

Contents

	Page
Abstract (Thai)	(3)
Abstract (English)	(4)
Acknowledgments	(5)
Contents	(7)
List of Tables	(9)
List of Figures	(12)
Abbreviations and Symbols	(15)
Chapter	
1 INTRODUCTION	1
1.1 Introduction	1
1.2 Literature reviews	5
1.3 Objectives	10
2 MATERIALS AND METHODS	11
2.1 Materials	11
2.2 Instruments	13
2.3 Synthesis of ligands	14
2.4 Synthesis of complexes	15
2.5 Techniques for structural determination	16
3 RESULTS	19
3.1 Synthesis and characterization of dmsazpy and desazpy Ligands	19
3.1.1 Synthesis of dmsazpy and desazpy ligands	19
3.1.2 Characterization of dmsazpy and desazpy ligands	21

Contents (continued)

	Page
3.2 Synthesis and characterization of Ru(DMSO)₂Cl₂ and Ru(L)₂Cl₂	
(L= dmsazpy and desazpy) complexes	39
3.2.1 Synthesis and characterization of Ru(DMSO) ₂ Cl ₂ complex	39
3.2.2 Synthesis of Ru(L) ₂ Cl ₂ (L= dmsazpy and desazpy) complexes	42
3.2.3 Characterization of Ru(L) ₂ Cl ₂ (L= dmsazpy and desazpy) complexes	44
3.2.4 X-ray structure of Ru(dmsazpy) ₂ Cl ₂ complexes	74
3.3 Electrochemistry of complexes	86
4 DISCUSSION	96
4.1 Electrospray mass spectrometry	97
4.2 Infrared spectroscopy	100
4.3 Proton nuclear magnetic resonance spectroscopy	102
4.4 UV-Visible absorption spectroscopy	105
4.5 X-ray structures determination	107
4.6 Electrochemistry	112
5 SUMMARY	118
Bibliography	121
Appendix	127
A. Cut off solvents	128
B. Bond distances (\AA) and bond angles (°)	129
C. Cyclic voltammograms	145
Vitae	151

List of Tables

Table	Page
1 The solubility of dmsazpy and desazpy ligands	21
2 Elemental analysis data of dmsazpy and desazpy ligands	22
3 Electrospray mass spectroscopic data of dmsazpy ligand	22
4 Electrospray mass spectroscopic data of desazpy ligand	23
5 IR data of dmsazpy ligand	26
6 IR data of desazpy ligand	27
7 ^1H NMR data of dmsazpy ligand	30
8 ^1H NMR data of desazpy ligand	31
9 UV-Visible spectral data of azpy, dmsazpy and desazpy ligands	35
10 IR data of $\text{Ru}(\text{DMSO})_4\text{Cl}_2$ complex	39
11 The solubility of <i>trans</i> - and <i>cis</i> - $\text{Ru}(\text{L})_2\text{Cl}_2$ complexes	43
12 Elemental analysis data of <i>trans</i> - and <i>cis</i> - $\text{Ru}(\text{L})_2\text{Cl}_2$ ($\text{L} = \text{dmsazpy}$ and desazpy) complexes	44
13 Electrospray mass spectroscopic data of <i>trans</i> - $\text{Ru}(\text{dmsazpy})_2\text{Cl}_2$ complex	45
14 Electrospray mass spectroscopic data of <i>trans</i> - $\text{Ru}(\text{desazpy})_2\text{Cl}_2$ complex	46
15 Electrospray mass spectroscopic data of <i>cis</i> - $\text{Ru}(\text{dmsazpy})_2\text{Cl}_2$ complex	46
16 Electrospray mass spectroscopic data of <i>cis</i> - $\text{Ru}(\text{desazpy})_2\text{Cl}_2$ complex	47
17 IR data of <i>trans</i> - $\text{Ru}(\text{dmsazpy})_2\text{Cl}_2$ complex	52
18 IR data of <i>trans</i> - $\text{Ru}(\text{desazpy})_2\text{Cl}_2$ complex	52

Lists of Table (continued)

Table	Page
19 IR data of <i>cis</i> -Ru(dmsazpy) ₂ Cl ₂ complex	53
20 IR data of <i>cis</i> -Ru(desazpy) ₂ Cl ₂ complex	53
21 ¹ H NMR data of <i>trans</i> -Ru(dmsazpy) ₂ Cl ₂ complex	60
22 ¹ H NMR data of <i>trans</i> -Ru(desazpy) ₂ Cl ₂ complex	60
23 ¹ H NMR data of <i>cis</i> -Ru(dmsazpy) ₂ Cl ₂ complex	61
24 ¹ H NMR data of <i>cis</i> -Ru(desazpy) ₂ Cl ₂ complex	62
25 UV-Visible spectral data of <i>trans</i> -Ru(dmsazpy) ₂ Cl ₂ complex	67
26 UV-Visible spectral data of <i>trans</i> -Ru(desazpy) ₂ Cl ₂ complex	67
27 UV-Visible spectral data of <i>cis</i> -Ru(dmsazpy) ₂ Cl ₂ complex	68
28 UV-Visible spectral data of <i>cis</i> -Ru(desazpy) ₂ Cl ₂ complex	68
29 The crystallographic data of <i>trans</i> -Ru(dmsazpy) ₂ Cl ₂ and <i>trans</i> -Ru(azpy) ₂ Cl ₂ complexes	76
30 The selected bond distances (Å) and angles (°) and their estimated standard deviations for <i>trans</i> -Ru(dmsazpy) ₂ Cl ₂ and <i>trans</i> -Ru(azpy) ₂ Cl ₂	77
31 The dihedral angles of different planes in <i>trans</i> -Ru(dmsazpy) ₂ Cl ₂ and in <i>trans</i> -Ru(azpy) ₂ Cl ₂ complexes	78
32 The crystallographic data of <i>cis</i> -Ru(dmsazpy) ₂ Cl ₂ and <i>cis</i> -Ru(azpy) ₂ Cl ₂ complexes	81
33 The selected bond distances (Å) and angles (°) and their estimated standard deviations for <i>cis</i> -Ru(dmsazpy) ₂ Cl ₂ and <i>cis</i> -Ru(azpy) ₂ Cl ₂	82
34 The dihedral angles of different planes in <i>cis</i> -Ru(dmsazpy) ₂ Cl ₂ and in <i>cis</i> -Ru(azpy) ₂ Cl ₂ complexes	83

List of Table (continued)

Table	Page
35 The cyclic voltammetric data of dmsazpy and desazpy ligands in 0.1 M TBAH CH ₃ CN at scan rate 50 mV/s (ferrocene used as an internal standard, ΔE = 54 mV)	87
36 The cyclic voltammetric data of <i>trans</i> - and <i>cis</i> -Ru(L) ₂ Cl ₂ (L= dmsazpy and desazpy) 0.1 M TBAH CH ₃ CN at scan rate 50 mV/s compared with <i>trans</i> - and <i>cis</i> -Ru(azpy) ₂ Cl ₂ (ferrocene used as an internal standard, ΔE = 54 mV)	91
37 The selected mode of vibration and absorption spectral data of RuL ₂ Cl ₂ complexes (L = dmsazpy and desazpy)	101
38 ¹ H NMR data for dmsazpy, desazpy <i>trans</i> - and <i>cis</i> -Ru(L) ₂ Cl ₂ (L = dmsazpy and desazpy) complexes	102
39 Bond distances of all complexes (Å)	109
40 Bond distances and stretching mode of N=N in <i>trans</i> - and <i>cis</i> -Ru(L) ₂ Cl ₂ (L = dmsazpy and desazpy) complexes	111
41 The selected bond distances and formal potentials of all Ruthenium(II) complexes	116
42 The solvent for UV-Visible spectrum and the minimum values for measurement	128
43 The bond distances (Å) and bond angles (°) of <i>trans</i> -Ru(dmsazpy) ₂ Cl ₂ complex	129
44 The bond distances (Å) and bond angles (°) of <i>cis</i> -Ru(dmsazpy) ₂ Cl ₂ complex	137

List of Figures

Figure	Page
1 The structures of azpy, dmsazpy and desazpy ligands	3
2 Five possible isomers of Ru(L) ₂ Cl ₂ (L = dmsazpy and desazpy) complexes	4
3 Electrospray mass spectrum of dmsazpy ligand	24
4 Electrospray mass spectrum of desazpy ligand	25
5 IR spectrum of dmsazpy ligand	28
6 IR spectrum of desazpy ligand	29
7 Structures of dmsazpy and desazpy ligands with proton numbering systems	30
8 ¹ H NMR spectrum of dmsazpy ligand	33
9 ¹ H NMR spectrum of desazpy ligand	34
10 UV-Visible absorption spectrum of dmsazpy ligand in CHCl ₃	37
11 UV-Visible absorption spectrum of desazpy ligand in CHCl ₃	38
12 IR spectrum of Ru(DMSO) ₄ Cl ₂ complex	41
13 Electrospray mass spectrum of <i>trans</i> -Ru(dmsazpy) ₂ Cl ₂ complex	48
14 Electrospray mass spectrum of <i>trans</i> -Ru(desazpy) ₂ Cl ₂ complex	49
15 Electrospray mass spectrum of <i>cis</i> -Ru(dmsazpy) ₂ Cl ₂ complex	50
16 Electrospray mass spectrum of <i>cis</i> -Ru(desazpy) ₂ Cl ₂ complex	51
17 IR spectrum of <i>trans</i> -Ru(dmsazpy) ₂ Cl ₂ complex	55
18 IR spectrum of <i>trans</i> -Ru(desazpy) ₂ Cl ₂ complex	56
19 IR spectrum of <i>cis</i> -Ru(dmsazpy) ₂ Cl ₂ complex	57
20 IR spectrum of <i>cis</i> -Ru(desazpy) ₂ Cl ₂ complex	58
21 The structures of <i>trans</i> -Ru(dmsazpy) ₂ Cl ₂ (1) and <i>trans</i> -Ru(desazpy) ₂ Cl ₂ (2) complexes with proton numbering systems	59

Lists of Figures (continued)

Figure	Page
22 The structures of <i>trans</i> -Ru(dmsazpy) ₂ Cl ₂ (1) and <i>trans</i> -Ru(desazpy) ₂ Cl ₂ (2) with proton numbering systems	61
23 ¹ H NMR spectrum of <i>trans</i> -Ru(dmsazpy) ₂ Cl ₂ complex	63
24 ¹ H NMR spectrum of <i>trans</i> -Ru(desazpy) ₂ Cl ₂ complex	64
25 ¹ H NMR spectrum of <i>cis</i> -Ru(dmsazpy) ₂ Cl ₂ complex	65
26 ¹ H NMR spectrum of <i>cis</i> -Ru(desazpy) ₂ Cl ₂ complex	66
27 UV-Visible absorption spectra of <i>trans</i> -Ru(dmsazpy) ₂ Cl ₂ in CHCl ₃ and dimethyl sulfoxide	70
28 UV-Visible absorption spectra of <i>trans</i> -Ru(desazpy) ₂ Cl ₂ in CHCl ₃ and dimethyl sulfoxide	71
29 UV-Visible absorption spectra of <i>cis</i> -Ru(dmsazpy) ₂ Cl ₂ in CHCl ₃ and dimethyl sulfoxide	72
30 UV-Visible absorption spectra of <i>cis</i> -Ru(desazpy) ₂ Cl ₂ in CHCl ₃ and dimethyl sulfoxide	73
31 Molecular structure of <i>trans</i> -Ru(dmsazpy) ₂ Cl ₂ complex	79
32 Molecular structure of <i>cis</i> -Ru(dmsazpy) ₂ Cl ₂ complex	85
33 Cyclic voltammograms of (A) dmsazpy and (B) desazpy in 0.1 M TBAH CH ₃ CN at scan rate 50 mV/s	89
34 Cyclic voltammograms of (A) <i>trans</i> -Ru(dmsazpy) ₂ Cl ₂ and (B) <i>trans</i> -Ru(desazpy) ₂ Cl ₂ (L= dmsazpy and desazpy) in 0.1 M TBAH CH ₃ CN at scan rate 50 mV/s	93

Lists of Figures (continued)

Figure	Page
35 Cyclic voltammograms of (A) <i>cis</i> -Ru(dmsazpy) ₂ Cl ₂ and (B) <i>cis</i> -Ru(desazpy) ₂ Cl ₂ (L= dmsazpy and desazpy) in 0.1 M TBAH CH ₃ CN at scan Rate 50 mV/s	94
36 Cyclic voltammograms of quasi-reversible couples of Ru(II/III) scaneed with various scan rate (50-1000 mV/s)	95
37 Cyclic voltammograms of ligand group I (A) dmsazpy, (B) desazpy scanned with various scan rate (50-1000 mV/s)	145
38 Cyclic voltammograms of ligand group II (A) dmsazpy, (B) desazpy scanned with various scan rate (50-1000 mV/s)	146
39 Cyclic voltammograms of (A) <i>N,N</i> -dimethylaniline and (B) <i>N,N</i> -diethylaniline scaneed with various scan rate (50-1000 mV/s)	147
40 Cyclic voltammograms of couple I in oxidation range of A-D <i>trans</i> - and <i>cis</i> -Ru(L) ₂ Cl ₂ (L=dmsazpy and desazpy) by varying scan rates (50-2000 mV/s)	148
41 Cyclic voltammograms of couple II in oxidation range of A-D <i>trans</i> - and <i>cis</i> -Ru(L) ₂ Cl ₂ (L=dmsazpy and desazpy) by varying scan rates (50-2000 mV/s)	149
42 Cyclic voltammograms of reduction range in <i>trans</i> - and <i>cis</i> -Ru(L) ₂ Cl ₂ (L=dmsazpy and desazpy) by varying scan rate (50-2000 mV/s)	150

ABBREVIATIONS AND SYMBOLS

azpy	=	2-(phenylazo)pyridine
dmsazpy	=	2-(<i>N,N</i> -dimethylphenylazo)thiazole
desazpy	=	2-(<i>N,N</i> -diethylphenylazo)thiazole
L	=	ligand
ES-MS	=	Electrospray Mass Spectrometry
IR	=	Infrared
NMR	=	Nuclear Magnetic Resonance
UV	=	Ultraviolet
CV	=	Cyclic voltammetry
mmol	=	millimole
g	=	gram
mg	=	milligram
h	=	hour
mL	=	milliliter
°C	=	degree celcius
min.	=	minutes
A.R.grade	=	Analytical reagent grade
R _f	=	retardation factor
TLC	=	Thin-Layer Chromatography
<i>m/z</i>	=	a value of mass divided by charge
Rel. abun.	=	relative abundance
cm ⁻¹	=	reciprocal centimeter (wavenumber)
s	=	singlet
d	=	doublet
t	=	triplet

ABBREVIATIONS AND SYMBOLS (continued)

δ	=	chemical shift relative to TMS
J	=	coupling constant
ppm	=	part per million
δ	=	chemical shift
Hz	=	hertz
MHz	=	megahertz
H-n	=	position of protons
CDCl ₃	=	deuteriochloroform
TMS	=	tetramethylsilane
nm	=	nanometer
λ_{max}	=	maximum wavelength
ν	=	absorption frequencies
ϵ	=	molar extinction coefficient
MLCT	=	metal-to-ligand charge transfer
HOMO	=	Highest Occupied Molecular Orbital
LUMO	=	Lowest Unoccupied Molecular Orbital
\AA	=	angstrom unit
$^\circ$	=	degree
mV/s	=	millivolt per second
V	=	Volt
A	=	Ampere
CH ₂ Cl ₂	=	dichloromethane
CHCl ₃	=	chloroform

DMF = dimethylformamide

DMSO = dimethyl sulfoxide

CH₃CN = acetonitrile