

2 MATERIALS AND METHODS

2.1 Materials

2.1.1 Chemical substances

Materials from Fluka AG, Switzerland

2-Aminobenzothiazole, $C_7H_6N_2S$, A.R. grade

Nitrosobenzene, C_6H_5NO , A.R. grade

Ruthenium(III)chloride trihydrate, $RuCl_3 \cdot 3H_2O$, A.R. grade

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

Materials from Merck

Silica gel 60 (0.040-0.063 nm) GF₂₅₄

Sodium hydroxide, NaOH, A.R. grade

Materials from Riedel-de Haen

Lithium chloride, LiCl, A.R. grade

2.1.2 Solvents

Solvents from BDH Laboratory Supplies

Chloroform, $CHCl_3$, A.R. grade

Solvents from Lab-Scan analytical sciences

Acetonitrile, CH_3CN , A.R. grade

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

Solvents from Merck

Dichloromethane, CH_2Cl_2 , A.R. grade

Ethanol, C_2H_5OH , A.R. grade

The solvents for column chromatography, dichloromethane and hexane, were reagent grade and 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 with use of a Carlo Erba EA 1108 Elemental Analyzer (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 recorded on a Perkin Elmer Spectrum GX FT-IR spectrophotometer from 370 to 4,000 cm^{-1} in the KBr pellets.

2.2.5 UV-Visible Absorption Spectroscopy

UV-Visible absorption spectra were recorded in the range 200-800 nm by Hewlett Packard 8425A diode array spectrophotometer.

2.2.6 Nuclear Magnetic Resonance Spectroscopy

1D and 2D NMR spectra were collected in CDCl_3 using a Varian UNITY SNOVA 500 MHz FT-NMR spectrometer. Tetramethylsilane (Me_4Si) was used as an internal standard.

2.2.7 Cyclic Voltammetry

Electrochemical measurements were performed by using cyclic voltammetry technique with Echem 1.5.1 program. Cyclic voltammograms were obtained using a glassy carbon working electrode, a platinum wire auxiliary electrode and a platinum disc reference electrode. The supporting electrolyte was tetrabutylammonium hexafluorophosphate (TBAH) in dichloromethane. At the end of each experiment, ferrocene was added as an internal standard. All potentials were quoted VS the ferrocene/ferrocenium couple (Fc/Fc^+). The argon gas was bubbled through the solution prior to each measurement.

2.2.8 X-ray Diffractometer

The X-ray crystal structures of *ctc*- $[\text{Ru}(\text{bsazpy})_2\text{Cl}_2]$ and *cct*- $[\text{Ru}(\text{bsazpy})_2\text{Cl}_2]$ complexes were determined by Smart APEX CCD diffractometer with SHELXTL NT (Version 6.12) programs.

2.3 Synthesis of ligand

2-(Phenylazo)benzothiazole ligand (bsazpy)

The 2-(phenylazo)benzothiazole ligand was obtained from the reaction between 2-aminobenzothiazole and nitrosobenzene. The 2-aminobenzothiazole (0.451 g, 3 mmol) was added to 3.75 mL of warm 20 M NaOH solution with stirring in water bath. Then 15 mL of benzene and nitrosobenzene (0.321 g, 3 mmol) were added to the solution. The solution mixture was heated in water-bath for 2 h and was extracted five times with 5 mL portions of benzene. The crude product was purified by column chromatography. The red-orange band was eluted with the hexane-dichloromethane mixture. Evaporation of solvent gave red-orange solid and the yield was 34%.

2.4 Synthesis of complexes

Synthesis of $[\text{Ru}(\text{bsazpy})_2\text{Cl}_2]$

To the ethanolic solution of 2-(phenylazo)benzothiazole (0.050 g, 0.363 mmol), LiCl (0.080 g) and $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (0.016 g, 0.077 mmol) were added and the mixture was heated in water bath for 7 h. Then the solution mixture was filtered and evaporated to dryness. The residue was purified by column chromatography and the dichloromethane-hexane mixture was used as the eluting solvent. Three geometrical isomers were collected as dark-green (%yield = 18), green (%yield = 56) and light-green (%yield = 18) isomers respectively.

The green isomer was recrystallized from the dichloromethane-acetonitrile mixture and the light-green isomer was recrystallized from the dichloromethane-hexane mixture. Both obtained crystals were suitable for X-ray diffraction analysis.