

## Chapter 2

### METHOD OF STUDY

#### 2.1 Materials

##### 2.1.1 Chemical substances

###### Product of Fluka Chemical.

1. 2,2':6',2''-Terpyridine,  $C_{18}H_{11}N_3$ , A.R. grade

###### Products of E. Merck.

1. Silica gel 60 (0.040-0.063 nm) GF<sub>254</sub>
2. Sodium hydroxide, NaOH, A.R. grade
3. Triethylamine,  $N(CH_2CH_3)_3$ , A.R. grade

###### Products of BDH Chemical Ltd.

1. Sodium nitrite,  $NaNO_2$ , A.R. grade
2. Silver nitrate,  $AgNO_3$ , A.R. grade

###### Products of Aldrich Chemical Cl., Inc.,

1. 2-Aminopyridine,  $C_5H_6N_2$ , A.R. grade
2. Ammonium hexafluorophosphate,  $NH_4PF_6$ , A.R. grade
3. *N,N*-Dimethyl-4-nitrosoaniline,  $C_8H_{10}N_2O$ , A.R. grade
4. *N,N*-Diethyl-4-nitrosoaniline,  $C_{10}H_{14}N_2O$ , A.R. grade
5. Ruthenium(III)trichloride hydrate,  $RuCl_3 \cdot 3H_2O$ , A.R. grade

###### Product of Riedel-de Haen

1. Lithium chloride, LiCl, A.R. grade

###### Product of Hopkin & Williams

1. Ammonium tetrafluoroborate,  $NH_4BF_4$ , A.R. grade

**2.1.2 Solvent (all other chemicals were reagent grade and purified by distillation and collected from their boiling point.)**

Product of Lab-Scan Analytical Science

1. Acetonitrile,  $\text{CH}_3\text{CN}$ , A.R. grade
2. Hexane,  $\text{C}_6\text{H}_{12}$ , A.R. grade
3. Dichloromethane,  $\text{CH}_2\text{Cl}_2$ , A.R. grade
4. Dimethyl sulfoxide,  $(\text{CH}_3)_2\text{SO}$ , A.R. grade
5. Methanol,  $\text{CH}_3\text{OH}$ , A.R. grade
6. Toluene,  $\text{C}_7\text{H}_8$ , A.R. grade

Product of E. Merck.

1. Absolute ethanol,  $\text{C}_2\text{H}_5\text{OH}$ , A.R. grade
1. Acetone,  $\text{C}_3\text{H}_6\text{O}$ , A.R. grade
2. Methanol,  $\text{CH}_3\text{OH}$ , A.R. grade

Product of J.T. Baker

1. Ether,  $(\text{C}_2\text{H}_5)_2\text{O}$ , A.R. grade

Product of Farmitalia Carbo Erba.

1. *N,N*-dimethylformamide,  $\text{C}_3\text{H}_7\text{NO}$ , A.R. grade
2. Ethylacetate,  $\text{C}_4\text{H}_8\text{O}$ , A.R. grade

## 2.2. Preparation of Ligands

The 2-(4'-*N,N*-dimethylaminophenylazo)pyridine (dmazpy) and 2-(4'-*N,N*-diethylaminophenylazo)pyridine (deazpy) ligands were prepared by modification of previous literature methods (Krause and Krause, 1980).

2.2.1 Synthesis of 2-(4'-*N,N*-dimethylaminophenylazo)pyridine (dmazpy) ligand.

2-aminopyridine (1.290 g, 0.014 mole) was added to a sodium hydroxide solution (12 mL, 25 M), which was gently heated in water bath and 4 mL of toluene and 1 mL of acetonitrile were also added. *N,N*-dimethyl-4-nitrosoaniline (2.05 g, 0.014 mole) was slowly added and the mixture was warmed further for 45 min. The reaction mixture was refluxed for 8.30 h. The solution was extracted three times with each of 15 mL of toluene. The toluene solution was evaporated to dryness. The product was dissolved in dichloromethane and purified with column chromatography (hexane:ethyl acetate = 1:1 by volume). The red band was collected and after evaporation the title compound was obtained as solid. The yield was 28 %.

2.2.2 Synthesis of 2-(4'-*N,N*-diethylaminophenylazo)pyridine (deazpy) ligand.

The 2-(4'-*N,N*-diethylaminophenylazo)pyridine ligand was prepared by the same process as 2-(4'-*N,N*-dimethylaminophenylazo)pyridine. 2-Aminopyridine (1.981 g, 0.021 mole) and *N,N*-diethyl-4-nitrosoaniline (3.750 g, 0.021 mole) were used in this reaction. The yield was 12 %.

### 2.3. Preparation of Complexes

$\text{Ru}^{\text{III}}(\text{tpy})\text{Cl}_3$  complex was synthesized by literature method (Sullivan, *et al.* 1980). The  $[\text{Ru}(\text{tpy})(\text{dmazpy})\text{Cl}]\text{PF}_6$  and  $[\text{Ru}(\text{tpy})(\text{deazpy})\text{Cl}]\text{PF}_6$  complexes were prepared by modified literature methods (Takeuchi, *et al.*, 1984). The  $[\text{Ru}(\text{tpy})(\text{dmazpy})\text{X}]\text{PF}_6$  and  $[\text{Ru}(\text{tpy})(\text{deazpy})\text{X}]\text{PF}_6$  complexes, where  $\text{X} = \text{NO}_2^-$ ,  $\text{CH}_3\text{CN}$ , were prepared by modification of previous literature methods (Hecker, *et al.*, 1991).

#### 2.3.1 Preparation of Trichloro(2,2':6',2''-terpyridine)ruthenium(III) complex, $\text{Ru}(\text{tpy})\text{Cl}_3$ .

65 mg (0.13 mmol) of  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  and 63 mg (0.13 mmol) of 2,2':6,2''-terpyridine was added to 20 mL of absolute ethanol in a 50 mL round-bottom flask. The mixture was heated at reflux for 3 h while vigorous magnetic stirring was maintained. After this time the reaction was cooled to room temperature, and the fine brown powder appeared. The solid was filtered and washed with 20 mL of absolute ethanol followed by 20 mL of ether and air-dried. The yield was 84.17% (202 mg).

#### 2.3.2 Preparation of Chloro(2-(4'-*N,N*-dimethylaminophenylazo)pyridine (2,2':6,2''-terpyridine)ruthenium(II) chloride complex, $[\text{Ru}(\text{tpy})(\text{dmazpy})\text{Cl}]\text{Cl}$ .

$\text{Ru}(\text{tpy})\text{Cl}_3$  (0.201 g, 0.48 mmol), 2-(4'-*N,N*-dimethylaminophenylazo)pyridine (dmazpy) (0.105 g, 0.46 mmol) and LiCl (0.107 g, 2.5 mmol) were added to 16 mL of a 3:1 (by volume) ethanol / water solvent mixture. Triethylamine (0.5 mL) was added as a reductant, and the mixture was degased with argon for 15 min. Then, the solution was heated at reflux with stirring for 4 h, evaporated to dryness and

dissolved in a minimum of methanol. The product was purified by column chromatography using a 2:1 (by volume) acetone / water as the eluent. The first purple band was collected, concentrated and dissolved in a minimum amount of ethanol. After 2 days, the resulting precipitate from ethanol was separated from solution by vacuum filtration, washed with 15 mL of ether. The procedure produced 0.237 g of a dry black solid. A typical yield for this method was 81 %.

2.3.3 Preparation of Chloro(2-(4'-*N,N*-dimethylaminophenylazo)pyridine (2,2':6',2''-terpyridine)ruthenium(II) hexafluorophosphate complex,  $[\text{Ru}(\text{tpy})(\text{dmazpy})\text{Cl}]\text{PF}_6$ .

A 40 mg (0.063 mmol) of  $[\text{Ru}(\text{tpy})(\text{dmazpy})\text{Cl}]\text{Cl}$  was dissolved in 15 mL methanol. A 5 mL of saturated aqueous  $\text{NH}_4\text{PF}_6$  was added dropwise to the solution. After 2 days, the black microcrystalline was collected by filtration, washed with a minimum volume of ether and air-dried. Yield 0.043 mg (91.58 %) was obtained.

2.3.4 Preparation of Nitro(2-(4'-*N,N*-dimethylaminophenylazo)pyridine (2,2':6',2''-terpyridine)ruthenium(II) hexafluorophosphate complex,  $[\text{Ru}(\text{tpy})(\text{dmazpy})\text{NO}_2]\text{PF}_6$ .

A 52 mg (0.082 mmol) sample of  $[\text{Ru}(\text{tpy})(\text{dmazpy})\text{Cl}]\text{Cl}$  and 35 g (0.164 mmol) of  $\text{AgNO}_3$  in 20 mL of 1:1 (by volume) acetone/water solvent mixture were heated at reflux for 4 h. Then  $\text{AgCl}$  was filtered off. The purple solution was heated for 10 min and 0.113 mg (1.642 mmol) of  $\text{NaNO}_2$  was added to the solution. The mixture was refluxed for 4 h, then the color was changed from purple to blue. Then the solution was cooled to room temperature and reduced the volume. A 20 mg

(0.164 mmol) of  $\text{NH}_4\text{PF}_6$  was added to the solution. The small black microcrystalline precipitated after 3 days. The solid was filtered and washed with 15 mL of ether and air-dried. The yield was 63%.

2.3.5 Preparation of Acetonitrile(2-(4'-*N,N*-dimethylaminophenylazo)pyridine (2,2':6',2''-terpyridine)ruthenium(II) hexafluorophosphate complex,  $[\text{Ru}(\text{tpy})(\text{dmazpy})\text{CH}_3\text{CN}](\text{PF}_6)_2$ .

A 59 mg (0.093 mmol) of  $[\text{Ru}(\text{tpy})(\text{dmapy})\text{Cl}]\text{Cl}$  and 55 g (32.6 mmol) of  $\text{AgNO}_3$  in 20 mL of acetone : water = 1:1 were heated at reflux for 4 h. Then, the mixture was filtered to remove  $\text{AgCl}$  and the solution was concentrated. The residue was dissolved in 20 mL of acetonitrile and refluxed for 5 h. The solution was evaporated and purified by column chromatography using acetonitrile as the eluent. The final blue band was collected. A 20 mg (0.164 mmol) of  $\text{NH}_4\text{PF}_6$  was added to the solution. The small black microcrystalline precipitated after 1 day. The yield was 42 %.

2.3.6 Preparation of Chloro(2-(4'-*N,N*-diethylaminophenylazo)pyridine (2,2':6',2''-terpyridine)ruthenium(II) chloride complex,  $[\text{Ru}(\text{tpy})(\text{deazpy})\text{Cl}]\text{Cl}$ .

This complex was synthesized using procedure analogous to the method of  $[\text{Ru}(\text{tpy})(\text{dmazpy})\text{Cl}]\text{Cl}$  complex, but the *dmazpy* ligand was taken place by *deazpy* ligand. The yield for this method was 86 %.

2.3.7 Preparation of Chloro(2-(4'-*N,N*-diethylaminophenylazo)pyridine (2,2':6',2''-terpyridine)ruthenium(II) hexafluorophosphate complex,  $[\text{Ru}(\text{tpy})(\text{deazpy})\text{Cl}]\text{PF}_6$ .

This complex was prepared in the same method as  $[\text{Ru}(\text{tpy})(\text{dmazpy})\text{Cl}]\text{PF}_6$  complex. The dmazpy ligand was replaced by an equivalent amount of deazpy. The yield was 86 %.

2.3.8 Preparation of Nitro(2-(4'-*N,N*-diethylaminophenylazo)pyridine (2, 2':6', 2''-terpyridine)ruthenium(II) hexafluorophosphate complex,  $[\text{Ru}(\text{tpy})(\text{deazpy})\text{NO}_2]\text{PF}_6$ .

The synthesis was done by similar method to that of  $[\text{Ru}(\text{tpy})(\text{dmazpy})\text{NO}_2]\text{PF}_6$  complex. The dmazpy ligand was replaced by deazpy ligand. The yield was 64%.

2.3.9 Preparation of Acetonitrile(2-(4'-*N,N*-diethylaminophenylazo)pyridine (2,2':6',2''-terpyridine)ruthenium(II) hexafluorophosphate complex,  $[\text{Ru}(\text{tpy})(\text{deazpy})\text{CH}_3\text{CN}](\text{PF}_6)_2$ .

These complex was synthesized using procedure analogous to the method of  $[\text{Ru}(\text{tpy})(\text{dmazpy})\text{CH}_3\text{CN}](\text{PF}_6)_2$  complex, but the deazpy ligand was used instead of dmazpy ligand. The yield was 47%.

## 2.4. Equipments

### 2.4.1 Melting Point Apparatus

Melting point of the ligands and the complexes were measured on Thomas Hoover Capillary melting point apparatus, range in 30-300 °C

### 2.4.2 Elemental analysis

Elemental analysis data were obtained by using Carlo Erbra EA 1108 Elemental Analyser (University of Bristol, UK.).

### 2.4.3 The Electrospray and The Fast-atom bombardment (FAB) Mass Spectrometry

Electrospray mass spectra were measured on a VG Quattro triple quadrupole system mass spectrometer with alcohol mobile phase (Wollogong University, Australia).

Fast-atom bombardment (FAB) mass spectra were recorded on a VG Autospec instrument (University of Bristol, UK.).

### 2.4.4 UV-Visible Absorption Spectroscopy

Ultraviolet and visible absorption spectra were recorded by using a Hewlett Packard 8425A diode array spectrophotometer.



#### 2.4.5 Infrared Spectroscopy

Infrared spectra were obtained by using a Perkin Elmer Spectrum GX FT-IR spectrophotometer from 370 to 4,000  $\text{cm}^{-1}$ . All samples were prepared in KBr pellets.

#### 2.4.6 Nuclear Magnetic Resonance Spectroscopy

$^1\text{H}$  NMR spectra were recorded in  $\text{CDCl}_3$  and  $d_6$ -DMSO with a FT-NMR Varian UNITY SNOVA 500-MHz with  $\text{Me}_4\text{Si}$  as an internal standard.

#### 2.4.7 Cyclic Voltammetry

Electrochemical experiments were performed using a CS-2000 (Cypress) and Echem 5.0. A platinum disc working electrode, a platinum gauze auxiliary electrode, and a  $\text{Ag}/\text{AgNO}_3$  reference electrode were used in a three-electrode configuration. Electrochemical measurements were done in  $\text{CH}_3\text{CN}$ , and 10 mM tetra-n-butylammonium hexafluorophosphate ( $[\text{NBu}_4]\text{PF}_6$ ) was used as supporting electrolyte. Ferrocene was added at the end of each experiment as an internal standard. All potentials were quoted vs the ferrocene/ferrocenium couple ( $\text{Fc}/\text{Fc}^+$ ). The solvent was used as received. The nitrogen gas was bubbled through the solution prior to each measurement.

#### 2.4.8 X-ray Diffractometer

The X-ray structure of 2-(4'-*N,N*-dimethylaminophenylazo)pyridine (dmazpy) was determined by CCD X-ray diffractometer with Siemens Smart program (Crystallography Center, University of Western Australia, Nedlands, Australia).

The X-ray structure of 2-(4'-*N,N*-diethylaminophenylazo)pyridine (deazpy) was determined by CCD X-ray diffractometer with teXsan program (School of chemistry, Suranaree University of Technology, Nakhon Ratchasima, Thailand).

The X-ray structure of [Ru(tpy)(dmazpy)Cl]BF<sub>4</sub> and [Ru(tpy)(dmazpy)NO<sub>2</sub>]BF<sub>4</sub> complexes were determined by CCD X-ray diffractometer with teXsan program (Department of Chemistry, Faculty of Science, Monash University, Clayton, Victoria, Australia).