscopic Analysis

Mass spectroscopic analyses were performed on a Hewlett-Packard HP 6890 Series GC System with mass selective indicator and a Shimadzu GCMS system QP5050A.

3.2.4 Melting Point

Melting points were recorded on a Fargo MP-ID melting point apparatus in glass capillaries and are uncorrected.

3.2.5 CHN Analysis

The carbon, hydrogen and nitrogen elemental compositions of samples from this work were obtained from a Perkin Elmer 2400 CHN Elemental Analyzer.

3.3 X-Ray Crystallography

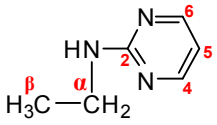
The crystal data were collected from a Bruker SMART APEX CCD diffractometer. The structure was solved by direct method, an approach based on statistical analyses of intensities, using the SHELXTL software package for structure refinement.

3.4 Fluorescence Studies

The fluorescence measurements were carried out in quartz cells, using an Hitachi fluorescence spectrophotometer Model F-2000 at room temperature. All the compounds with the same concentration (å $2.5x10^{-4}$ M) were prepared in methanol and DMSO.

3.5 Preparation of Ligands

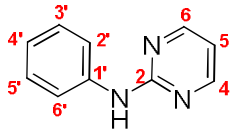
3.5.1 2-N-Ethylaminopyrimidine (L1)



L1

2-Chloropyrimidine (0.7915 g) was added to ethylamine (15.00 cm^3) and heated under reflux with continuous stirring for 4 hours. The mixture was then cooled and a minimum volume of water was added and extracted with ether. Evaporation of solvent gave the crude product, which was then repeatedly washed with chloroform to give the light yellow solid. Yield : 0.6765 g, 86%; m.p : 58 ï 62 ^oC; IR (cm^{-1}) : 3258.34 (ν_{N-H}), 2970.57 (ν_{C-H}), 1595.76 ($\nu_{C=Npym}$), 1534.05 ($\nu_{C=C}$); ^{1}H-NMR δ_H ppm (400MHz, $CDCl_3$) : 8.24, d, 2H (H-4, H-6), *J*=4.9 Hz, 6.47, t, 1H (H-5), *J*=4.9 Hz, 5.17, s, 1H (N-H), 3.45, q, 2H (H-Ŭ), 1.21, t, 3H (H-ƀ), *J*=7.3 Hz; ^{13}C-NMR δ_C ppm (100.4MHz, $CDCl_3$) : 162.29 (C-2), 158.01 (C-4, C-6), 110.37 (C-5), 36.23 (C-Ŭ), 14.89 (C-ƀ); GCMS : Found M^+ = 123.00; $C_6H_9N_3$ requires M^+ = 123.08.

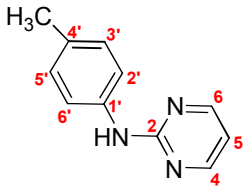
3.5.2 2-N-Anilinopyrimidine (L2)



L2

2-Chloropyrimidine (5.4153 g) was added to aniline (4.50 cm^3) and heated under reflux for 4 hours. Absolute ethanol was used as a solvent and was added dropwise. The reaction mixture was then extracted with ether. The ethereal layer was washed with water and dried over anhydrous sodium sulphate. Evaporation of solvent gave a crude product which was then recrystallised from ethylacetate to give a colourless crystals. Yield : 0.4740 g, 70%; m.p : 110 ï 114 ^oC; IR (cm^{-1}) : 3258.06 (ν_{N-H}), 1578.10 ($\nu_{C=Npym}$), 1537.26 ($\nu_{C=C}$); ^{1}H-NMR δ_H ppm (400MHz, $CDCl_3$) : 8.40, d, 2H (H-4, H-6), *J*=4.9 Hz, 7.59, d, 2H (H-2ô, H-6ô), *J*=7.6 Hz, 7.34, t, 3H (H-3ô, H-5ô, N-H), *J*=7.6 Hz, 7.03, t, 1H (H-4ô), *J*=7.6 Hz, 6.69, t, 1H (H-5), *J*=4.9 Hz; ^{13}C-NMR δ_C ppm (100.4MHz, $CDCl_3$) : 160.21 (C-2), 157.98 (C-4, C-6), 139.35 (C-1ô), 128.94 (C-2ô, C-6ô), 122.74 (C-4ô), 119.53 (C-3ô, C-5ô), 112.52 (C-5); GCMS : Found M^+ = 170.00; $C_{10}H_9N_3$ requires M^+ = 171.08.

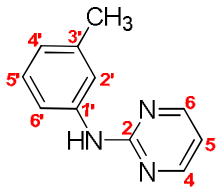
3.5.3 2-N-(p-Methylanilino)pyrimidine (L3)



L3

2-Chloropyrimidine (3.1714 g), which was dissolved in an absolute ethanol was added to *p*-toluidine (3.00 cm^3). The mixture was refluxed for about 5 hours. The reaction mixture was then cooled and the residue slurry was extracted with ether. The ether extracts were washed with water and dried over anhydrous sodium sulphate. Evaporation of solvent gave the product, a colourless crystals. Yield : 2.1248 g, 67%; m.p : 130 ï 132 ^oC; IR (cm^{-1}) : 3258.42 (ν_{N-H}), 1595.76 ($\nu_{C=Npym}$), 1534.05 ($\nu_{C=C}$); ^{1}H-NMR δ_H ppm (400MHz, $CDCl_3$) : 8.39, d, 2H (H-4, H-6), *J*=4.6 Hz, 7.47, d, 2H (H-3ô, H-5ô), *J*=6.4 Hz, 7.14, d, 2H (H-2ô, H-6ô), *J*=8.3 Hz, 6.67, t, 1H (H-5), *J*=4.9 Hz, 2.32, s, 3H (-CH_3); ^{13}C-NMR δ_C ppm (100.4MHz, $CDCl_3$) : 160.91 (C-2), 157.99 (C-4, C-6), 136.65 (C-1ô), 132.50 (C-4ô), 129.45 (C-3ô, C-5ô), 120.07 (C-2ô, C-6ô), 112.20 (C-5), 20.79 (-CH_3); GCMS : Found M^+ = 184.00; $C_{11}H_{11}N_3$ requires M^+ = 185.10.

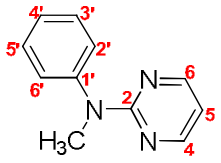
3.5.4 2-N-(m-Methylanilino)pyrimidine (L4)



L4

m-Toluidine (3.00 cm^3) was added to a solution of 2-chloropyrimidine (3.1714 g) in absolute ethanol and heated under reflux for about 5 hours. The mixture was evaporated and the residue slurry was extracted with ether. The combined ether layer were then washed with water and dried over anhydrous sodium sulphate. Evaporation of ether gave the product, a colourless crystal. Yield : 1.8394 g, 58%; m.p : 85 ï 88 ^oC; IR (cm^{-1}) : 3257.43 (ν_{N-H}), 1573.91 ($\nu_{C=Npym}$), 1534.27 ($\nu_{C=C}$); ^{1}H-NMR δ_H ppm (400MHz, $CDCl_3$) : 8.42, d, 2H (H-4, H-6), *J*=4.9 Hz, 7.61, d, 1H (H-2ô, H-6ô), *J*=8.3 Hz, 7.34, t, 1H (H-5ô), *J*=7.6 Hz, 7.05, t, 1H (H-5), *J*=7.6 Hz, 6.72, d, 1H (H-4ô), *J*=4.9 Hz, 2.17, s, 3H ($-CH_3$); ^{13}C-NMR δ_C ppm (100.4MHz, $CDCl_3$) : 160.29 (C-2), 157.98 (C-4, C-6), 139.19 (C-1ô), 138.79 (C-3ô), 128.78 (C-5ô), 123.66 (C-2ô), 120.17 (C-4ô), 116.71 (C-5), 112.41 (C-6ô), 21.58 ($-CH_3$); GCMS : Found M^+ = 184.00; $C_{11}H_{11}N_3$ requires M^+ = 185.10.

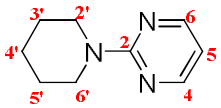
3.5.5 2-N-Methylanilinopyrimidine (L5)



L5

N-Methylaniline (5.00 cm^3) was added to a solution of 2-chloropyrimidine (5.3983 g) in absolute ethanol. The mixture was heated under reflux for about 2 hours and was extracted with ether. The ethereal layer was washed with water. Evaporation of solvent gave a crude product which was then recrystallised from ethylacetate to give a colourless crystals. Yield : 3.0230 g, 56%; m.p : 48 ï 50 ^oC; IR (cm^{-1}) : 3036.45 (ν_{N-H}), 2943.74 (ν_{C-H}), 1581.81 ($\nu_{C=Npym}$), 1550.79 ($\nu_{C=C}$); ^{1}H-NMR δ_H ppm (400MHz, $CDCl_3$) : 8.32, d, 2H (H-4, H-6), *J*=8.3 Hz, 7.20 ï 7.41, m, 5H (H-2ô, H-3ô, H-4ô, H-5ô, H-6ô), 6.54, t, 1H (H-5), *J*=4.9 Hz, 3.50, s, 3H ($-CH_3$); ^{13}C-NMR δ_C ppm (100.4MHz, $CDCl_3$) : 162.79 (C-2), 157.64 (C-4, C-6), 145.98 (C-1ô), 129.18 (C-3ô, C-5ô), 126.57 (C-4ô), 125.86 (C-5), 110.72 (C-2ô, C-6ô), 38.67 ($-CH_3$); GCMS : Found M^+ = 184.00; $C_{11}H_{11}N_3$ requires M^+ = 185.10.

3.5.6 2-N-Piperidinopyrimidine (L6)



L6

2-Chloropyrimidine (1.5812 g), piperidine (15.00 cm^3) and ethanol (15.00 cm^3) were heated under reflux for 2 hours. The mixture was evaporated and the residue slurry was extracted with ether. The ether extracts were washed with water and dried over anhydrous sodium sulphate. Evaporation of solvent gave the product, a yellowish brown liquid. Yield : 1.2170 g, 77%, IR (cm^{-1}) : 2933.02 (ν_{C-H}), 1586.01 ($\nu_{C=Npym}$), 1545.40 ($\nu_{C=C}$); ^{1}H-NMR δ_H ppm (400MHz, $CDCl_3$) : 8.27, d, 2H (H-4, H-6), *J*=4.6 Hz, 6.40, t, 1H (H-5), *J*=4.9 Hz, 3.78, m, 4H (H-2ô, H-6ô), 1.56 ï 1.65, m, 6H (H-3ô, H-4ô, H-5ô); ^{13}C-NMR δ_C ppm (100.4MHz, $CDCl_3$): 161.70 (C-2), 157.70 (C-4, C-6), 108.99 (C-5), 44.76 (C-2ô, C-6ô), 25.73 (C-3ô, C-5ô), 24.88 (C-4ô); GCMS : Found M^+ = 163.00; $C_9H_{13}N_3$ requires M^+ = 163.11.

3.6 Preparation of Copper Complexes

3.6.1 Tetra-μ-acetato-κ^{8}O:O'-bis{[N-ethylpyrimidin-2-amine]copper(II)}(CuL1)

A solution of copper (II) acetate (0.1000 g) in acetonitrile (15.00 cm^3) was added dropwise to a solution of **L1** (0.1356 g) in acetonitrile (15.00 cm^3) and trimethylorthoformate (9.00 cm^3) with continuous stirring and heated at 50 ï 60^{o}C. A green precipitate was formed after one day. The precipitate was filtered and the dark blue powder was dried over silica gel in vacuum desiccators for overnight. It was then recrystallized from acetonitrile to give blue crystals, **CuL1**. Yield: 0.0786 g, 62%. m.p: 208 ï 212 ^{o}C. *Anal*. Calc. for $Cu_2(C_2H_3O_2)_4(C_6H_9N_3)_2$: C, 38.42; H, 4.92; N, 13.78. Found: C, 38.98; H, 3.72; N, 13.51%. IR: ν (cm^{-1}) 3323.79 (ν_{N-H}); 1585.85 ($\nu_{C=Npym}$); 1541.78 ($\nu_{C=C}$); 478.06 (ν_{Cu-N}).

3.6.2 Tetra-μ-acetato-κ^{8}O:O'-bis{[N-(pyrimidin-2-yl)aniline-κN]copper(II)}(CuL2)

A solution of copper (II) acetate (0.1000 g) in acetonitrile (15.00 cm^3) was added dropwise to a solution of **L2** (0.1885 g) in acetonitrile (15.00 cm^3) and trimethylorthoformate (9.00 cm^3). The mixture was heated at 50 ï 60^{o}C with stirring. A blue precipitate was formed after few days. The solid was filtered off and the blue powder formed then dried over silica gel in vacuum desiccators for overnight, which was then recrystallized from acetonitrile to give blue crystals, **CuL2**. Yield: 0.1282 g, 68%. m.p: 206 ï 210 ^{o}C. *Anal*. Calc. for $Cu_2(C_2H_3O_2)_4(C_{10}H_9N_3)_2$: C, 47.67; H, 4.29; N, 11.91. Found: C, 48.58; H, 3.92; N, 12.07%. IR: ν (cm^{-1}) 3316.03 (ν_{N-H}); 1597.54 ($\nu_{C=Npym}$); 1572.77 ($\nu_{C=C}$); 494.14 (ν_{Cu-N}).

3.6.3 Tetra-μ-acetato-κ^{8}O:O'-bis{[N-(pyrimidin-2-yl)4-methylaniline-κN] copper(II)} (CuL3)

A solution of copper (II) acetate (0.1000 g) in acetonitrile (15.00 cm^3) was added dropwise to a solution of **L3** (0.2040 g) in acetonitrile (15.00 cm^3) and trimethylorthoformate (9.00 cm^3) with continuous stirring and heated at 50 ï 60^{o}C. The solid was filtered and dried over silica gel in vacuum desiccators for overnight. The crude product was recrystallized from acetonitrile to give blue crystals**,** **CuL3**. Yield : 0.1346 g, 66%. m.p: 198 ï 202 ^{o}C. *Anal*. Calc. for $Cu_2(C_2H_3O_2)_4(C_{11}H_{11}N_3)_2$: C, 49.12; H, 4.67; N, 11.46. Found: C, 49.25; H, 4.36; N, 11.32%. IR: ν (cm^{-1}) 3325.46 (ν_{N-H}); 1606.94 ($\nu_{C=Npym}$); 1572.22 ($\nu_{C=C}$); 442.27 (ν_{Cu-N}).

3.6.4 Tetra-μ-acetato-κ^{8}O:O'-bis{[N-(pyrimidin-2-yl)3-methylaniline-κN] copper(II)} (CuL4)

A solution of copper (II) acetate (0.1000 g) in acetonitrile (15.00 cm^3) was added dropwise to a solution of **L4** (0.2040 g) in acetonitrile (15.00 cm^3) and trimethylorthoformate (9.00 cm^3) with continuous stirring and heated at 50 ï 60^{o}C. A dark blue precipitate was formed after few days. The precipitate was filtered and the blue powder was dried over silica gel in vacuum desiccators for overnight. The crude product was recrystallized from acetonitrile to give blue crystals, **CuL4**. Yield : 0.0857 g, 42%. m.p: 214 ï 218 ^{o}C. *Anal.* Calc. for $Cu_2(C_2H_3O_2)_4(C_{11}H_{11}N_3)_2$: C, 49.12; H, 4.67; N, 11.46. Found: C, 50.13; H, 4.38; N, 11.24%. IR: ν (cm^{-1}) 3293.43 (ν_{N-H}); 1601.42 ($\nu_{C=Npym}$); 1572.35 ($\nu_{C=C}$); 500.11 (ν_{Cu-N}).

3.6.5 Attempted to Prepare Tetra-μ-acetato-κ^{8}O:O'-bis{[N-(pyrimidin-2-yl) N-methylaniline-κN] copper(II)} (CuL5)

A solution of copper (II) acetate (0.1000 g) in acetonitrile (15.00 cm^3) was added dropwise to a solution of **L5** (0.2040 g) in acetonitrile (15.00 cm^3) and trimethylorthoformate (9.00 cm^3) with continuous stirring and heated at 50 ï 60^{o}C. A dark green solution was obtained and left at room temperature for several days. Evaporation of solution gave green slurry. No desired product obtained.

3.6.6 Attempted to Prepare Tetra-μ-acetato-κ^{8}O:O'-bis{[N-(pyrimidin-2-yl) piperidine-κN] copper(II)} (CuL6)

A solution of copper (II) acetate (0.1000 g) in acetonitrile (15.00 cm^3) was added dropwise to a solution of **L6** (0.1798 g) in acetonitrile (15.00 cm^3) and trimethylorthoformate (9.00 cm^3) with continuous stirring and heated at 50 ï 60^{o}C. A brown solution was obtained and left at room temperature for several days. Evaporation of solution gave brown slurry. No desired product obtained.