

CONTENTS

	Pages
บทคัดย่อ	(3)
ABSTRACT	(4)
ACKNOWLEDGEMENT	(5)
THE RELEVANCE OF THE RESEARCH WORK	(6)
CONTENTS	(7)
LIST OF TABLES	(10)
LIST OF FIGURES	(12)
LIST OF ABBREVIATIONS	(16)
1 INTRODUCTION	1
1.1 Introduction	1
1.2 Literatures reviews	3
1.3 Objectives	10
2 MATERIALS AND METHODS	11
2.1 Materials	11
2.1.1 Chemical Substances	11
2.1.2 Solvents	11
2.2 Instruments	12
2.2.1 Melting Point Apparatus	12
2.2.2 Elemental Analysis	12
2.2.3 Fast-Atom Bombardment (FAB) Mass Spectrometry	12
2.2.4 Infrared Spectroscopy	12
2.2.5 UV-Visible Absorption Spectroscopy	12
2.2.6 Nuclear Magnetic Resonance Spectroscopy	13
2.2.7 Cyclic Voltammetry	13

CONTENTS (continued)

	Pages
2.2.8 X-ray Diffractometer	13
2.3 Synthesis of ligand	14
2.4 Synthesis of complexes	14
3 RESULTS AND DISCUSSION	15
3.1 Synthesis of ligand	15
3.2 Characterization of ligand	16
3.2.1 Elemental Analysis	16
3.2.2 Fast-Atom Bombardment (FAB) Mass Spectrometry	17
3.2.3 UV-Visible Absorption Spectroscopy	19
3.2.4 Infrared Spectroscopy	21
3.2.5 Nuclear Magnetic Resonance Spectroscopy	24
3.2.6 Cyclic Voltammetry	33
3.3 Synthesis of complexes	37
3.4 Characterization of complexes	39
3.4.1 Elemental Analysis	39
3.4.2 Fast-Atom Bombardment (FAB) Mass Spectrometry	40
3.4.3 UV-Visible Absorption Spectroscopy	44
3.4.4 Infrared Spectroscopy	49
3.4.5 Nuclear Magnetic Resonance Spectroscopy	54
3.4.6 Cyclic Voltammetry	78
3.4.7 X-ray Crystallography	84
4 CONCLUSION	93
REFERENCE	95

CONTENTS (continued)

	Pages
APPENDIX	99
VITAE	125

LIST OF TABLES

Tables	Pages
1. The physical properties of the bsazpy ligand	15
2. Elemental analysis data of the bsazpy ligand	17
3. FAB mass spectroscopic data of the bsazpy ligand	17
4. The electronic spectral data of the bsazpy ligand	19
5. The selected infrared spectroscopic data of the bsazpy ligand	21
6. ^1H NMR and ^{13}C NMR spectroscopic data of the bsazpy ligand	25
7. Cyclic voltammetric data of bsazpy and azpy in 0.1 M TBAH dichloromethane at scan rate 50 mV/s (ferrocene as internal standard)	33
8. The physical properties of the $[\text{Ru}(\text{bsazpy})_2\text{Cl}_2]$ complexes	37
9. Elemental analysis data of the $[\text{Ru}(\text{bsazpy})_2\text{Cl}_2]$ complexes	39
10. FAB mass spectrometric data of the $[\text{Ru}(\text{bsazpy})_2\text{Cl}_2]$ complexes	40
11. The electronic spectral data of the $[\text{Ru}(\text{bsazpy})_2\text{Cl}_2]$ complexes	44
12. The selected IR spectroscopic data of the bsazpy ligand and the $[\text{Ru}(\text{bsazpy})_2\text{Cl}_2]$ complexes	49
13. ^1H NMR and ^{13}C NMR spectroscopic data of <i>ctc</i> - $[\text{Ru}(\text{bsazpy})_2\text{Cl}_2]$	55
14. ^1H NMR and ^{13}C NMR spectroscopic data of <i>cct</i> - $[\text{Ru}(\text{bsazpy})_2\text{Cl}_2]$	63
15. ^1H NMR and ^{13}C NMR spectroscopic data of <i>ttt</i> - $[\text{Ru}(\text{bsazpy})_2\text{Cl}_2]$	72
16. Cyclic voltammetric data of the $[\text{Ru}(\text{bsazpy})_2\text{Cl}_2]$ complexes in 0.1 M TBAH dichloromethane at scan rate 50 mV/s (ferrocene as internal standard)	78
17. Comparison of electronic and redox properties of the $[\text{Ru}(\text{bsazpy})_2\text{Cl}_2]$ complexes	79
18. Crystallographic data for <i>ctc</i> - $[\text{Ru}(\text{bsazpy})_2\text{Cl}_2]$	86
19. Selected bond distances (\AA) and angles ($^\circ$) for <i>ctc</i> - $[\text{Ru}(\text{bsazpy})_2\text{Cl}_2]$	87

LIST OF TABLES (continued)

Tables	Pages
20. Crystallographic data for <i>cct</i> -[Ru(bsazpy) ₂ Cl ₂]	89
21. Selected bond distances (Å) and angles (°) for <i>cct</i> -[Ru(bsazpy) ₂ Cl ₂]	90
22. Solvents for UV-Visible spectrum and the minimum values for measurement	100
23. Bond distances (Å) and bond angles (°) for <i>ctc</i> -[Ru(bsazpy) ₂ Cl ₂]	101
24. Bond distances (Å) and bond angles (°) for <i>cct</i> -[Ru(bsazpy) ₂ Cl ₂]	110

LIST OF FIGURES

Figures	Pages
1. The structures of the azpy and bsazpy ligands	3
2. The structure of the bsazpy ligand	16
3. FAB mass spectrum of the bsazpy ligand	18
4. UV-Visible absorption spectrum of bsazpy in CH ₂ Cl ₂	20
5. IR spectrum of the bsazpy ligand	23
6. The atom numbering scheme of bsazpy	24
7. ¹ H NMR spectrum of bsazpy in CDCl ₃ (500 MHz)	28
8. ¹ H- ¹ H COSY NMR spectrum of bsazpy in CDCl ₃ (500 MHz)	29
9. ¹³ C NMR spectrum of bsazpy in CDCl ₃ (500 MHz)	30
10. DEPT NMR spectrum of bsazpy in CDCl ₃ (500 MHz)	31
11. ¹ H- ¹³ C HMQC NMR spectrum of bsazpy in CDCl ₃ (500 MHz)	32
12. Cyclic voltammogram of bsazpy in 0.1 M TBAH CH ₂ Cl ₂ at scan rate 50 mV/s	35
13. Cyclic voltammogram of azpy in 0.1 M TBAH CH ₂ Cl ₂ at scan rate 50 mV/s	36
14. Five possible isomers of the [RuL ₂ Cl ₂] complexes	38
15. FAB mass spectrum of <i>ctc</i> -[Ru(bsazpy) ₂ Cl ₂]	42
16. FAB mass spectrum of <i>cct</i> -[Ru(bsazpy) ₂ Cl ₂]	43
17. UV-Visible absorption spectrum of <i>ctc</i> -[Ru(bsazpy) ₂ Cl ₂] in CH ₂ Cl ₂	46
18. UV-Visible absorption spectrum of <i>cct</i> -[Ru(bsazpy) ₂ Cl ₂] in CH ₂ Cl ₂	47
19. UV-Visible absorption spectrum of <i>ttt</i> -[Ru(bsazpy) ₂ Cl ₂] in CH ₂ Cl ₂	48
20. IR spectrum of <i>ctc</i> -[Ru(bsazpy) ₂ Cl ₂]	51
21. IR spectrum of <i>cct</i> -[Ru(bsazpy) ₂ Cl ₂]	52
22. IR spectrum of <i>ttt</i> -[Ru(bsazpy) ₂ Cl ₂]	53

LIST OF FIGURES (continued)

Figures	Pages
23. The atom numbering scheme of <i>ctc</i> -[Ru(bsazpy) ₂ Cl ₂]	54
24. ¹ H NMR spectrum of <i>ctc</i> -[Ru(bsazpy) ₂ Cl ₂] in CDCl ₃ (500 MHz)	57
25. ¹ H- ¹ H COSY NMR spectrum of <i>ctc</i> -[Ru(bsazpy) ₂ Cl ₂] in CDCl ₃ (500 MHz)	58
26. ¹³ C NMR spectrum of <i>ctc</i> -[Ru(bsazpy) ₂ Cl ₂] in CDCl ₃ (500 MHz)	59
27. DEPT NMR spectrum of <i>ctc</i> -[Ru(bsazpy) ₂ Cl ₂] in CDCl ₃ (500 MHz)	60
28. ¹ H- ¹³ C HMQC NMR spectrum of <i>ctc</i> -[Ru(bsazpy) ₂ Cl ₂] in CDCl ₃ (500 MHz)	61
29. The atom numbering scheme of <i>cct</i> -[Ru(bsazpy) ₂ Cl ₂]	62
30. ¹ H NMR spectrum of <i>cct</i> -[Ru(bsazpy) ₂ Cl ₂] in CDCl ₃ (500 MHz)	65
31. ¹ H- ¹ H COSY NMR spectrum of <i>cct</i> -[Ru(bsazpy) ₂ Cl ₂] in CDCl ₃ (500 MHz)	66
32. ¹³ C NMR spectrum of <i>cct</i> -[Ru(bsazpy) ₂ Cl ₂] in CDCl ₃ (500 MHz)	67
33. DEPT NMR spectrum of <i>cct</i> -[Ru(bsazpy) ₂ Cl ₂] in CDCl ₃ (500 MHz)	68
34. ¹ H- ¹³ C HMQC NMR spectrum of <i>cct</i> -[Ru(bsazpy) ₂ Cl ₂] in CDCl ₃ (500 MHz)	69
35. The atom numbering scheme of <i>ttt</i> -[Ru(bsazpy) ₂ Cl ₂]	70
36. ¹ H NMR spectrum of <i>ttt</i> -[Ru(bsazpy) ₂ Cl ₂] in CDCl ₃ (500 MHz)	73
37. ¹ H- ¹ H COSY NMR spectrum of <i>ttt</i> -[Ru(bsazpy) ₂ Cl ₂] in CDCl ₃ (500 MHz)	74
38. ¹³ C NMR spectrum of <i>ttt</i> -[Ru(bsazpy) ₂ Cl ₂] in CDCl ₃ (500 MHz)	75
39. DEPT NMR spectrum of <i>ttt</i> -[Ru(bsazpy) ₂ Cl ₂] in CDCl ₃ (500 MHz)	76
40. ¹ H- ¹³ C HMQC NMR spectrum of <i>ttt</i> -[Ru(bsazpy) ₂ Cl ₂] in CDCl ₃ (500 MHz)	77

LIST OF FIGURES (continued)

Figures	Pages
41. Cyclic voltammogram of <i>ctc</i> -[Ru(bsazpy) ₂ Cl ₂] in 0.1 M TBAH CH ₂ Cl ₂ at scan rate 50 mV/s	81
42. Cyclic voltammogram of <i>cct</i> -[Ru(bsazpy) ₂ Cl ₂] in 0.1 M TBAH CH ₂ Cl ₂ at scan rate 50 mV/s	82
43. Cyclic voltammogram of <i>ttt</i> -[Ru(bsazpy) ₂ Cl ₂] in 0.1 M TBAH CH ₂ Cl ₂ at scan rate 50 mV/s	83
44. The crystal structure of <i>ctc</i> -[Ru(bsazpy) ₂ Cl ₂] (H-atom omitted)	88
45. The crystal structure of <i>cct</i> -[Ru(bsazpy) ₂ Cl ₂] (H-atom omitted)	92
46. Cyclic voltammogram of bsazpy (A) and azpy (B) with various scan rate 50-1000 mV/s in the reduction range	119
47. Cyclic voltammogram of <i>ctc</i> -[Ru(bsazpy) ₂ Cl ₂] – couple I (Ru ^{III} /Ru ^{II}) (A) in the oxidation range and couple II (B), couple III (C) in the reduction range with various scan rates 50-1000 mV/s	120
48. Cyclic voltammogram of <i>cct</i> -[Ru(bsazpy) ₂ Cl ₂] – couple I (Ru ^{III} /Ru ^{II}) (A) in the oxidation range and couple II (B), couple III (C) in the reduction range with various scan rates 50-1000 mV/s	121
49. Cyclic voltammogram of <i>ttt</i> -[Ru(bsazpy) ₂ Cl ₂] – couple I (Ru ^{III} /Ru ^{II}) (A) in the oxidation range and couple II (B), couple III (C) in the reduction range with various scan rates 50-1000 mV/s	122
50. Cyclic voltammogram of <i>ctc</i> -[Ru(azpy) ₂ Cl ₂] in 0.1 M TBAH CH ₂ Cl ₂ at scan rate 50 mV/s	123

LIST OF FIGURES (continued)

Figures	Pages
51. Cyclic voltammogram of <i>ctc</i> -[Ru(azpy) ₂ Cl ₂] – couple I (Ru ^{III} /Ru ^{II}) (A) in the oxidation range and couple II (B), couple III (C) in the reduction range with various scan rates 50-1000 mV/s	124

LIST OF ABBREVIATIONS

Å	=	Angstrom unit ($1\text{\AA} = 10^{-10}$ meter)
A.R. grade	=	Analytical reagent grade
azpy	=	2-(phenylazo)pyridine
bpy	=	2,2'-bipyridine
bsazpy	=	2-(phenylazo)benzothiazole
CH_3CN	=	Acetonitrile
CHCl_3	=	Chloroform
CH_2Cl_2	=	Dichloromethane
cm^{-1}	=	Wave number
CV	=	Cyclic voltammetry
d	=	doublet
dd	=	doublet of doublet
DMF	=	<i>N,N</i> -dimethylformamide
DMSO	=	Dimethyl sulfoxide
FAB-MS	=	Fast-Atom Bombardment Mass Spectrometry
g	=	gram
h	=	hour
Hz	=	Hertz
IR	=	Infrared
<i>J</i>	=	coupling constant
K	=	Kelvin
mL	=	milliliter
mmol	=	millomole
mV/s	=	millivolt per second

LIST OF ABBREVIATIONS (continued)

m/z	=	a value of mass divided by charge
MLCT	=	metal to ligand charge transfer
MW	=	molecular weight
nm	=	nanometer
NMR	=	Nuclear Magnetic Resonance
phen	=	1,10-phenanthroline
ppm	=	part per million
Rel. Abun.	=	Relative abundance
s	=	singlet
t	=	triplet
TMS	=	Tetramethylsilane
UV-Vis	=	Ultraviolet-Visible
°	=	degree
λ_{max}	=	Maximum wavelength
ϵ	=	Molar extinction coefficient
δ	=	Chemical shift relative to TMS