

Chapter 2

MATERIALS AND METHODS

2.1 Materials

2.1.1 Chemical substances

Materials from Fluka.

1. Ruthenium(III) trichloride trihydrate, $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, A.R. grade
2. 2-Aminothiazole, $\text{C}_3\text{H}_4\text{N}_2\text{S}$, A.R. grade
3. Tetra-*n*-butylammonium hexafluorophosphate, $[\text{NBu}_4]\text{PF}_6$,
A.R. grade

Materials from Merck.

1. Silica gel 60 GF₂₅₄
2. Propionic acid, $\text{C}_3\text{H}_6\text{O}_2$, A.R. grade

Materials from T.J. Baker

1. Sodium nitrite, NaNO_2 , A.R. grade
2. Sulfuric acid, H_2SO_4 , A.R. grade

Material from Analytical Carlo Erba

1. Ammonium acetate, $\text{CH}_3\text{COONH}_4$, A.R. grade

Material from Lab-scan analytical sciences.

1. Acetic acid glacial, CH_3COOH , A.R. grade

2.1.2 Solvents (all other chemicals were reagent grade and used without further purification)

Materials from Lab-scan analysis sciences.

1. Dimethyl sulfoxide, $(\text{CH}_3)_2\text{SO}$, A.R. grade
2. Acetonitrile, CH_3CN , A.R. grade
3. Toluene, C_7H_8 , A.R. grade
4. Hexane, C_6H_{12} , A.R. grade

Materials from Analytical Carlo Erba

1. Chloroform, CHCl_3 , A.R. grade
2. Ethylacetate, $\text{C}_4\text{H}_8\text{O}_2$, A.R. grade
3. *N,N*-dimethylformamide, $\text{C}_3\text{H}_7\text{NO}$, A.R. grade
4. *N,N*-dimethylaniline, $(\text{CH}_3)_2\text{NC}_6\text{H}_5$, A.R. grade

Materials from Merck

1. Acetone, $\text{C}_3\text{H}_6\text{O}$, A.R. grade
2. Dichloromethane, CH_2Cl_2 , A.R. grade
3. Ethanol, $\text{C}_2\text{H}_5\text{OH}$, A.R. grade

Material from Fluka.

1. *N,N*-diethylaniline, $(\text{C}_2\text{H}_5)_2\text{NC}_6\text{H}_5$, A.R. grade

Material from T.J. Baker

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

2.1.3 The solvents, dichloromethane and hexane, for column chromatography were purified by distillation and collected from their boiling points.

2.2 Instruments

- 2.2.1 Melting point of all compounds were measured on an Electrothermal melting point apparatus (Electrothermal 9100).
- 2.2.2 Elemental analysis data were obtained from Mahidol University, Thailand.
- 2.2.3 Electrospray mass spectra were recorded on a VG Quattro triple quadrupole Mass Spectrometer.
- 2.2.4 Infrared spectra ($4000\text{-}400\text{ cm}^{-1}$) were recorded on a Perkin Elmer Spectrum GX FTIR- Spectrophotometer and far IR spectra ($400\text{-}200\text{ cm}^{-1}$) were measured on a Perkin Elmer 783 Infrared Spectrophotometer in KBr pellets.
- 2.2.5 Proton nuclear magnetic resonance spectra ($^1\text{H NMR}$) were recorded on a Varian UNITY SNOVA 500 MHz FTNMR Spectrometer at ambient temperature. Tetramethylsilane (TMS) was used as internal reference.
- 2.2.6 UV-Visible absorption spectra were monitored in the range 200-820 nm. by Hewlett Packard 8452A array Spectrophotometer.
- 2.2.7 X-ray diffraction data were collected on a Nonius Kappa CCD X-ray Diffractometer with TeXsan program.
- 2.2.8 Electrochemical measurements were carried out using cyclic voltammetric technique. The measurements were obtained from Cypress system Version 6.0 computer controlled electroanalysis system. A platinum disk was used as the working electrode. The counter electrode was a platinum gauze and Ag/AgNO_3 was used as the reference electrode. Ferrocene was added as an internal standard to the electrochemical cell. The supporting electrolyte was tetrabutylammonium hexafluorophosphate (TBAH) in acetonitrile solvent.

2.3 Synthesis of ligands

2.3.1 Synthesis of 2-(*N,N*-dimethylphenylazo)thiazole ligand (dmsazpy)

The 2-(*N,N*-dimethylphenylazo)thiazole ligand was obtained from the reaction of 2-Aminothiazole with *N,N*-dimethylaniline and sodium nitrite. Sodium nitrite, NaNO₂ (0.177 g., 2.46 mmol) was slightly added to the cool solution of 5 mL of concentrated sulfuric acid at 0-5°C with stirring. The 3 mL of the mixture of propionic acid and acetic acid (1:5 V/V) and 2-Aminothiazole (0.246 g., 2.46 mmol) were added, respectively. After the reaction mixture was stirred for 30 min., 0.31 mL (0.246 mmol) of *N,N*-dimethylaniline in 3 mL of the mixture of propionic acid and acetic acid (1:5 V/V) was added. The solution was neutralized with saturated ammonium acetate to pH 7. Then, the solution was poured into 50 mL of water and kept it overnight at 4°C. The solution mixture was extracted with CH₂Cl₂ and evaporated to small volume. Purification was carried out by column chromatography technique on silica gel using CH₂Cl₂:Hexane (2:3 V/V) as eluent. The red band was collected and evaporated to dryness. The 0.29 g of solid was obtained. (% yield = 50.8, m.p. 172-172.5 °C)

2.3.2 Synthesis of 2-(*N,N*-diethylphenylazo)thiazole ligand (desazpy)

The 2-(*N,N*-dimethylphenylazo)thiazole ligand was synthesized by using the similar procedure as 2-(*N,N*-dimethylphenylazo)thiazole ligand. But *N,N*-diethylaniline (0.39 mL, 2.46 mmol) was used instead of the *N,N*-dimethylaniline. The 0.33 g. of red solid was obtained. (% yield = 51.6, m.p.169-169.6 °C).

2.4 Synthesis of complexes

2.4.1 Synthesis of dichlorotetrakis(dimethyl sulfoxide)ruthenium(II) complex or $[\text{Ru}(\text{DMSO})_4\text{Cl}_2]$

The $\text{Ru}(\text{DMSO})_4\text{Cl}_2$ complex was prepared according to the literature method (Evans, *et al.*, 1973). Ruthenium trichloride trihydrate, $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (0.042 g., 0.2 mmol) was refluxed in dimethyl sulfoxide (0.2 mL, 0.8 mmol) for 5 min. The solution was changed from dark-brown to orange-brown, then it was cooled to room temperature and 0.6 mL of acetone was added. The reaction mixture was stored in a desiccator for 7-10 days. The orange crystals were filtered and washed with diethyl ether. The yield was 0.084 g. (% yield = 72 %, m.p. 120°C).

2.4.2 Syntheses of *trans*-dichlorobis(2-*N,N*-dimethylphenylazothiazole)-ruthenium(II) complex or *trans*- $[\text{Ru}(\text{dmsazpy})_2\text{Cl}_2]$ and *cis*-dichlorobis(2-*N,N*-dimethylphenylazothiazole)ruthenium(II) complex or *cis*- $[\text{Ru}(\text{dmsazpy})_2\text{Cl}_2]$

$\text{Ru}(\text{DMSO})_4\text{Cl}_2$ complex (0.025 g., 0.05 mmol) and dmsazpy ligand (0.034 g., 0.14 mmol) were refluxed in chloroform (15 mL) for 21 h. The solution changed from red-brown to dark purple. The solution was filtered and evaporated to dryness. The residue was purified by column chromatography on silica gel. The greenish-blue band of *trans*- $\text{Ru}(\text{dmsazpy})_2\text{Cl}_2$ complex was isolated from the mixture of toluene and acetonitrile (2:1 V/V). The pink-purple was also isolated as *cis*- $\text{Ru}(\text{dmsazpy})_2\text{Cl}_2$. The yield of *trans*- $\text{Ru}(\text{dmsazpy})_2\text{Cl}_2$ was 0.014 g. (% yield = 43.8, m.p. > 300°C). Recrystallization of *trans*- $\text{Ru}(\text{dmsazpy})_2\text{Cl}_2$ in dichloromethane

resulted in good crystals suitable for X-ray diffraction analysis. The yield of the *cis* isomer was 0.07 g. (% yield = 22.04, m.p. more than 300°C). The *cis*-Ru(dmsazpy)₂Cl₂ complexes were recrystallized from the mixture of dichloromethane and toluene (4:1 V/V) at room temperature for 5-7 days.

2.4.3 Syntheses of *trans*-dichlorobis(2-*N,N*-diethylphenylazothiazole)-ruthenium(II) complex or *trans*-[Ru(desazpy)₂Cl₂] and *cis*-dichlorobis(2-*N,N*-diethylphenylazothiazole)ruthenium(II) complex or *cis*-[Ru(desazpy)₂Cl₂]

The synthesis was similarly to that of *trans*-Ru(dmsazpy)₂Cl₂ complex and *cis*-Ru(dmsazpy)₂Cl₂. The dmsazpy was replaced by an equivalent of desazpy ligand (0.026 g., 0.10 mmol). The yield of the *trans* isomer was 0.015 g. (% yield = 48.57 %, m.p. > 300°C). The yield of the *cis* form was 0.006 g. (% yield = 17.14 %, m.p. > 300°C).

2.5 Techniques for structural determination

2.5.1 Electrospray mass spectrometry (ES-MS)

ES-MS is an useful technique to confirm molecular structure of compounds by considering their *m/z* values. The ES technique has been developed to study inorganic and organometallic structures.

2.5.2 Infrared spectroscopy (IR)

IR is commonly used to detect characteristic frequencies of functional groups in compounds. The compounds have to absorb the infrared frequency range and show vibration modes of molecule at different frequencies. For this research

complexes absorb in the IR medium region ($4000\text{-}650\text{ cm}^{-1}$) and far IR region ($650\text{-}200\text{ cm}^{-1}$) for molecular vibrations.

2.5.3 Proton Nuclear Magnetic Resonance Spectroscopy (^1H NMR)

^1H NMR is another technique to identify structure of compounds. It is related to molecular arrangement. The chemical shifts (δ) data provide information concerning the electron density about a giving molecules. The resonance frequency of proton is relatively in sensitive to its environment. However, other features also affect NMR parameters.

2.5.4 UV-Visible absorption spectrometry (UV-Vis)

UV-Visible absorption is a roughly technique to characterize complexes but useful for describing colored. The chromophoric groups in compounds give rise to absorption to the ultra-violet region ($200\text{-}800\text{ nm}$). The colors of transition-metal compounds are usually attributable to electronic transitions involved d orbitals. These transitions are of two main types. One type is "d-d transition" which gives pale colors. In the other type is the "charge transfer transition" which gives dark colors.

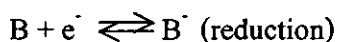
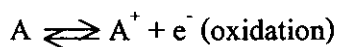
2.5.5 X-ray structure determination

The molecular structure of $\text{Ru}(\text{dmsazpy})_2\text{Cl}_2$ are confirmed by X-ray analyses. These techniques provide highly accurate stereochemical information (including absolute configurations for optically active species). In this work, The CCD is used as detector. The TeXsan programs is used for solving crystal data and the Xtal program is used to study the crystal structure.

2.5.6 Cyclic Voltammetry (CV)

The cyclic voltammetry is an electrochemical method which leads to the knowledge of redox phenomena. It shows current-potential curve, which is called cyclic voltammogram. In general, a typical voltammetric experiment utilizes three types of electrodes (Eklund and Bond, 1998).

The working electrode that is the electrode at which the reaction of interest takes place, e.g. the simple one-electron oxidation-reduction processes are given below



These electrode are typically made an inert and electrically conducting material. The common electrodes are made of platinum and some forms of carbon (i.e. glassy carbon or graphite).

The reference electrode is the electrode that provides a fixed reference couple against the potential of working electrode measured, e.g. the Ag/Ag^+ electrode which the potentials are accurately known relative to the standard hydrogen electrode (SHE).

The counter/auxiliary electrode is the electrode that consists of a large surface area piece of platinum (wire or gauze) or carbon (disk or rod) placed directly into the test solution. Since the current flows through the counter electrode, it must have sufficiently large surface area relative to working electrode to prevent limitation of current flowing in the circuit. The current measured in a voltammetric experiment flows between the working and counter electrode.