

## 2 MATERIALS AND METHODS

### 2.1 Materials

#### 2.1.1 Chemical substances

##### Materials from Fluka

2-Aminopyrazine,  $C_4H_7N_3$ , A.R. grade

Nitrosobenzene,  $C_6H_5NO$ , A.R. grade

Tetrabutylammonium hexafluorophosphate,  $[NBu_4]PF_6$ , A.R. grade

##### Materials from Merck

Silica gel 60 (0.040-0.063 nm) GF<sub>254</sub>

Sodium hydroxide, NaOH, A.R. grade

##### Materials from Aldrich

Ruthenium(III) chloride hydrate,  $C_{12}H_8N_2 \cdot H_2O$ , A.R. grade

#### 2.2.2 Solvents

##### Solvent from Analyzed' Reagent

1-Propanol,  $CH_3CH_2CH_2OH$ , A.R. grade

##### Solvents from Lab. Scan analytical science

Acetonitrile,  $CH_3CN$ , A.R. grade

Chloroform,  $CH_2Cl$ , A.R. grade

Dichloromethane,  $CH_2Cl_2$ , A.R. grade

Dimethyl sulfoxide, DMSO, A.R. grade

Hexane,  $C_6H_{14}$ , A.R. grade

### Solvent from Merck

Hydrochloric acid, HCl, A.R. grade

### Solvent from M&B Laboratory Chemical

Dimethylformamide, HCON(CH<sub>3</sub>)<sub>2</sub>, A.R. grade

The solvents, dichloromethane, hexane, and ethylacetate, for column chromatography were purified by distillation prior to use.

## **2.2 Instruments**

### **2.2.1 Melting Point Apparatus**

Melting points of all compounds were measured on an Electrothermal melting point apparatus (Electrothermal 9100).

### **2.2.2 Elemental Analysis**

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

### **2.2.3 Fast-atom bombardment (FAB) Mass spectrometry**

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

### **2.2.4 Infrared Spectroscopy**

Infrared spectra were collected by using KBr pellets on a Perkin Elmer Spectrum GX FT-IR Spectrophotometer from 370 - 4,000 cm<sup>-1</sup>.

### 2.2.5 UV-Visible Absorption Spectroscopy

A Hewlett Peckard 8425A diode array spectrophotometer was used to record the electronic spectra in the range 200-800 nm.

### 2.2.6 Nuclear Magnetic Resonance Spectroscopy

1D and 2D NMR spectra were recorded in  $\text{CDCl}_3$  solution with a Varian UNITY SNOVA 500-MHz FT-NMR spectrometer and Bruker AVANCE 300-MHz. Tetramethylsilane ( $\text{Si}(\text{CH}_3)_4$ ) was used as an internal standard.

### 2.2.7 Cyclic Voltammetry

Electrochemical experiments were carried out using cyclic voltammetry technique. The program was Echem1.5.1. Cyclic voltammograms were obtained using a glassy carbon working electrode, a platinum wire auxiliary electrode and a platinum disc reference electrode. All potentials were quoted vs the ferrocene/ferrocenium ion in acetonitrile. The electrolyte was tetrabutylammonium hexafluorophosphate (TBAH). The argon was bubbled through the solution prior to each measurement.

### 2.2.8 X-ray Diffractometer

The structures of the *ctc*- $[\text{Ru}(\text{azine})_2\text{Cl}_2]$  and the *tcc*- $[\text{Ru}(\text{azine})_2\text{Cl}_2]$  complexes were determined by Smart APEX CCD diffractometer with the SHELXTL NT (version 6.12) programs.

## 2.3 Synthesis of ligand

The 2-(phenylazo)pyrazine (azine) ligand was prepared by modified literature method (Krause and Krause, 1980).

2-Aminopyrazine (283 mg, 2.97 mmol) reacted with nitrosobenzene (324 mg, 3.02 mmol) in the mixture of 20 M NaOH and 10 mL of benzene solution. The reaction mixture was heated in the water bath at 50-60 °C with stirring for 3 h. The mixture was extracted with benzene. The brown reaction mixture was evaporated to one fifth of the original volume and transferred to silica gel column packed with hexane. The red-orange band was eluted with hexane-ethylacetate (9:1) mixture, which was collected and evaporated to dryness. The yield is 52 % (283 mg).

## 2.4 Syntheses of complexes

### 2.4.1 *ctc* and *ccc* - [Ru(azine)<sub>2</sub>Cl<sub>2</sub>] (The Blue complexes)

The *ctc* and *ccc*-[Ru(azine)<sub>2</sub>Cl<sub>2</sub>] complexes were prepared by mixing of RuCl<sub>3</sub>·3H<sub>2</sub>O (10 mg, 0.05 mmol) and 2-(phenylazo)pyrazine ligand (30 mg, 0.15 mmol) in dimethylformamide (50 mL) at reflux for 6 h. The solvent was removed. The residue was purified by column chromatography. The dichloromethane was used as an eluent. The first and the last blue bands were eluted with dichloromethane-ethylacetate (9:1) mixture. The isolated product consisted two isomers (*ctc* and *ccc*-[Ru(azine)<sub>2</sub>Cl<sub>2</sub>]). The yield of *ctc* isomer is 50 % (13 mg) and that of the *ccc* isomer is 20 % yield (5 mg).

### 2.4.2 *tcc* -[Ru(azine)<sub>2</sub>Cl<sub>2</sub>] (The green complex)

The *tcc*-[Ru(azine)<sub>2</sub>Cl<sub>2</sub>] complex was synthesized by using the same procedure described for the *ctc* and the *ccc*-[Ru(azine)<sub>2</sub>Cl<sub>2</sub>] complexes. The dimethylformamide was replaced by 1-propanol. The yield of the *tcc* isomer (green color) is 22 % (8 mg).