Synthesis and Characterization of New Ruthenium-Tungsten Bimetallic Complex Equipped With Anchoring Ligand

PK Wardani¹, D Anggraini¹, A Awaluddin¹, MB Kassim²,³ and K Arifin²,*

¹Departement of Chemistry, Faculty of Mathematic and Natural Science, University of Riau, Kampus Bina Widya, Km 12.5 Simpang Baru, Pekanbaru, Riau, Indonesia
²Fuel Cell Institute, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor Malaysia
³School of Sciences and Food Technology, Faculty of Science and Technology Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia

*corresponding author : khuzaim@ukm.edu.my

Abstract. A new ruthenium-tungsten bimetallic complex equipped carboxylic as anchoring ligand and thiocyanate as bridging ligand has successfully synthesized. Ruthenium complex and tungsten hexacarbonyl are used as starting materials. The synthesis process involves two-step reactions in one-pot with ultraviolet light and monitored by FTIR spectroscopy. The final product fully characterized by UV-Vis, FTIR, ¹HNMR, ¹³CNMR, and LCMS spectroscopies analysis confirms that the product is a bimetallic complex with molecular formula Ru(C₁₂H₈N₂O₄)₂-(NCS)₂-W(CO)₄. Cyclic voltammetry of the complex exhibit one reversible redox couple, two quasi-reversible redox couples and one irreversible redox peak. The complex absorbs light energy in a wider solar spectrum compared to related ruthenium complex. The complex is supposed to be a good dye-sensitizer to improve TiO₂ photoelectrode performance in artificial photosynthesis applications.

1. Introduction
Transition metal complex molecules are crucial in photosynthetic systems. The complex molecules present as a catalyst, chromophores or electron relay. Complex molecule based on ruthenium metal is the most studied in the artificial photosynthetic application due to excellent electrochemical, catalytic activity and photophysical properties for many applications [1-5]. The complex is used as a dye-sensitizer to a wide bandgap semiconductor of a solar cell, such as in Gratzel cell [6]. Changing the optical properties of transition metal complexes with ligand modification is an interesting field of research because it will produce a molecule that can absorb light energy in a wide wavelength range, efficient electron transfer, and long-lived excited states [7,8]. In addition to modifying ligands, the use of a bimetallic complex molecule expected can improve the monometallic complex performance [5].

The bimetallic complex has an advantage of exhibit intramolecular energy which can increase lifetime during the reaction [9]. The complex can be homo-bimetallic complex or hetero-bimetallic complex. The homo-bimetallic complex is a complex that has two metals center with the same atom [10], whereas a hetero-bimetallic complex is a complex that has two metals center with a different atom [11]. Compared with homo-bimetallic complex, the hetero-bimetallic complex is more studied [12]. Most of the reported bimetallic complex has long and non-rigid bridging ligands that will affect to electron transfer process from one metal center to another [10,13].
A bimetallic complex based on ruthenium-tungsten metals as dye sensitizer has been reported previously. Two of metal center connected by double thiocyanate ligands, which is a short and rigid ligand. However, complexes containing previously synthesized ruthenium-tungsten do not have anchoring ligand like a carboxylic functional groups [5]. The absence of anchoring ligands causes the complex cannot be a good sensitizer. It will not be bonded covalently to the surface like TiO₂, and as a consequence, the photoelectrode performance will not increase [5].

The preparation of bimetallic complexes generally has a long reaction pathway [9,11]. Here, we report a new ruthenium-tungsten bimetallic complex equipped with carboxylic groups as anchoring ligand and thiocyanate as bridging ligands. Thiocyanate is used as a bridging ligand between metals because it includes a simple bridging ligand. Thiocyanate has unpaired electrons in S and N atoms, so it is possible to bind tungsten carbonyl to S atom and ruthenium complexes on N atoms. The synthesis process involves two-step reactions in one-pot and irradiated with ultra violet (UV) light. The one-pot method is used in this synthesis because it is effective for two reaction steps in the same reactor so that it has a simple step-level reaction path. In addition, the advantage of using a one-pot synthesis procedure is that it can minimize chemical waste and save reaction time [14]. The final product fully characterized by Ultraviolet–visible (UV-Vis), Fourier-transform infrared (FTIR), Proton & Carbon nuclear magnetic resonance (¹H NMR and ¹³CNMR) and Liquid chromatography–mass spectrometry (LCMS) spectroscopies analysis.

2. Experimental

2.1. Synthesis of bimetallic complexes

The bimetallic complexes with molecular formula Ru(C₁₂H₈N₂O₄)₂(NCS)₂-W(CO)₆ (III) which is abbreviated as Ru-W were prepared using one-pot synthesis method, by react of [Ru(C₁₂H₈N₂O₄)₂(NCS)₂] complex (II) and W(CO)₆ (I). A solution of tungsten hexacarbonyl (W(CO)₆) (30 mg, 1 mol) in THF (40ml) was reflux and irradiated with UV light under nitrogen atmosphere at room temperature for 2 hours to generate the W(CO)₆-THF intermediate [5]. Ru(C₁₂H₈N₂O₄)₂(NCS)₂ (14.96 mg, 1 mol) as precursor was added directly to the reaction mixture, which then reflux for 6 hours irradiated with UV light. The UV radiation is used in this synthesis to accelerate the formation of complex molecules. After that, the crude reaction was reflux again for 20 hours without irradiated UV light (Figure 1). The reaction monitored by FTIR spectroscopy until desired peaks appear and differ from the starting material peaks. Then the solvent (THF) was removed and the solid was filtered to produce black solid product (6.5 mg).

2.2 Characterization

The UV-Vis, FTIR, ¹H NMR, ¹³CNMR and LCMS spectroscopies used to characterize the molecular structure and electronic transition. The absorption spectra of the complex in ethanol at room temperature were recorded using UV-Vis λ 35 Perkin Elmer 1000-200 nm. The FTIR recorded using Perkin Elmer Spectrum 400 FT-IR/NIR with Imaging System. The ¹H NMR and ¹³CNMR (FT-NMR Bruker, AVANCE III HD 400 MHz) spectra of the Ru-W bimetallic complexes were recorded in DMSO-d₆ to predict the position of proton and carbon. Direct infused is a method used in LCMS (Dionex(LC)/Bruker(MS), MicroToF) analysis.

2.3 Electrochemical study

The cyclic voltammetry study of Ru-W bimetallic complex was performed in three-electrode electrochemical system. Platinum wire as a counter electrode, platinum disk as a working electrode and Ag/AgCl as reference electrode. The redox potentials of the complex (1x10⁻⁵) were measured in a solution of DMF that contain 0.1 M TBAPF₆ as supporting electrolyte in nitrogen atmosphere at room temperature and scan rate of 0.1 Vs⁻¹.
3. Result and Discussion

The FTIR spectra of Ru-W bimetallic complex showed a strong signal in 2107 cm\(^{-1}\) and medium signal in 2067 cm\(^{-1}\) that characteristic of two thiocyanate as bridging ligand (-NCS-). The functional groups of carboxylic (-COO) showed at 1726 cm\(^{-1}\) (strong) and 1618 cm\(^{-1}\) (medium). The carbonyl groups (-CO) from tungsten carbonyl showed at 1976 cm\(^{-1}\) (weak), 1918 cm\(^{-1}\) (strong) and 1875 cm\(^{-1}\) (weak). The IR spectra of Ru-W bimetallic complex confirms the coordination mode of the tungsten carbonyl to ruthenium complex via thiocyanate bridging ligand.

\(^1\)HNMR (DMSO-d\(_6\), 400 MHz) spectra showed that the bimetallic molecule complex was asymmetric. In \(^1\)HNMR showed the chemical shift at 6.87 ppm (s, 1H), 7.60 ppm (dd, 1H), 7.77 ppm (d, 1H), 8.36 ppm (dd, 1H), 8.99 ppm (d, 1H), 9.16 ppm (d, 1H) and 9.43 ppm (d, 1H). The \(^1\)HNMR spectra was compare and identical with the product obtained one-pot reaction method by Jitchati et al. \([15]\). \(^1\)HNMR spectra compared with product obtained one-pot reaction method by Jitchati et al. because proton from the bimetallic complex come from the precursor that is standard ruthenium complex. The \(^{13}\)CNMR (100 MHz, DMSO-d\(_6\)) of Ru-W bimetallic complexes showed resonances in the expected regions. Four signal of carbonyl groups from tungsten showed at 194.67 ppm, 196.66 ppm, 201.66 ppm and 201.94 ppm. The four carbon from carboxylic groups was observed at 159.08 ppm, 165.48 ppm, 165.93 ppm and 178.32 ppm also, the thiocyanate carbon was observed at 66.17 ppm and 68.74 ppm. The last characterization of Ru-W bimetallic complex is LCMS, to make sure the molecular weight and confirm the structure of bimetallic complexes. The spectra of LCMS showed the bimetallic complex has molecular weight 1000.8884 m/z. The theoretical molecular weight of bimetallic complex is 1001.5205 m/z, when compared to the results obtained from LCMS experiment spectra have molecular weight similarity up to 99.94%. These results can confirm that the Ru-W bimetallic complex was successfully synthesized by the one-pot synthesis method.

The UV-Vis spectrum of bimetallic complex in ethanol showed three absorption band at 315 nm (A= 2.133), 400 nm (A= 0.817), and 540 nm (A= 0.812) which were assign to metal to ligand charge transfer (MLCT). The absorption intensity of bimetallic complex is higher than the standard ruthenium complex. In addition, there is a shift in the wavelength in the visible light region for the Ru-W bimetallic complex, this indicates that the light absorption of the Ru-W bimetallic complex is better.
than the standard ruthenium complex. The Ru-W bimetallic complex are highly soluble in polar protic solvent (water, ethanol, methanol), soluble enough in polar aprotic solvent (tetrahydrofuran, dimethyl formamide, dimethyl sulfoxide) and insoluble in nonpolar solvent. The analytical data of bimetallic complexes are in good agreement with the molecular structure proposed.

The electrochemical properties of Ru-W bimetallic complex were investigated by cyclic voltammetry with three-electrode system in DMF and TBAPF$_6$. The Ru-W bimetallic complex voltammogram shown in Figure 2. The Ru-W bimetallic complex shown several redox processes corresponding to one reversible redox couple (E1), two quasi-reversible redox couples (E2, E3) and one irreversible redox peak (E4) at room temperature. The reversible redox couple was identified as E1 with $E_{1/2}$ $0.196$ V ($\Delta E_p = 147$ mV) associated to formal reduction of Ru(III)/(II). Two quasi-reversible redox couples were identified as E2 and E3 with $E_{1/2}$ $0.198$ V ($\Delta E_p = 149$ mV) and $0.552$ V ($\Delta E_p = 105$ mV) are associated to formal oxidation of W(I)/W(II) and W(0)/W(I). The potential irreversible peak is identified as E4 can be reduction peak of the ligand around the complex. Differences in potential values and shifts in oxidation or reduction numbers depend on the substituents around the metal [16]. One reversible redox couple and two quasi-reversible redox couples when compared with the ferrocene standard can be observed as one-electron redox processes. All the properties of bimetallic complex show that the Ru-W bimetallic complexes can be a dye sensitizer agent to improve the performance of the TiO$_2$ photoelectrode in artificial photosynthesis applications.

![Cyclic voltammogram of Ru-W bimetallic complex (1x10^3) in DMF with TBAPF$_6$ (0.1M) supporting electrolyte and scan rate at 0.1Vs$^{-1}$](image)

**Figure 2.** Cyclic voltammogram of Ru-W bimetallic complex (1x10$^3$) in DMF with TBAPF$_6$ (0.1M) supporting electrolyte and scan rate at 0.1Vs$^{-1}$

4. Conclusion
A bimetallic complex based on ruthenium and tungsten metals with carboxylic as anchoring ligand and thiocyanate as bridging ligand has successfully synthesized and characterized by spectroscopic techniques. The molecular formula of bimetallic complex is Ru(C$_{12}$H$_3$_N$_2$O$_4$)$_2$-(NCS)$_2$W(CO)$_4$ with a molecular weight of 1000.8884 m/z. The results of UV-Vis spectra indicated that the bimetallic complex has better absorption than the standard ruthenium complex. The electrochemical test results show that ruthenium metal undergoes a formal reduction reaction Ru(III)/Ru(II) while tungsten metal
undergoes a formal oxidation reaction from W(0)/W(II) through the redox stage W(0)/W(I) and W(I)/W(II). The electrochemical and photophysical properties of Ru-W bimetallic complex shown that complex can improve the performance of the TiO$_2$ photoelectrode in artificial photosynthesis applications.

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