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

Uraiwan Changsaluk and Kanidtha Hansongnern

Abstract

Changsaluk, U. and Hansongnern, K.
Dichlorobis(5-methyl-2-(phenylazo)pyridine)ruthenium(II) complex: characterization and NMR spectroscopy

The new azoimine functionalized ligand, 5-methyl-2-(phenylazo)pyridine (5mazpy) was synthesized. It reacted with RuCl₃.3H₂O in ethanolic solution to give the isomeric [Ru(5mazpy)₂Cl₂] 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 confirmed by elemental analysis. The ¹H and ¹³C NMR spectra of complex exhibited two sets of ligand peaks, this indicated that both 5mazpy ligands were in different environments. Therefore, the [Ru(5mazpy)₂Cl₂] complex has no C₂-symmetry. Results from UV-Visible absorption spectroscopy show that the complex exhibited the t₂(Ru) → π→ π*, π→ π*(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

Changsaluk, U. and Hansongnern, K.
Dichlorobis(5-methyl-2-(phenylazo)pyridine)ruthenium(II) complex: characterization and NMR spectroscopy
Received, 3 October 2005       Accepted, 22 December 2005

Ph.D Student in Chemistry, 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

1Ph.D Student in Chemistry, 2Ph.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
Received, 3 October 2005       Accepted, 22 December 2005
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)Cl₂], showed remarkably high cytotoxicity against a series of tumor-cell lines (Velders et al., 2000). Furthermore, the complex of [Ru(azpy)Cl₂] has been used as a catalyst in epoxidation reaction (Barf et al., 1995). The [Ru(papm)₂Cl₂] (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, similar to azpy but contains a methyl group (-CH₃) at the fifth position on the pyridine ring. We would like to study the effect of 5mazpy ligand on the chemistry of [Ru(5mazpy)₂Cl₂] compared with that of [Ru(azpy)₂Cl₂]. From the previous report, [Ru(azpy)₂Cl₂] can occur in five geometrically isomeric forms: trans-cis-cis (tcc), trans-trans-trans (ttt), cis-trans-cis (etc), 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, etc-[Ru(azpy)₂Cl₂], tcc-[Ru(azpy)₂Cl₂], and ccc-[Ru(azpy)₂Cl₂] (Krause and Krause, 1980). Their structures were confirmed by X-ray crystallography. The etc and tcc isomers have C₂-symmetry while ccc-isomer has C₁-symmetry. Since the ccc-isomer lacks C₂-symmetry, it was readily recognized from NMR spectra. In this work, the NMR spectroscopic technique was used to identify the configuration of [Ru(5mazpy)₂Cl₂].
Materials and Methods

Materials
6-amino-3-methylpyridine and nitroso-benzene were purchased from Fluka. RuCl₃·3H₂O 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 CDCl₃ on a Varian UNITY SNOVA 500 MHz FT-NMR spectrometer at ambient temperature with Me₄Si 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 auxiliary electrode, and platinum disc reference electrode were used in three-electrode configur-
Dichlorobis(5-methyl-2-(phenylazo)pyridine)
ruthenium(II) complex

Changsaluk, U. and Hansongnern, K.

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-methylpyridine (3.13 mmol) was added to the benzene solution and the mixture was stirred on water bath. Then NaOH was added to the reaction. Nitrosobenzene (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 CH₂Cl₂ : Hexane (1:9 v/v). The yield of 5mazpy ligand was 62%.

Synthesis of [Ru(azpy)₂Cl₂]
The [Ru(azpy)₂Cl₂] complex was prepared by modified literature method (Krause and Krause, 1980). The mixture of 0.10 g (0.48 mmol) of RuCl₃,3H₂O 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 dichloromethane and purified by column chromatography on silica gel. Three isomers of [Ru(azpy)₂Cl₂] were isolated. The purple ccc-[Ru(azpy)₂Cl₂] band was selected and eluted by using a mixture of dichloromethane and ethylacetate (9:1) resulting in 30% of ccc-[Ru(azpy)₂Cl₂] complex.
### Table 1. Analytical\(^a\), UV-Vis spectra\(^b\), voltammetric data\(^c\) and melting point.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Analysis (%)</th>
<th>(\lambda_{max}), nm (10(^{-3}) (\varepsilon), M(^{-1}) cm(^{-1}))</th>
<th>Oxidation potential</th>
<th>Reduction potential</th>
<th>Melting point (ºC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(5\text{mazpy})</td>
<td>72.92 (73.08)</td>
<td>(5.63 (5.62)) (22.58 (21.30))</td>
<td>448(0.4), 324(16.0)</td>
<td>-1.62(94)</td>
<td>77-78</td>
</tr>
<tr>
<td>([\text{Ru}(5\text{mazpy})_2\text{Cl}_2])</td>
<td>49.64 (50.89)</td>
<td>(3.37 (3.91)) (15.61 (14.84))</td>
<td>576(12.6), 338(21.5)</td>
<td>0.62(82)</td>
<td>-1.17(85), -1.51 (^d)</td>
</tr>
<tr>
<td>(c\text{ccc}=[\text{Ru}(\text{azpy})_2\text{Cl}_2])</td>
<td>49.64 (49.08)</td>
<td>(3.37 (3.50)) (15.61 (15.83))</td>
<td>576(12.2), 334(21.1)</td>
<td>0.66(95)</td>
<td>-1.08(67), -1.54 (^d)</td>
</tr>
</tbody>
</table>

\(^a\) Calculated values are given in parentheses
\(^b\) In CH\(_2\)Cl\(_2\)
\(^c\) In CH\(_2\)Cl\(_2\), 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 [\(\delta\)/ppm, \(J\)/Hz].

<table>
<thead>
<tr>
<th>compound</th>
<th>3-H(^d)</th>
<th>4-H(^e)</th>
<th>5-H(^e)</th>
<th>6-H(^d)</th>
<th>8-H(^e)</th>
<th>9-H(^e)</th>
<th>10-H(^f)</th>
<th>-CH(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>azpy(^a)</td>
<td>7.78 (8.0)</td>
<td>8.04 (8.5, 8.5)</td>
<td>7.57 (7.5, 5.0)</td>
<td>8.75 (5.0)</td>
<td>8.02 (7.5, 2.0)</td>
<td>7.64 (^g)</td>
<td>7.64 (^g)</td>
<td></td>
</tr>
<tr>
<td>(5\text{mazpy})(^b)</td>
<td>7.76 (8.5)</td>
<td>7.69 (8.0, 2.0)</td>
<td>(8.56) (^c)</td>
<td>8.04 (7.5, 2.0)</td>
<td>(7.52) (^c)</td>
<td>(7.52) (^c)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ccc-[Ru(azpy)_2Cl_2](^b)</td>
<td>(A) 8.55 (8.0)</td>
<td>8.18 (8.0, 7.5)</td>
<td>(7.49) (6.0)</td>
<td>7.89 (9.0, 1.0)</td>
<td>7.42 (8.0, 8.5)</td>
<td>7.54 (7.5, 7.5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(B) 8.66 (8.0)</td>
<td>8.40 (8.0, 7.5)</td>
<td>(9.69) (5.5)</td>
<td>6.73 (8.5, 1.0)</td>
<td>(7.29) (8.0, 8.0)</td>
<td>7.45 (7.5, 7.5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Ru}(5\text{mazpy})_2\text{Cl}_2])(^b)</td>
<td>(A) 8.27 (8.0)</td>
<td>7.69 (8.0, 1.0)</td>
<td>(7.03) (^c)</td>
<td>7.77 (8.5, 1.5)</td>
<td>7.38 (8.5, 8.0)</td>
<td>7.45 (7.5, 7.5)</td>
<td>2.20 (^d)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(B) 8.40 (8.0)</td>
<td>7.93 (8.0, 1.5)</td>
<td>(9.58) (^c)</td>
<td>6.68 (8.5, 1.0)</td>
<td>7.18 (8.0, 7.5)</td>
<td>7.25 (7.5, 7.5)</td>
<td>2.56 (^e)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) In acetone-\(d_6\)
\(^b\) In CDCl\(_3\)
\(^c\) doublet of doublet
\(^d\) doublet
\(^e\) triplet
\(^f\) singlet
\(^g\) doublet
\(^h\) 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)Cl\(_2\)] complex exhibited \(\nu(N=N)\) 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 exhibited transitions at 448 nm (\(\varepsilon \sim 400 \text{ M}^{-1} \text{ cm}^{-1}\)) and 324 nm (\(\varepsilon \sim 16,000 \text{ M}^{-1} \text{ cm}^{-1}\)), corresponding to intraligand transitions, \(n \rightarrow \pi^*\) and \(\pi \rightarrow \pi^*\), 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)_2Cl\(_2\)] complex were synthesized to compare with 5mazpy and [Ru(5mazpy)_2Cl\(_2\)]. The NMR spectra were used to support the structures of compounds. The \(^1\)H NMR spectra of azpy and ccc-[Ru(azpy)_2Cl\(_2\)] 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)_2Cl\(_2\)] in acetone-\(d_6\).](image-url)
Dichlorobis(5-methyl-2-(phenylazo)pyridine) ruthenium(II) complex

Changsaluk, U. and Hansongnern, K.

(7.57 ppm) and H3 (7.78 ppm). The known ccc-[Ru(azpy)2Cl2] complex (Seal, 1984) has C₁-symmetry and the two azpy ligands are not equivalent. Therefore, the ¹H and ¹³C NMR spectra exhibited two sets of ligand peaks (Figures 3 and 4). The spectral data of 5mazpy ligand and [Ru(5mazpy)₂Cl₂] which were carried out in CDCl₃ are summarized in Table 2. The methyl signal has been particularly useful in determining isomer configuration. The ¹H NMR spectrum of [Ru(5mazpy)₂Cl₂] exhibited two methyl signals of equal intensities at 2.20 ppm and 2.56 ppm. This indicated that the [Ru(5mazpy)₂Cl₂] complex has no C₂-symmetry. From the [Ru(azpy)₂Cl₂] complex only ccc-isomer has C₁-symmetry (Seal, 1984). Therefore, the configuration of the [Ru(5mazpy)₂Cl₂] complex should be cis-cis-cis configuration. In the case of C₁-symmetry in the [Ru(5mazpy)₂Cl₂] complex, the ¹H 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)₂Cl₂] which was carried out in the same solvent (CDCl₃). In addition, the ¹³C NMR signals assignments were based on the HMOC spectrum and are summarized in Table 3. The ¹³C NMR spectrum of [Ru(5mazpy)₂Cl₂] 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...
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$_2$Cl$_2$ 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)$_2$Cl$_2$].
Figure 6. The $^{13}$C NMR spectra of $[\text{Ru}(5\text{mazpy})_2\text{Cl}_2]$ in CDCl$_3$.

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 $\text{ccc-}[\text{Ru}(5\text{mazpy})_2\text{Cl}_2]$ has been observed at -1.17 V.
Dichlorobis(5-methyl-2-(phenylazo)pyridine) ruthenium(II) complex

V and in \( ccc-[\text{Ru(azpy)}_2\text{Cl}_2]\) at -1.08 V. The cathodic response in \( ccc-[\text{Ru(5mazpy)}_2\text{Cl}_2]\) and \( ccc-[\text{Ru(azpy)}_2\text{Cl}_2]\) 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 \( ccc-[\text{Ru(5mazpy)}_2\text{Cl}_2]\) complex (-1.17 V) occurred at a higher potential than the \( ccc-[\text{Ru(azpy)}_2\text{Cl}_2]\) complex (-1.08 V). These results show that the azpy ligand is a slightly better \( \pi \)-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 \( ^1\text{H} \) and \( ^1\text{C} \) and \( ^1\text{H}-^1\text{H} \) COSY NMR spectra of this complex exhibited two sets of ligand peaks, this indicated that both 5mazpy ligands were in different environments. The \([\text{Ru(5mazpy)}_2\text{Cl}_2]\) complex has \( C_1 \)-symmetry, therefore the configuration of the \([\text{Ru(5mazpy)}_2\text{Cl}_2]\) 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.

Acknowledgments

The authors would like to thank the Postgraduate Education and Research Program in Chemistry, Thailand Research Fund (Grant No. BRG 4680018), Department of Chemistry, Faculty of Science, and the Graduate School at Prince of Songkla University for financial supports. We are thankful to Prof. Neil Connelly (School of chemistry, University of Bristol, U.K.) for results of elemental analyses.

References


