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SNYTHESIS AND CHARACTERIZATION OF HYDRATED TRIS (2, 2'-BIPYRIDINE) DICHLORIDE RUTHENIUM (II) COMPLEX AND ITS ELECTROCATALYTIC ACTIVITY TOWARDS CARBON DI OXIDE REDUCTION

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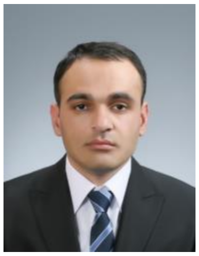

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ABSTRACT

A new convenient method for the synthesis of hydrated tris (2, 2'-bipyridine) dichloride ruthenium (II) complex has been developed. We introduced the chlorosulfonic acid as a chlorinating reagent during our synthetic process which replace the hexafluorophosphate radical of the [Ru (bpy) $_3$] (PF6)$_2$ complex with chloride, form hydrated Tris [Ru (bpy) $_3$] (Cl)$_2$ complex. The corresponding complex is characterized with UV-Visible, IR, CV, 1 H and C 13 NMR spectroscopic technique. The synthesized hydrated ruthenium complex was then checked as an electrocatalyst for the reduction of carbon dioxide in a designed electrolytic cell. The carbon dioxide gas in the aqueous solution of Tris (2, 2'-bipyridine) ruthenium (II) dichloride catalyst, at the potential of 1.5 V reduced to methane gas, examined with FTIR spectrometer.

Keywords: Chlorosulfonic acid, 2,2'-bipyridine, Spectroscopic study, Cyclic voltammetry, Electrocatalytic reduction.

INTRODUCTION

Tris (2, 2'-bipyridine) ruthenium (II) complex has been extensively studied and widely used in photocatalysis, electrocatalysis and photoelectrochemical cells [1]. In particular, their ability to function as tuneable pigments in dye-sensitized solar cells (DSSC) has attracted considerable attention [2]. Moreover, the unique combination of chemical stability and redox property of the tris (2, 2'-bipyridine) ruthenium complex plays an important role of a photocatalyst for the reduction of carbon dioxide in aqueous solution forming hydrogen gas, carbon monoxide and formic acid [3-4]. Previously many methods were used for the synthesis of tris (2, 2'-bipridine) ruthenium (II) dichloride complex, which have tedious long procedures [5-6]. In this paper we report a new convenient method for the synthesis of tris (2, 2'-bipyridine) ruthenium (II).X_2 complexes ($X=PF_6$, Cl) with good yields, and also the electrocatalytic use of tris (2, 2'-bipyridine) ruthenium (II) dichloride complex for the reduction of carbon dioxide. The ruthenium complex and its catalytic results were then fully characterized with spectroscopic techniques. The UV-Visible study for our complex tris (2, 2'-bipyridine) ruthenium (II) dichloride showed the UV-Visible absorption at 455 nm in water. The reported data showed that the absorption maxima changed for the ruthenium complex when solubilized in different solvents and if bonded with other substances [7-8]. The ruthenium complex structure confirmed from the 1 H, C 13 NMR and IR spectrums. The electrochemical study of tris (2, 2'-bipyridine) ruthenium (II) dichloride show one-electron redox process Ru (II)/ Ru (III), also reported elsewhere [9-10].We further investigate the electrocatalytic activity of the tris (2, 2'-bipyridine) ruthenium (II) dichloride complex for the carbon dioxide reduction in aqueous solution at pH 8. The electrolytic cell used during the carbon dioxide reduction process designed such likes; its cathode was made from the steel wire gauze, which acts as a multi cathode system providing large surface area for the reduction of carbon dioxide. The potential of 1.5 V was given to the electrolytic cell during the carbon dioxide reduction process for 1 h period of time. The carbon dioxide reduction results were then examined with FTIR spectrometer showed that the tris (2, 2'-bipyridine) ruthenium (II) dichloride complex act as an electrocatalyst reduced the carbon dioxide to methane gas.

RESULT & DISCUSSION

The infrared spectra observed with (Varian 640-IR) FTIR Spectrometer in the range of 400- 4000 nm. The IR spectrum of ruthenium bipyridine complex was measured on the ATR Zn-Se alloy plate, using the scanning method. The gases formed during the catalytic reduction of carbon dioxide, their IR spectrum were observed within IR gas cell (pike technology) having dimensions 100 mm long and 25 mm in a diameter, using the KBr window. The 1 H and C 13 NMR spectrums were measured with Varian 500 MHz NMR spectrometer using the deuterated dimethyl sulfoxide solvent ($Me_2SO\text{-}d_6$). The UV-Visible spectra of the ruthenium complex was measured in distill water (solvent) using the Optizen 3220 UV-Visible spectrometer. The electrochemical measurements done with the help of electrochemical analyzer (Model 100 B, USA) and a three electrodes cell stand. The three electrodes were used, Ag/AgCl/3 M NaCl electrode as a reference electrode, glassy carbon electrode as a working electrode and the platinum electrode as an auxiliary electrode. Furthermore, the electrocatalytic reduction of carbon dioxide was carried out in a 5-neck glass jar act as an electrolytic cell. The electrolytic cell was connected to a carbon dioxide gas cylinder, hydrogen gas source and with a programmable power supply (HM 7044), providing voltage during the carbon dioxide reduction process.

MATERIALS

All chemicals were of regent-grade and used as received. The ruthenium trichloride trihydrate 99.98%, Chlorosulfonic acid 99%, and NH_4PF_6 99.99%, were obtained from the Sigma-Aldrich. The 2, 2'-bipyridine was purchased from the TCI Japan. The anhydrous solvents were used throughout the synthesis.

EXPERIMENTAL SECTION

Synthesis of Ru (bipy) $_3(PF_6)_2$

The 'Ruthenium-blue' solution was prepared according to the described procedure [11]. The (0.5 g) of hydrated ruthenium trichloride salt was dissolved in mixed solution of ethanol (15ml) and water (10ml), and then refluxed under inert argon till to the formation of blue solution which takes approximately 4 hour. The (1.5 g) 2, 2'-bipyridine (bpy) in (10 ml) ethanol were then added to this ruthenium blue solution and refluxed for another 30 minutes under argon forming dark red solution. The dark red solution was then cooled up to room temperature and added to it under stirring (1.5 g) of NH_4PF_6 in (10 ml) of distill water, upon which it immediately formed the brown red precipitate of Ru (bpy) $_3(PF_6)_2$ complex. The precipitate was separated through filtration and put in a freezer drier to evaporate the solvents.

Synthesis of [Ru (bipy) $_3$] (Cl) $_2$ .xH_2O

The (1 g) Ru (bpy) $_3(PF_6)_2$ complex was dissolved in (30 ml) of anhydrous chloroform, using (250 ml) three necks round bottom flask. The reaction flask was connected to a reflux condenser and constant dropping funnel. The anhydrous calcium chloride tubes were connected to the reflux condenser and constant dropping funnel to keeps the reaction flask from the moisture. The reaction mixture heat at a 65 $^{\circ}$C temperature for 15mintues under inert argon and then added to it slowly (3 ml) of pure Chlorosulfonic acid through the constant dropping funnel. The reaction mixture was then refluxed for 1 h, forming a creamy green precipitate. The creamy green precipitate was cooled and concentrated to 10ml using rotary evaporator. The creamy green precipitate was then dissolved in (10 ml) of anhydrous ethanol forming dark orange solution, if insoluble materials remained inside filtered it from the solution. The (15 ml) of anhydrous diethyl ether was added to the dark orange solution, upon which it immediately formed the red-orange microcrystals of [Ru (bpy) $_3$] (Cl) $_2$ .xH_2O complex. The crystals were separated upon filtration and then washed two times with (5 ml) anhydrous diethyl ether. The ruthenium complex crystals were put in a freezer drier over night to remove the solvents. The tris (2, 2'-bipyridine) ruthenium (II) dichloride complex was obtained with a good yield of 81%.

UV-Visible spectra

The UV-visible spectra for the ruthenium complex was measured in distill water. The absorption spectra of Ru [(bpy) $_3$] (Cl) $_2$ .xH_2O complex at different concentrations show the maximum absorption at 455 nm as depicted in Figure 1.

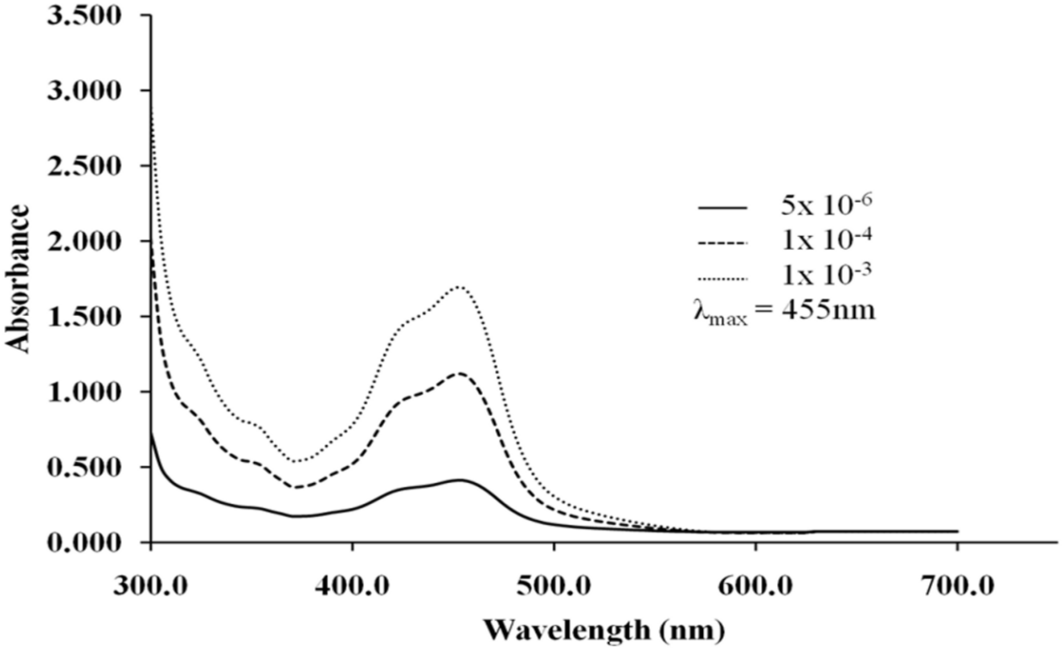

Figure 1: UV-Visible absorption spectrum of Ru [(bpy)$_3$] (Cl)$_2$ complex at different concentrations of (1x10^{-4}, 1x10^{-5}, and 10x10^{-6} M) in distilled water.

IR Spectrum

The IR spectrum of Ru [(bpy) $_3$] (Cl) $_2$ .xH_2O complex is shown in Figure 2.

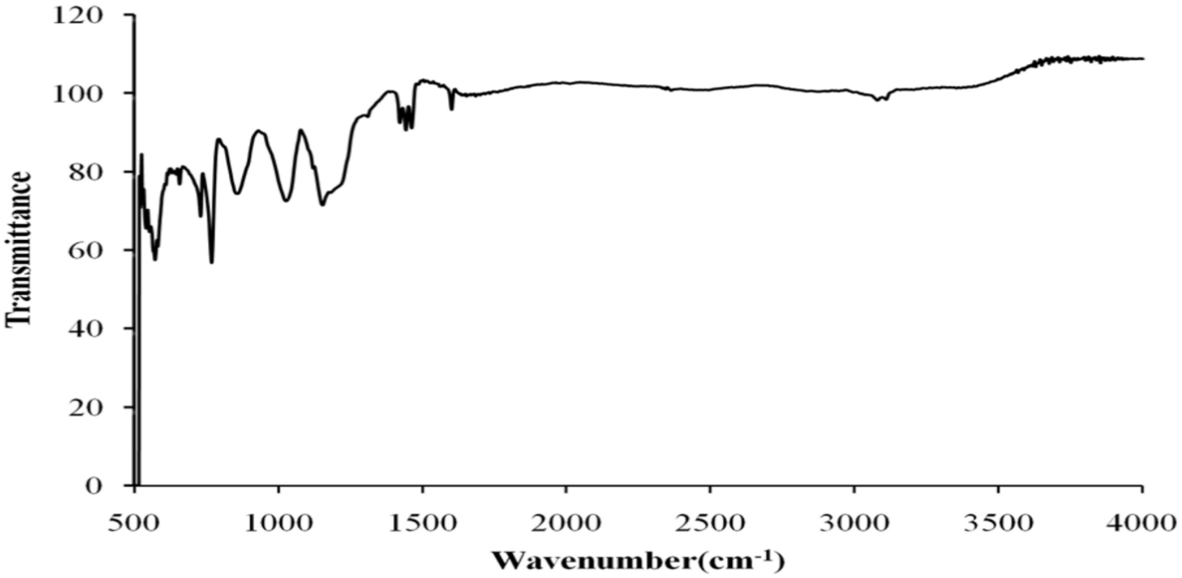

Figure 2: FTIR spectrum of Ru [(bpy)$_3$] (Cl)$_2$ complex detected on ATR (Zn-Se) plate, used the scanning method within the range of 400-4000 cm^{-1}.

The IR spectrum showing ring frequencies of the bipyridine ring at a1602, 1463, 1443 and 1423 cm^{-1}(assigned to $\nu_{C=C}$ and $\nu_{C=N}$) [14].The spectrum shows two new bands at 1443 and 1310 cm^{-1}, this is impossible to determine with certainty the origin of these bands, is evident that ruthenium metal cheated with 2,2'-bipyridine ligand showing the ruthenium-nitrogen skeletal vibration, and such like peaks were not observed in the free ligand spectrum [15]. The absorption band between 1216-1122 cm^{-1} and 1000-600 cm^{-1} were assigned to hydrogen dependent absorptions and inplane hydrogen deformation modes [16].

NMR Spectrum

The 1 H, 13 C NMR spectrums of the Ru [(bipy) $_3$] (Cl) $_2$ .xH_2O complex were recorded on 500 MHz NMR Spectrometer. The deuterated 99.9% Me_2SO-d_6 was used as a NMR solvent containing tetramethylsilane as a standard reference. All the NMR experiments were carried out under room temperature (298 K).The 1 H spectrum of the ruthenium complex shown in Figure 3(a).

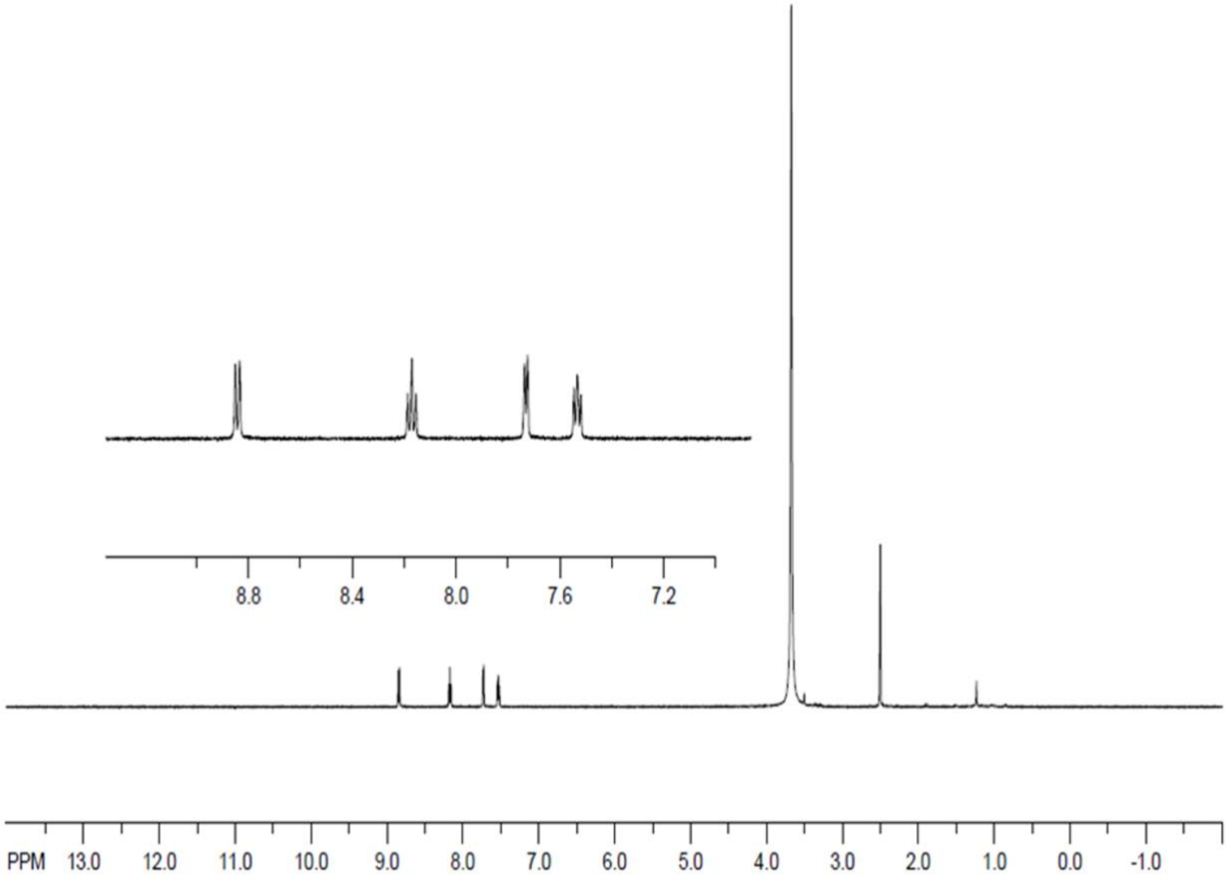

Figure 3 (a): 1 H NMR spectrum of the Ru [(bpy) $_3$] (Cl) $_2$ complex in the Me_2SO-d_6 solvent at 298 K.

The peaks at 1.223 ppm and 3.674 ppm indicate diethyl ether and water solvents respectively. The 2, 2'-bipyridine NMR spectrum shown in the expanded form having two doublets and two triplets peaks illustrates downfield chemical shifts for the 2 and 3 bipyridine ring protons and upfield chemical shifts for ring proton 4 and 5. The C 13 NMR spectrum depicted in the Figure 3(b),

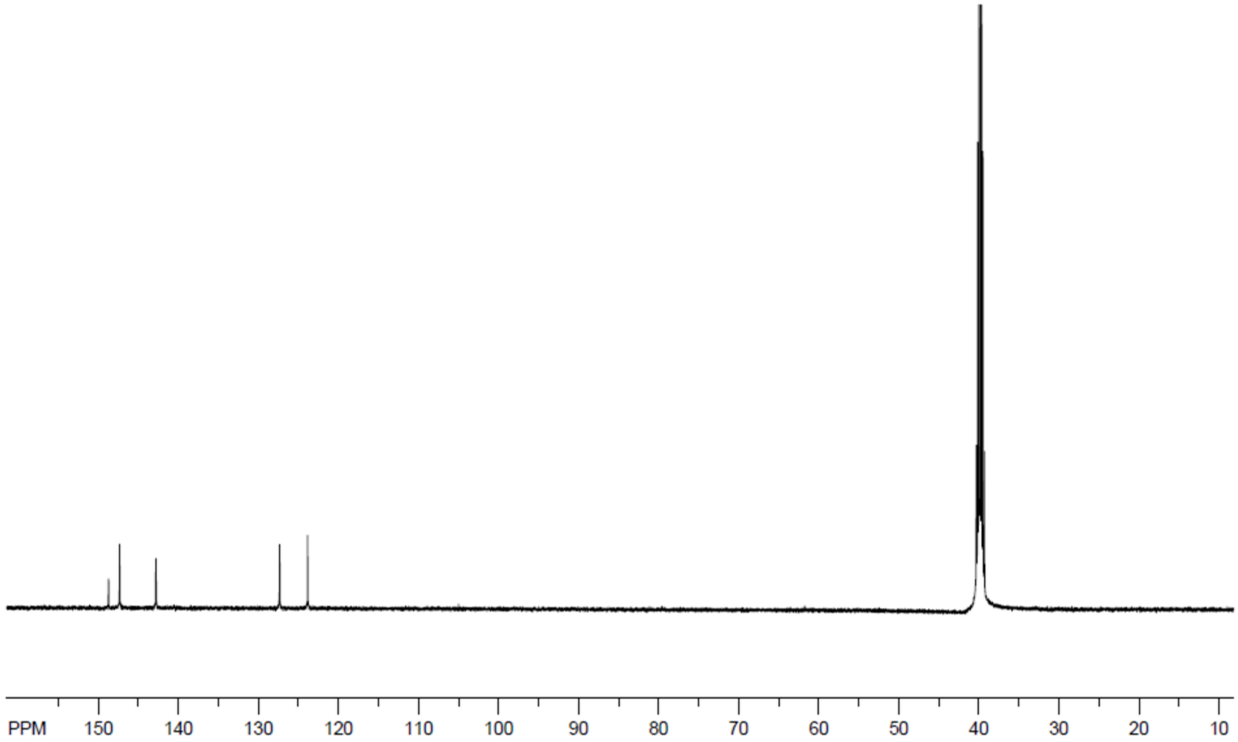

Figure 3 (b): C 13 NMR spectrum of the Ru [(bpy) $_3$] (Cl) $_2$ complex in the Me_2SO-d_6 solvent at 298K.

showing that the C3, C5 and C4 of 2,2'-bipyridine ligand in Ru [(bpy) $_3$] (Cl) $_2$ complex shows downfield chemical shift and the remaining two carbon of the 2,2'-bipyridine ligand C6 and C2 shows upfield chemical shift. The change in the carbon chemical shift is due to the magnetic anisotropy of polarization of the heterocyclic bipyridine rings, and also due to the ligand-metal chelation which changed the electronic density within the 2, 2'-bipyridine ligands [17]. We compared the 1 H and C 13 chemical shifts of our ruthenium complex with the 1 H and C 13 chemical shifts of free 2, 2'-bipyridine ligand, illustrates in (Table 1) and (Table 2) respectively.

Table: 1 1H NMR chemical shifts for the ruthenium complex recorded at a ppm scale.

$[Ru(bpy)_3]Cl_2 . xH_2O$		2,2'-bipyridine	
1H δ (ppm)	Assignment	1H δ (ppm)	Assignment
7.5 (triplet)	3	7.4	3
7.7 (doublet)	5	7.9	5
8.1 (triplet)	4	8.5	4
8.8 (doublet)	2	8.7	2

*δ = Chemical shift; ppm = parts per million

Table: 2 13 C NMR chemical shifts for the ruthenium complex recorded at a ppm scale.

$[Ru(bpy)_3]Cl_2 . xH_2O$		2,2'-bipyridine	
C13 δ (ppm)	Assignment	C13 δ (ppm)	Assignment
123.8	3	120.7	3
127.3	5	124.1	5
142.7	4	137.2	4
147.3	2	149.3	2
148.6	6	155.6	6

The 2, 2'-bipyridine ligand shows great variation in chemical shifts after chelation with ruthenium metal [17-18].

Cyclic Voltammetric Study

Cyclic voltammetric study of the Ru $[(bpy)_3] (Cl)_2 .xH_2O$ complex was performed on three electrode system. We used glassy carbon electrode as a working electrode, platinum electrode as a counter electrode and Ag/AgCl as a reference electrode. The cyclic voltammetric study of the Ru $[(bpy)_3] (Cl)_2$

complex shows one electron reversible cyclic voltammogram [19]. The cyclic voltammetric study of our tris bipyridine ruthenium (II) dichloride complex (1mmol), in 0.1M electrolytic KCl aqueous solution also gives one electron reversible cyclic voltammogram, within potential sweeps from -1.5 to 2.0 V. The cyclic voltammogram of the ruthenium complex was obtained at the scan rate of 50, 100 and 150 mVs^{-1}, showing the ruthenium complex Ru (II)/ Ru (III) redox state is depicted in Figure 4.

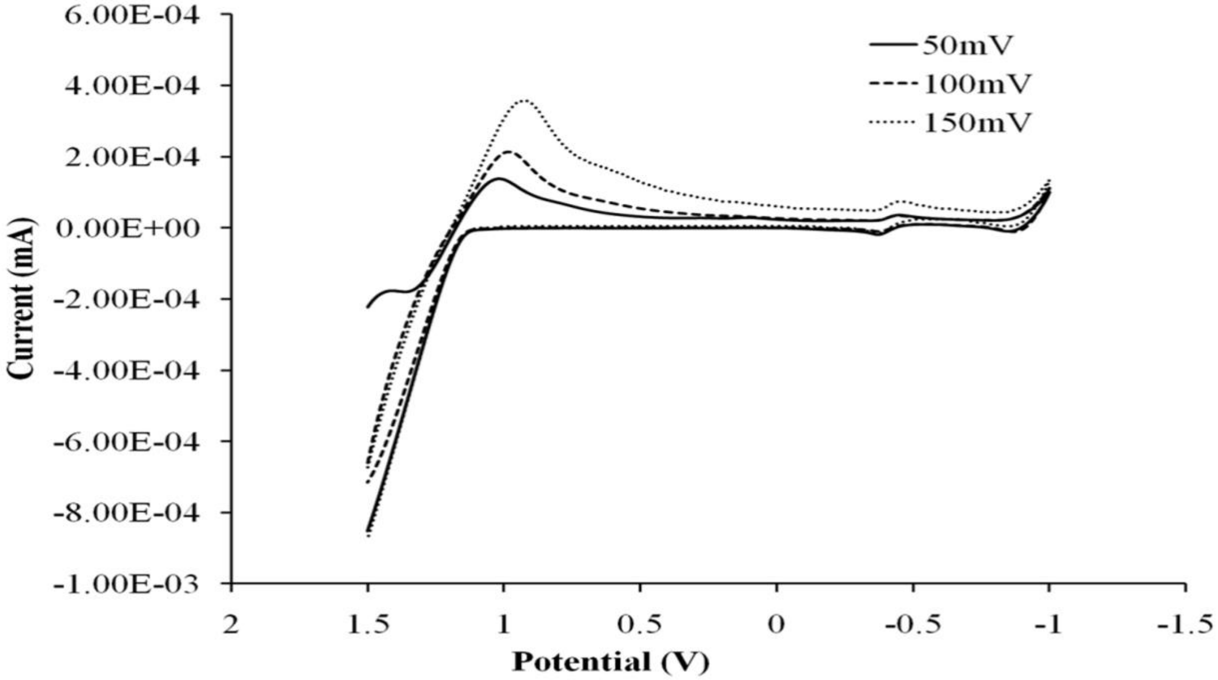

Figure 4: Cyclic voltammogram of Ru [(bpy)$_3$] (Cl)$_2$ complex at the scan rates of 50, 100 and 150 mVs^{-1} in the aqueous 0.1 M KCl electrolytic solution.

Electrocatalytic Reduction of Carbon Dioxide

The Ru [(bpy)$_3$] (Cl)$_2$ complex was investigate as an electrocatalyst for the reduction of carbon dioxide in aqueous media at a room temperature. The carbon dioxide reduction process was performed in a five neck gas jar which acts as an electrolytic cell. The cathode of the electrolytic cell designed from the steel wire gauze, which acts as a multi cathode system. The cathode fitted in the gas jar such like, that surrounded the single stannous anode rod, which is embedded in the middle of the gas jar. The two electrodes were then connected to a programmable power supply HM 7044 and adjusted its voltage to 1.5 V. The electrolytic cell was sealed up from the atmosphere, and also vacuumed before starting the experiment is depicted in Figure 5.

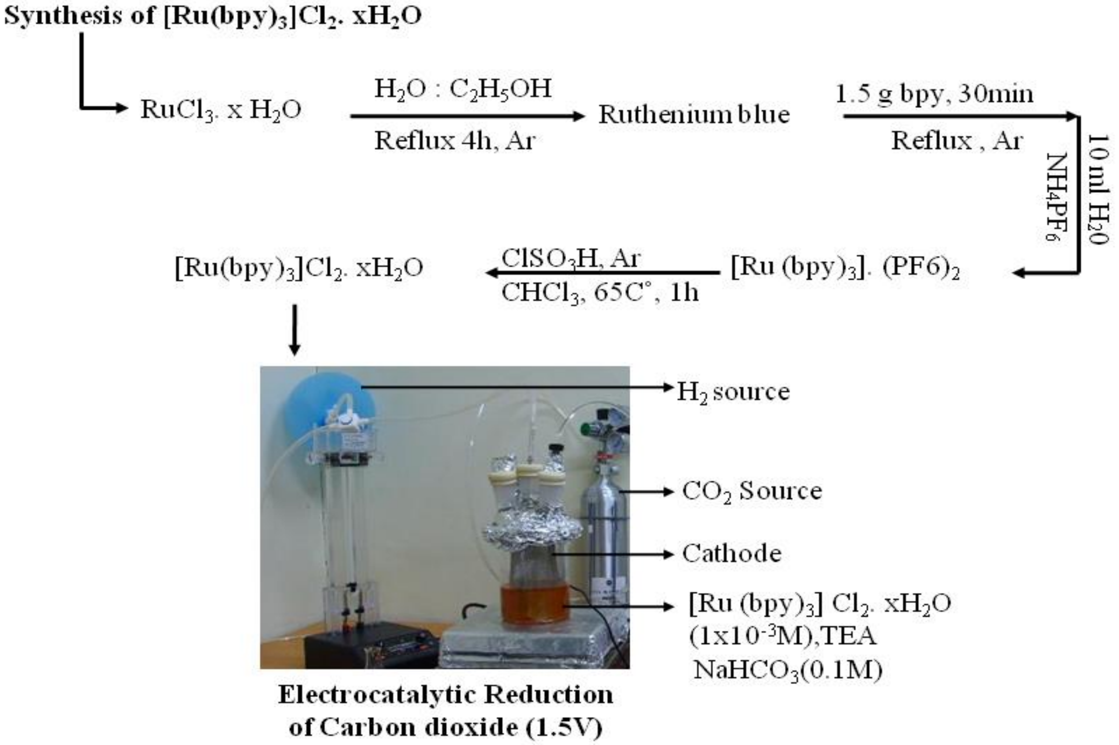

Figure 5: Designed electrolytic cell for the catalytic reduction of carbon dioxide.

The electrolytic cell contained 100 ml of $1x10^{-3}$ M Ru $[(bpy)_3]$ $(Cl)_2$ catalyst solution, made in the 0.1 M $NaHCO_3$ electrolytic aqueous solution. The carbon dioxide reduction process was carried under basic condition, using the pH 8 [20]. The triethanolamine (TEA) were used as an electron donor source during the carbon dioxide reduction. The catalytic solution was first saturated with carbon dioxide gas and then passed from it hydrogen gas slowly throughout the reaction process by means of a long needle, embedded in the electrolytic cell. The voltage of 1.5 V was given to the electrolytic cell for one hour period of time. The electrodes were then disconnected from the voltage source after one hour, putting a long needle syringe in the electrocatalytic cell to collect the gases formed during the carbon dioxide reduction process. The gases were checked with IR, using the IR gas cell which is vacuumed before use. The IR spectrum results shows that the carbon dioxide reduced to methane gas as depicted in Figure 6(a).

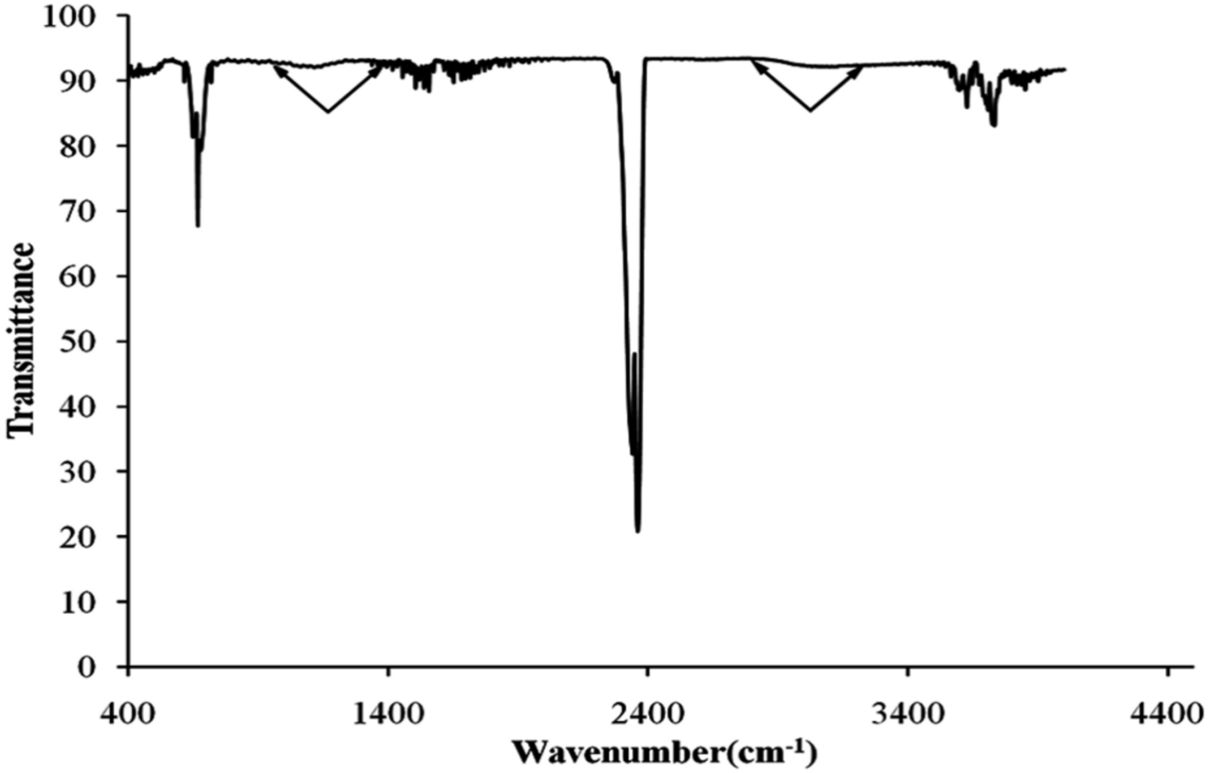

Figure 6 (a): FTIR spectrum of methane gas formed from the electrocatalytic reduction of carbon dioxide at 1.5 V, checked within the IR- gas cell, used scan range 400-4000 cm^{-1}.

We also compared our results with the IR spectrum of pure methane and carbon dioxide gases mixture as depicted in Figure 6(b).

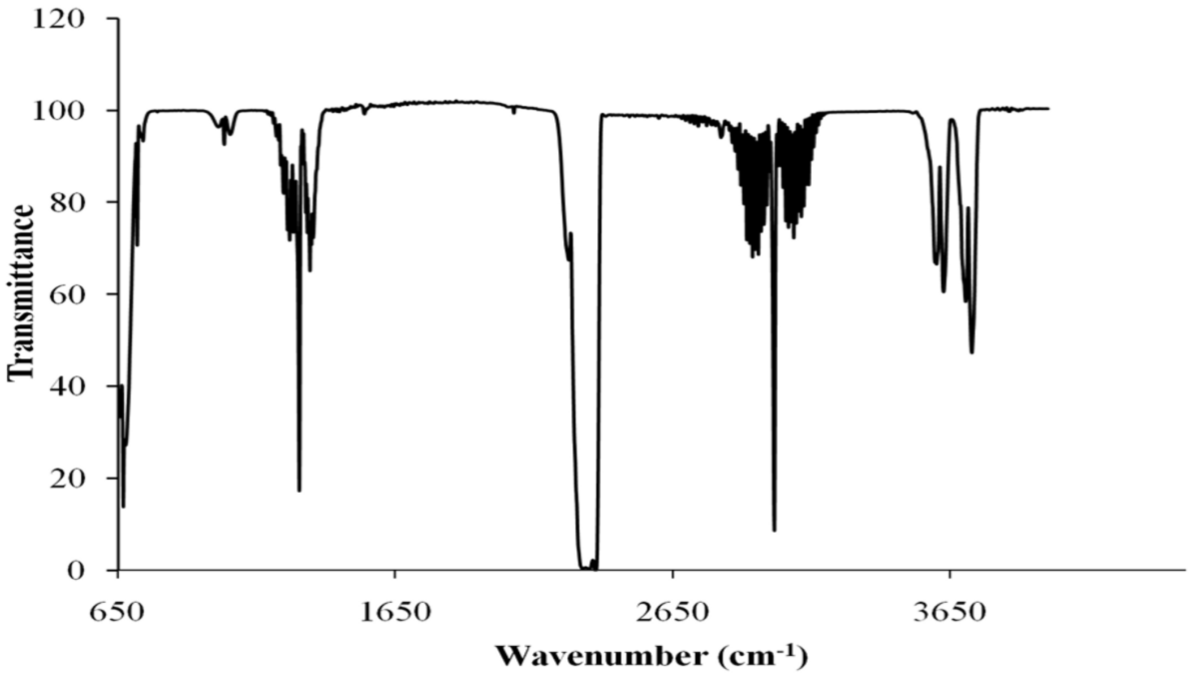

Figure 6 (b): FTIR spectrum of pure methane and carbon dioxide gas mixture detected within the IR- gas cell, used the scanning method within the range of 650-4000 cm^{-1}.

The gas IR spectrum of the carbon dioxide reduction process shows two new peaks. The first one board peak shown with arrow in the range of 1400-1025cm^{-1} and second one board peak shown in the range of 3015-2920cm^{-1} respectively, indicating the bending and stretching mode of C-H bond of methane gas [21].The noisy peak form in the 1890-1400cm^{-1} range showing water peak. The methane peak is not sharp due to the trace concentration of methane gas formed and also due to the unreacted carbon dioxide gas and water vapors [21-22]. The reduction of the carbon dioxide to methane gas is eight electron acceptance processes. The triethanolamine donate electrons to the ruthenium bipyridine catalyst for the carbon dioxide reduction [23-24].

$$CO_2 + 8H^+ + 8TEA \longrightarrow CH_4 + 4H_2O + 8TEA^+$$

$$[Ru\,(bpy)_3]^{2+} + TEA \longrightarrow [Ru\,(bpy)_3]^+ + TEA^+$$

The proton for the reduction of carbon dioxide comes either from oxidized amine, water or from the substance which use as a hydrogen gas source [25].

CONCLUSION

We synthesized tris (2, 2'-bipyridine).Cl_2 ruthenium (II) complex using a new convenient method. The tris (2, 2'-bipyridine) $(PF_6)_2$ ruthenium (II) complex were synthesized first, used the ruthenium blue solution. We replaced successfully the secondary ligand PF_6 of tris (2, 2'-bipyridine) $(PF_6)_2$ ruthenium (II) complex with chloride radical, reacting it with Chlorosulfonic acid, which results into the formation of hydrated tris (2, 2'-bipyridine).Cl_2 ruthenium (II) complex. The structure of tris (2, 2'-bipyridine).Cl_2 ruthenium (II) complex was confirmed from 1 H and C 13 NMR and FTIR like spectroscopic techniques. The UV-Visible absorption spectra in aqueous solvent at 455nm confirmed that our complex is in the ruthenium (II) oxidation state. The electrochemical study for our ruthenium complex in the aqueous electrolytic potassium chloride solution showed one electron reduction process Ru^{II}/Ru^{III}. The tris (2, 2'-bipyridine).Cl_2 ruthenium (II) complex act as an electrocatalyst reduced the carbon dioxide to methane gas at the potential of 1.5 V. The FTIR spectrum results confirmed the methane gas formation.

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REFERENCES

[1] Kuppuswamy Kalyanasundaram, *Coordination Chemistry Review*, **1982**, 46, 244.

[2] Mohammad Khaja Nazeeruddin, Michael Gratzel, *Struct Bond*, **2007**, 123, 175.

[3] Jean-Marie Lehn, Raymond Ziessel, *proceedings of the National Academy of Sciences USA*, **1982**, 79, 704.

[4] Jean-Marie Lehn, Raymond Ziessel, *Journal of Organomettalic*, Chemistry, **1990**, 382, 173.

[5] Zhiqin Ji, Songping D Huang, Ana R Guadalupe, *Inorganic Chimica Acta*, **2000**,305,134.

[6] Hartmut Yersin, Erich Gallhuber, Arnd Vogler, Horst Kunkely, *Journal of American Chemical Society*, **1983**, 105, 4156.

[7] Fred E Lytle, David M Hercules. *Journal of American Chemical Society*, **1969**, 91:2, 257.

[8] Shikao Shi, Ji Zhou, Ruilong Zong, Jianping Ye, *Journal of Luminescence*, **2007**, 122-123, 220.

[9] Giovanni Carlo Fiaccabrino, Milena Koudelka-Hep, Yun-Tai Hsueh, D Scott Collins, Rosemary L Smith, *Analytical Chemistry*, **1998**, 70, 4161.

[10] Ramasamy Ramaraj, Christian Kabbe, Fritz Scholz, *Journal of Electrochem, Communications*, **2000**, 2, 194.

[11] Togano Tadashi, Nagao Noriharu, Tsuchida Mitsuko, Kumakura Hiromi, Hisamatsu Kumiko, Howell F Scott, Mukaida Masao, *Inorganic Chimica Acta*, **1992**, 195, 225.

[12] Testurou Handa, Motoko Sakai, Masayuki Nakagaki, *Journal of American Chemical Society*, **1986**, 90, 3380.

[13] William H Quayle, Jack H Lunsford, *Inorganic Chemistry*, **1982**, 21, 103.

[14] Shi Dao-Jun, Masao Kaneko, *Journal of Photochemistry and Photobiology, A: Chemistry*, **1990**, 51, 161.

[15] R G Inskeep, *Journal of Inorganic Nuclear Chemistry*, **1962**, 24, 776.

[16] J S Strukl, J L Walter, *Journal spectrochimica Acta*, **1971**, 27A, 221.

[17] Guillermo Orellana, Carlos Alvarez Ibarra, Jorge Santoro, *Inorganic Chemistry*, **1988**, 27, 1030.

[18] Yasuhiko Ohsawa, M. Keith DeArmond, Kenneth W. Hanck, Charles G. Moreland, *Journal of American Chemical Society*, **1985**, 107, 5386.

[19] Baoqiang Lv, Anshu Ren, Yun Luo, Hongyan Yuan, Dan Xiao, *Russian Journal of Electrochemistry*, **2008**, 44, 1051.

[20] Masashi Azuma, Kazuhito Hashimoto, Masahiro Hiramoto, *Journal of Electrochemical Society*, **1990**, 137, 1778.

[21] Joseph Z. Su, Malgosia Kanabus-Kaminska, FTIR Gas Measurement in Home Smoke Alarm Tests. IRC- RR. **2002**, 107, 25: http://irc.nrc-cnrc.gc.ca/ircpubs.

[22] Robert L. Spellicy, Imacc Industrial Monitor & Control Crop, Round Rock, Texas, **2009**. 9: http://www.docstoc.com/docs/14923067/FTIR-Monitoring.

[23] Etsuko Fujita, Daniel L. DuBois, Carbon dioxide Fixation. BNL- 67078, Brookhaven National Lab Upton NY 34, **2005**: www.osti.gov/bridge/servlets/purl/752960-T3jXzX/webviewable/.

[24] Matthew R. Hudson, Electrochemical Reduction of Carbon dioxide. USA, **2005**, 15: http://www2.potsdam.edu/exochemistry/ElectroRednCO2.pdf.

[25] F. Richard Keene, Carol Creutz, Norman Sutin, *Coordination Chemistry Reviews*, **1985**, 64, 260.