

Ruthenium(II) Complexes of Mixed Bipyridyl and Dithiolate Ligands: Synthesis, Characterization and Electrochemical Studies

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We report the synthesis, characterization and electrochemical studies of four ruthenium(II) complexes of mixed bipyridyl and dithiolate ligands. The complexes formulated as [Ru(L₁)(dcbpy)], [Ru(L₂)(dcbpy)], [Ru(L₃)(dcbpy)] and [Ru(L₄)(dcbpy)] where L₁ = dipotassium ethoxycarbonyl-1-cyanoethylene-2,2-dithiolate, L₂ = dipotassium bis(ethoxycarbonyl)ethane-2,2-dithiolate, L₃ = dipotassium cyanodithio-imidocarbonate, L₄ = dipotassium 2,2-dicyanoethylene-2,2-dithiolate and dcbpy = 4,4-dicarboxylic-2,2-bipyridine. The ligands and complexes were characterized by FTIR, UV-Vis, PL, NMR spectroscopic techniques, cyclic and square wave voltammetry. The FT-IR spectra studies confirmed the coordination of the ligands to the Ru(II) ion. Electronic absorption indicates that the geometry around the metal ion is 4 coordinate square planar. The ruthenium(II) complexes showed good redox properties from the CV and SWV measurements. All the complexes exhibited strong photoluminescence intensity ratios in the red regions, which indicated good electrochemical abilities.

Keywords: Dithiolate; 4, 4-dicarboxylic-2,2-bipyridine; spectroscopy; photophysical studies; voltammetry.

1. INTRODUCTION

Dithiolate ligands have attracted many researchers due to their good electronic and chemical properties [1-3]. They were reported to have interesting physical and spectroscopic properties and their applications include conductivity, magnetism, and catalysis [4-6]. Dithiolates are bidentate ligands with two sulfur donor atoms and are unsaturated [7-9]. Their ligands can coordinate in binary or heterobimetallic manner with metal ions [7]. They usually form a stable square planar geometry around

transition metal ions [9]. Metal complexes containing dithiolate ligands such as ruthenium (Ru) bipyridyl complex with $C_2S_2N_2$ and S_2COEt as the S-donor ligands have been reported. The properties of the two series of $C_2S_2N_2$ and S_2COEt includes significant highest HOMO contribution from the sulfur-donor ligand and the HOMO largely located at the center of the Ru metal ion. The dianionic $C_2S_2N_2$ has a greater electron capability than the monoanionic S_2COEt that causes destabilization of the metal *d*-orbital and lower the energy of metal-to-ligand charge transfer transitions [10, 11]. Ruthenium(II) complexes have been investigated for their uses in solar cells due to key features they possess which include absorption bands in the visible region with a relatively large molar extinction coefficient and luminescent properties [13-16]. However, amongst all other metals which have been used in the sensitization of solar cells, ruthenium has been found to be the most efficient of all [17]. A study of Ru(II) diamine dithiolate complexes for sensitization of nanocrystalline TiO_2 film was reported by Islam *et al.* to have strong electron donating ligands [12]. The complexes synthesized showed a broad and intense MLCT in the visible range [12]. In this paper we report the synthesis, characterization, photophysical and electrochemical studies of Ru(II) complexes of mixed ligands of bipyridyl and dithiolates.

2. EXPERIMENTAL

2.1. Materials and Methods

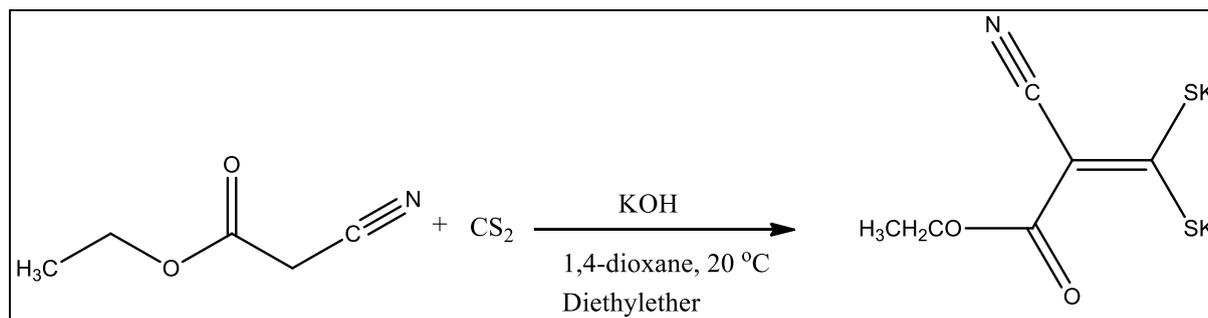
Chemicals were of analytical grade and used as obtained without purification. All chemicals and solvents were bought from Associated Chemical Enterprises (ACE), Merck and Sigma Aldrich. Chemical used include: $RuCl_2(DMSO)_4$, ethylcyanoacetate, cyanamide, malononitrile, carbon disulfide, 1,4-dioxane, diethyl malonate, diethyl ether, 2,2'-bipyridyl-4,4'-dicarboxylic acid, and methanol. Infrared spectroscopy was collected on FTIR-ATR Perkin Elmer 4000 Hz spectrophotometer in the range 4000-400 cm^{-1} . Absorption and emission spectra were measured on a Perkin-Elmer Lambda 25 UV-Vis spectrophotometer and Perkin-Elmer Lambda 45 Fluorimeter. For all the complexes, cyclic voltammetry and square wave were performed using an auto lab potentiostat instrument with a pseudo silver/silver chloride (Ag/AgCl) reference electrode, a glassy carbon working electrode and an auxiliary platinum (Pt) counter electrode. The ligands were synthesized with slightly modification as described in literature [18]. All the complexes were synthesized as reported by Evans [19].

2.2. Preparation of ligands

2.2.1. Preparation of dipotassium ethoxycarbonyl-1-cyanoethylene-2, 2-dithiolate (L_1)

Potassium hydroxide (1.12 g, 20 mmol) was suspended in 1, 4-dioxane (100 mL) and a solution of ethyl cyanoacetate (1.06 mL, 10 mmol) and carbon disulfide (0.60 mL, 10 mmol) in 1, 4-dioxane (50 mL) was added with stirring and cooled to maintain a temperature of 15-20 °C for 4 h (Scheme 1). After the addition, the suspension was filtered, washed with dioxane-ether in 1:1 ratio and dried. Yield: 90%,

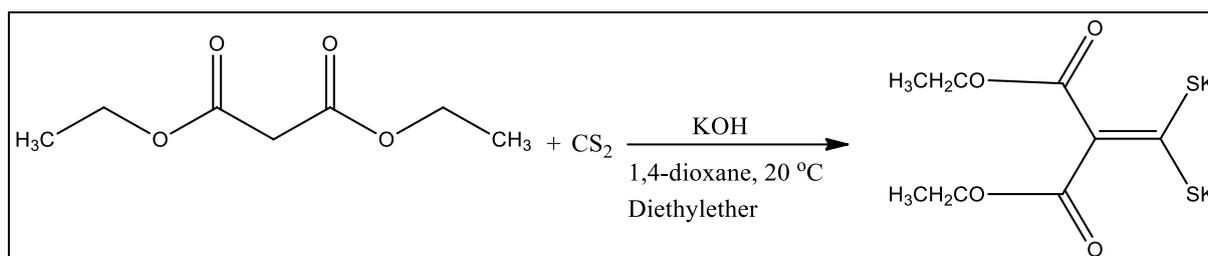
m.p: 250 °C, Selected IR $\nu(\text{cm}^{-1})$: C-S (870), $\text{C}\equiv\text{N}$ (2108), C=O (1652). ^1H NMR ($\text{DMSO-}d_6$) δ 1.16 (t, 3H, CH_3), 3.98 (q, 2H, $-\text{OCH}_2$).



Scheme 1. Synthesis of L1

2.2.2. Preparation of dipotassium bis(ethoxycarbonyl)ethene-2, 2-dithiolate (L_2)

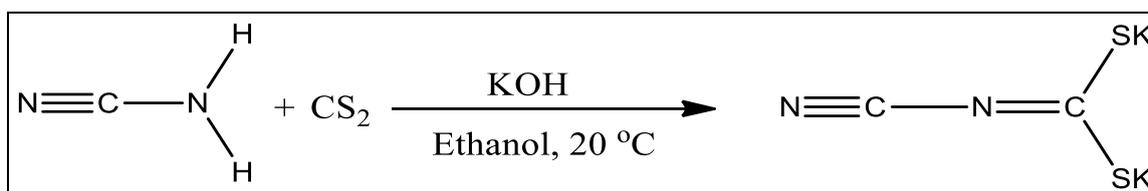
The procedure was similar to that of L_1 . In a conical flask, a solution of diethyl malonate (1.52 mL, 10 mmol) and carbon disulfide (0.604 mL, 10 mmol) in dioxane (50 mL) was added into a solution of potassium hydroxide in dioxane (100 mL). The mixture was stirred and cooled to maintain the temperature of 15-20 °C for 4 h (Scheme 2). The suspension was filtered, wash with dioxane-ether in 1:1 ratio and dried in a desiccator. Yield: 94%, m.p: 250 °C, Selected IR $\nu(\text{cm}^{-1})$: C-S (950), C=O (1652). ^1H NMR ($\text{DMSO-}d_6$) δ 1.18 (t, 3H, CH_3), 3.84 (q, 2H, $-\text{OCH}_2$).



Scheme 2. Synthesis of L_2

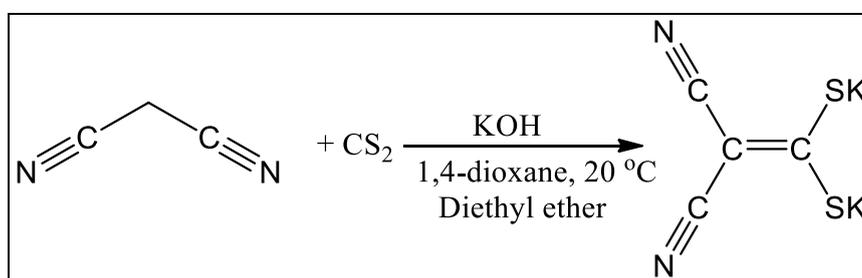
2.2.3. Preparation of dipotassium cyanodithio-imidocarbonate (L_3)

The procedure was the same as the previous ligands. Potassium hydroxide (1.12 g, 20 mmol) was suspended in ethanol (100 mL) and a solution of cyanamide (0.42 g, 10 mmol) and carbon disulfide (0.604 mL, 10 mmol) in ethanol (50 mL) was added with stirring and cooled to maintain a temperature of 15-20 °C for 4 h (Scheme 3). After the addition, the suspension was filtered, washed with ethanol-ether in 1:1 ratio and dried. Yield: 88%, m.p: 220 °C, Selected IR $\nu(\text{cm}^{-1})$: C-S (910), $\text{C}\equiv\text{N}$ (2200), N=C (1010).

Scheme 3. Synthesis of L₃

2.2.4. Preparation of dipotassium 2,2-dicyanoethylene-2,2-dithiolate (L₄)

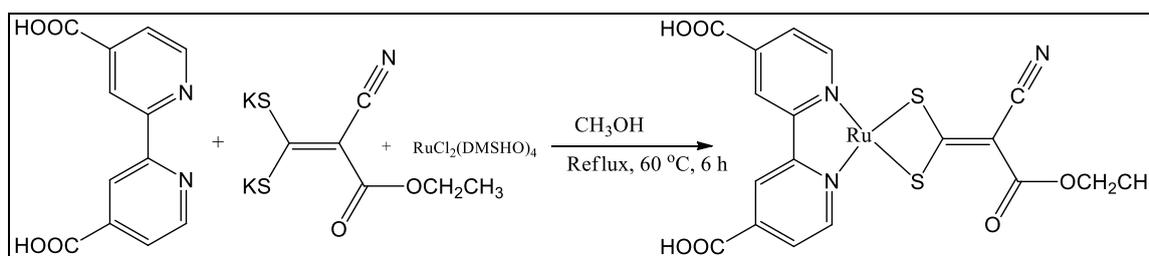
The same procedure was used for the synthesis of L₄. In a conical flask, potassium hydroxide (1.12 g, 20 mmol) was dissolved in 1,4-dioxane (100 mL). In a separate beaker, a solution of malononitrile (0.661 g, 10 mmol) and carbon disulfide (0.604 mL, 10 mmol) in 1,4-dioxane (50 mL) was prepared. This solution was added into the potassium hydroxide solution with stirring and cooled to maintain a temperature of 15-20 °C for 4 h (Scheme 4). The precipitate formed was filtered, washed with dioxane-ether in 1:1 ratio and dried. Yield: 95%, m.p: 250 °C, Selected IR $\nu(\text{cm}^{-1})$: C-S (952), C \equiv N (2174), C=C (1300). ¹³C NMR (DMSO-*d*₆) δ 84.5 (C=C), 120.06 (C \equiv N), 156.01 (C—C), 166.56 (C—S).

Scheme 4. Synthesis of L₄.

2.3. Synthesis of ruthenium(II) complexes

2.3.1. Synthesis of [Ru(L₁)(dcbpy)]Cl

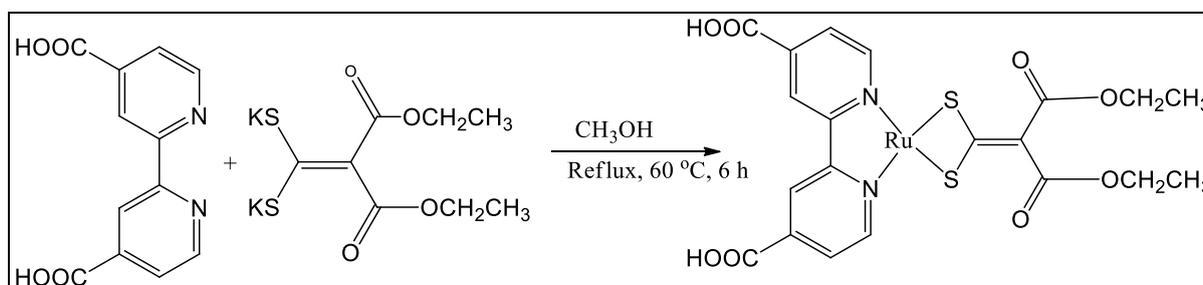
A sample of RuCl₂(DMSO)₄ (0.19 g, 0.40 mmol) was dissolved in 30 mL of methanol, followed by dcbpy (0.10 g, 0.40 mmol) as a solid. The mixture was refluxed at 60 °C for 3 h while stirring under N₂ gas. After 3 h, L₁ (0.11 g, 0.40 mmol) in methanol was added to the flask and refluxed for another 3 h (Scheme 5). The reaction mixture was cooled at room temperature before removing the solvent on a rotary evaporator. The resulting solid was washed three times with water then with acetone. The solution was then filtered through a sintered glass crucible, dried in the desiccator and weighed. Yield: 42%, m.p: 250 °C, Selected IR $\nu(\text{cm}^{-1})$: C-S (821), C \equiv N (2150), O=H (3408-2964). ¹H NMR (DMSO-*d*₆) δ = 0.81 (t, 3H, CH₃), 1.11 (q, 2H, —OCH₂).



Scheme 5. Synthesis of [Ru(L₁)(dcbpy)]

2.3.2. Synthesis of [Ru(L₂)(dcbpy)] C2

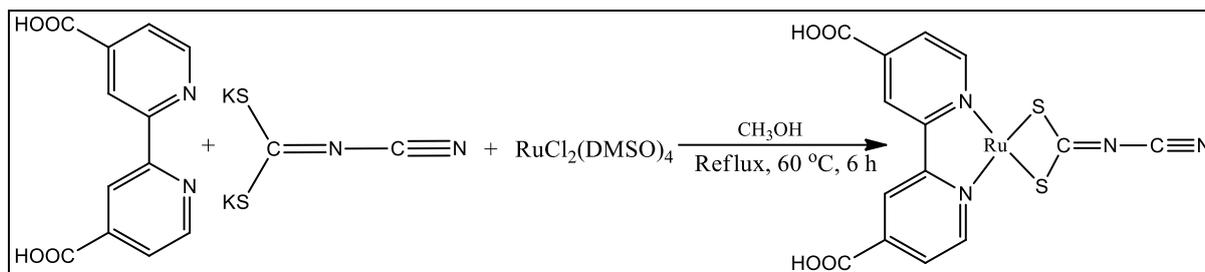
Into a two neck flask, RuCl₂(DMSO)₄ (0.19 g, 0.40 mmol) was dissolved in 30 mL of methanol, followed by dcbpy (0.10 g, 0.40 mmol) as a solid. The mixture was refluxed for 3 h under N₂ gas at 60 °C followed by the addition of L₂ (0.10 g, 0.40 mmol). The mixture was refluxed for 3 h (Scheme 6). The reaction mixture was cooled at room temperature before removing the solvent on a rotary evaporator. The precipitate was washed three times with water to remove the by-products. The solution was then filtered through a sintered glass crucible, dried in the desiccator and weighed. Yield: 51%, m.p: 240 °C, selected IR v(cm⁻¹): C-S (856), C≡O (1766), O=H (3035-2839). ¹H NMR (DMSO-*d*₆) δ = 0.63 (t, 3H, CH₃), 1.01 (q, 2H, —OCH₂).



Scheme 6. Synthesis of [Ru(L₂)(dcbpy)]

2.3.3. Synthesis of [Ru(L₃)(dcbpy)] C3

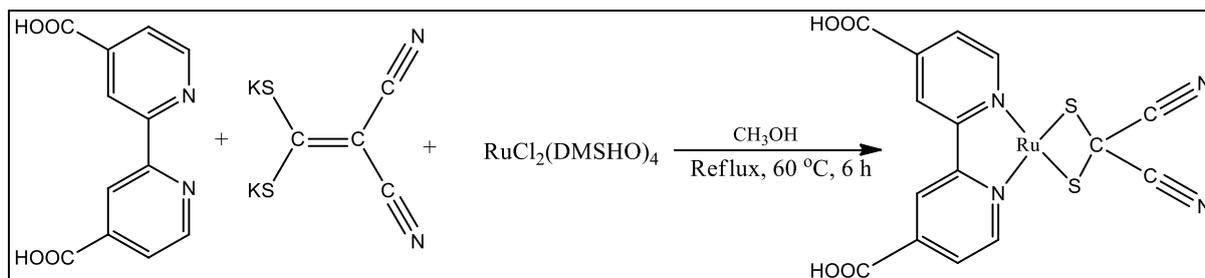
RuCl₂(DMSO)₄ (0.19 g, 0.40 mmol) was dissolved in 30 mL of methanol, followed by dcbpy (0.10 g, 0.40 mmol) as a solid. The mixture was refluxed under N₂ environment at 60 °C for 3 h. After 3 h, L₃ (0.156 g, 0.40 mmol) in methanol was added. The solution was refluxed for another 3 h (Scheme 7). The solvent was removed using a rotary evaporator. The precipitate was washed three times with water and acetone. The solution was then be filtered through a sintered glass crucible, dried in the desiccator and weighed. Yield: 54%, m.p: 240 °C, selected IR v(cm⁻¹): C-S (981), C≡N (2111), O=H (3423-3105). ¹H NMR (DMSO-*d*₆) δ 6.96-8.5 (dcbpy protons), 8.63 (O-H).



Scheme 7. Synthesis of [Ru(L₃)(dcbpy)]

2.3.4. Synthesis of [Ru(L₄)(dcbpy)] C4

A sample of RuCl₂(DMSO)₄ (0.19 g, 0.40 mmol) was dissolved in 30 mL of methanol, followed by dcbpy (0.10 g, 0.40 mmol) as a solid. The mixture was refluxed at 60 °C for 3 h while stirring under N₂ gas. After 3 h, L₄ (0.18 g, 0.40 mmol) was added to the solution and the mixture was refluxed for 3 h (Scheme 8). The reaction mixture was cooled at room temperature before removing the solvent on a rotary evaporator. The resulting solid was washed three times with water to remove the salt and acetone. The solution was then filtered through a sintered glass crucible, dried in the desiccator and weighed. Yield: 60%, m.p: 230 °C, Selected IR ν(cm⁻¹); C-S (910), C≡N (2104), O-H (3400-3169). ¹H NMR (DMSO-*d*₆) δ 8.79 (dcbpy protons). 9.01 (O-H).



Scheme 8. Synthesis of [Ru(L₄)(dcbpy)]

3. RESULT AND DISCUSSION

3.1. Synthesis of metal complexes and physicochemical properties

Ruthenium(II) complexes were prepared by reacting RuCl₂(DMSO)₄ precursor with dithiolate derivatives and 4,4-dicarboxylic-2,2'-bipyridine in a stoichiometric ratio of 1:1:1. Molar conductivity measurements confirmed that ligands are electrolytes with results higher than 20 μS/cm and complexes are non-electrolytes with results lower than 20 μS/cm [2]. Color changes were observed in the process of syntheses in which the initial yellow colour of the precursor complex changed to brown upon coordination of ligands to Ru(II) ions. Physicochemical properties of studied compounds are presented in Table 1.

Table 1. Physiochemical properties of compounds

Compounds	%Yield	Colour	Melting point (°C)	Conductivity Measurements ($\mu\text{S}/\text{cm}$)
L ₁	90	Yellow	250	79.4
L ₂	94	Yellow	250	49.7
L ₃	88	Yellow	220	68.6
L ₄	95	Yellow	250	139.6
C ₁	42	Dark brown	250	7.99
C ₂	51	Dark brown	240	9.01
C ₃	54	Dark brown	240	5.75
C ₄	60	Brown	230	6.18

3.2. Infrared spectra of the ligands and complexes

Relevant FTIR data are presented in Table 2. The infrared spectra of the ligands and the corresponding Ru(II) complexes were compared and assigned on careful comparison. The stretching frequencies found at 2108 cm^{-1} , 2200 cm^{-1} and 2174 cm^{-1} for L₁, L₂ and L₄, respectively, were assigned to the $\nu(\text{C}\equiv\text{N})$ stretching vibrations [2]. Both L₁ and L₂ exhibited carbonyl groups with stretching vibration modes of 1670 cm^{-1} and 1724 cm^{-1} for L₁ and L₂, respectively. The stretching modes at 887 cm^{-1} , 950 cm^{-1} , 920 cm^{-1} and 952 cm^{-1} for L₁, L₂, L₃ and L₄, respectively were due to $\nu(\text{C}-\text{S})$ frequencies. For the complexes, it was observed that all the characteristic peaks shifted to lower vibrational frequencies as compared to free dithiolate ligands. The peaks of interest were $\nu(\text{O}-\text{H})$, $\nu(\text{S}-\text{C}\equiv\text{N})$ and $\nu(\text{C}-\text{S})$. The vibration frequencies for $\nu(\text{O}-\text{H})$ were found at a range of 3600-2660 cm^{-1} for all the synthesized complexes. The strong prominent peaks observed at 2211 cm^{-1} for C₁, 2110 cm^{-1} for C₃ and 2137 cm^{-1} for C₄ are attributed to the $\nu(\text{S}-\text{C}\equiv\text{N})$ of the thiocyanate moiety [22-23]. The stretching modes of $\nu(\text{C}-\text{S})$ were blue shifted in the complexes as compared to their free ligands. This could be attributed to the coordination of the metal ion and S-donor atoms present in the dithiolate ligands [24-27].

Table 2. Relevant FT-IR data of the ligands and corresponding Ru(II) complexes

Compound	$\nu(\text{C}\equiv\text{N})$	$\nu(\text{O}-\text{H})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}-\text{S})$
L ₁ (cm^{-1})	2108	—	1652	887
L ₂ (cm^{-1})	—	—	1724	950
L ₃ (cm^{-1})	2200	—	—	920
L ₄ (cm^{-1})	2174	—	—	952
C ₁ (cm^{-1})	2211	3408-2964	1625	821
C ₂ (cm^{-1})	2110	3035-2839	1766	856
C ₃ (cm^{-1})	—	3423-3105	1681	918
C ₄ (cm^{-1})	2137	3600-2660	1704	910

3.3. Electronic spectra

The UV-Vis spectra of the ligands (L₂-L₄) showed two bands at the range of 313-390 nm and L₁ showed three bands at a range of 316-380 nm (Figure 1). The absorption peaks were ascribed to $n-\pi^*$ and $\pi-\pi^*$ transitions. Relevant electronic data for the Ru(II) complexes are presented in Table 1. The

spectra of C₁ displayed three absorption peaks at 318 and 380 nm that were due to MLCT and the peak at 441 nm was due to $^4T_{2g} \rightarrow ^2T_{2g}$ transitions (Table 3). The same transitions were obtained for C₂-C₄. The broad and intense MLCT transitions are due to the carboxylic anchoring groups in the bipyridyl ligands that allowed an extended delocalization of acceptor orbital of the MLCT excited states [28-30]. A blue-shifted wavelength was observed for C₂ compared to C₁, C₃ and C₄ which may be due to the increase in the energy of the LUMO of the ligands [31, 32]. The proposed geometries of the complexes are square planar as indicated by spectroscopic studies and the ligands are coordinated in a bidentate manner to the ruthenium ion as shown in Schemes 5-8.

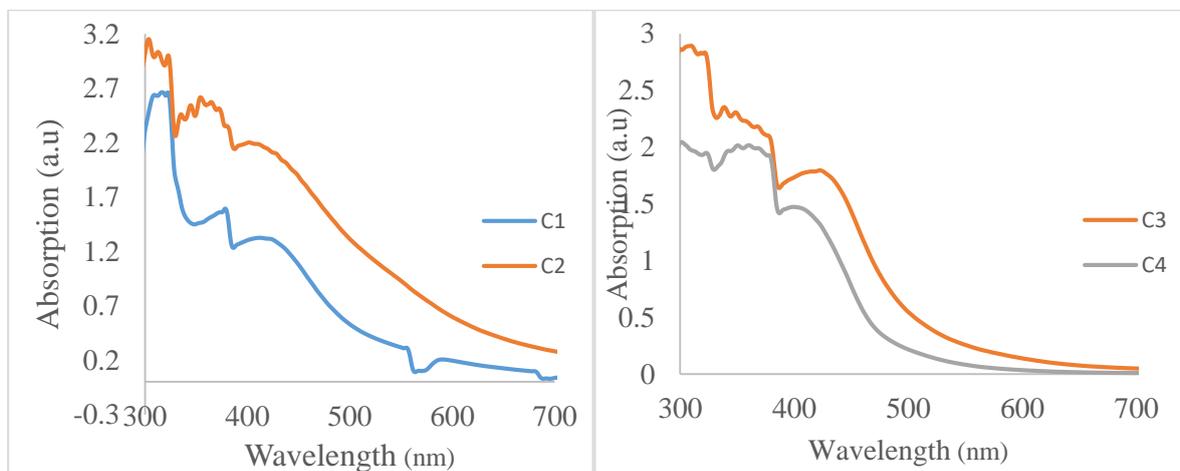


Figure 1. Overlay electronic spectra for complexes (C₁-C₄).

Table 3. Electronic spectra of complex C₁-C₄

Complexes	MLCT (nm)	$^4T_{2g} \rightarrow ^2T_{2g}$ (nm)
C ₁	316, 380	441
C ₂	318, 366	421
C ₃	313, 375	426
C ₄	319, 368	414

3.4. Emission spectra of Ru(II) complexes (C₁-C₄)

In the Ru(II) emission spectra (Figure 2), a common broad band above 400 nm with different emission intensities were observed for all the complexes [21-23]. The emission for C₁ was relative to C₂ and C₃ was relative to C₄. It was observed that C₃ and C₄ emission spectra are red shifted by 1 nm compared to C₁ and C₂. The red shift was due to the extended π -conjugation of the ligand that stabilizes the MLCT state. The emission spectra of C₁ and C₂ are blue shifted by 1 nm to C₃ and C₄. The blue shift was attributed to the lower intra-ligand charge transfer transitions that originated from LUMO of the electron donating groups of the ligand [28].

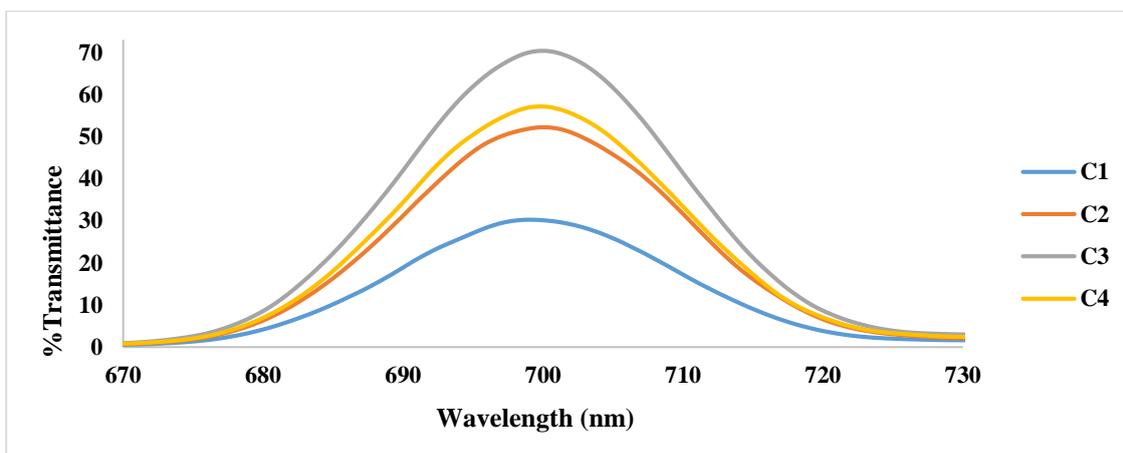


Figure 1. Emission spectra of Ru(II) complexes (C₁-C₄)

3.5. NMR spectra of complexes C₁-C₄

The ¹H NMR spectra of all the compounds were obtained in DMSO solution (Figures 3-6). For the ligands, triplet signals at 1.16 ppm for CH₃ and a quartet at 3.98 ppm for the O—CH₂ were obtained from the spectrum of L₁. The ¹H NMR spectrum of L₂ displayed triplet signal at 1.18 ppm due to CH₃ and a quartet at 3.84 ppm for O—CH₂. The ¹H NMR spectrum of C₁ displayed triplets at 0.81 ppm and a quartet at 1.11-1.26 ppm for CH₃ and O—CH₂ respectively [2, 8]. The CH₂ groups of the aromatic ring present in dcbpy were observed at 7.84-7.94 ppm and 8.78-8.95 ppm respectively. The protons of the O—CH₂ group was observed as a quartet at 1.01-1.27 ppm and the protons of the CH₃ group was observed as triplet at 0.63 ppm for C₂. Complex C₃ and C₄ displayed CH₂ from dcbpy groups at 6.96-8.15 ppm and 8.79-9.01 ppm, respectively.

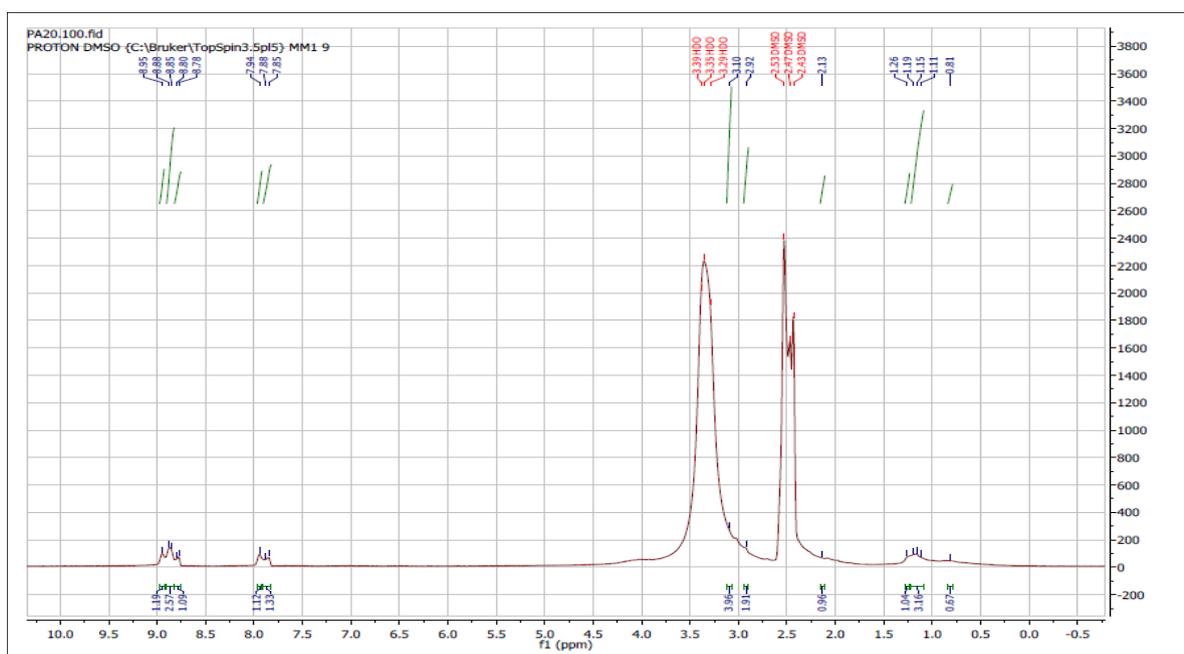


Figure 2. ¹H NMR spectra for C₁.

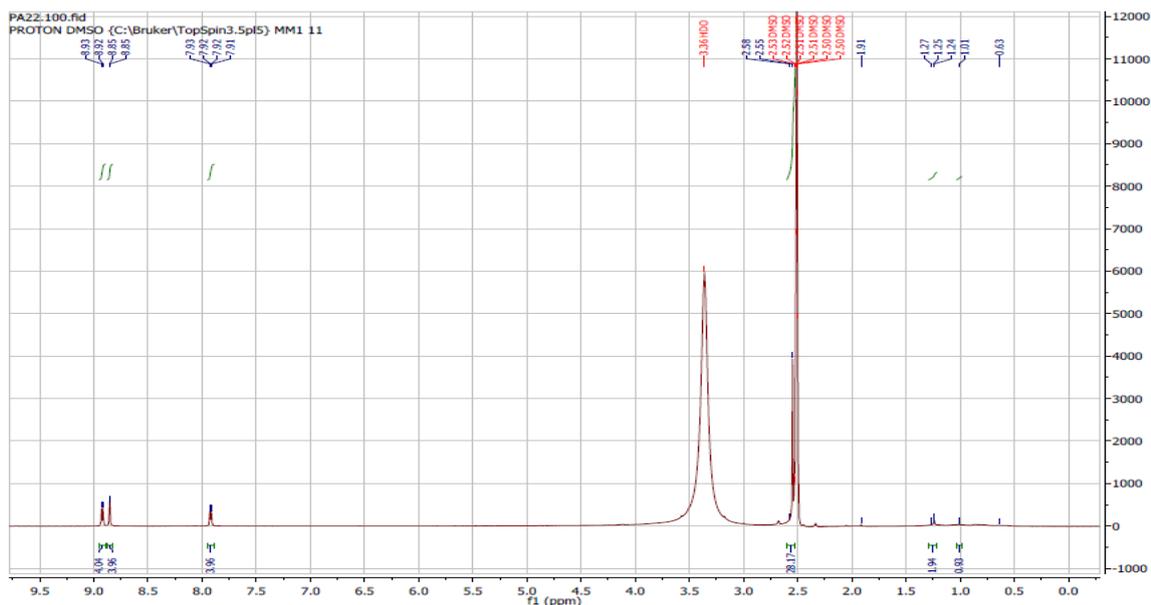


Figure 3. ¹H NMR spectra for C₂.

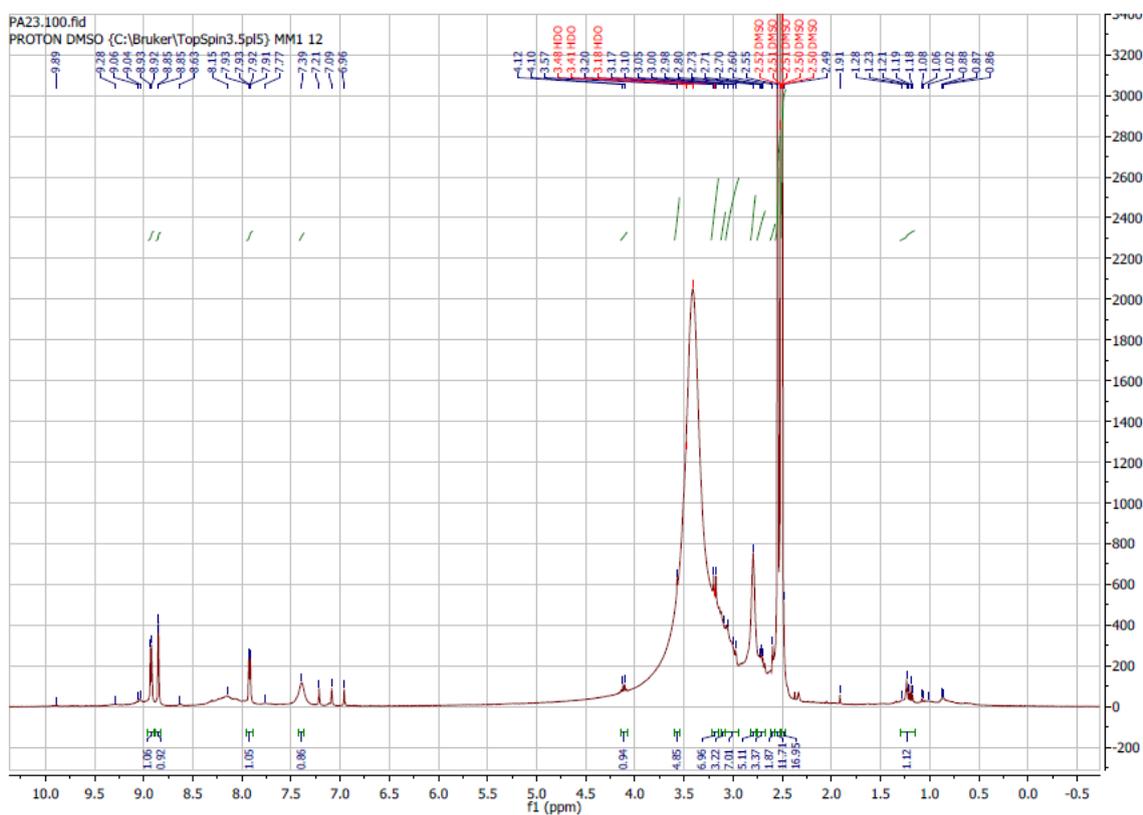


Figure 4. ¹H NMR spectra for C₃.

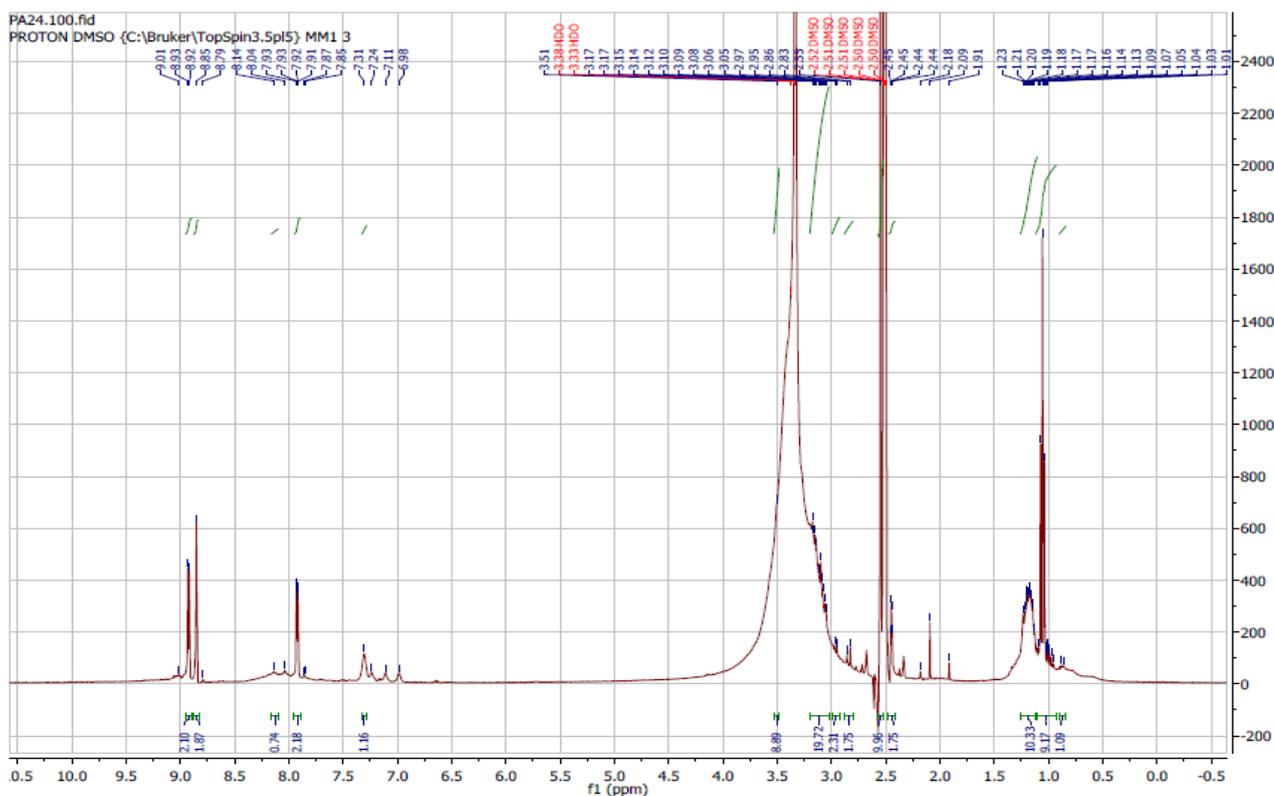


Figure 6. ^1H NMR spectra for C_4 .

3.6. Electrochemical studies of the ruthenium(II) complexes

The cyclic and square wave voltammogram of the complexes in DMSO were studied at a scan rate of 25 mV/s and tetrabutylammonium hexafluorophosphate as a supporting electrolyte in the potential range -1.5 to +1.5 V using Ag|AgCl electrode. The voltammogram (Figures 7a-d) displayed $\text{Ru}(\text{III})/\text{Ru}(\text{II})$ couple at positive potential and a ligand-base reduction at negative potentials. The irreversible reductions at -0.80 V for C_1 , -0.92 V for C_2 and -0.86 V for C_3 were due to the π -conjugation bonds present in the ligands. For C_4 , one reversible reduction peak was shown at -0.89 V and was attributed to the $\text{C}\equiv\text{N}$ moiety that are π -donor groups that enhance the electron density of the complex [31-34].

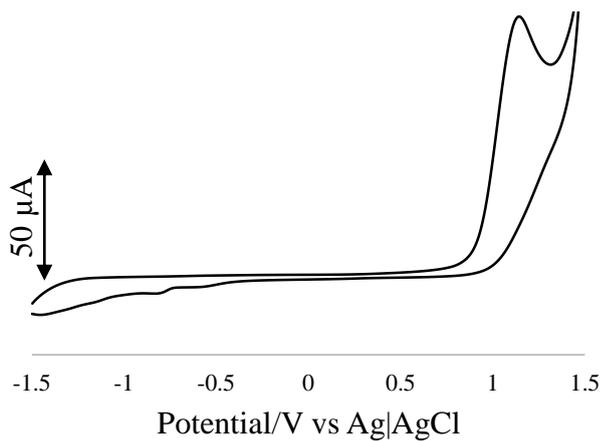


Figure 7a₁: CV of C₁.

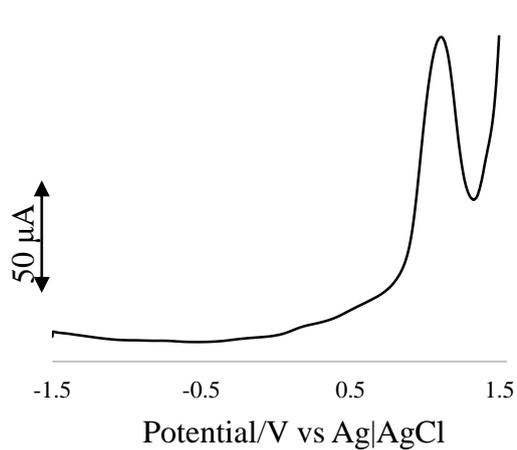


Figure 7a₂: SW of C₁.

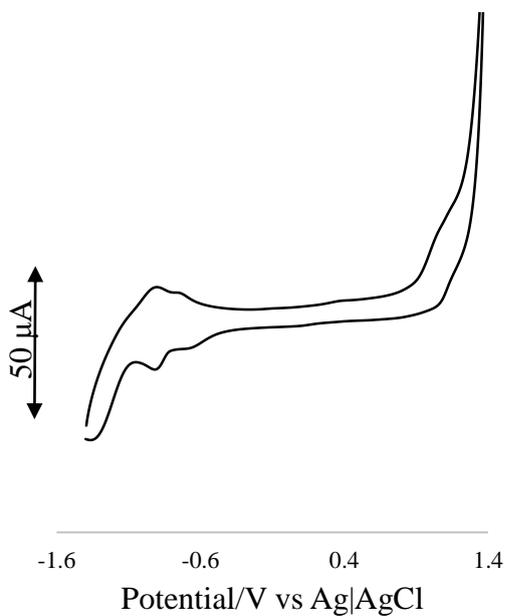


Figure 7b₁: CV of C₂.

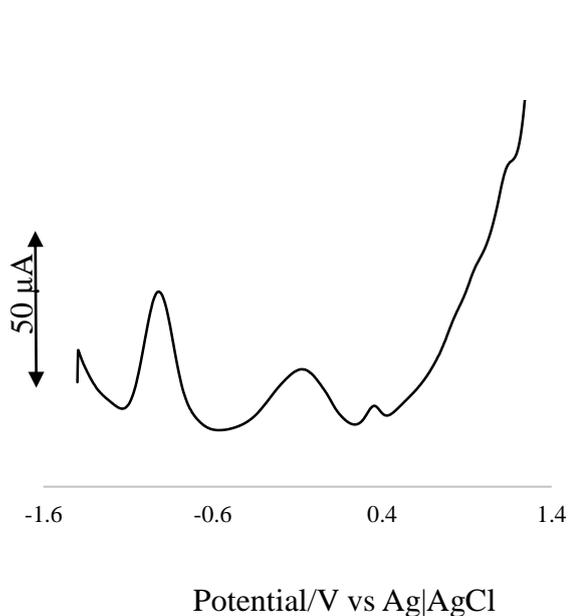


Figure 7b₂: SW of C₂.

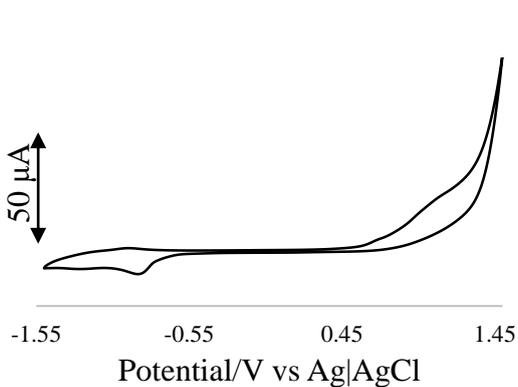


Figure 7c₂: SW of C₃.

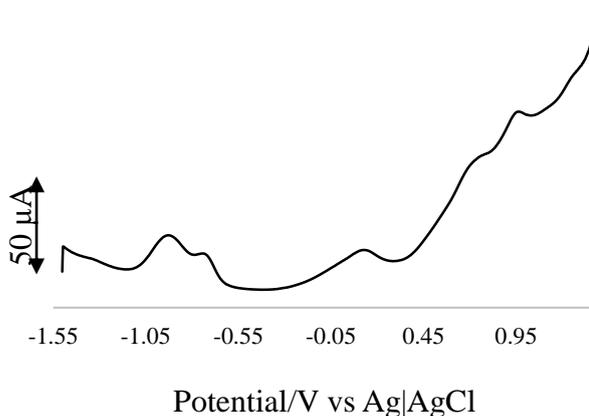
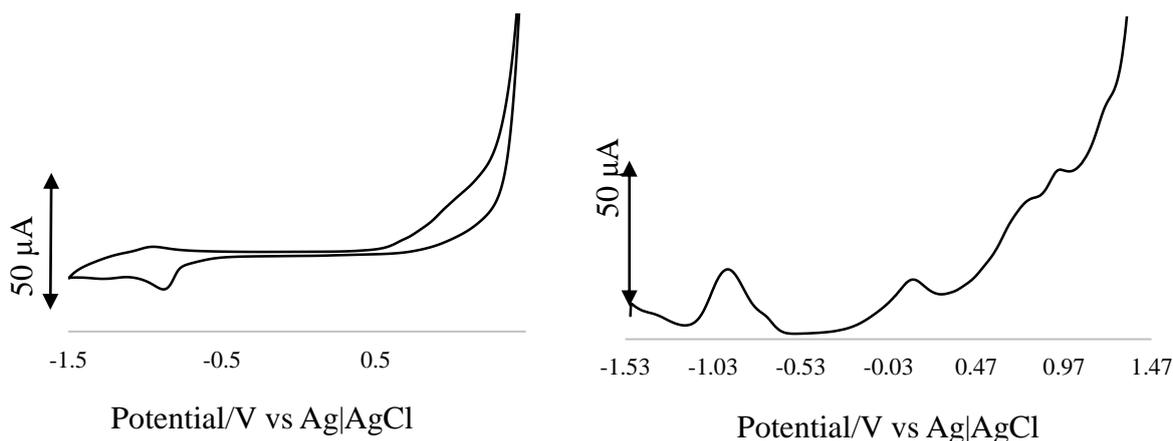


Figure 7c₂: SW of C₃.

Figure 7d₁: CV of C₄.Figure 7d₂: SW of C₄.**Figure 7.** The cyclic and square wave voltammogram of the complexes

The more positive reductions were an indication of an additional π -conjugation bond (C=C, C \equiv N) from the dithiolate ligands. The quasi reversible oxidation peak was displayed at +1.08 V in C₁ and was assigned to Ru^(III)/Ru^(II) redox couple. For C₂, C₃ and C₄, the metal center wave couple were found at +1.07 V, +0.94 V and +1.09 V, respectively.

4. CONCLUSION

Ru(II) complexes of mixed bipyridyl and dithiolate ligands were successfully synthesized and spectroscopically characterized. Molar conductivity measurements showed that the dithiolate ligands were electrolytes and the Ru(II) complexes were non-electrolyte in aqueous solution. FTIR spectra studies confirmed the coordination of 4,4-dicarboxylic-2,2-bipyridine and dithiolate ligands in bidentate chelating mode to form RuN₂S₂ centre. Electronic spectra studies of the Ru(II) complexes confirmed the proposed square planar geometries around the Ru(II) ion. Cyclic voltammetry of all the Ru(II) complexes were consistent with one irreversible ligand based reduction. The more negative reduction potentials were ascribed to the extended π -conjugation in the ligand which enhanced photo-electrochemical properties of the ruthenium(II) complexes.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this paper.

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