ORIGINAL ARTICLE

Dichlorobis(5-methyl-2-(phenylazo)pyridine) ruthenium(II) complex: characterization and NMR spectroscopy

Uraiwan Changsaluk[1] and Kanidtha Hansongnern[2]

Abstract

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The new azoimine functionalized ligand, 5-methyl-2-(phenylazo)pyridine (5mazpy) was synthesized. It reacted with $RuCl_3.3H_2O$ in ethanolic solution to give the isomeric $[Ru(5mazpy)_2Cl_2]$ complexes. One of the isomers was characterized by infrared spectroscopy, nuclear magnetic resonance spectroscopy, UV-Visible absorption spectroscopy, and cyclic voltammetry. Results from infrared spectroscopy show that the N=N stretching mode in the complex appeared at a lower frequency than that in the free ligand. The formulation of complex was comfirmed by elemental analysis. The ^1H and ^{13}C NMR spectra of complex exhibited two sets of ligand peaks, this indicated that both 5mazpy ligands were in different environments. Therefore, the $[Ru(5mazpy)_2Cl_2]$ complex has no C_2-symmetry. Results from UV-Visible absorption spectroscopy show that the complex exhibited the $t_2(Ru) \rightarrow \pi^*(5mazpy)$ MLCT transitions in the visible region. Redox studies showed the Ru(III)/Ru(II) couple at +0.62 V and two azo reductions couple at -1.17 V and -1.51 V versus ferrocene couple.

Key words : ruthenium, 5-methyl-2-(phenylazo)pyridine, azoimine

[1]Ph.D Student in Chemistry, [2]Ph.D.(Chemistry), Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla 90112 Thailand.
Corresponding e-mail: kanidtha.h@psu.ac.th
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บทคัดย่อ

อุไรวรรณ ช่างสลัก และ ขนิษฐา หาญสูงเนิน

การยืนยันโครงสร้าง และนิวเคลียร์แมกเนติกเรโซแนนซ์ สเปกโทรสโกปีของสารประกอบเชิงซ้อนของโลหะรูทีเนียมที่มีลิแกนด์เป็น 5-methyl-2-(phenylazo)pyridine

ว. สงขลานครินทร์ วทท. ธ.ค. 2548 27(ฉบับพิเศษ 3) : 739-749

ได้สังเคราะห์ลิแกนด์เอโซอิมีนตัวใหม่ คือ 5-methyl-2-(phenylazo)pyridine (5mazpy) ลิแกนด์ใหม่ 5mazpy นี้เมื่อนำมาทำปฏิกิริยากับ $RuCl_3.3H_2O$ ในตัวทำละลายเอทานอล เกิดเป็นไอโซเมอร์ของสารประกอบ $[Ru(5mazpy)_2Cl_2]$ หลายตัว ได้ศึกษาเคมีของไอโซเมอร์ของสารประกอบ $[Ru(5mazpy)_2Cl_2]$ หนึ่งไอโซเมอร์ โดยเทคนิคอินฟราเรดสเปกโทรสโกปี นิวเคลียร์แมกเนติกเรโซแนนซ์สเปกโทรสโกปี เทคนิคการวัดการดูดกลืนแสง และเทคนิคไซคลิก-โวลแทมเมทรี ผลจากเทคนิคอินฟราเรดสเปกโทรสโกปี แถบการยืดของ N=N ในสารประกอบเชิงซ้อนปรากฏที่ความถี่ต่ำกว่าในลิแกนด์อิสระ มีการยืนยันสูตรเคมีของสารประกอบด้วยเทคนิคการวิเคราะห์หาปริมาณธาตุที่เป็นองค์ประกอบสเปกตรัม ^1H และ ^{13}C NMR แสดงสัญญาณของลิแกนด์เป็นสองชุด แสดงว่าลิแกนด์ทั้งสองจัดตัวอยู่ในสภาพแวดล้อมที่ต่างกัน ดังนั้นสารประกอบ $[Ru(5mazpy)_2Cl_2]$ จึงไม่มีแกนสมมาตร C_2 ผลจากเทคนิคการวัดการดูดกลืนแสงมีการถ่ายโอนอิเล็กตรอนจากโลหะไปยังลิแกนด์ (MLCT) ในช่วงแสงที่มองเห็นได้ การศึกษาทางไฟฟ้าเคมี แสดงคู่พีคของ Ru(III)/Ru(II) ที่ค่าศักย์ไฟฟ้า +0.62 โวลต์ และคู่พีคของเอโซ ที่ -1.17 โวลต์ และ -1.51 โวลต์ เมื่อเทียบกับคู่พีคของเฟอโรซีน

ภาควิชาเคมี คณะวิทยาศาสตร์ มหาวิทยาลัยสงขลานครินทร์ อำเภอหาดใหญ่ จังหวัดสงขลา 90112

The ruthenium(II) complexes containing azoimine (-N=N-C=N-) and imine (-N=C-C=N-) functional units have been chosen for study of their chemistry. The advantage of the azoimine functional unit is that it has a strong ability to stabilize metal centers in the lower oxidation states, such as Ru(II), Os(II), Pd(II), Pt(II), Ag(I), and Cu(I). There are a variety of applications of the ruthenium(II) complexes with azoimine ligands, such as the ruthenium(II) with 2-(phenylazo) pyridine (azpy), $[Ru(azpy)_2Cl_2]$, showed remarkably high cytotoxicity against a series of tumor-cell lines (Velders *et al*., 2000). Furthermore, the complex of $[Ru(azpy)_2Cl_2]$ has been used as a catalyst in epoxidation reaction (Barf *et al*., 1995). The $[Ru(papm)_2Cl_2]$ (papm = 2-(phenylazo)pyrimidine) complex has an important activity of antibiotics and antimicrobials (Santra *et al*., 1999). In this work, our interest is to synthesize the complex of Ru(II) with the new azoimine ligand, 5-methyl-2-(phenylazo)pyridine (5mazpy). The structures of ligands are shown in Figure 1. The 5mazpy is an unsymmetric bidentate N,N'-donor center, is similar to azpy but contains a methyl group ($-CH_3$) at the fifth position on the pyridine ring. We would like to study the effect of 5mazpy ligand on chemistry of $[Ru(5mazpy)_2Cl_2]$ compared with that of $[Ru(azpy)_2Cl_2]$. From the previous report, $[Ru(azpy)_2Cl_2]$ can occur in five geometrically isomeric forms : *trans-cis-cis* (*tcc)*, *trans-trans-trans* (*ttt*), *cis-trans-cis* (*ctc*), *cis-cis-trans* (*cct*), and *cis-cis-cis* (*ccc*) by considering the order of the coordinating pairs of Cl, N(pyridine), and N'(azo), respectively (Figure 2). However, only three isomers have been reported, namely, *ctc*-$[Ru(azpy)_2Cl_2]$, *tcc*-$[Ru(azpy)_2Cl_2]$, and *ccc*-$[Ru(azpy)_2Cl_2]$ (Krause and Krause, 1980). Their structures were confirmed by X-ray crystallography. The *ctc* and *tcc* isomers have C_2-symmetry while *ccc*-isomer has C_1-symmetry. Since the *ccc*-isomer lacks C_2-symmetry, it was readily recognized from NMR spectra. In this work, the NMR spectroscopic technique was used to identify the configuration of $[Ru(5mazpy)_2Cl_2]$.

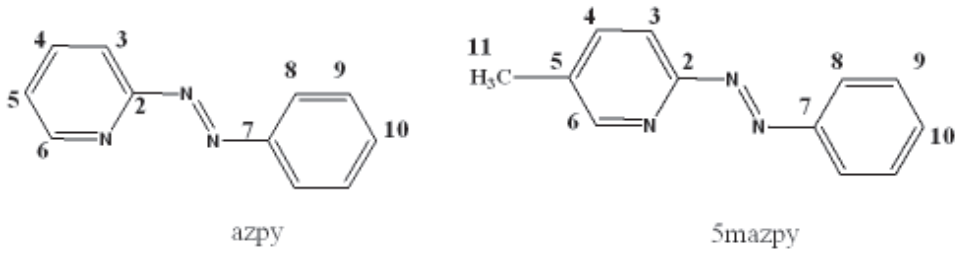

Figure 1. Structures of 2-(phenylazo)pyridine (azpy) and 5-methyl-2-(phenylazo)pyridine (5mazpy).

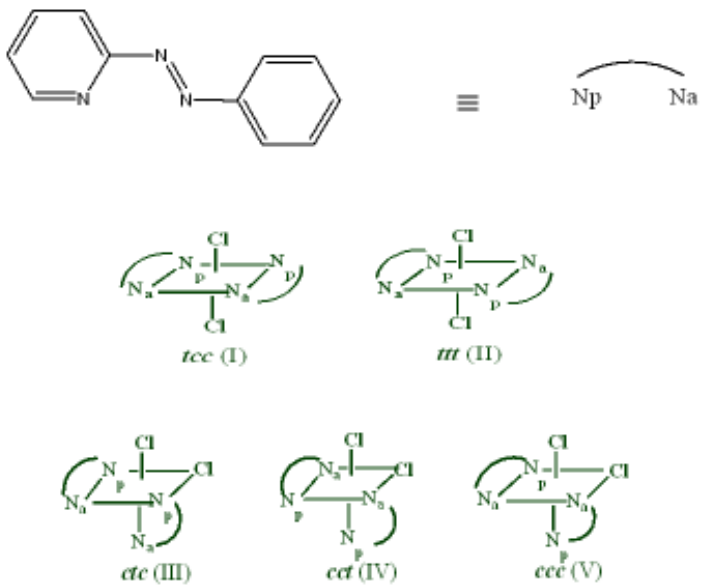

Figure 2. The five possible $[Ru(azpy)_2Cl_2]$ isomers.

Materials and Methods

Materials

6-amino-3-methylpyridine and nitrosobenzene were purchased from Fluka. $RuCl_3.3H_2O$ was digested three times with conc. HCl and evaporated to dryness before use as described previously (Misra *et al*., 1998). The solvents, dichloromethane and hexane, for column chromatography, were purified by distillation prior to use.

Instrumentation

Elemental analyses were performed by Carlo Erbra EA 1108 elemental analyzer. Infrared spectra were measured on a Perkin Elmer Spectrum GX FT-IR spectrophotometer from 370 to 4,000 cm^{-1}. All samples were prepared in the KBr pellets. Ultraviolet and visible absorption spectra were measured on a UV-Vis spectrophotometer SPECORD S100. 1D and 2D NMR spectra were measured in $CDCl_3$ on a Varian UNITY SNOVA 500 MHz FT-NMR spectrometer at ambient temperature with Me_4Si as an internal standard. Electrochemical properties were measured using MacLab (4e AD Instruments) with potentiostat (Serial No p068). The program was EChem 1.5.1. A glassy carbon working electrode, platinum wire auxilary electrode, and platinum disc reference electrode were used in three-electrode configur-

ation. The supporting electrolyte was tetra-*n*-butylammonium hexafluorophosphate (TBAH) in CH_3CN. Ferrocene was added at the end of each experiment as an internal standard. All potentials were quoted vs the ferrocene/ferricinium couple ($FeCp_2/FeCp_2^+$). The solvent was used as received. Argon gas was bubbled through the solution prior to each measurement.

Synthesis

Synthesis of 2-(phenylazo)pyridine (azpy)

The 2-(phenylazo)pyridine ligand was prepared by literature method (Krause and Krause, 1980). 2-Aminopyridine (0.45 g, 4.78 mmol) reacted with nitrosobenzene (0.60 g, 5.60 mmol) in the mixture of 20 M NaOH 13.5 mL and 10 mL of benzene with stirring. The reaction mixture was heated on the water bath for 45 min. The reaction mixture was extracted five times with 5 mL portions of benzene, then the solvent was removed by rotary evaporator. The residue was purified by column chromatography on a silica gel with a mixture of hexane and ethylacetate as the eluting solvent. The orange band was collected. The yield was 35%.

Synthesis of 5-methyl-2-(phenylazo) pyridine (5mazpy)

The 5-methyl-2-(phenylazo)pyridine ligand was prepared by modified literature method (Krause and Krause, 1980). 6-Amino-3-methyl-pyridine (3.13 mmol) was added to the benzene solution and the mixture was stirred on water bath. Then NaOH was added to the reaction. Nitroso-benzene (3.16 mmol) in small portions was added to the reaction then the reaction mixture was refluxed for 8 h. The green solution became brown. The product was extracted with benzene and evaporated to dryness. The residue was purified by column chromatography on silica gel. The orange band was eluted with the mixture of CH_2Cl_2 : Hexane (1:9 v/v). The yield of 5mazpy ligand was 62%.

Synthesis of $[Ru(azpy)_2Cl_2]$

The $[Ru(azpy)_2Cl_2]$ complex was prepared by literature method (Krause and Krause, 1980). The mixture of 0.10 g (0.48 mmol) of $RuCl_3.3H_2O$ and 0.20 g (1.09 mmol) of 2-(phenylazo)pyridine in dimethylformamide (30 mL) was refluxed, with magnetic stirring for 10 h. The solution mixture was filtered and solvent was removed. The residue was dissolved in a minimum volume of dichloro-methane and purified by column chromatography on silica gel. Three isomers of $[Ru(azpy)_2Cl_2]$ were isolated. The purple *ccc*-$[Ru(azpy)_2Cl_2]$ band was selected and eluted by using a mixture of dichloromethane and ethylacetate (9:1) resulting in 30% of *ccc*-$[Ru(azpy)_2Cl_2]$ complex.

Synthesis of $[Ru(5mazpy)_2Cl_2]$

The $[Ru(5mazpy)_2Cl_2]$ complex was prepared by modified literature method (Krause and Krause, 1980). The ruthenium complex, $[Ru(5mazpy)_2Cl_2]$, was prepared by the reaction between $RuCl_3.3H_2O$ (0.24 mmol) and 5mazpy (0.53 mmol) in ethanol. After the mixture was refluxed for 6 h, the solution was evaporated to dryness. The dried product was dissolved in a small volume of $CHCl_3$ and purification of the compound was carried out by column chromato-graphy on silica gel. The purple band was collected. The yield of this complex was 20%.

Results and Discussion

Synthesis

5-methyl-2-(phenylazo)pyridine was syn-thesized by condensing nitrosobenzene with 6-amino-3-methylpyridine in dry benzene under refluxing conditions for 8 h. Purification was carried out by chromatography. The ligand is a new azoimine ligand and acts as a N,N'-bidentate chelating molecule. Ethanolic solutions of 5mazpy with $RuCl_3$ under reflux afforded the $[Ru(5mazpy)_2Cl_2]$ complex. One of the isomers was separated and its configuration was studied by NMR spectroscopic technique. The melting points of the 5mazpy ligand and complexes are shown in Table 1.

Spectra

Infrared spectroscopy of compounds was recorded in a KBr disc in the 4000-400 cm^{-1} region. The 5mazpy ligand showed medium peaks at

Table 1. Analytical[a], UV-Vis spectral[b], voltammetric data[c] and melting point.

Compound	Analysis (%)			λ_{max}, nm (10^{-3} ε, M^{-1} cm^{-1})	Oxidation potential	Reduction potential	Melting point (ºC)
	C	H	N		$E_{1/2}$(ΔE,mV)	$E_{1/2}$(ΔE,mV)	
5mazpy	72.92	5.63	22.58	448(0.4), 324(16.0)		-1.62(94)	77-78
	(73.08)	(5.62)	(21.30)				
[Ru(5mazpy)$_2$Cl$_2$]	49.64	3.37	15.61	576(12.6), 338(21.5)	0.62(82)	-1.17(85), -1.51[d]	327-328
	(50.89)	(3.91)	(14.84)				
ccc-[Ru(azpy)$_2$Cl$_2$]	49.64	3.37	15.61	576(12.2), 334(21.1)	0.66(95)	-1.08(67), -1.54[d]	321-322
	(49.08)	(3.50)	(15.83)				

[a] Calculated values are given in parentheses
[b] In CH_2Cl_2
[c] In CH_2Cl_2, supporting electrolyte, TBAH (0.1 M); solute concentration, 10^{-3} M; scan rate, 100 mVs^{-1}.
[d] cathodic peak

Table 2. ^{1}H NMR data for the compounds [δ/ppm, J/Hz].

compound		3-H[d]	4-H[e]	5-H[e]	6-H[d]	8-H[e]	9-H[f]	10-H[f]	-CH_3
azpy[a]		7.78 (8.0)	8.04 (8.5, 8.5)	7.57 (7.5, 5.0)	8.75 (5.0)	8.02 (7.5, 2.0)	7.64[g]	7.64[g]	
5mazpy[b]		7.76 (8.5)	7.69 (8.0, 2.0)		8.56[c]	8.04 (7.5, 2.0)	7.52[g]	7.52[g]	2.43[c]
ccc-[Ru(azpy)$_2$Cl$_2$][a]	(A)	8.55 (8.0)	8.18 (8.0, 7.5)	7.56 (8.0, 5.5)	7.49 (6.0)	7.89(9.0, 1.0)	7.42 (8.0, 8.5)	7.54 (7.5, 7.5)	
	(B)	8.66 (8.0)	8.40 (8.0, 7.5)	8.08 (8.0, 5.5)	9.69 (5.5)	6.73 (8.5, 1.0)	7.29 (8.0, 8.0)	7.45 (7.5, 7.5)	
[Ru(5mazpy)$_2$Cl$_2$][b]	(A)	8.27 (8.0)	7.69 (8.0, 1.0)		7.03[c]	7.77(8.5, 1.5)	7.38 (8.5, 8.0)	7.45 (7.5, 7.5)	2.20[c]
	(B)	8.40 (8.0)	7.93 (8.0, 1.5)		9.58[c]	6.68 (8.5, 1.0)	7.18 (8.0, 7.5)	7.25 (7.5, 7.5)	2.56[c]

[a] In acetone-d_6 [b] In $CDCl_3$ [c] singlet [d] doublet
[e] doublet of doublet [f] triplet [g] multiplet

1605-1440 cm^{-1}, corresponding to C=C and C=N stretching in the pyridine ring of the ligand. The sharp band at 1389 cm^{-1} was assigned to the N=N stretching, which occurred at a lower frequency than that in azpy (1421 cm^{-1}) (Krause and Krause, 1980). This stretching mode was used to be considered the π-acid property in azo complexes. The 5mazpy ligand contains a methyl group in pyridine ring at the fifth position. The methyl group donated electron into π*-orbital of azo. Then the bond order of N=N (azo) decreased and the vibrational energies decreased (Thongkum, 2004). The [Ru (5mazpy)$_2$Cl$_2$] complex exhibited ν(N=N) at 1320 cm^{-1}, red shifted by 69 cm^{-1} from the free 5mazpy ligand, which is evidence of good indication of N-coordination. UV-Visible spectral studies of the complex reveal absorptions within the range 200-800 nm. The free 5mazpy ligand exbibited transitions at 448 nm (ε~400 M^{-1} cm^{-1}) and 324 nm (ε~16,000 M^{-1} cm^{-1}), corresponding to intraligand transitions, n→π* and π→π*, respectively. The complex displayed intense bands in the UV-Visible region at 338 nm and in at 576 nm assigned to intraligand transition and metal-to-ligand charge-transfer transition, respectively.

The azpy ligand and *ccc*-[Ru(azpy)$_2$Cl$_2$] complex were synthesized to compare with 5mazpy and [Ru(5mazpy)$_2$Cl$_2$]. The NMR spectra were used to support the structures of compounds. The ^{1}H NMR spectra of azpy and *ccc*-[Ru(azpy)$_2$Cl$_2$] were carried out in acetone-d_6. The peak assignment was supported by using simple correlation ^{1}H-^{1}H COSY NMR spectroscopy. The azpy ligand showed 6 signals for nine protons of the pyridine ring and the phenyl ring. On the pyridine ring, the H6 (8.75 ppm) located next to H4 (8.04 ppm) and was affected by nitrogen of azo function which caused the signal to shift to lower field than H5

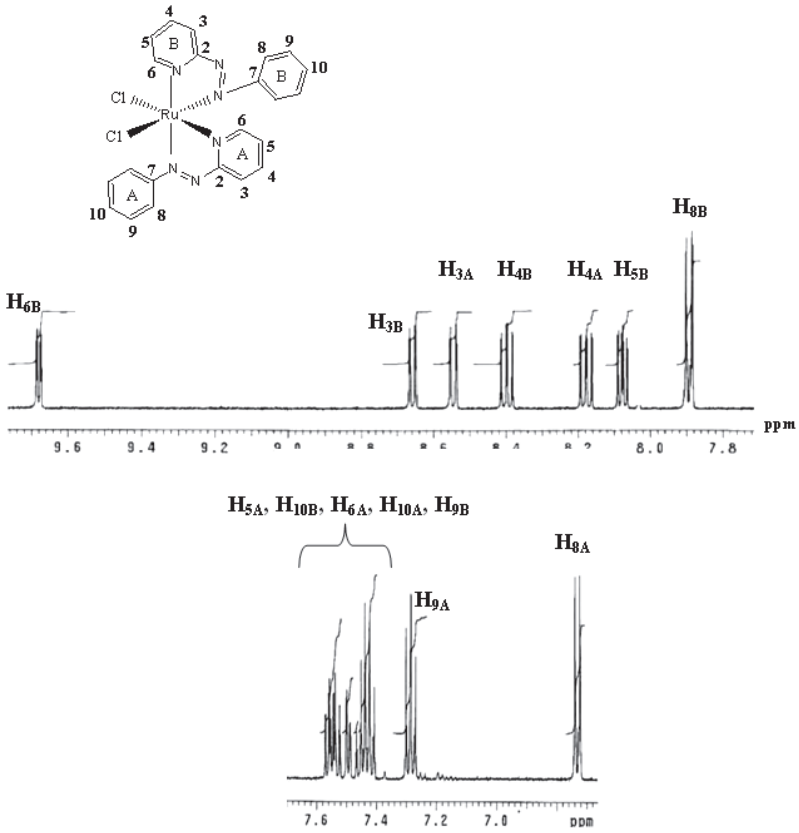

Figure 3. The ^{1}H NMR spectrum of *ccc*-[Ru(azpy)$_2$Cl$_2$] in acetone-d_6.

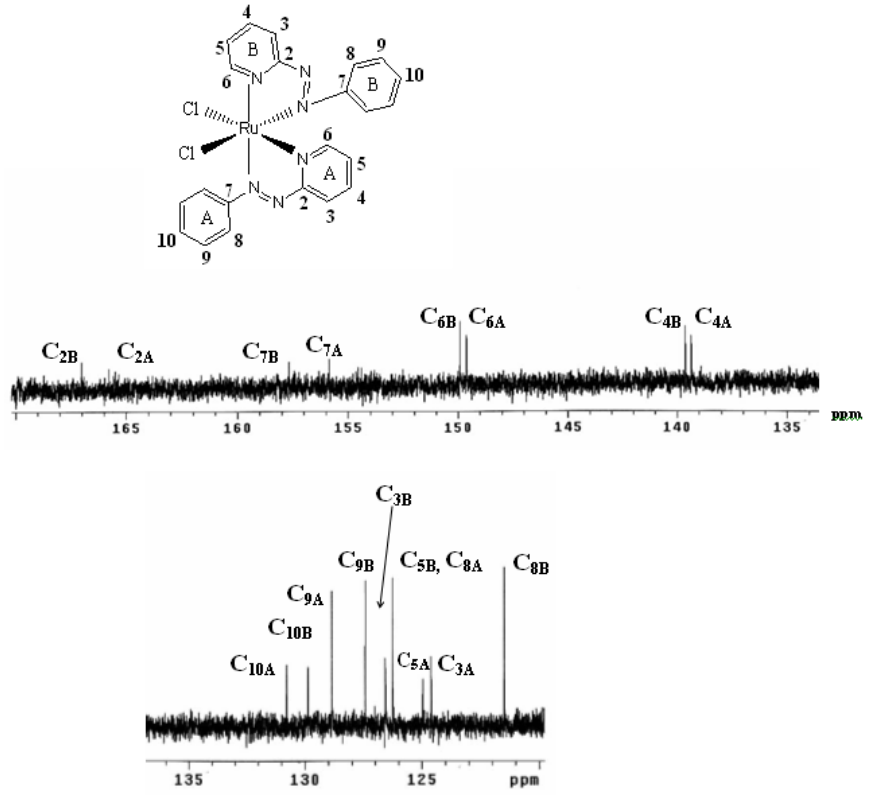

Figure 4. The ^{13}C NMR spectrum of *ccc*-[Ru(azpy)$_2$Cl$_2$] in acetone-d_6.

(7.57 ppm) and H3 (7.78 ppm). The known *ccc*-[Ru(azpy)$_2$Cl$_2$] complex (Seal, 1984) has C_1-symmetry and the two azpy ligands are not equivalent. Therefore, the ^{1}H and ^{13}C NMR spectra exhibited two sets of ligand peaks (Figures 3 and 4). The spectral data of 5mazpy ligand and [Ru(5mazpy)$_2$Cl$_2$] which were carried out in CDCl$_3$ are summarized in Table 2. The methyl signal has been particularly useful in determining isomer configuration. The ^{1}H NMR spectrum of [Ru(5mazpy)$_2$Cl$_2$] exhibited two methyl signals of equal intensities at 2.20 ppm and 2.56 ppm. This indicated that the [Ru(5mazpy)$_2$Cl$_2$] complex has no C_2-symmetry. From the [Ru(azpy)$_2$Cl$_2$] complex only *ccc*-isomer has C_1-symmetry (Seal, 1984). Therefore, the configuration of the [Ru(5mazpy)$_2$Cl$_2$] complex should be *cis-cis-cis* configuration. In the case of C_1-symmetry in the [Ru(5mazpy)$_2$Cl$_2$] complex, the ^{1}H NMR spectrum (Figure 5) exhibited two sets of ligand peaks, which have been fully assigned using 2D COSY NMR spectroscopy. The NMR spectrum showed that the pyridine protons were mostly affected when compared to the phenyl protons. The H3(A, B) and H6(B) signals were shifted to downfield while H6(A), H8(A, B), H9(A, B) and H10(A, B) were shifted upfield from those of the free ligand. The proton H6(B) appeared at the lower field than H6(A) because it was trans to the N=N mode (electron withdrawing group) while proton H6(A) was trans to chloride (Velder *et al*., 2004). This is similar that the result of *ccc*-[Ru(azpy)$_2$Cl$_2$] which was carried out in the same solvent (CDCl$_3$). In addition, the ^{13}C NMR signals assignments were based on the HMQC spectrum and are summarized in Table 3. The ^{13}C NMR spectrum of [Ru(5mazpy)$_2$Cl$_2$] shows 20 signals of 24 carbons (Figure 6). The carbon 8, 9 in phenyl ring A and B in complex resonate symmetrically at different position. The signals of carbon C6 occurred at a lower field than

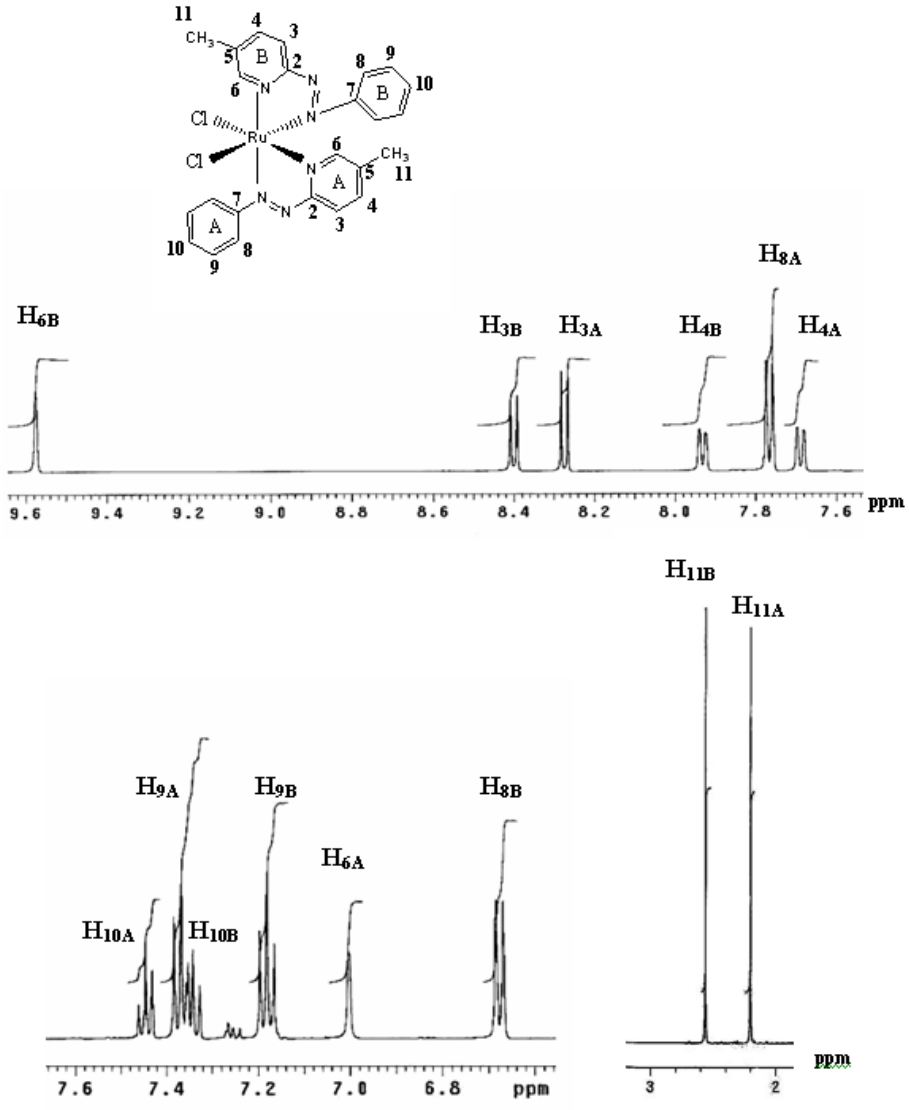

Figure 5. The ^{1}H NMR spectrum of [Ru(5mazpy)$_2$Cl$_2$] in CDCl$_3$.

that of other methine carbons because it was located next to the nitrogen atoms on pyridine ring. The signal carbon of CH_3 (C11) appeared at the highest field 19.0 ppm (A) and 19.6 ppm (B).

Electrochemistry

The electrochemical behaviour of the complexes in CH_2Cl_2 was examined by cyclic voltammetry. The voltammogram (Figure 7) of complexes displayed metal oxidation on the positive potential and ligand reductions on the negative potential with respect to ferrocene. The results are given in Table 1. The measurements were carried out at a scan rate of 100 mV/s in dichloromethane. For the [Ru(azpy)$_2$Cl$_2$] and [Ru (5mazpy)$_2$Cl$_2$] complexes, in the potential range 0.00 to +1.50 V at scan rate 100 mV/s reversible oxidative response was observed corresponding to the Ru(III)/Ru(II) couple. In comparison with the azpy complex, the *ccc*-[Ru(azpy)$_2$Cl$_2$] showed this behaviour couple at the +0.66 V, $E_{1/2}$, which was more positive than that of *ccc*-[Ru(5mazpy)$_2$

Table 3. ^{13}C NMR data for the compounds [δ/ppm].

compound		2-C	3-C	4-C	5-C	6-C	7-C	8-C	9-C	10-C	11-C
azpy[a]		164.1	114.1	139.3	126.3	150.1	153.1	123.9	133.0	130.1	
5mazpy[b]		161.1	138.8	115.2	135.6	149.8	152.4	123.5	129.1	131.9	18.4
ccc-[Ru(azpy)$_2$Cl$_2$][a]	(A)	165.8	124.6	139.4	125.0	149.6	155.9	126.2	128.8	130.8	
	(B)	167.0	126.6	139.6	126.2	149.9	157.7	121.5	127.4	129.9	
[Ru(5mazpy)$_2$Cl$_2$][b]	(A)	163.5	125.8	139.3	136.2	148.1	155.4	125.6	127.6	130.9	19.0
	(B)	165.2	124.2	137.9	136.6	149.5	157.2	121.3	128.7	129.6	19.6

[a] **In acetone-d_6**
[b] **In CDCl$_3$**

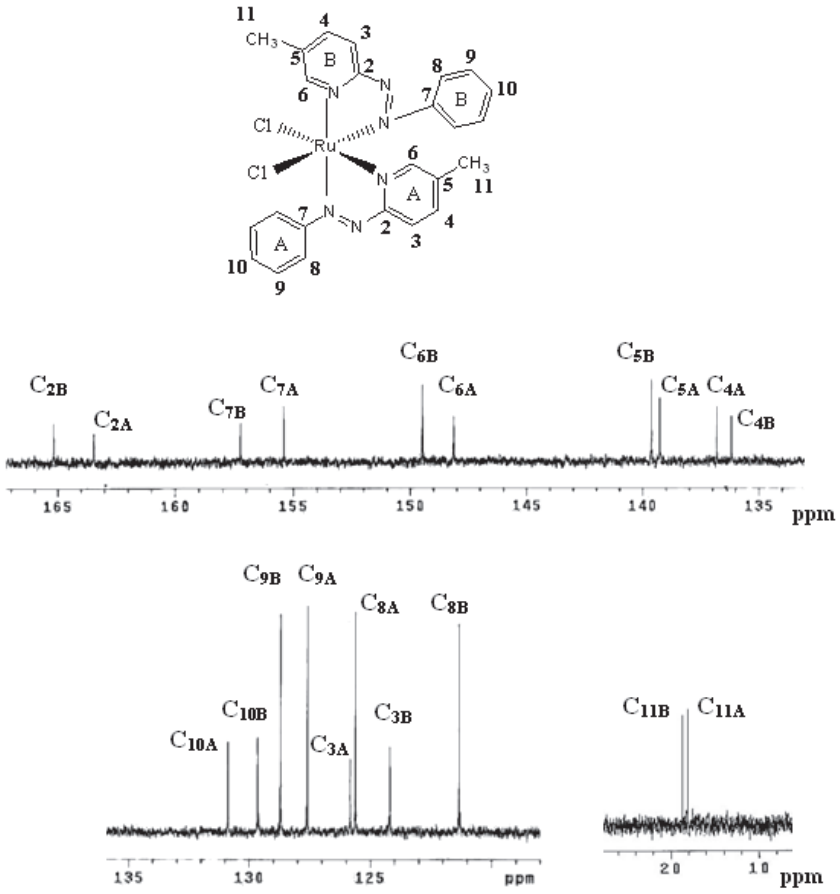

Figure 6. The ^{13}C NMR spectra of [Ru(5mazpy)Cl$_2$] in CDCl$_3$.

Cl$_2$] (+0.62 V).

In the potential range 0 to -2.0 V, reductive responses were observed under similar conditions using a glassy carbon working electrode. The reduction potentials were compared with the results from the free ligand. The 5mazpy ligand displayed one quasi-reversible two electron reduction response with peak to peak separation at 94 mV. There are one reversible couple and one cathodic peak in reduction range in both ruthenium(II) complexes. The first reduction in *ccc*-[Ru(5mazpy)$_2$Cl$_2$] has been observed at -1.17

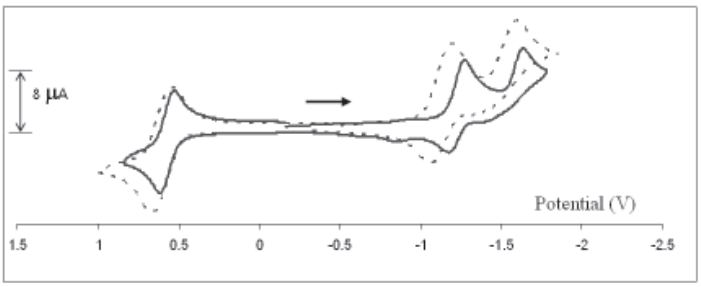

Figure 7. The cyclic voltammograms of $[Ru(5mazpy)_2Cl_2]$ (——) and $[Ru(azpy)_2Cl_2]$ (----) in 0.1 M TBAH CH_2Cl_2 solution at scan rate 100 mV/s (ferrocene as an internal standard)

V and in *ccc*-$[Ru(azpy)_2Cl_2]$ at -1.08 V. The cathodic response in *ccc*-$[Ru(5mazpy)_2Cl_2]$ and *ccc*-$[Ru(azpy)_2Cl_2]$ were -1.51 V and -1.54 V, respectively. It is due to the acceptance of electron at the azo function. The first reduction couple of the *ccc*-$[Ru(5mazpy)_2Cl_2]$ complex (-1.17 V) occurred at a higher potential than the *ccc*-$[Ru(azpy)_2Cl_2]$ complex (-1.08 V). These results show that the azpy ligand is a slightly better π-accepter than the 5mazpy ligand.

Conclusion

All of the compounds were characterized by using elemental analysis, IR spectroscopy, UV-Visible absorption spectroscopy, 1D and 2D NMR spectroscopy. Their electrochemical properties were studied by cyclic voltammetry. Results from IR spectroscopy showed that the N=N stretching frequency of compound was shifted to a lower value compared to that of the free ligand. The ^{1}H and ^{13}C and ^{1}H-^{1}H COSY NMR spectra of this complex exhibited two sets of ligand peaks, this indicated that both 5mazpy ligands were in different environments. The $[Ru(5mazpy)_2Cl_2]$ complex has C_1-symmetry, therefore the configuration of the $[Ru(5mazpy)_2Cl_2]$ complex should be *cis-cis-cis* configuration. In addition, the complex displayed intense absorption bands at 576 nm (assigned to the metal-to-ligand charge-transfer, MLCT) and at 338 nm (assigned to intraligand transition) in dichloromethane.

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