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AN INVESTIGATION OF HOLE-TRANSFER AND ANTIFERROMAGNETIC
SUPEREXCHANGE IN ASYMMETRIC DINUCLEAR RUTHENIUM
COMPLEXES

By
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the Faculty of Graduate Studies and Research
in partial fulfillment of
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Abstract

An electrochemical and magnetic moment approach to assessing the degree of electronic and antiferromagnetic exchange coupling respectively in asymmetric dinuclear complexes is outlined. First, the monomers from which these systems are constituted were synthesized by substituting *trans* ammine in mononuclear $[\text{Ru}(\text{NH}_3)_5(2,3\text{-Cl}_2\text{pcyd})][\text{ClO}_4]_2$ with various nitrogen heterocycles of varying σ -donor strength. Six mononuclear ruthenium(III) and corresponding ruthenium(II) complexes of 2,3- Cl_2 phenylcyanamide monoanion ligand, $\text{trans}-[(L_n)\text{Ru}(\text{NH}_3)_{5-n}(2,3\text{-Cl}_2\text{pcyd})]^{m+}$, were synthesized and characterized, where L_n is 3,5-dimethylpyridine, pyridine, 2,6-dimethylpyrazine, pyrazine, methylpyrazinium cation ($n = 1$, tetraammines), and 2,2'-bipyridine ($n = 2$, triammine). The results showed that the metal-ligand coupling measured, H_{LM} increases as energetic matching between metal and ligand orbitals is increased. However, at a certain threshold, when L_n is mepyz⁺, the calculated H_{LM} decreases with better energetic matching between the metal and ligand orbitals. This has been accounted for in terms of an increasing degree of covalency that results in a poor estimate of dipole moment length in the model used to calculate H_{LM} .

Three dinuclear complexes, $\text{trans}-[L_n\text{Ru}(\text{NH}_3)_{5-n}\text{-dicyd-Ru}(\text{NH}_3)_5][\text{PF}_6]_4$ where L_n = pyridine, pyrazine ($n = 1$), and 2,2'-bipyridine ($n = 2$) were synthesized and characterized via magnetic resonance, electrochemical and infrared and electronic absorption spectroscopy techniques. This data along with that of the analogous symmetric complex, $[\text{Ru}(\text{NH}_3)_5\text{-dicyd-Ru}(\text{NH}_3)_5][\text{PF}_6]_4$, allowed a test of the predictive capabilities of the CNS theoretical model of metal-metal coupling. The free energy of resonance exchange and the antiferromagnetic exchange constants were calculated from metal-

metal coupling elements derived from the CNS model and the metal-ligand coupling elements derived from Hush-Mulliken model, respectively. These calculated values were compared to the values of the symmetric pentaammine complex studied previously and from the complexes' solvent-dependent, room-temperature magnetic moments. Magnetic data showed that the asymmetric complexes had slightly enhanced coupling compared to the symmetric pentaammine complex. However, the theoretical estimates of the free energy of resonance exchange were in poor agreement with those of the symmetric pentaammine complex and this was suggested to be due to a poor estimate of the transition dipole moment length.

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*I dedicate this thesis to my dear wife Wangûi
and to
Ciana cia mîthiima yakwa.*

"If I had the gift of being able to speak in other languages without learning them, and could speak every language there is in all the heaven and earth...or if I had the gift of foresight and knew what was going to happen in future, knew everything and understood all the secret truths and mysteries and possessed all knowledge...and if I had sufficient faith so that I could speak to a mountain and make it move...and if I bestowed all that I have to feed the poor and I surrendered my body to be burned in order that I may glory. If I had and could do all these without love, it would be of no value whatsoever to me. The greatest is Love."

St. Paul

Table of Content

	Page
Acceptance Sheet	ii
Abstract	iii
Acknowledgements	v
Dedication	vi
Table of Contents	vii
List of Tables	xii
List of Figures	xv
List of Schemes	xxv
List of Appendices	xxvi
List of Abbreviations	xxvii
 CHAPTER 1: INTRODUCTION	 1
1.1 BACKGROUND	2
1.2 METAL-METAL COUPLING IN SYMMETRIC MIXED-VALENCE COMPLEXES	 6
1.2.1 Superexchange	6
1.2.2 Thermodynamics of Mixed-Valence Complexes	9
1.2.3 Theoretical Models For Metal- Metal Coupling	12
1.3 METAL-METAL COUPLING IN ASYMMETRIC DINUCLEAR COMPLEXES	 21

1.4	SOLVENTS DONOR-ACCEPTOR INTERACTION	25
1.5	MAGNETIC ELECTRON EXCHANGE	30
1.5.1	Charge Transfer Model for Antiferromagnetic Exchange	31
1.5.2	Bridging Ligand Mediated Electron Exchange	32
1.6	EXPERIMENTAL DETERMINATION OF MAGNETIC MOMENTS	37
1.6.1	Evaluation of Magnetic Moments of Complexes in Solution	37
1.7	RESEARCH GOALS	40
	CHAPTER 2: EXPERIMENTAL	43
2.1	STARTING MATERIALS	43
2.1.1	Reagents for Ligand Synthesis	43
2.1.2	Reagents for Metal Complex Synthesis	43
2.1.3	Electrolyte	44
2.1.4	Cyclic Voltammetry Internal Reference	44
2.1.5	Chromatography	44
2.1.6	Compressed Gases	45
2.1.7	Solvents	45
2.2	METAL COMPLEX PRECURSOR SYNTHESIS	47
2.2.1	Chloropentaammineruthenium(III) Chloride $[(\text{NH}_3)_5\text{RuCl}][\text{Cl}_2]$	47
2.2.2	<i>Trans</i> -Chlorotetraaminesulfonylruthenium(II) Chloride <i>Trans</i> - $[\text{Ru}(\text{NH}_3)_4(\text{SO}_2)\text{Cl}]\text{Cl}$	48

2.3	LIGAND SYNTHESIS	50
2.3.1	Preparation of <i>N</i> -Methylpyrazinium Tosylate	50
2.4	SYNTHESIS OF THE MONONUCLEAR COMPLEXES OF 2,3-Cl ₂ Hpcyd	51
2.4.1	Preparation of [Ru(NH ₃) ₅ (2,3-Cl ₂ pcyd)][PF ₆] ₂	51
2.4.2	Preparation of <i>Trans</i> -[(3,5-Me ₂ py)Ru(NH ₃) ₄ (2,3-Cl ₂ pcyd)] [ClO ₄] ₂	52
2.4.3	Preparation of <i>Trans</i> -[(pyridine)Ru(NH ₃) ₄ (2,3-Cl ₂ pcyd)] [ClO ₄] ₂	53
2.4.4	Preparation of <i>Trans</i> -[(2,6-Me ₂ pyz)Ru(NH ₃) ₄ (2,3-Cl ₂ pcyd)] [ClO ₄]	55
2.4.5	Preparation of <i>Trans</i> -[(pyz)Ru(NH ₃) ₄ (2,3-Cl ₂ pcyd)] [ClO ₄]	57
2.4.6	Preparation of <i>Trans</i> -[(Mepyz)Ru(NH ₃) ₄ (2,3-Cl ₂ pcyd)] [ClO ₄] ₂	58
2.4.7	Preparation of <i>Mer</i> -[(bpy)Ru(NH ₃) ₃ (2,3-Cl ₂ pcyd)] [ClO ₄] ₂	60
2.5	SYNTHESIS OF ASYMMETRIC DINUCLEAR COMPLEXES	62
2.5.1	Preparation of <i>Trans</i> -[(py)Ru(NH ₃) ₄ (dicyd)Ru(NH ₃) ₅] [PF ₆] ₄	62
2.5.2	Preparation of <i>Trans</i> -[(pyz)Ru(NH ₃) ₄ (dicyd)Ru(NH ₃) ₅] [PF ₆] ₄	64
2.5.3	Preparation of <i>Mer</i> -[(bpy)Ru(NH ₃) ₃ (dicyd)Ru(NH ₃) ₅] [PF ₆] ₄	66
2.6	PHYSICAL MEASUREMENTS	68

2.6.1	Infrared Spectroscopy	68
2.6.2	Electronic Absorption Spectroscopy	68
2.6.3	Cyclic Voltammetry	68
2.6.4	Spectroelectrochemistry	69
2.6.5	Elemental Analyses	70
2.7	TECHNIQUES	71
2.7.1	ITO Preparation and Etching	71
2.7.2	Ag/AgCl Reference Electrode Preparation	71
2.8	THEORETICAL CALCULATIONS	72
2.8.1	Non-linear Curve Fitting	72
CHAPTER 3: RESULTS		73
3.1	MONONUCLEAR COMPLEXES	73
3.1.1	Infrared Spectroscopy	73
3.1.2	Electronic Absorption Spectroscopy	77
3.1.3	Electrochemical Studies	95
3.1.4	Spectroelectrochemical Studies	100
3.2	DINUCLEAR COMPLEXES	116
3.2.1	Synthesis	117
3.2.2	Synthetic Strategies	119
3.2.3	Infrared Spectroscopy	122
3.2.4	Electronic Absorption Spectroscopy	125
3.2.5	Cyclic Voltammetry	140
3.2.6	Spectroelectrochemistry	153
3.2.7	Solution Magnetic Susceptibility Measurements	162

3.2.8	^1H NMR Spectroscopy of the Asymmetric Complexes	170
CHAPTER 4: DISCUSSION		185
4.1.	MONONUCLEAR COMPLEXES	185
4.1.1	Electronic Absorption Spectroscopy	185
4.1.2	Electrochemistry	199
4.2.	ASYMMETRIC DINUCLEAR COMPLEXES	203
4.2.1	Electronic Absorption Spectroscopy	205
4.2.2	Cyclic Voltammetry	209
4.2.3	Spectroelectrochemistry	217
4.2.4	Testing the CNS Model	217
4.2.5	Solution Magnetic Susceptibility and Antiferromagnetic Exchange Measurements	221
4.3	CONCLUSION AND FUTURE STUDIES	225
APPENDIX		228
REFERENCES		230

List of Tables

Table	Page
1.1 Donor Number Values for Solvents	25
3.1 Infrared Band Energies (cm^{-1}) for Selected Characteristic Vibrations of the Mononuclear Complexes	75
3.2 Electronic Absorption Spectroscopy Data for <i>trans</i> - $[(\text{NH}_3)_5\text{Ru}^{\text{III}}(2,3\text{-Cl}_2\text{pcyd})]^{2+}$ as a Function of Solvent	82
3.3 Electronic Absorption Spectroscopy Data for <i>trans</i> - $[(3,5\text{-Me}_2\text{py})\text{Ru}^{\text{III}}(\text{NH}_3)_4(2,3\text{-Cl}_2\text{pcyd})]^{2+}$ as a Function of Solvent	83
3.4 Electronic Absorption Spectroscopy Data for <i>trans</i> - $[(3,5\text{-Me}_2\text{py})\text{Ru}^{\text{II}}(\text{NH}_3)_4(2,3\text{-Cl}_2\text{pcyd})]^+$ as a Function of Solvent	84
3.5 Electronic Absorption Spectroscopy Data for <i>trans</i> - $[(\text{pyridine})\text{Ru}^{\text{III}}(\text{NH}_3)_4(2,3\text{-Cl}_2\text{pcyd})]^{2+}$ as a Function of Solvent	85
3.6 Electronic Absorption Spectroscopy Data for <i>trans</i> - $[(\text{pyridine})\text{Ru}^{\text{II}}(\text{NH}_3)_4(2,3\text{-Cl}_2\text{pcyd})]^+$ as a Function of Solvent	86
3.7 Electronic Absorption Spectroscopy Data for <i>trans</i> - $[(2,6\text{-Me}_2\text{pyz})\text{Ru}^{\text{III}}(\text{NH}_3)_4(2,3\text{-Cl}_2\text{pcyd})]^{2+}$ as a Function of Solvent	87
3.8 Electronic Absorption Spectroscopy Data for <i>trans</i> - $[(2,6\text{-Me}_2\text{pyz})\text{Ru}^{\text{II}}(\text{NH}_3)_4(2,3\text{-Cl}_2\text{pcyd})]^+$ as a Function of Solvent	88
3.9 Electronic Absorption Spectroscopy Data for <i>trans</i> - $[(\text{pyz})\text{Ru}^{\text{III}}(\text{NH}_3)_4(2,3\text{-Cl}_2\text{pcyd})]^{2+}$ as a Function of Solvent	89
3.10 Electronic Absorption Spectroscopy Data for <i>trans</i> - $[(\text{pyz})\text{Ru}^{\text{II}}(\text{NH}_3)_4(2,3\text{-Cl}_2\text{pcyd})]^+$ as a Function of Solvent	90
3.11 Electronic Absorption Spectroscopy Data for <i>trans</i> - $[(\text{Mepyz})\text{Ru}^{\text{III}}(\text{NH}_3)_4(2,3\text{-Cl}_2\text{pcyd})]^{3+}$ as Function of Solvent	91
3.12 Electronic Absorption Spectroscopy Data for <i>trans</i> - $[(\text{Mepyz})\text{Ru}^{\text{II}}(\text{NH}_3)_4(2,3\text{-Cl}_2\text{pcyd})]^{2+}$ as Function of Solvent	92
3.13 Electronic Absorption Spectroscopy Data for <i>mer</i> - $[(\text{bpy})\text{Ru}^{\text{III}}(\text{NH}_3)_3(2,3\text{-Cl}_2\text{pcyd})]^{2+}$ as a Function of Solvent	93

3.14	Electronic Absorption Spectroscopy Data for <i>mer</i> - [(bpy)Ru ^{II} (NH ₃) ₃ (2,3-Cl ₂ pcyd)] ⁺ as a Function of Solvent	94
3.15	Ru(III/II) Reduction Couples and ΔE values as a Function of Solvent Seven Mononuclear Complexes	96
3.16	Infrared Band Energies for the Asymmetric Ru _a (III)-Ru _b (III) Dinuclear Complexes Bridged by dicyd ²⁻	123
3.17	Electronic Absorption Spectroscopy Data for [Ru(NH ₃) ₅ (dicyd)Ru(NH ₃) ₅][PF ₆] ₄ as a Function of Solvent	136
3.18	Deconvoluted Electronic Absorption Spectroscopy Data for <i>trans</i> - [(pyridine)Ru(NH ₃) ₄ (dicyd)Ru(NH ₃) ₅][PF ₆] ₄ in Various Solvents	137
3.19	Deconvoluted Electronic Absorption Spectroscopy Data for <i>trans</i> - [(pyrazine)Ru(NH ₃) ₄ (dicyd)Ru(NH ₃) ₅][PF ₆] ₄ in Various Solvents	138
3.20	Deconvoluted Electronic Absorption Spectroscopy Data for <i>trans</i> - [(bipyridine)Ru(NH ₃) ₃ (dicyd)Ru(NH ₃) ₅][PF ₆] ₄ in Various Solvents	139
3.21	Redox Couples and Compropotionation Constants as a Function of Solvent for [Ru(NH ₃) ₅ -dicyd-Ru(NH ₃) ₅][PF ₆] ₄	143
3.22	Redox Couples and Compropotionation Constants as a Function of Solvent for [(pyridine)Ru(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅][PF ₆] ₄	144
3.23	Redox Couples and Compropotionation Constants as a Function of Solvent for [(pyrazine)Ru(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅][PF ₆] ₄	145
3.24	Redox Couples and Compropotionation Constants as a Function of Solvent for [(bipyridine)Ru(NH ₃) ₃ -dicyd-Ru(NH ₃) ₅][PF ₆] ₄	146
3.25	Estimated Energy of the IT band, , of the Asymmetric Complexes from Spectroelectrochemical Measurement in Various Solvents	155
3.26	Magnetic data of [Ru(NH ₃) ₅ -dicyd-Ru(NH ₃) ₅][PF ₆] ₄ in Various Deuterated Solvents	164
3.27	Magnetic data of <i>trans</i> -[(pyridine)Ru(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅][PF ₆] ₄ in Various Deuterated Solvents	165
3.28	Magnetic data of <i>trans</i> -[(pyrazine)Ru(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅][PF ₆] ₄ in Various Deuterated Solvents	166
3.29	Magnetic data of <i>mer</i> -[(bipyridine)Ru(NH ₃) ₃ -dicyd-Ru(NH ₃) ₅][PF ₆] ₄	

	in Various Deuterated Solvents	167
3.30	Magnetic Moments and Antiferromagnetic Exchange Constants for Dinuclear Complexes in Various Deuterated Solvents	168
3.31	Solvent –Dependent ^1H NMR Chemical Shift Data of $[\text{Ru}(\text{NH}_3)_5\text{-dicyd-Ru}(\text{NH}_3)_5][\text{PF}_6]_4$	180
3.32	Solvent Dependent ^1H NMR Chemical Shift Data of <i>trans</i> -[(pyridine) $\text{Ru}(\text{NH}_3)_4\text{-dicyd-Ru}(\text{NH}_3)_5][\text{PF}_6]_4$	180
3.33	Solvent Dependent ^1H NMR Chemical Shift Data of <i>trans</i> -[(pyrazine) $\text{Ru}(\text{NH}_3)_4\text{-dicyd-Ru}(\text{NH}_3)_5][\text{PF}_6]_4$	181
3.34	Solvent –Dependent ^1H NMR Chemical Shift Data of <i>mer</i> -[(bipyridine) $\text{Ru}(\text{NH}_3)_3\text{-dicyd-Ru}(\text{NH}_3)_5][\text{PF}_6]_4$	181
4.1	ΔE_{asy} Values of the Asymmetric Complexes	216
4.2	Solvent Dependent ΔG_i Values of the Asymmetric Complexes	216
4.3	Effective Coupling of the Metal Centers, H_{MM}^2/E_{IT} in Nitromethane	219
4.4	Effective Coupling of the Metal Centers, H_{MM}^2/E_{IT} in Acetonitrile	219
4.5	Effective Coupling of the Metal Centers, H_{MM}^2/E_{IT} in Acetone	220
4.6	Effective Coupling of the Metal Centers, H_{MM}^2/E_{IT} in in DMSO	220
4.7	Energy Difference Between Ground State and LMCT Excited State, associated with $h_{d\pi}^a$ for dicyd $^{2-}$ Bridged Asymmetric Complexes	222
4.8	Calculated Antiferromagnetic Exchange Constants for Ruthenium(III) Dinuclear Complexes as a Function of Solvent	223

List of Figures

Figure	Page
1.1 The Creutz-Taube ion	2
1.2 Donor and acceptor sites separated by a bridge	3
1.3 Potential energy curves representing initial and final states for symmetric mixed valence complexes	4
1.4 Two superexchange pathways in the mixed-valence ruthenium dinuclear complexes bridged by a π -system ligand	7
1.5 Interaction of the ruthenium d_{xz} orbitals with pyrazine π -LUMO and dicyd ²⁻ π -HOMO	8
1.6 Potential energy curves for symmetric mixed valence complexes	13
1.7 $\Delta G_r'$ values versus theoretical, H_{ad}^2/E_{IT} values for the penta-, tetra-, and triammine complexes	15
1.8 Potential energy profiles for the donor $M_a LM_b$, acceptor $M_a^- LM_b^+$, and intermediate charge transfer $M_a L^+ M_b^-$ states	17
1.9 $\Delta G_r'$ values versus H_{ad}^2/E_{IT} values for the penta-, tetra-, and triammine complexes	20
1.10 Mulliken theoretical analysis scheme of donor-acceptor interactions and its application to the asymmetric mixed-valence case	21
1.11 Schematic illustration of how the potential surfaces respond to asymmetric ligand substitution processes	22
1.12 Donor-acceptor solvent interactions	26
1.13 Two types of magnetic interaction showing how free paramagnetic ions form a dimer via diamagnetic bridging ligand	30
1.14 Mixing of F and I state, and potential energy diagram representing this in the charge transfer model for antiferromagnetic exchange	31
1.15 Plot of calculated versus estimated antiferromagnetic exchange constants or the complexes in aprotic solvents	36

3.1	Ruthenium bonding to various resonance forms of phenylcyanamide anion ligand	74
3.2	Infrared spectrum of $[\text{Ru}(\text{NH}_3)_5(2,3\text{-Cl}_2\text{pcyd})][\text{ClO}_4]_2$	76
3.3	Infrared spectrum of $[\text{trans}-(\text{Mepyz})\text{Ru}(\text{NH}_3)_4(2,3\text{-Cl}_2\text{pcyd})]^{2+}$	76
3.4	Resonance stabilized anionic phenylcyanamide π system showing nonbonding electrons that can delocalize into the π system	78
3.5	A qualitative MO energy level diagram showing the relative energies of the $b_1^* \leftarrow b_1$ LMCT transition for pcyd^-	79
3.6	MO diagram of mononuclear ruthenium(II)-phenylcyanamide complex showing the MLCT transition	80
3.7	Electronic absorption spectra of $[(\text{NH}_3)_5\text{Ru}^{\text{III}}(2,3\text{-Cl}_2\text{pcyd})]^{2+}$ in various solvents	82
3.8	Electronic absorption spectra of $\text{trans}-[(3,5\text{-Me}_2\text{py})\text{Ru}^{\text{III}}(\text{NH}_3)_4(2,3\text{-Cl}_2\text{pcyd})]^{2+}$ in various solvents	83
3.9	Electronic absorption spectra of $\text{trans}-[(3,5\text{-Me}_2\text{py})\text{Ru}^{\text{II}}(\text{NH}_3)_4(2,3\text{-Cl}_2\text{pcyd})]^+$ in various solvents	84
3.10	Electronic absorption spectra of $\text{trans}-[(\text{py})\text{Ru}^{\text{III}}(\text{NH}_3)_4(2,3\text{-Cl}_2\text{pcyd})]^{2+}$ in various solvents	85
3.11	Electronic absorption spectra of $\text{trans}-[(\text{pyridine})\text{Ru}^{\text{II}}(\text{NH}_3)_4(2,3\text{-Cl}_2\text{pcyd})]^+$ in various solvents	86
3.12	Electronic absorption spectra of $\text{trans}-[(2,6\text{-Me}_2\text{pyz})\text{Ru}^{\text{III}}(\text{NH}_3)_4(2,3\text{-Cl}_2\text{pcyd})]^{2+}$ in various solvents	87
3.13	Electronic absorption spectra of $\text{trans}-[(2,6\text{-Me}_2\text{pyz})\text{Ru}^{\text{II}}(\text{NH}_3)_4(2,3\text{-Cl}_2\text{pcyd})]^+$ in various solvents	88
3.14	Electronic absorption spectra of $\text{trans}-[(\text{pyz})\text{Ru}^{\text{III}}(\text{NH}_3)_4(2,3\text{-Cl}_2\text{pcyd})]^{2+}$ in various solvents	89
3.15	Electronic absorption spectra of $\text{trans}-[(\text{pyz})\text{Ru}^{\text{II}}(\text{NH}_3)_4(2,3\text{-Cl}_2\text{pcyd})]^+$ in various solvents	90
3.16	Electronic absorption spectra of $\text{trans}-[(\text{Mepyz})\text{Ru}^{\text{III}}(\text{NH}_3)_4(2,3\text{-Cl}_2\text{pcyd})]^{3+}$ in various solvents	91

3.17	Electronic absorption spectra of <i>trans</i> - [(Mepyz)Ru ^{II} (NH ₃) ₄ (2,3-Cl ₂ pcyd)] ²⁺ in various solvents	92
3.18	Electronic absorption spectra of <i>mer</i> - [(bpy)Ru ^{III} (NH ₃) ₃ (2,3-Cl ₂ pcyd)] ²⁺ in various solvents	93
3.19	Electronic absorption spectra of <i>mer</i> - [(bpy)Ru ^{II} (NH ₃) ₃ (2,3-Cl ₂ pcyd)] ⁺ in various solvents	94
3.20	Cyclic voltammogram of <i>trans</i> - [Ru(NH ₃) ₅ (2,3-Cl ₂ pcyd)] ²⁺ in DMSO	97
3.21	Cyclic voltammogram of <i>trans</i> - [(3,5-Me ₂ py)Ru(NH ₃) ₄ (2,3-Cl ₂ pcyd)] ²⁺ in nitromethane	97
3.22	Cyclic voltammogram of <i>trans</i> - [(pyridine)Ru(NH ₃) ₄ (2,3-Cl ₂ pcyd)] ²⁺ in acetonitrile	98
3.23	Cyclic voltammogram of <i>trans</i> - [(2,6-Me ₂ pyz)Ru(NH ₃) ₄ (2,3-Cl ₂ pcyd)] ²⁺ in acetonitrile	98
3.24	Cyclic voltammogram of <i>trans</i> - [(pyz)Ru(NH ₃) ₄ (2,3-Cl ₂ pcyd)] ²⁺ in acetone	99
3.25	Cyclic voltammogram of <i>trans</i> - [(Mepyz)Ru(II)(NH ₃) ₄ (2,3-Cl ₂ pcyd)] ²⁺ in acetonitrile	99
3.26	Cyclic voltammogram of <i>mer</i> - [(bpy)Ru(NH ₃) ₄ (2,3-Cl ₂ pcyd)] ²⁺ in nitromethane	99
3.27	Spectroelectrochemical data for <i>trans</i> -[Ru(NH ₃) ₅ (2,3-Cl ₂ pcyd)] ²⁺ in NM	102
3.28	Spectroelectrochemical data for <i>trans</i> -[Ru(NH ₃) ₅ (2,3-Cl ₂ pcyd)] ²⁺ in AN	102
3.29	Spectroelectrochemical data for <i>trans</i> - [Ru(NH ₃) ₅ (2,3-Cl ₂ pcyd)] ²⁺ in AC	103
3.30	Spectroelectrochemical data for <i>trans</i> -[Ru(NH ₃) ₅ (2,3-Cl ₂ pcyd)] ²⁺ in DMSO	103
3.31	Spectroelectrochemical data for <i>trans</i> -[(3,5-Me ₂ py)Ru(NH ₃) ₄ (2,3-Cl ₂ pcyd)] ²⁺ in NM	104

3.32	Spectroelectrochemical data for <i>trans</i> -[(3,5-Me ₂ py)Ru(NH ₃) ₄ (2,3-Cl ₂ pcyd)] ²⁺ in AN	104
3.33	Spectroelectrochemical data for <i>trans</i> -[(3,5-Me ₂ py)Ru(NH ₃) ₄ (2,3-Cl ₂ pcyd)] ²⁺ in AC	105
3.34	Spectroelectrochemical data for <i>trans</i> -[(3,5-Me ₂ py)Ru(NH ₃) ₄ (2,3-Cl ₂ pcyd)] ²⁺ in DMSO	105
3.35	Spectroelectrochemical data for <i>trans</i> -[(py)Ru(NH ₃) ₄ (2,3-Cl ₂ pcyd)] ²⁺ in NM	106
3.36	Spectroelectrochemical data for <i>trans</i> -[(py)Ru(NH ₃) ₄ (2,3-Cl ₂ pcyd)] ²⁺ in AN	106
3.37	Spectroelectrochemical data for <i>trans</i> -[(py)Ru(NH ₃) ₄ (2,3-Cl ₂ pcyd)] ²⁺ in AC	107
3.38	Spectroelectrochemical data for <i>trans</i> -[(py)Ru(NH ₃) ₄ (2,3-Cl ₂ pcyd)] ²⁺ in DMSO	107
3.39	Spectroelectrochemical data for <i>trans</i> -[(2,6-Me ₂ pyz)Ru(II)(NH ₃) ₄ (2,3-Cl ₂ pcyd)] ²⁺ in NM	108
3.40	Spectroelectrochemical data for <i>trans</i> -[(2,6-Me ₂ pyz)Ru(II)(NH ₃) ₄ (2,3-Cl ₂ pcyd)] ²⁺ in AN	108
3.41	Spectroelectrochemical data for <i>trans</i> -[(2,6-Me ₂ pyz)Ru(II)(NH ₃) ₄ (2,3-Cl ₂ pcyd)] ²⁺ in AC	109
3.42	Spectroelectrochemical data for <i>trans</i> -[(2,6-Me ₂ pyz)Ru(II)(NH ₃) ₄ (2,3-Cl ₂ pcyd)] ²⁺ in DMSO	109
3.43	Spectroelectrochemical data for <i>trans</i> -[(pyz)Ru(II)(NH ₃) ₄ (2,3-Cl ₂ pcyd)] ²⁺ in NM	110
3.44	Spectroelectrochemical data for <i>trans</i> -[(pyz)Ru(II)(NH ₃) ₄ (2,3-Cl ₂ pcyd)] ²⁺ in AN	110
3.45	Spectroelectrochemical data for <i>trans</i> -[(pyz)Ru(II)(NH ₃) ₄ (2,3-Cl ₂ pcyd)] ²⁺ in AC	111
3.46	Spectroelectrochemical data for <i>trans</i> -[(pyz)Ru(II)(NH ₃) ₄ (2,3-Cl ₂ pcyd)] ²⁺ in DMSO	111

3.47	Spectroelectrochemical data for <i>trans</i> -[(Mepyz)Ru(NH ₃) ₄ (2,3-Cl ₂ pcyd)] ²⁺ in NM	112
3.48	Spectroelectrochemical data for <i>trans</i> -[(Mepyz)Ru(NH ₃) ₄ (2,3-Cl ₂ pcyd)] ²⁺ in AN	112
3.49	Spectroelectrochemical data for <i>trans</i> -[(Mepyz)Ru(NH ₃) ₄ (2,3-Cl ₂ pcyd)] ²⁺ in AC	113
3.50	Spectroelectrochemical data for <i>trans</i> -[(Mepyz)Ru(NH ₃) ₄ (2,3-Cl ₂ pcyd)] ²⁺ in DMSO	113
3.51	Spectroelectrochemical data for <i>mer</i> -[(bpy)Ru(III)(NH ₃) ₃ (2,3-Cl ₂ pcyd)] ²⁺ in NM	114
3.52	Spectroelectrochemical data for <i>mer</i> -[(bpy)Ru(III)(NH ₃) ₃ (2,3-Cl ₂ pcyd)] ²⁺ in AN	114
3.53	Spectroelectrochemical data for <i>mer</i> -[(bpy)Ru(III)(NH ₃) ₃ (2,3-Cl ₂ pcyd)] ²⁺ in AC	115
3.54	Spectroelectrochemical data for <i>mer</i> -[(bpy)Ru(III)(NH ₃) ₃ (2,3-Cl ₂ pcyd)] ²⁺ in DMSO	115
3.55	Infrared spectrum of <i>trans</i> -[pyRu(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅] ⁴⁺	123
3.56	A MO scheme for the orbitals resulting from π -interactions that shows origins of Ru _a -NCN and Ru _b -NCN LMCT bands	127
3.57	Electronic absorption spectra of [Ru(NH ₃) ₅ (dicyd)Ru(NH ₃) ₅] ⁴⁺ in all solvents	128
3.58	Electronic absorption spectra of <i>trans</i> -(pyridine)Ru(NH ₃) ₄ (dicyd)Ru(NH ₃) ₅] ⁴⁺ in all solvents	128
3.59	Electronic absorption spectra of <i>trans</i> - [(pyrazine)Ru(NH ₃) ₄ (dicyd)Ru(NH ₃) ₅] ⁴⁺ in all solvents	129
3.60	Electronic absorption spectra of <i>mer</i> - [(bipyridine)Ru(NH ₃) ₃ (dicyd)Ru(NH ₃) ₅] ⁴⁺ in all solvents	129
3.61	Gaussian band fit of the LMCT transition profile of <i>trans</i> - [(py)Ru(NH ₃) ₄ (dicyd)Ru(NH ₃) ₅] ⁴⁺ in NM	130

3.62	Gaussian band fit of the LMCT transition profile of <i>trans</i> -[(py)Ru(NH ₃) ₄ (dicyd)Ru(NH ₃) ₅] ⁴⁺ in AN	130
3.63	Gaussian band fit of the LMCT transition profile of <i>trans</i> -[(py)Ru(NH ₃) ₄ (dicyd)Ru(NH ₃) ₅] ⁴⁺ in AC	131
3.64	Gaussian band fit of the LMCT transition profile of <i>trans</i> -[(py)Ru(NH ₃) ₄ (dicyd)Ru(NH ₃) ₅] ⁴⁺ in DMSO	131
3.65	Gaussian band fit of the LMCT transition profile of <i>trans</i> -[(pyz)Ru(NH ₃) ₄ (dicyd)Ru(NH ₃) ₅] ⁴⁺ in NM	132
3.66	Gaussian band fit of the LMCT transition profile of <i>trans</i> -[(pyz)Ru(NH ₃) ₄ (dicyd)Ru(NH ₃) ₅] ⁴⁺ in AN	132
3.67	Gaussian band fit of the LMCT transition profile of <i>trans</i> -[(pyz)Ru(NH ₃) ₄ (dicyd)Ru(NH ₃) ₅] ⁴⁺ in AC	133
3.68	Gaussian band fit of the LMCT transition profile of <i>trans</i> -[(pyz)Ru(NH ₃) ₄ (dicyd)Ru(NH ₃) ₅] ⁴⁺ in DMSO	133
3.69	Gaussian band fit of the LMCT transition profile of <i>mer</i> -[(bpy)Ru(NH ₃) ₃ (dicyd)Ru(NH ₃) ₅] ⁴⁺ in NM	134
3.70	Gaussian band fit of the LMCT transition profile of <i>mer</i> -[(bpy)Ru(NH ₃) ₃ (dicyd)Ru(NH ₃) ₅] ⁴⁺ in AN	134
3.71	Gaussian band fit of the LMCT transition profile of <i>mer</i> -[(bpy)Ru(NH ₃) ₃ (dicyd)Ru(NH ₃) ₅] ⁴⁺ in AC	135
3.72	Gaussian band fit of the LMCT transition profile of <i>mer</i> -[(bpy)Ru(NH ₃) ₃ (dicyd)Ru(NH ₃) ₅] ⁴⁺ in DMSO	135
3.73	Cyclic voltammogram of <i>trans</i> -[(pyridine)Ru(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅] ⁴⁺ in NM	147
3.74	Cyclic voltammogram of <i>trans</i> -[(pyridine)Ru(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅] ⁴⁺ in AN	147
3.75	Cyclic voltammogram of <i>trans</i> -[(pyridine)Ru(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅] ⁴⁺ in AC	148
3.76	Cyclic voltammogram of <i>trans</i> -[(pyridine)Ru(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅] ⁴⁺ in DMSO	148

3.77	Cyclic voltammogram of <i>trans</i> -[(pyrazine)Ru(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅] ⁴⁺ in NM	149
3.78	Cyclic voltammogram of <i>trans</i> -[(pyrazine)Ru(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅] ⁴⁺ in AN	149
3.79	Cyclic voltammogram of <i>trans</i> -[(pyrazine)Ru(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅] ⁴⁺ in AC	150
3.80	Cyclic voltammogram of <i>trans</i> -[(pyrazine)Ru(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅] ⁴⁺ in DMSO	150
3.81	Cyclic voltammogram of <i>mer</i> -[(bipyridine)Ru(NH ₃) ₃ -dicyd-Ru(NH ₃) ₅] ⁴⁺ in NM	151
3.82	Cyclic voltammogram of <i>mer</i> -[(bipyridine)Ru(NH ₃) ₃ -dicyd-Ru(NH ₃) ₅] ⁴⁺ in AN	151
3.83	Cyclic voltammogram of <i>mer</i> -[(bipyridine)Ru(NH ₃) ₃ -dicyd-Ru(NH ₃) ₅] ⁴⁺ in AC	152
3.84	Cyclic voltammogram of <i>mer</i> -[(bipyridine)Ru(NH ₃) ₃ -dicyd-Ru(NH ₃) ₅] ⁴⁺ in DMSO	152
3.85	Spectroelectrochemical data for <i>trans</i> -[(pyradine)Ru(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅] ⁴⁺ in NM	156
3.86	Spectroelectrochemical data for <i>trans</i> -[(pyradine)Ru(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅] ⁴⁺ in AN	156
3.87	Spectroelectrochemical data for <i>trans</i> -[(pyradine)Ru(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅][PF ₆] ₄ in AC	157
3.88	Spectroelectrochemical data for <i>trans</i> -[(pyradine)Ru(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅][PF ₆] ₄ in DMSO	157
3.89	Spectroelectrochemical data for <i>trans</i> -[(pyrazine)Ru(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅][PF ₆] ₄ in NM	158
3.90	Spectroelectrochemical data for <i>trans</i> -[(pyrazine)Ru(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅][PF ₆] ₄ in AN	158
3.91	Spectroelectrochemical data for <i>trans</i> -[(pyrazine)Ru(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅][PF ₆] ₄ in AC	159

3.92	Spectroelectrochemical data for <i>trans</i> -[(pyrazine)Ru(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅][PF ₆] ₄ in DMSO	159
3.93	Spectroelectrochemical data for <i>mer</i> -[(bipyridine)Ru(NH ₃) ₃ -dicyd-Ru(NH ₃) ₅][PF ₆] ₄ in NM	160
3.94	Spectroelectrochemical data for <i>mer</i> -[(bipyridine)Ru(NH ₃) ₃ -dicyd-Ru(NH ₃) ₅][PF ₆] ₄ in AN	160
3.95	Spectroelectrochemical data for <i>mer</i> -[(bipyridine)Ru(NH ₃) ₃ -dicyd-Ru(NH ₃) ₅][PF ₆] ₄ in AC	161
3.96	Spectroelectrochemical data for <i>mer</i> -[(bipyridine)Ru(NH ₃) ₃ -dicyd-Ru(NH ₃) ₅][PF ₆] ₄ in DMSO	161
3.97	400 MHz ¹ H NMR spectrum of <i>trans</i> -[pyRu(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅][PF ₆] ₄ in nitromethane-d ₃	171
3.98	400 MHz ¹ H NMR spectrum of <i>trans</i> -[pyRu(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅] in nitromethane-d ₃ showing the pyridine and dicyd ²⁻	171
3.99	400 MHz ¹ H NMR COSY of <i>trans</i> -[pyRu(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅] in nitromethane-d ₃ showing the pyridine and dicyd ²⁻	172
3.100	400 MHz ¹ H NMR spectrum of <i>trans</i> -[pyRu(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅] in acetone-d ₆ showing the pyridine hydrogen resonances	173
3.101	400 MHz ¹ H NMR spectrum of <i>trans</i> -[pyzRu(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅] in nitromethane-d ₃ showing the pyrazine hydrogen resonances	174
3.102	400 MHz ¹ H NMR spectrum of <i>trans</i> -[pyzRu(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅] in nitromethane-d ₃	174
3.103	400 MHz ¹ H NMR spectrum of <i>trans</i> -[pyzRu(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅] in nitromethane-d ₃ showing the pyrazine hydrogen resonances	175
3.104	400 MHz ¹ H NMR spectrum of <i>trans</i> -[pyzRu(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅] in acetone-d ₆ showing the pyrazine hydrogen resonances	175
3.105	400 MHz ¹ H NMR spectrum of <i>trans</i> -[pyzRu(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅] in DMSO-d ₆ showing the pyrazine hydrogen resonances	176
3.106	400 MHz ¹ H NMR spectrum of <i>trans</i> -[bpyRu(NH ₃) ₃ -dicyd-Ru(NH ₃) ₅] in nitromethane-d ₃ showing the hydrogen resonances	177
3.107	400 MHz ¹ H NMR spectrum of <i>mer</i> -[bpyRu(NH ₃) ₃ -dicyd-Ru(NH ₃) ₅]	

	in nitromethane-d ₃ showing the hydrogen resonances	177
3.108	400 MHz ¹ H NMR COSY and NOESY of <i>mer</i> -[bpyRu(NH ₃) ₃ -dicyd-Ru(NH ₃) ₅] in nitromethane-d ₃	178
3.109	400 MHz ¹ H NMR spectrum of <i>mer</i> -[bpyRu(NH ₃) ₃ -dicyd-Ru(NH ₃) ₅] in acetone-d ₆ showing the hydrogen resonances	179
3.110	400 MHz ¹ H NMR spectrum of <i>mer</i> -[bpyRu(NH ₃) ₃ -dicyd-Ru(NH ₃) ₅] in DMSO-d ₆ showing the hydrogen resonances	179
4.1	Plot of LMCT transition energy versus solvent donor number of mononuclear complexes	186
4.2	Plot of MLCT transition energy versus solvent donor number of mononuclear complexes	187
4.3	MO scheme showing the MLCT transitions in mononuclear complexes under study	190
4.4	Plot of oscillator strength versus LMCT transition energy as a function of solvent for the mononuclear complexes	193
4.5	Plot of H_{LM} coupling element versus solvent donor number for mononuclear complexes	196
4.6	Plot of oscillator strength versus MLCT transition energy as a function of solvent for the mononuclear complexes	197
4.7	Plot of H_{ML} coupling element versus solvent donor number for tetraammine mononuclear complexes	199
4.8	Redox potential as a function of solvent donor number for the mononuclear complexes	201
4.9	Variation of ruthenium(III/II) reduction couples of the mononuclear complexes from most to least donating solvent	202
4.10	A simple MO diagram for LMCT transition in symmetric dinuclear Ru ^{III} -Ru ^{III} complex bridged with π -HOMO ligand	206
4.11	Plot of E_{LMCT} transition energy of Ru_b^{III} -NCN chromophore versus solvent donor strength	207
4.12	Schematic representation of how donor acceptor interaction between coordinated amines and solvent	208

4.13	Solvent dependent $Ru_b^{III/II}$ redox couples of the dimer for symmetric pentaammine and asymmetric complexes	210
4.14	Solvent dependent $Ru_a^{III/II}$ redox couples of the dimer for symmetric pentaammine and asymmetric tetrammine-pyridine	211
4.15	Polarization of dicyd ²⁻ bridging ligand	212
4.16	Variation of $L^{-/2-}$ redox potential with solvent donor properties when <i>trans</i> -ammine is asymmetrically substituted with stronger π -acceptor	213
4.17	Plot of ΔG_c versus solvent donor strength for dinuclear complexes when <i>trans</i> -ammine is asymmetrically substituted with weaker σ -donor	215
4.18	Plot of calculated versus estimated antiferromagnetic exchange constants for the three asymmetric tetrammine-pyridine	224

List of Schemes

Scheme		Page
1.1	Involvement of LMCT Excited state in Superexchange Mechanism	33
3.1	π -bonding interaction between Ru(III) and cyanamide anionic ligand	79
3.2	The πd - $L\pi^*$ interaction	81
3.3	Metal-Centered and Ligand-Centred couples of Mononuclear Complexes	95
3.4	Scheme for synthesis of Asymmetric Dinuclear Complexes	117
3.5	Electrochemical Processes for Metal Centered and Ligand Centered events in Dinuclear Systems	141
4.1	Interaction between Ruthenium(II)-methylpyrazinium π -bond and NH_3	189

List of Appendices

Appendix		Page
1	Metal-Ligand Coupling Elements of Symmetric and Asymmetric Complexes from Mononuclears LMCT bands as a Function of Solvent	228
2	Generated Data used to determine Theoretical Antiferromagnetic Exchange, $-J_{AF}$	229

List of Abbreviations

AC	acetone
AN	acetonitrile
bpy	2,2-bipyridine
Calcd	calculated
COSY	Correlated SpectroscopY (Homonuclear Shift Correlation)
CV	cyclic voltammetry
Dicyd ²⁻	1,4-dicyanamidobenzene dianion
DMSO	dimethylsulfoxide
E_{IT}	energy of the intervalence transition
f	oscillator strength
Fc	ferrocene
ΔG_{asy}	free energy due to asymmetry
ΔG_c	free energy of comproportionation
ΔG_e	electrostatic free energy
ΔG_{ex}	free energy of antiferromagnetic exchange
ΔG_i	inductive free energy of
ΔG_r	free energy of resonance exchange
ΔG_s	entropic free energy of
ΔG_{th}	thermal barrier of electron transfer
H	metal-metal coupling
H_{ad} (or H_{ab})	acceptor-donor coupling element (Hush model)

$H_{MM'}$	metal-metal coupling (CNS model)
HOMO	Highest Occupied Molecular Orbitals
IT	intervalence transition
K_c	comproportionation constant
LMCT	Ligand-to-Metal Charge Transfer
LUMO	Lowest Unoccupied Molecular Orbital
MMCT	metal-to-metal charge transfer
NM	nitromethane
NIR	Near-infrared
NMR	nuclear magnetic resonanace
NOESY	Nuclear Overhauser Enhancement Spectroscopy
OTTLE	optically transparent thin-layer electrode
pcyd ²⁻	phenylcyanamide
pentaammine	complex with the form $\text{Ru}(\text{NH}_3)_5\text{-L}$
py	pyridine
pyz	pyrazine
TBAB	tetrabutylammonium bromide
TBAH	tetrabutylammonium hexafluorophosphahate
tetraammine	complex with the form $(\text{py})\text{Ru}(\text{NH}_3)_4\text{-L}$ or $(\text{pyz})\text{Ru}(\text{NH}_3)_4\text{-L}$
triammine	$(\text{bpy})\text{Ru}(\text{NH}_3)_3\text{-L}$
UV-Vis-NIR	Ultraviolet-Visible-near Infrared

CHAPTER 1

INTRODUCTION

Polynuclear transition metal complexes represent an interesting class of coordination compounds which often display intriguing spectroscopic, magnetic and electrochemical properties. The elucidation of the nature and extent of the electronic interactions between metal centers in these complexes is an interesting area of research that continues to offer challenging fundamental problems.¹ Studies in this area have been driven by the desire to understand the role of long-range electron transfer in many biological processes² as well as practical functions associated with metal-metal interaction. Novel molecular materials may be prepared by considering these complexes as molecular building blocks. Polymerization and retention of electron delocalization between blocks then leads to a long-chain molecular wire.³ Polypyridyl ruthenium complexes have received much attention for their possible roles in photochemical molecular devices, such as molecular light switches,⁴ multielectron-transfer catalysts for water splitting,⁵ or solar energy harvesters.⁶

Understanding the factors that control metal-metal interactions is central to the purposeful synthesis of molecular materials and to the tuning of their properties. In such systems, the electronic interaction of metal centers are mediated by the orbitals of the bridge, and the interplay between metal and bridging orbitals are thus central in determining the behavior of the resultant system.⁷ Electronic transitions have probability, and this property in a complex contains information about the magnitude of electronic coupling between metal centers.

1.1 BACKGROUND

Metal-metal interactions in a given system may arise from Coulombic interactions or from direct coupling of the metals' wavefunctions. When the two metal centers interact sufficiently, it is possible for an electron to be transferred between them, thus forming a complex containing metal centers of inequivalent oxidation state, the so-called mixed-valence complexes.^{7,8} This is a common phenomenon,⁹ and Prussian blue, which has a cyanide-bridged Fe(III)-Fe(II) structure, was one of the first chemical materials to be described.¹⁰ Among the first designed mixed-valence complexes was the pyrazine-bridged dimer synthesized by Creutz and Taube in late 1960s¹¹ Figure 1.1.

Figure 1.1: The Creutz-Taube ion.

The conceptual and theoretical framework for understanding thermal outer-sphere electron transfer had earlier on been provided by Marcus in a series of publications between 1957 and 1958.¹² Ten year later, mixed-valence materials were reviewed and classified by Robin and Day,¹³ and Allen and Hush.¹⁴ One of the primary frameworks for understanding this area was then published by Hush,¹⁵ who forged a theoretical connection between electronic coupling and the energy and band shape of an intervalence charge-transfer band in the mixed valence systems. In this formalism, Hush linked the

spectroscopic properties of mixed-valence complexes to the intermolecular electron transfer theory of Marcus.

Since then, the well laid foundations to the understanding of the properties of molecular mixed-valence systems began to attract great interest. This is because of the new properties exhibited when significant electron coupling between the donor and acceptor sites is present, and because of the relationships between the optical properties and the electron transfer rates of the species. Mixed-valence molecules contain donor (D) and acceptor (A) sites separated by a bridge (B), as in Figure 1.2.

Figure 1.2: Donor and acceptor sites separated by a bridge.

The degree of metal-metal coupling experienced in a symmetric mixed-valence complex can be described by using a potential energy diagrams as in Figure 1.3. In each diagram, the left-hand parabola represents the potential energy surface for $M_a - L - M_b$ and the right hand parabola represents the same for $M_a^- - L - M_b^+$, where M_b is the donor center, and M_a is the acceptor center, and L is the bridge. The energy needed to photoexcite the odd electron to the higher state at the same nuclear configuration is shown on Figure 1.3B as E_{IT} . This is also known as λ , the energy of the metal-to-metal charge transfer (MMCT) band. H is the metal-metal coupling element, which is a measure of any interaction between donor and acceptor metal ions.¹⁶

In the Robin and Day classification,^{13,14} mixed-valence systems are characterized as Class I, II or III, depending on the strength of the electronic interaction between the oxidized and reduced sites, ranging from essentially zero (Class I), to moderate (Class II), to very strong electronic coupling (Class III).

Figure 1.3: Potential energy curves representing initial and final states for symmetric mixed valence complexes in Class I, A; Class II, B; and Class III, C.

The properties of Class I systems are essentially those of the separate sites, as in Figure 1.3A. There is no splitting at the intersection of the potential energy curves and H is zero. Class II systems possess new optical and electronic properties in addition to those of the separate sites. In these systems, Hush's treatment predicts the existence of charge transfer band for optically induced electron-transfer, and that the properties of that charge transfer band will reflect the degree of coupling between the metal centers. Such an event is termed metal-to-metal charge transfer (MMCT) or more commonly, because the two metals have different oxidation state (valencies), an intervalence transfer (IT) band. An interaction between donor and acceptor occurs, causing splitting at the intersection of the potential energy curves and H is greater than zero. However, the interaction between the

sites is sufficiently weak that Class II systems are valence-trapped or charge-localized, and can be described by a double-well potential, as shown in Figure 1.3B. In Class III systems, the interaction of the donor and acceptor sites is so great that two separate minima are no longer discernible and the energy surface features a single minimum. A perturbation treatment is no longer valid, as the interaction between donor and acceptor is so great that the electron is completely delocalized and the system has its own unique properties devoid of those of the separate sites, as in Figure 1.3C.

Since 1969, when Creutz and Taube reported their novel dinuclear complex,¹¹ a great body of work on the study of mixed-valence complexes has come into being.⁷ Dinuclear complexes based on the ruthenium(III/II) complex have played a central role in the study of mixed-valence chemistry, because of their rich and versatile redox chemistry, in association with their d^5/d^6 configuration. They also normally present favourable kinetic properties and are thermodynamically stable. Reviews in 1983 by Creutz,^{7a} and in 1994 by Crutchley,^{7b} have discussed advances in this field in detail.

1.2 METAL-METAL COUPLING IN SYMMETRIC MIXED-VALENCE COMPLEXES

Metal-metal coupling arises from the mixing of metal donor and acceptor orbitals. This mainly occurs through two major routes: through direct overlap of the metal orbitals or through superexchange. When donor and acceptor centers are separated by a bridge, Figure 1.2, the geometric distance between the metal centers is sufficiently large that direct overlap of the electronic wavefunctions is negligible. Electronic coupling occurs indirectly by mixing of metal-based donor and acceptor orbitals with orbitals of appropriate symmetry in the bridge. This is what is described as superexchange.^{16,17}

1.2.1 Superexchange

Superexchange can occur by two mechanisms, one of which will be preferred because of the energetics of the system. Electron-transfer superexchange occurs when the bridging ligand's lowest unoccupied π -molecular orbitals (π -LUMO) provides the pathway, and the mechanistic steps consist of an initial electron transfer from the donor metal to the empty bridge orbital, and a simultaneous electron transfer from the bridge to the acceptor metal. The concerted event is that of an electron moving from the donor end of the system to the acceptor end, as in Figure 1.4A.

The pathway through the ligand's highest occupied π -molecular orbital (π -HOMO) is known as hole-transfer superexchange and is shown for a mixed-valence ruthenium complex in Figure 1.4B. The mechanism of the concerted superexchange event can be represented as two stepwise electron transfer events, the first between the bridging ligand's π -HOMO and ruthenium(III) (π -acceptor) orbitals and the second

between the ruthenium(II) (π -donor) orbitals and the bridging ligand π -HOMO. Because the concerted event effectively represents an electron hole moving across the system from the acceptor to the donor end, the mechanism shown in Figure 1.4 is termed as hole-transfer superexchange.^{16,17}

Figure 1.4: Two superexchange pathways in the mixed-valence ruthenium dinuclear complexes bridged by a π -system ligand.

In metal complexes, the superexchange mechanism can be probed by making changes in the bridging ligand, the metal, the ancillary ligands, and/or the solvent. Electronic delocalization is enhanced by the mixing of electronic donor and acceptor wavefunctions and the bridging ligand is thus intimately involved in superexchange. For effective mediation and coupling, and for superexchange to occur, the ligand must possess an orbital spanning the entire molecule, which is symmetrically and energetically matched to the metal centers' orbitals such that it can interact simultaneously with both donor and acceptor centers.^{7b} It is thus not surprising that to obtain substantial coupling, an extended π -system is necessary, as in Figure 1.5, whereas coupling via a σ -framework is typically far weaker.¹⁸

Figure 1.5: Diagram showing the interaction of the ruthenium d_{xz} orbitals with pyrazine π -LUMO and dicyd²⁻ π -HOMO, the most likely pathways for electron and hole-transfer superexchange, respectively.

The role of the nature of the ancillary ligand and the metal center on the extent of coupling have been shown by Curtis *et al.* He observed decreasing metal-metal coupling in a series of analogous of the Creutz-Taube ion as σ -donating amines were systematically replaced by increasing by π -accepting ligands.^{1,19} This behaviour is consistent with electron transfer superexchange. On the other hand, Crutchley *et al.*¹⁶ have shown that, for a series of ruthenium mixed-valence complexes bridged by dicyd²⁻, replacing an ammine by π -accepting ligands increases the metal-metal coupling, and this is consistent with hole-transfer superexchange.

1.2.2 Thermodynamics of Mixed-Valence Complexes

The extent of metal-metal coupling in a mixed-valence complex determines to a large extent its stability and electronic properties. Theoretical models (see Section 1.2.3) use charge transfer spectral data to derive metal-metal coupling and distinguish between various 'classes' of mixed-valence complexes. Cyclic voltammetry (CV) allows one to directly determine experimentally the stability of a mixed-valence state via the comproportionation constant, K_c , which is defined by the equilibrium in Equation 1.1 for a Class I or Class II complex,

or Equation 1.2 for a Class III complex

These equations can be viewed as the sum of the two metal-centered redox events defined by Equation 1.3

Thus, the cyclic voltammetry experiment yields directly a free energy of comproportionation by first calculating the separation between the metal-centered couples, $\Delta E = E_{m2}^o - E_{m1}^o$, and relating this quantity to K_c via the Nernst equation,

$$\Delta G_c = -nF\Delta E = -RT \ln K_c \dots\dots\dots 1.4$$

K_c is usually related to the difference in potential (in volts) between metal-centered reduction couples (ΔE) and the more useful form of this equation is

$$K_c = 10^{16.91\Delta E} \dots\dots\dots 1.5$$

in which the prefactor has been numerically evaluated at 298 K for a one-electron event. For Class III complexes, K_c is usually very large ($>10^3$) due to strong bonding interactions between donor and acceptor wavefunctions, resulting in delocalization of the odd electron. For Class II complexes, K_c is usually less than 10^3 .²⁰

As will be discussed in Section 1.2.3, the evaluation of theoretical models of metal-metal coupling for mixed-valence complexes requires a measure of free energy of comproportionation, ΔG_c determined from K_c . A number of factors relating to the stability of the reactant and product complexes contribute to the magnitude of K_c , and, because of this, the free energy of comproportionation, ΔG_c , may only be considered a qualitative measure of metal-metal coupling when the resonance exchange term contribution is dominant.

Sutton and Taube proposed²¹ the following four distinct contributions to the magnitude of ΔG_c ,

$$\Delta G_c = \Delta G_s + \Delta G_e + \Delta G_i + \Delta G_r \dots\dots\dots 1.6$$

where ΔG_s reflects the statistical distribution of the comproportionation equilibrium, ΔG_e accounts for the electrostatic repulsion of the two like-charged metal centers, ΔG_i is an inductive factor dealing with competitive coordination of the bridging ligand by the metal ions, and ΔG_r is the free energy of resonance exchange the only component of ΔG_c which represents "actual" metal-metal coupling.

As noted later in a personal communication by Sutin and demonstrated experimentally by Evans *et al.*,¹⁶ an additional term is needed when there is significant stabilization of the Ru(III)-Ru(III) complex by antiferromagnetic exchange. This term, ΔG_{ex} , is then a fifth contributing factor to the magnitude of ΔG_c ,

$$\Delta G_c = \Delta G_s + \Delta G_e + \Delta G_i + \Delta G_r + \Delta G_{ex} \dots\dots\dots 1.7$$

Unlike the other four terms, which all favours the mixed-valence product of Equation 1.1, ΔG_{ex} measures a stabilizing influence upon a reactant complex, and thus is of opposite sign to the remaining terms of this equation. In systems where superexchange occurs via the electron-transfer pathway, an energetic mismatch of the ligand π -LUMO and the ruthenium(III) πd orbitals should lead to a small or insignificant magnitude of ΔG_{ex} . In hole-transfer systems, however, the magnitude of ΔG_{ex} may be such that ignoring this term leads to misleadingly low estimates of resonance exchange.^{16,17}

In the weak-coupling case for symmetric systems, it has been shown²² that

$$\Delta G_r' = H^2 / E_{IT} \dots\dots\dots 1.8$$

where $\Delta G_r'$ (the free energy of resonance per mixed-valence complex), is a measure of metal-metal interaction,¹⁶ whereas, for the strongly coupled Class III systems, Figure 1.6,

$$\Delta G_r' = H - \Delta G_{th} \dots\dots\dots 1.9$$

where ΔG_{th} is the thermal energy barrier to electron transfer in the related Class I system.

1.2.3 Theoretical Models For Metal- Metal Coupling

For the last four decades, there has been an advent of theoretical models to describe the properties of mixed-valence complexes.²³ Amongst these, two principal models have generally been used to describe metal-metal coupling: the classical two-state model of Hush,¹⁵ and the CNS (Creutz, Newton, and Sutin)²⁴ model that focuses on the superexchange mechanism.

The Hush Model

Hush's model has been, since its inception, the mainstay of analysis of mixed-valence complexes. Its conceptual simplicity and ease of application has made it the tool of choice for synthetic chemists in understanding thermal and photoinduced electron transfer. Hush's treatment is essentially an application of Mulliken's theories²⁵ to the specific question of intervalence transfer bands in mixed-valence complexes and is based on a consideration of the oscillator strength, f , of the experimentally measured intervalence band.

For a symmetric mixed-valence complex, the simplest case for electron transfer is illustrated by the potential energy diagram in Figure 1.6A, constructed for a two-state system. The light lines of the potential energy surfaces represent the diabatic initial and

final states for a non-mixing symmetric mixed-valence complex. In this representation, the electron is coupled between donor and acceptor by a single oscillator that has the same frequency in both the initial and final states. E_{IT} , which is also referred to as E_{op} , is the optical energy required to photoexcite an electron between initial and final states at the same nuclear configuration (intervalence transition energy). The free energy ΔG_{th} represents the activation barrier to thermal electron transfer, whose pathway arises when initial and final states are vibronically coupled. In the absence of any interaction between donor and acceptor metal ion, the resonance exchange integral, H , is zero and such behavior is representative of Class I mixed-valence system.

Figure 1.6: Potential energy curves for symmetric mixed-valence complexes.

If the diabatic states are now allowed to mix to form normalized adiabatic states, the resultant potential energy diagram is that given in bold lines in Figure 1.6A. The thermal activation barrier, ΔG_{th} , decreases as H increases with the onset of donor-acceptor coupling. In the high-temperature limit, where tunneling effects may be ignored,

Hush showed that both the single-frequency model and the dielectric-continuum model results in Equation 1.10 for weakly coupled, symmetric Class II mixed-valence complexes¹⁵

$$E_{op} = 4E_{th} \dots\dots\dots 1.10$$

In the high-temperature limit, Hush stated that the band shapes will tend to be Gaussian, and that Equation 1.11 may be used to relate the experimental bandwidth in cm^{-1}

$$\Delta\nu_{1/2} = (2310E_{op})^{1/2} \dots\dots\dots 1.11$$

Hush's ubiquitous equation for evaluating the donor-acceptor coupling element, H , also referred to as H_{ad} or H_{ab} , is derived from a perturbation treatment of the oscillator strength, f , of the intervalence band which is observed experimentally and which can be approximated by Equation 1.12 and is unitless.

$$f = 4.61 \times 10^{-9} (\epsilon_{\max} \Delta\nu_{1/2}) \dots\dots\dots 1.12$$

For weakly coupled systems, the intensity, $\epsilon_{\max}$, of the intervalence transition can be related to the extent of coupling H_{ad} between donor and acceptor by Equation 1.13

$$H_{ad} = \frac{2.06 \times 10^{-2}}{r} (\epsilon_{\max} \Delta\nu_{1/2} E_{IT})^{1/2} \dots\dots\dots 1.13$$

where H_{ad} is the donor-acceptor coupling element, in cm^{-1} , r is the transition moment length (typically as the donor-acceptor separation in Δ , from crystallographic data) and $\epsilon_{\max}$, $\Delta\nu_{1/2}$, and E_{IT} are the molar absorptivity ($\text{M}^{-1}\text{cm}^{-1}$), bandwidth at half-height (cm^{-1}), and energy of the band maximum ($\nu_{\max}$ or E_{op}) in cm^{-1} , respectively, of the intervalence band.

As mixing of electron donor and acceptor wave functions increases, covalency is approached, and for mixed-valence complexes, a perturbation treatment (i.e. Hush

theory) is no longer valid. H_{ad} becomes sufficiently large that coupling between the two centres is such that the thermal barrier to electron transfer disappears. This is the Class III regime of Robin and Day,¹³ as shown in Figure 1.6B. For a Class III system, the relationship between H_{ad} and E_{op} (cm^{-1}) may be described by Equation 1.14

$$H_{ad} = E_{op}/2 \dots\dots\dots 1.14$$

The Hush model has been demonstrated to be successful in predicting bandwidths for weakly coupled mixed-valence complexes. In the mixed-valence dicyd²⁻ bridged complexes studied by Evans *et al*¹⁶ the Hush model was appropriate for weakly coupled systems but it was demonstrated that, as coupling was increased, the correlation between the theoretical model and experiment became more scattered, as in Figure 1.7. To some degree, this may be attributed to the value of r in equation 1.13, which should get smaller as the extent of donor-acceptor mixing increases. A more appropriate model for strongly coupled mixed-valence complexes was developed by Creutz, Newton and Sutin.²⁴

Figure 1.7: Plot of experimental $\Delta G_r^\ddagger$ values versus theoretically calculated H_{ad}^2/E_{IT} (Hush Model) values for the pentaammine (circles), tetraammine (squares), and triammine (triangles) complexes. Data from reference 16.

The CNS Model

Hush's theoretical model is strictly limited in scope to the treatment of weakly coupled systems. In 1994, Creutz, Newton, and Sutin (CNS) reported a novel approach to the problem of evaluating metal-metal coupling elements in strongly coupled mixed-valence complexes.²⁴ Whereas Hush's model considers the intensity of the intervalence transition band, the CNS theory approaches the matter by focusing on the superexchange mechanism, rather than the oscillator strength f of the IT band, in modeling metal-metal coupling in mixed-valence complexes. The CNS inventors showed that Equation 1.13 can be used to calculate metal-ligand coupling elements, $h_{d\pi}$, for any donor-acceptor system, provided that overlap may be neglected and the charge transfer transition dipole moment lies along the donor-acceptor bonding axis. Therefore, an alternative form of Equation 1.13 is

$$h_{d\pi} = \frac{3.03 \times 10^2}{r} (v_{\max} f)^{1/2} \dots\dots\dots 1.15$$

where $v_{\max}$ is band maximum in cm^{-1} , f is oscillator strength of a single metal-ligand charge transfer chromophore, and r is transition moment length which is usually taken to be the separation between donor and acceptor in Δ . The metal-ligand coupling element, $h_{d\pi}$, is usually referred to as H_{LM} or H_{ML} when the superexchange pathway is hole-transfer or electron transfer respectively.

In practice, the metal-ligand coupling element could then be determined by replacing the intervalence spectral data with the corresponding metal-to-ligand or ligand-to-metal charge transfer spectral data. This treatment retains the advantageous ease of application of the Hush model but is more generally applicable.

Consider a prototypical dinuclear complex of the form $M_a - L - M_b$ which is described by diabatic wave functions showing the odd electron localized, respectively, on the donor (M_b) and acceptor (M_a) ends of the complex as shown in Figure 1.8.

Figure 1.8: Diabatic (dashed lines) and adiabatic (solid lines) potential energy profiles for the donor M_aLM_b , acceptor $M_a^-LM_b^+$, and intermediate charge transfer $M_aL^+M_b^-$ states. The charge transfer events are labelled as initial (i), final (f), and intervalence (IT). Adapted from reference 17.

For each superexchange pathway (electron- or hole-transfer), the diabatic wave-functions can mix via a single charge-transfer excited state shown in the figure above. Assuming no direct overlap of the metal orbitals due to their spacial separation, H_{ad} can be assumed to be zero. Since the electron transfer superexchange pathway is expressed by MLCT bands, and the hole-transfer superexchange pathway by LMCT bands, the coupling elements H_{ML} , $H_{M'L}$, H_{LM} , and $H_{LM'}$ can be calculated. Their respective energy gaps can similarly be represented as E_{ML} , E_{LM} , and E_{IT} , where the first and second terms are both

E_{CT}^i for electron-transfer and hole-transfer superexchange pathways, respectively, as in Figure 1.8.

Considering only the electron transfer pathway, Newton determined an expression, Equation 1.16, for $H_{MM'}$ from consideration of the optical transition moment of the intervalence transition.²⁵

$$H_{MM'} = H_{ML}H_{M'L} \left[\left(\frac{1}{2\Delta E_{ML}} + \frac{1}{\Delta E_{M'L}} \right) \right] \dots\dots\dots 1.16$$

which expands to Equation 1.17 when contributions from both possible superexchange pathways are considered

$$H_{MM'} = \frac{H_{ML}H_{M'L}}{2\Delta E_{ML}^{eff}} + \frac{H_{LM}H_{LM'}}{\Delta E_{LM}^{eff}} \dots\dots\dots 1.17$$

Equation 1.17 is the general equation for the effective (i.e. indirect) coupling of the metal centres. The coupling element $H_{MM'}$ of this equation is the effective metal-metal coupling, while the coupling elements in the two terms on the right-hand side of the equation are associated with metal-ligand interactions of the electron-transfer and hole-transfer pathways, respectively. The denominators are reduced energy gaps between metal and ligand orbitals. The subscript nomenclature may be understood given that the electron-transfer pathway is associated with metal-to-ligand charge transfer (MLCT) bands in the electronic spectrum of the complex, while the hole-transfer pathway is associated with ligand-to-metal (LMCT) bands, as seen in Figure 1.8.

The energetics of a given system will often cause one pathway to dominate, in which case only the term of Equation 1.17 dealing with that pathway need be considered. Since the systems described by this thesis undergo hole-transfer superexchange preferentially, only the second term of Equation 1.17 is considered. For these systems,

the adiabatic coupling element H_{LM} represents a “normal” LMCT coupling element between the ligand and a ruthenium(III) center, i.e. event labeled 1 in Figure 1.4B, while $H_{LM'}$ represents an LMCT involving the donor metal M_b bearing instantaneously, the acceptor metal’s oxidation state.²⁴ This means that the ruthenium(III) center (with all its bond lengths and its solvation sphere) must possess the inner and outer coordination appropriate to a ruthenium(II) centre. Since this latter quantity is experimentally unavailable, the assumption that $H_{LM} = H_{LM'}$ must be made, introducing an intrinsic error into Equation 1.18, the practical form of Equation 1.17.

$$H_{MM'} = \frac{H_{LM}^2}{\Delta E_{LM}^{eff}} \dots\dots\dots 1.18$$

The effective energy gap for hole-transfer case is simply the reduced energy difference between E_{CT}^i and E_{CT}^f , and may be evaluated experimentally according to Equation 1.19

$$\Delta E_{LM}^{eff} = [0.5(\frac{1}{E_{LMCT}} + \frac{1}{E_{LMCT} - E_{IT}})]^{-1} \dots\dots\dots 1.19$$

where $E_{LMCT} = E_{CT}^i$ and $E_{LMCT} - E_{IT} = E_{CT}^f$ as in Figure 1.8.

Equation 1.19 is the only part of the CNS model which requires an experimental determination of the intervalence transition band. If a reasonable estimate of E_{IT} can be made, $H_{MM'}$ may be determined exclusively using data from the charge transfer spectra of the fully oxidized complex. In fact, estimates of $H_{MM'}$ have been made using data from mononuclear complexes.²⁴ A new study by Evans *et al.*¹⁷ showed this model breaking down with more strongly coupled complexes, as seen by the curvature in the data point distribution of Figure 1.9. This implies that the more strongly coupled complexes in this

study may be bordering on Class III behavior, where the approximations used to derive Equation 1.15 no longer apply.

Figure 1.9: Plot of experimental $\Delta G_r'$ values versus theoretically calculated H_{ad}^2/E_{IT} values (CNS Model) for the pentaammine (circles), tetraammine (squares), and triammine (triangles) complexes. Figure reproduced from reference 16.

1.3 METAL-METAL COUPLING IN ASYMMETRIC DINUCLEAR COMPLEXES

In conjunction with electrochemical data, Mulliken treatment of donor-acceptor interactions can be used in such a way as to address the issue of metal-metal coupling in asymmetric dinuclear complexes. Figure 1.10A illustrates a simple mixing scheme used by Mulliken in the development of his resonance structure theory in charge transfer complexes.^{26,27} The basis set consists of the hypothetical zero-order 'no-bond' diabatic state of energy E_1^0 (donor's HOMO energy relative to vacuum)¹ which has the exchanging electron fully localized on the donor end, M_b , and the 'dative' diabatic state of energy E_2^0 , where the electron is fully localized on the acceptor end, M_a . If the diabatic states are now allowed to mix using a variational treatment, they give rise to a stabilized ground-state wavefunction of energy E_g and a destabilized, excited-state combination of energy E_e .

Figure 1.10: A: Simple two-state Mulliken theoretical analysis scheme of donor-acceptor interactions and B: its application to the asymmetric mixed-valence dinuclear case.

Figure 1.10B shows how Mulliken formalism applies to the case of asymmetric mixed-valence dinuclear complexes such as the one used in this study. A major point of difference, compared to the organic-donor acceptor complexes typically addressed using this theory, is that now most of the zero-order splitting Δ originates in the Frank-Condon energy associated with vertical electron transfer ¹.

Figure 1.11: Schematic illustration of how the potential surfaces respond to asymmetric ligand substitution processes.

As shown in Figure 1.11, asymmetric substitution of an ammine in ruthenium center b of symmetric dinuclear complex $[(NH_3)_5 Ru_b^{II}(dicyd)Ru_a^{III}(NH_3)_5]^{3+}$ with a nitrogen heterocycle such as pyridine or pyrazine ligand will clearly create redox asymmetry. It can be seen from this figure that this will result in a perturbation δE_1^o in the energy of the no-bond state, E_1^o , as well as in a perturbation δE_2^o in the energy E_2^o of the excited-state, compared to the symmetric case. An important underlying assumption

here is that the surfaces are harmonic and that the asymmetric ligand substitution process does not significantly change their shapes or displacement in nuclear configurational space.

The new redox asymmetry of the dinuclear complex, ΔE_{asy} , will affect the difference between metal-centered redox couple potentials, $\Delta E = E_{m2}^o - E_{m1}^o$, of the asymmetric dinuclear complex and hence ΔG_c in a very predictable way. Curtis *et al.*¹ have pointed out this factor in their studies of asymmetric dinuclear complexes bridged by a pyrazine ligand which preferentially utilizes π -LUMO in charge-transfer. The redox asymmetry in a given dinuclear system, as depicted by quantity ΔE_{asy} in Figure 1.11, therefore contributes directly to the magnitude of ΔG_c and this requires the thermodynamic Equation 1.7 to be revisited. Including such a term, Equation 1.7 is therefore expanded to the form of Equation 1.20

$$\Delta G_c = \Delta G_s + \Delta G_e + \Delta G_i + \Delta G_r + \Delta G_{ex} + \Delta E_{asy} \dots\dots\dots 1.20$$

The free energy of comproportionation ΔG_c results from the formation of two mixed-valence complexes, Equation 1.1. To be consistent with the theoretical analysis, the free energy of comproportionation must be considered per mixed-valence complex,

$$\Delta G_c' = 0.5\Delta G_c \dots\dots\dots 1.21$$

By analogy, the free energy of resonance exchange can be defined per mixed-valence complex as

$$\Delta G_r' = 0.5\Delta G_r \dots\dots\dots 1.22$$

and the redox asymmetry per mixed-valence complex as

$$\Delta E_{asy}' = 0.5\Delta E_{asy} \dots\dots\dots 1.23$$

ΔG_{th} for ruthenium ammine complexes varies from 2000 to 3000 cm^{-1} ²² and, as it will be later shown, most of the complexes of this study have metal-metal coupling elements that fall below this range. Accordingly, the intermediate coupling case in Figure 1.6A provides the best description for the majority of the complexes of this study and the theoretical value of the free energy of resonance exchange will be derived from Equation 1.18. The CNS approach appears to be the more suitable model for determining the metal-metal coupling in the asymmetric mixed-valence complexes of this study, based on the improved correlation between experiment and theory of strongly coupled, Class II symmetric complexes.^{16,17}

1.4 SOLVENTS DONOR-ACCEPTOR INTERACTION

The outer-sphere perturbations based on solvent have received careful attention from most researchers working on mixed-valence complexes. It has been noted that complexes with ammine ancillary ligands often exhibit markedly different solvent dependencies.²⁰ A number of empirical parameters for solvent polarity exist, as outlined in a review by Reichardt.²⁸ The Donor Numbers (DN) of Gutmann, based on the reaction enthalpies of various donors with SbCl_5 under fixed conditions, have been adopted by many researchers as the empirical solvent parameter of choice as they presumably measure a specific molecular property, the ‘donor strength’ of the solvent.²⁹ Numerous studies in our group¹⁶ and others^{30,31} have confirmed the appropriateness of donor number for modeling solvation effects. Table 1.1 shows solvents that have been used in this study and their donor numbers.

Table 1.1: Donor number values for solvents.

Solvent	Donor Number
Nitromethane	2.7
Acetonitrile	14.1
Acetone	17.0
Dimethyl Sulfoxide	29.8

Meyer *et al*³⁰ have described solvent perturbation as similar to hydrogen-bonding interactions between solvent lone pair and ammine protons. At the microscopic level, the solvent effect appears to come from an interaction involving electron-pair donation from

a solvent molecule to the N-H bond, Figure 1.12A. The net effect of this hydrogen bonding interaction is an electron density increase at the metal center, where the limiting case is a complete loss of an ammine proton and formation of an amido complex (Figure 1.12B). Because of an increased nuclear charge and more acidic N-H groups, the stabilizing effect of such electron-pair donation from the solvent will be greater for ruthenium(III) than for ruthenium(II), and the effect will increase as solvent donor number increases.

Figure 1.12: Donor-acceptor interaction involving electron pair from the solvent to the ammine protons.

Studies on $[(\text{bpy})_2\text{ClOs-pyz-Ru}(\text{NH}_3)_5]^{4+}$ complexes by Meyer *et al*³² showed that preferential solvation of the ammine at the ruthenium center was sufficient to induce electron transfer in the mixed-valence complex such that the Os(III)-Ru(II) complex in weak donor solvents becomes the Os(II)-Ru(III) complex in stronger donor solvents.^{31,32,33} The preferential solvation of amines bonded to ruthenium(III) stabilizes the ruthenium(III) oxidation state and provides a solvent barrier to electron transfer from osmium(II).

In the complexes of our study, there will always be a π -symmetric d-orbital on ruthenium which can accept electron density from the N-H σ -bond as a result of solvent-ammine donor-acceptor interactions. As the electron density on the metal center is increased by interactions with the solvent via the ammine ligands, the energy of the $d\pi$ orbitals is increased. This destabilization of metal d-orbitals increases the energy gap to the π -HOMO orbitals of the cyanamide moiety and, as a result, this reduces the overlap of metal-ligand orbitals in these complexes,¹⁶ and, as a consequence, the LMCT oscillator strength is expected to be attenuated.

The delocalized valency of Class III complexes provides stabilization akin to conjugation in organic compounds¹⁷ and, the system thus resists outer-sphere perturbations which would remove this condition and as such, E_{op} for Class III complexes is solvent-independent. In Class III complexes, the transitions are characterized as electron excitations rather than charge transfer events, and the interaction between the two metal ions is so large that there is no thermal barrier to electron transfer between them. This large coupling results in complete blending of oxidation states as the odd electron is delocalized over both metal ions sites. In this limit, there is no longer a structural difference between the sites and local solvent dipole orientations are averaged. The odd electron occupies a delocalized molecular orbital and the electron transfer rate can be described as being equivalent to electron mobility within this orbital.⁹ As a result, the oxidation state described for a molecule such as one in Figure 1.1 becomes Ru(II.5)-Ru(II.5) rather than Ru(III)-Ru(II).³² A further criterion for Class III behavior is the metal-to-metal charge transfer band shape having a high-energy tail.

For Class II systems, however, the transitions are charge transfers and according to Marcus-Hush theory, the solvent dependence of E_{op} on outer-sphere reorganization should correlate linearly with the reciprocals of solvent's optical and static dielectric constants.^{15b,7} Dielectric continuum theory treats solvents as structureless and has successfully been applied to the solvent dependence of optical electron transfer for weakly coupled Class II complexes, Equation 1.24. According to this theory, the solvent dependence of the absorption band energies is characterized by microscopic dielectric constants, the static dielectric constant (D_s) and the optical dielectric constant (D_{op}).^{15b}

From Hush theory, E_{op} for a weakly coupled, symmetric mixed-valence system can be approximated by Equation 1.24

$$E_{op} = \lambda_i + \lambda_o + \Delta E' \dots\dots\dots 1.24$$

where λ_i is the inner-sphere reorganization energy and λ_o is the outer-sphere reorganization energy. $\Delta E'$ takes into account any additional energy associated with the excitation to either a spin-orbit or ligand field excited state. If λ_i and $\Delta E'$ are assumed to be solvent-independent for a given Class II system, then variations in E_{op} with solvent should be proportional to the solvent term $(D_{op}^{-1} - D_s^{-1})$ found in the Marcus-Hush expression for λ_o . The linear correlation between E_{op} and $(D_{op}^{-1} - D_s^{-1})$ has been demonstrated for a number of weakly coupled symmetric Class II mixed-valence complexes,³³ thereby giving support to the Marcus-Hush model.

However, consideration of a solvent dielectric is not appropriate for the polyamine complexes of this thesis because of the solvent-donor ammine-acceptor interactions shown in Figure 1.12. Indeed, a study by Curtis *et al.*³⁰ on mixed-valence

systems showed that the interactions between coordinated ammine and donor solvents change the redox asymmetry within the molecule and this is the principal contributor to the change in the intervalence band energies.

1.5 MAGNETIC ELECTRON EXCHANGE

The simplest case of magnetic exchange in dinuclear metal complexes is one in which low-spin metal centres are in the same oxidation state and are bridged by an organic molecule, L, i.e.

The ruthenium(III) ion possesses a single unpaired electron with spin, $S = 1/2$ and the intramolecular interaction between the two metal ions in a dimer can be described by the Hamiltonian

$$H = -2JS_aS_b \dots\dots\dots 1.25$$

where J is the exchange coupling constant. From this Hamiltonian arise two major types of interactions: When the exchange constant J is negative, the coupling is termed as antiferromagnetic, in which case the singlet ground-state and triplet state are separated in energy by $-2J$. When J is positive, one obtains ferromagnetic coupling, i.e. a spin-aligned or triplet ground-state, Figure 1.13.

Figure 1.13: Two types of magnetic interaction showing how free paramagnetic ($S = 1/2$) ions form a dimer via diamagnetic bridging ligand.

Whether a singlet or triplet ground-state is formed depends on the relative magnitude of antiferromagnetic (J_{AF}) and ferromagnetic (J_F) terms

$$2J = J_F + J_{AF} \dots\dots\dots 1.26$$

where J_F represents the overall spin pairing energy and J_{AF} is the energy released when the two spins are coupled³⁴ and reflects the extent of electron-exchange stabilization.

1.5.1 Charge Transfer Model for Antiferromagnetic Exchange

To explain the magnitude of J_{AF} , one can examine the extent of overlap between coupled metal magnetic orbitals³⁵ or parameters that reflect the extent of electron exchange stabilization.³⁶ The latter approach has the same framework as the one used to develop Marcus electron transfer theory and the Hush model for intervalence transition. The electron exchange interaction can be described as being the result of mixing of the charge transfer final state, F , with the initial state, I , as shown in Figure 1.14, where the requirements for mixing are such that the spins in the initial state be antiparallel and result in stabilization energy J_{AF} .

Figure 1.14: A) Mixing of charge transfer state F with state I , and
B) a potential energy diagram representing the mixing in the charge transfer model for antiferromagnetic exchange.

Figure 1.14 B shows potential energy surfaces that represents the initial and final states in which E_{op} is the metal-to-metal charge transfer (MMCT) energy between the states which are at the same nuclear configuration. The stabilization energy that results from the delocalization of electron density is represented by the resonance exchange energy, H_{ab} , and a factor that represents mixing of states, given by E_o' , the energy difference between initial and final states. Bertrand³⁴ gave the following relationship between J_{AF} and the extent of electron coupling, H_{ab}

$$J_{AF} = 2|H_{ab}|^2 / E_{op}' \dots\dots\dots 1.27$$

When the metal-metal separation is large, the ferromagnetic term, J_F , is usually believed to be small relative to J_{AF} , and as metal-metal separation increases, J_F is likely to be canceled out by second-order antiferromagnetic contributions.³⁷ Referring to Equation 1.27, the antiferromagnetic term, J_{AF} , is now a direct measure of the exchange coupling constant $-2J$, thus allowing the resonance exchange energy, H_{ab} , to be determined from Equation 1.27 if the coupling constant and MMCT energy have been determined. Although such a result is an approximation, it still seems a valuable guide in the design of exchange-coupled systems. Note that any factors such as solvents, ancillary ligands, and bridging ligand that perturb H_{ab} , will affect J_{AF} proportionally.

1.5.2 Bridging Ligand-Mediated Electron Exchange

In cases where metal ions are sufficiently separated to prevent through-space overlap of πd orbitals, antiferromagnetic coupling occurs via the superexchange mechanism, in which the bridging ligand's π -orbitals mediate exchange. For dicyd²⁻ ligand-bridged dinuclear ruthenium(III) complexes, the dianionic ligand is intimately

involved in metal-metal-metal coupling. Scheme 1.1 demonstrates the involvement of LMCT excited states in the superexchange mechanism.

Scheme 1.1: Involvement of LMCT Excited State in the Superexchange Mechanism

The unpaired electrons in the LMCT excited state can only couple if their spins are opposite. As a result, the mixing of the LMCT excited state with the ground-state stabilizes a ground state in which the electrons are antiparallel.

The LMCT transition produced as a result of interaction between metal and bridging ligand has a value whose measure is the energy gap between metal magnetic orbitals and the HOMO superexchange pathway.³⁸ The oscillator strength of these LMCT bands measures the extent of electronic interactions between the metal ions and the bridging ligand.³⁹ The energy gap ΔE between the metal magnetic orbitals and the HOMO can be estimated by^{39,40}

$$\Delta E = E_{op} - \lambda \dots\dots\dots 1.28$$

Where E_{op} is the energy of the LMCT transition and λ is a correction term that compensates the change in the inner- and outer-coordination sphere configuration resulting from a transition into a vibrationally excited level of the excited state.

Hay *et al.*⁴¹ theoretically showed that J_{AF} can be analysed in terms of pairwise interactions of dimeric molecular orbitals, with the square of splitting in energy between the members of a pair being a measure of the stabilization of the low-spin state. Their final result was shown to be equivalent to Anderson's theoretical treatment of

superexchange in insulators.³⁶ Other theoretical treatments have emphasized the importance of overlap between metal ions and the bridging ligand.⁴² The optimization of antiferromagnetic superexchange requires the simultaneous overlap of metal ions with bridging ligand molecular orbitals.⁴³ For effective overlap, the metal πd magnetic orbitals and the bridging ligand π -HOMO must be well matched in energy and symmetry, and the superexchange pathway must be continuous, spanning the entire bridging ligand.

By using valence-bond theory, the antiferromagnetic exchange coupling constant J_{AF} can be related to the metal-ligand coupling element according to the approach of Tuzek and Solomon,⁴⁴ whose expression for the exchange was

$$-J_{AF} = \frac{h_{d\pi}^4}{\Delta^2} \left(\frac{1}{U} + \frac{2}{E_{DCT}} \right) \dots\dots\dots 1.29$$

where the transfer integral (metal-ligand coupling element), $h_{d\pi}$, corresponds to a one-electron charge transfer between the bridging ligand and the metal (i.e., an LMCT transition), Δ is the energy difference between the ground state and the LMCT excited state associated with $h_{d\pi}$, U is the metal-to-metal charge-transfer MMCT transition energy, and E_{DCT} is the difference in energy between the ground and double-charge-transfer states. The singlet double-charge-transfer state corresponds to the simultaneous transition of one bridging ligand electron to each metal ion. It is not accounted for by Anderson theory and can have a significant contribution to ground-state antiferromagnetism.

It is expected that, for a series of similar transition-metal dinuclear complexes, the energies of the charge-transfer transitions will not vary appreciably and that the greatest influence on J_{AF} , according to Equation 1.29, will be the metal-ligand coupling element

$h_{d\pi}$. Creutz, Newton, and Sutin (CNS),^{30,45} have shown that the value of $h_{d\pi}$ can be determined from experimental CT band properties by using the expression from Mulliken and Hush, Equation 1.15. This equation is frequently assumed to be applicable only to very weakly coupled systems; however, CNS have shown that this equation is exact in the two-state model, provided that overlap can be neglected and that the charge transfer transition is polarized along the donor-acceptor axis.

Thus, for a dinuclear system, J_{AF} can be calculated, provided there exist reasonable estimates or actual values of MMCT and double-charge-transfer energies and an observable bridging ligand-to-metal charge transfer band. In addition, a true test of the above equations requires a comparison of a wide range of experimental exchange constants against those calculated. From room-temperature magnetic moment measurements, it is possible to calculate J values according to the method of Thompson and Ramaswamy,⁴⁶ whose expression for estimating the exchange constant for complexes in solution is given by Equation 1.30 at $T = 298\text{ K}$

$$-2J_{est} = kT \ln \left(\frac{3.0003g^2}{\mu_{eff}^2} - 3 \right) \dots\dots\dots 1.30$$

where g is the electron g -factor and has a value of about 2 for an electron with no orbital angular momentum. Utilization of the fully characterized symmetric dinuclear $[\{(\text{NH}_3)_5\text{Ru}\}_2\mu\text{-(dicyd)}][\text{PF}_6]_4$ ⁴⁷ complexes makes this test possible. The correlation between the theoretically determined J_{est} for data derived from aprotic solvents is quite good (Figure 1.15).

Figure 1.15: Plot of calculated versus estimated antiferromagnetic exchange constants of the complexes in aprotic solvents (solid circles) and in aqueous solutions (solid squares). The equation for the line is $2J_{est} = 1.5J_{AF} - 260$; $R^2 = 0.86$. Reproduced from reference 47.

1.6 EXPERIMENTAL DETERMINATION OF MAGNETIC MOMENTS

Although the measurements of the molar susceptibility of a solid compound over a broad temperature range is the traditional method employed to evaluate the exchange coupling constant experimentally,^{48,49,50} methods based on solution measurements are available.

1.6.1 Evaluation of Magnetic Moments of Complexes in Solution

The quantitative determination of the paramagnetic susceptibility of a compound in solution is possible through the Evans^{51,52} method. In this experiment, a coaxial capillary containing only the solvent and reference (TMS or DSS) is inserted into the sample solution (dissolved in the same solvent and containing the same reference) in a high-field NMR spectrometer. If the compound is paramagnetic, it will shift the reference peak for the reference in the sample, but not for the reference in the capillary tube. Thus two reference peaks will be seen with the splitting between them, Δf , dependent upon the degree of paramagnetism of the sample.^{37,47}

The gram susceptibility, χ_g (in mL g⁻¹) of the sample complex is given by

$$\chi_g = -3\Delta f / 4\pi\nu m + [\chi_o + \chi_o(d_o - d_s) / m] \dots\dots\dots 1.31$$

where, Δf , is the observed frequency shift (in Hz) of the reference resonance; ν is the fixed probe frequency (in Hz) of the NMR spectrometer; χ_o is the mass susceptibility (in mL g⁻¹) of the solvent; m is the mass (in g) of the complex per mL of solution; d_o and d_s

are the densities in (g mL⁻¹) of the solvent and solution, respectively. The term $\chi_o + \chi_o(d_o - d_s)/m$ represents a correction to this solvent mass susceptibility for any changes in solution density. In cases where the paramagnetism is large, this term is negligible,⁵³ and is also small for dilute solutions because $d_s \cong d_o + m$.

The mass susceptibility, χ_g , of the sample can be converted into the molar susceptibility, χ_m , by multiplying it by the molecular weight of the complex

$$\chi_m = \chi_g M = \frac{-3\Delta f M}{4\pi \nu m} \dots\dots\dots 1.32$$

where M is the molecular weight (in g mol⁻¹). For transition metal complexes, it is only possible to measure the net molar susceptibility, χ_m , of Equation 1.32 which is the sum of the paramagnetic (χ'_m) and diamagnetic (χ_d) contributions. χ'_m is given by

$$\chi'_m = \chi_m - \chi_d \dots\dots\dots 1.33$$

The molar diamagnetic susceptibility, χ_d , of a complex can be approximated by summing the molar diamagnetic contributions (Pascal's constants)⁵⁴ from all the atoms, χ_a , and from all the bonds in the functional groups, χ_b .

$$\chi_d = \sum_i \chi_{a_i} + \sum_j \chi_{b_j} \dots\dots\dots 1.34$$

From Equation 1.32, the sample's effective magnetic moment may be determined experimentally according to Equation

$$\mu_{eff} = 2.83\sqrt{\chi'_m} T \dots\dots\dots 1.35$$

where T is the temperature at which experiment was run (in K). The spin-only magnetic moment of the metal complexes can be calculated from various values of S,

$$\mu_{eff} = g[S(S+1)]^{1/2} \text{ in } \mu_B \dots\dots\dots 1.36$$

where S is the total spin quantum number of the system, $g \cong 2.0$ for an electron with no orbital angular momentum. In this spin-only model approximation, the number of unpaired electrons n is related to S by

$$S = n/2 \dots\dots\dots 1.37$$

and substituting for S and 2.0 for g in Equation 1.37,

$$\mu_{eff} = [n(n + 2)]^{1/2} \text{ in } \mu_B \dots\dots\dots 1.38$$

This equation allows one to calculate the number of unpaired electrons in a transition metal complex, if the effective moment has been determined experimentally. For low-spin ruthenium(III), experimental values of μ_{eff} range from 1.90 to 2.07 in μ_B ,⁵⁵ suggesting that a close-to-spin-only treatment is sufficient, with only a small contribution from orbital angular momentum.

1.7 RESEARCH GOALS

The focus of this research is to study metal-metal interactions in asymmetric dinuclear ruthenium(III) complexes through a series of specific inner- and outer-sphere perturbations. Intimately linked to this investigation is the need for a fundamental understanding of the electronic nature of the metal-ligand bonding interaction found in mononuclear systems. The aim of this study is therefore to provide the conceptual framework for the design of such systems and to this end, the main objectives of this research are to:

- 1) Synthesize a series of mononuclear ruthenium(III) complexes of the dichlorophenylcyanamide ($2,3\text{-Cl}_2\text{pcyd}^-$) monoanion ligand. These complexes will be examined by spectroscopic and electrochemical methods, and the inner- and outer-sphere perturbations of the ruthenium(III)-cyanamide π -bond that result from varying the solvent and the σ -donor strength of ligand *trans* to the cyanamide moiety.

Where L is

Note: A triammine complex is formed when a 2,2'-bipyridine ligand binds.

2) Synthesize and characterize ruthenium(II) complexes of 2,3-Cl₂pcyd⁻ and examine by spectroscopic and electrochemical methods the inner- and outer-sphere perturbation of the ruthenium-cyanamide and ruthenium heterocycle bonds that result from one-electron reduction of corresponding ruthenium(III) complexes.

3) Synthesize and characterize a series of asymmetric dinuclear ruthenium complexes of the dianionic ligand, 1,4-dicyanamidobenzene (dicyd²⁻), Ru_a(III)-Ru_b(III).

Inner- and outer-sphere perturbation of the ruthenium(III)-cyanamide π -bond of the above complexes will be examined by spectroscopic, electrochemical and magnetic methods. This will ascertain the metal-metal antiferromagnetic superexchange coupling that results from donor-acceptor interactions between solvent nonbonding electrons and the protons of the ammine ligands coordinated to ruthenium(III) and a variation of the σ -donor strength of the nitrogen heterocycle *trans* to the cyanamide moiety.

4) To generate by spectroelectrochemical methods, the mixed-valence $\text{Ru}_a(\text{III})$ - $\text{Ru}_b(\text{II})$ complexes of the dianionic ligand, dicyd²⁻. Spectroscopic and electrochemical techniques employed on this series of complexes will help in examining the outer- and inner-sphere perturbations of the ruthenium-cyanamide π -bond and hence the metal-metal hole-transfer superexchange.

CHAPTER 2

EXPERIMENTAL

2.1 STARTING MATERIALS

2.1.1 Reagents for Ligand Synthesis

Ammonium thiocyanate (reagent grade 97.5%, Aldrich Chemical Co.), benzoyl chloride (reagent grade 99%, Aldrich Chemical Co.), lead acetate trihydrate (reagent grade 99+%, Aldrich Chemical Co.), sodium hydroxide (reagent grade 97%, Anachemia), glacial acetic acid (reagent grade 99.7%, Aldrich Chemical Co.), 2,3-dichloroaniline (reagent grade 99%, Aldrich Chemical Co.), triethylamine (TEA, reagent grade 99.5%, Aldrich Chemical Co.), pyrazine (reagent grade 99%, Aldrich Chemical Co.), iodomethane (reagent grade 99%, Aldrich Chemical Co.), silver tosylate (reagent grade 99%, Aldrich Chemical Co.) and activated charcoal (BDH) were all used without further purification.

2.1.2 Reagents for Metal Complex Synthesis

Ruthenium(III) chloride (reagent grade 99%, Pressure Chemical Co.), hydrazine monohydrate (reagent grade 98%, Aldrich Chemical Co.), ammonium hexafluorophosphate (reagent grade 99.9%, Aldrich Chemical Co.), tetrabutylammonium bromide (reagent grade 99%, Aldrich Chemical Co.), sodium tetraphenylborate (reagent

grade 99.5%, Aldrich Chemical Co.), hydrochloric acid (reagent grade, Anachemia), sulfur dioxide (reagent grade 99.98%, Aldrich Chemical Co), sulfuric acid (reagent grade 95-98%, Anachemia), sodium bisulfite (reagent grade, Fisher Scientific Co.), pyridine (99%, Anachemia), 3,5-dimethylpyridine (reagent grade 99.5%, Aldrich Chemical Co.), 2,2'-dipyridyl (reagent grade 99.5%, Aldrich Chemical Co.), and 2,6-dimethylpyrazine (reagent grade 99.5%, Aldrich Chemical Co.) were all used without further purification. Zinc/mercury amalgam was prepared first by cleaning mossy zinc metal (reagent grade, 99.9%, Aldrich Chemical Co.) with 1M HCl and then treating it with saturated solution of mercury(II) chloride (reagent grade, 99% Aldrich Chemical Co.).

2.1.3 Electrolyte

Tetrabutylammonium hexafluorophosphate (reagent grade, 98%, Aldrich Chemical Co.) was recrystallized twice from ethanol and vacuum-dried overnight at 120 °C.

2.1.4 Cyclic Voltammetry Internal Reference

Dicyclopentadienyliron, more commonly known as ferrocene (reagent grade, J.T Baker Chemical Co.) was sublimed before it was used.

2.1.5 Chromatography

CM Sephadex C25 (Carboxymethyl Sephadex) cation exchange resin (bead size: 40-125 μ , Sigma Chemical Co.) was used as received. Used CM-Sephadex C25 Cation exchange resin was recycled by first washing with 1 L of a solution containing EDTA (30

g), sodium sulfite (20 g), and sodium hydroxide (80 g), and repeatedly and alternately washing with 1M HCl and 2M sodium hydroxide. This was pursued until the original white colour of the resin was reclaimed, at which point it was considered clean enough for re-use. Continuous washing with 1M NaCl was finally carried out until the pH of eluent was neutral and the Sephadex was stored in this form.

2.1.6 Compressed Gases

Argon (UHP grade, 99.99 %, Praxair) and sulfur dioxide (reagent grade, 99.98%, Aldrich Chemical Co., 99.98%) gases were used as received.

2.1.7 Solvents

Solvents for Synthesis

Acetonitrile (spectrograde, 99.9%, Aldrich Chemical Co.), nitromethane (99%, Aldrich Chemical Co.), methyl sulfoxide (spectrograde, 99.9%, Aldrich Chemical Co.), acetone (spectrograde, 99.9%, Aldrich Chemical Co.), anhydrous diethyl ether (99%, Caledon laboratory), methanol (Caledon laboratory 99%), and anhydrous ethanol (Commercial Alcohols Inc.) were used without further purification.

Solvents for Spectroscopy and Electrochemistry⁵⁶

Acetonitrile (anhydrous, 99.9%, Aldrich Chemical Co.) and methyl sulfoxide (anhydrous, 99.9%, Aldrich Chemical Co.), were distilled in glass under reduced pressure in the presence of activated alumina then stored under argon. Nitromethane (99%,

Aldrich Chemical Co.) was stored overnight over activated alumina, filtered and stored under argon. Acetone (HPLC grade, 99.9%, Aldrich Chemical Co.) was used without further purification.

Solvents for NMR Spectroscopy

Acetonitrile-d₃ (99.6 atom % D, CDN isotopes), DMSO-d₆ (99.9 atom% D, CDN isotopes), nitromethane-d₃ (99 atom% D, Aldrich Chemical Co.), and deuterium oxide (99.9 atom% D, Aldrich Chemical Co.), tetramethylsilane, TMS (NMR grade, 99.9%, Aldrich Chemical Co.) and the sodium salt of 2,2-dimethyl-2-silapentane-5-sulfonate, DSS (99 %, Aldrich Chemical Co.) were used as received.

2.2 METAL COMPLEX PRECURSOR SYNTHESIS

2.2.1 Chloropentaammineruthenium(III) Chloride

The synthesis of this precursor is a slight modification of the one described by Evans¹⁷ and generally based upon the method ascribed to Clarke.⁵⁷ Evans reported a problem with some batches of hydrazine monohydrate that resulted in extremely poor yield of product and formation of other by-products. The synthesis presented here is a modification designed to minimize interferences caused by the quality of hydrazine that resulted in large quantities of undesired side products and low yield of the desired compound. We did not observe the formation of copious quantities of ammonium salt after refluxing, as reported,¹⁶ as the solution was allowed to cool to only about 50 °C, instead of 4 °C.

$\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, 10 g was added very slowly to a solution of 82 mL (1.56 mol) hydrazine monohydrate in 100 mL water and the resultant burgundy solution allowed to stir for 16 h (typically overnight). The reaction vessel was put on an ice bath and 250 mL (2.15 mol) of concentrated HCl (37%) was carefully and slowly added to the reaction mixture. The addition of HCl resulted in boil-over, as the reaction tended to become self-catalytic. Using a large reaction vessel (2 L) was found to adequately curb this problem. In between these additions, a total of 10 g (0.17 mol) NaCl was also added into the reaction mixture. The reaction flask was fitted with a condenser column and heated to reflux for 2 h. The solution was allowed to cool to about 50 °C and the resultant orange crystals were collected by vacuum filtration, yielding 10.51 g (36 mmol) of crude

$\text{Ru}(\text{NH}_3)_5\text{Cl}_3$. A second crop was obtained by allowing the filtrate to cool in the refrigerator overnight. The copious amounts of ammonium salt that formed were filtered off and the filtrate was allowed to stand in the fume-hood for 2 days. More yellowish orange crystals of $\text{Ru}(\text{NH}_3)\text{Cl}_3$ formed which were filtered and air-dried, yielding 1.56 g. The first and the second crops were combined and recrystallized by boiling in 400 mL of 0.1 M HCl. The hot solution was filtered and allowed to cool in air overnight. Deep orange crystals 9.80 g (33 mmol, 70 % yield) were filtered, washed sparingly with 0.1 M HCl, and acetone and vacuum-dried giving.

2.2.2 *Trans*-Chlorotetraaminesulfonylruthenium(II) Chloride

Trans- $[\text{Ru}(\text{NH}_3)_4(\text{SO}_2)\text{Cl}]\text{Cl}$

This complex was prepared by a method similar to that by Vogt.⁵⁸ Chloropentaamineruthenium(III) chloride 10 g (34 mmol) was dissolved in 300 mL of water at about 80 °C. To this solution was added 4 equiv. of sodium bisulfite, 14.3 g, 136 mmol). When the orange crystals had completely dissolved, sulfur dioxide was slowly bubbled through the solution, which was kept at about 80 °C. After an induction period of about 20 minutes, faint yellow crystals started to form. The reaction conditions were maintained for 90 min, after which the system was cooled to room temperature with continuous saturation of SO_2 . The reaction vessel was tightly sealed and refrigerated overnight. The fine yellow crystals were collected by filtration and washed with acetone and ether, then vacuum-dried at room temperature. The yield of *trans*-bisulfitotetraamineruthenium(II) *trans*- $[\text{Ru}(\text{NH}_3)_4(\text{HSO}_3)_2]$ was 9.55 g (28 mmol). This

compound was dissolved in 800 mL of 6 M HCl by heating at boiling for 15 min. The colour of the solution rapidly darkened with heating from a yellow to a deep orange-brown color. The solution was filtered by vacuum while hot with a coarse frit, cooled in freezer overnight yielding crystals of $[\text{Ru}(\text{NH}_3)_4(\text{SO}_2)\text{Cl}]\text{Cl}$. These were collected by filtration, washed with 6 M HCl and methanol and vacuum dried at room temperature yielding 6.80 g (23 mmol).

2.3 LIGAND SYNTHESIS

The preparation of (2,3-dichlorophenyl)cyanamide, (2,3-Cl₂Hpcyd⁻) ligand was according to the procedure of Naklicki and has previously been reported.⁵⁹

2.3.1 Preparation of *N*-Methylpyrazinium Tosylate

Mepyz-OTs

The synthesis of this ligand was according to the method devised by Magnuson.⁶⁰ A mixture of 10 g (0.125 mol) of pyrazine and 26 mL (0.42 mol) of iodomethane was stored overnight in a glass-stoppered flask in the dark. The bright yellow *N*-methylpyrazinium iodide was collected by filtration, washed with ether and dried in air overnight, yielding 14.5 g. By leaving the filtrate in the dark for one week at room temperature, a second crop of 10 g of the yellow crystals was obtained. The iodide salt was converted to the tosylate salt by precipitation of silver iodide. Approximately 6.5 g of silver tosylate was dissolved in 60 mL water and mixed with a 5.0 g (23 mmol) solution of *N*-methylpyrazinium iodide. The solution was stirred at 40 °C and a yellow solid precipitated. The reaction was allowed to continue for 15 minutes at an elevated temperature of 50-60 °C. A spatula full of activated charcoal was introduced and the solution stirred for 5 min, then filtered. The filtrate was evaporated to dryness in a rotary vaporator at 45 °C and the solid obtained was dissolved in warm ethanol, and stored in the refrigerator overnight. The light yellow crystals of the tosylate salt that formed were filtered and washed with ether. A second crop was obtained by addition of ether to the

filtrate from the first crop. The yield of N-methylpyrazinium tosylate was 4.8 g (18 mmol).

2.4 SYNTHESIS OF THE MONONUCLEAR COMPLEXES OF 2,3-Cl₂Hpcyd

2.4.1 Preparation of [Ru^{III}(NH₃)₅(2,3-Cl₂pcyd)][PF₆]₂

The reagent complex, [Ru(NH₃)₅(OH₂)](PF₆)₂ was prepared following the method of Callahan *et al.*⁶¹ Pentaammineruthenium(III) chloride (1.50 g, 5.1 mmol) was dissolved in 150 mL of 0.1 M H₂SO₄. The solution mixture was degassed and purged once with argon and then reduced over fresh Zn/Hg amalgam in an ice bath for 40 minutes. This solution was transferred under argon into a flask containing 12 g NH₄PF₆. The reaction mixture was degassed and saturated once with argon and the yellow precipitate that formed was chilled for 1 h in the refrigerator. The faint yellow product was filtered in a glove bag under argon, and washed with degassed water, then diethyl ether before drying in vacuo overnight. Yield: 2.4 g (4.8 mmol). The title complex was prepared from this precursor by the method reported by Naklicki.⁵⁹ The ligand 2,3Cl₂Hpcyd (0.4 g 2.14 mmol) of was dissolved in 60 mL acetone containing 4 drops of HPF₆ acid. Freshly prepared [Ru(NH₃)₅(OH₂)](PF₆)₂ (0.6 g, 1.2 mmol) was added and the solution was stirred for 30 min in air. The colour turned from yellow to deep blue. This solution was filtered and excess TBAB was added. The resulting blue precipitate was filtered, dried in air, then dissolved in minimum water before being purified by cation exchange chromatography on CM-sephadex C25-120 resin, eluting with 0.5 M NaCl. The major blue band was collected and the product forced out of solution by the addition of excess NaBPh₄. The blue tetraphenylborate salt was filtered, metathesized to the bromide

salt, then finally metathesized to the hexafluorophosphate salt, which was air-dried overnight. This salt was dissolved in acetone and recrystallized by slow ether diffusion. The blue crystalline product was dried in vacuo. The overall approximate yield from the precursor was 0.40 g (47 %). Metathesis was also used to prepare a perchlorate salt sample for IR analysis was done. Elemental analysis: Calcd for $C_7N_7H_{18}Cl_2F_{12}P_2Ru + 0.19(CH_3)_2CO$: C, 13.51; N, 14.56; H, 2.87; Found: C, 13.10; N, 14.05; H, 2.98.

2.4.2 Preparation of

***Trans*-[(3,5-Me₂py)Ru(NH₃)₄(2,3-Cl₂pcyd)][ClO₄]₂**

Following a modified procedure of Chang *et al.*,⁶² *trans*-[Ru(NH₃)₄(SO₂)Cl]Cl, 0.40 g (1.3 mmol) was added to 20 mL of a warm 1:4 acetone:water mixture containing 2 g (~4X molar excess) of 3,5-dimethylpyridine. Sodium hydrogen carbonate (0.30 g) was then added and the solution was stirred for 40 min at 40-50 °C until the colour turned greenish yellow. The solution mixture was added and filtered into 500 mL acetone and chilled for 2 h. The yellow precipitate, *trans*-[Ru(NH₃)₄(SO₂)(3,5-Me₂py)][Cl₂], was collected, washed with acetone and anhydrous diethyl ether, then dried in vacuo. This product was then dissolved in 10 mL water and oxidized by slow addition of 20 mL of a 1:1 30 % H₂O₂/1 M HCl mixture. After 10 min, the product, *trans*-[Ru(NH₃)₄(SO₄)(3,5-Me₂py)][Cl], was precipitated out by adding it into 500 mL acetone and then chilling it for 2 h before filtering and drying in vacuo. This complex was dissolved in 10 mL water, and reduced over Zn/Hg amalgam for 10 minutes. The resulting yellowish-orange solution was transferred under argon into a flask containing 4 molar excess of solid NaBPh₄. The yellow product was stirred under argon and then filtered under argon and dried in vacuo. The ligand 2,3-Cl₂Hpcyd (0.5 g, 2.57 mmol) was dissolved in 100 mL of

acetone containing 5 drops of HPF_6 , and the solution was purged and saturated with argon twice. *Trans*-[(3,5- Me_2py) $\text{Ru}(\text{II})(\text{NH}_3)_4(\text{OH}_2)][\text{BPh}_4]_2$ (0.45 g, 0.49 mmol) was added and the solution was degassed and saturated with argon once more. The reaction was allowed to proceed overnight at room temperature, whereby it the color turned from yellow to green. The solution was transferred into an Erlenmeyer flask and stirred in air overnight. Excess TBAB was added and the green precipitate formed was filtered and washed with cold acetone before drying it in vacuo for 1 h. This green precipitate was dissolved in water and charged onto a Sephadex column and eluted with 0.5 M NaCl . Two bands were identified; the first yellow band, presumed to be unreacted starting material, and the second was the major product which was green-blue. To this eluent, was added 1.0 g NaBPh_4 and a green solid precipitated, which was filtered and dried in air overnight yielding 0.3 g of tetraphenylborate salt. This product was dissolved in 30 mL acetone and excess TBAB was added. A green precipitate formed, which was filtered and dried in air to yield 0.15 g of bromide salt. This salt was dissolved in 20 mL water and excess (2.0 g NaClO_4) was added. This solution was chilled in the refrigerator overnight. The blue solid that formed was filtered, dried and recrystallized by ether diffusion into an acetone solution at room temperature, affording greenish needles. The overall approximate yield from the precursor was 0.10 g (31%). Elemental analysis: Calcd for $\text{C}_{14}\text{N}_7\text{H}_{24}\text{Cl}_4\text{O}_8\text{Ru}$: C, 25.43; N, 14.83; H, 3.66; Found: C, 25.48; N, 14.66; H, 3.71

2.4.3 Preparation of

Trans-[(pyridine) $\text{Ru}^{\text{III}}(\text{NH}_3)_4(2,3\text{-Cl}_2\text{pcyd})][\text{ClO}_4]_2$

Excess pyridine (1.3 mL, 16 mmol) was added to 60 mL water and the solution heated to 40-50 °C. $(\text{NH}_3)_4\text{Ru}(\text{SO}_2)\text{Cl}_2$ (1.1 g, 3.6 mmol) was then added and the solution

was stirred at about 40 °C for 45 min.⁵⁰ The solution was filtered under gravity into a beaker containing 1 L acetone. The yellow precipitate that formed was filtered and dried in vacuo for 1 h yielding 1.37 g of (py)(NH₃)₄Ru(II)(SO₂)Cl₂. This product was dissolved in 40 mL water, filtered and a 40 mL 1:1 mixture of HCl (2M):H₂O₂ (30%) was added slowly. After stirring for 10 min, this solution was added into 1.4 L acetone with stirring. The yellow product that formed was filtered, washed with acetone and dried in vacuo for 1 h. The oxidized product yield was 1.17 g of (py)(NH₃)₄Ru(SO₄)Cl. This product was dissolved in 20 mL of water, filtered and reduced over 20 g freshly prepared Zn/Hg amalgam for 20 min. The solution was transferred under argon into 5.0 g solid NH₄PF₆ and the mixture was purged and saturated with argon once before chilling in the refrigerator for 2 h. The yellow product was filtered, washed with anhydrous ether and dried overnight in vacuo. The yield of [(py)(NH₃)₄Ru(OH₂)] [PF₆]₂ was 1.66 g. The ligand 2,3-Cl₂Hpcyd (0.4 g, 2.14 mmol) was dissolved in 100 mL acetone containing 5 drops of HPF₆. The solution was purged and saturated with argon twice. The complex [(py)(NH₃)₄Ru(OH₂)] [PF₆]₂ (0.4 g, 0.73 mmol) was added and the solution degassed and saturated with argon once more. The reaction was allowed to proceed overnight at room temperature, whereby the colour turned from yellow to green. The solution was transferred into an Erlenmeyer flask, and stirred in air for 6 h and the green colour intensified. Excess TBAB was added and the green precipitate was filtered and washed with cold acetone before drying it in vacuo for 1 h. The green precipitate was dissolved in water and charged in a Sephadex column and eluted with 0.5 M NaCl. Two bands were identified; the first yellow band, presumed to be unreacted starting material, and the second was the major product which was green-blue. To this eluent was added 1 g of

NaBPh₄ and a green precipitate was filtered and dried in air overnight, yielding 0.6 g of tetraphenylborate salt. This product was dissolved in 30 mL acetone and excess TBAB was added. A green precipitate was filtered and dried in air, yielding 0.2 g of bromide salt. This salt was dissolved in 20 mL water and excess NaClO₄ (2 g) was added and the mixture was chilled in the refrigerator overnight. The blue solid that formed was filtered, dried and recrystallized by ether diffusion into an acetone solution at room temperature, affording greenish needles. The overall approximate yield from the precursor was 0.21 g (11%). Elemental analysis: Calcd for C₁₂N₇H₂₀Cl₄O₈Ru + 0.5CH₃CN: C, 23.88; N, 16.07; H, 3.31; Found: C, 23.69; N, 15.80; H, 3.48.

2.4.4 Preparation of

***Trans*-[(2,6-Me₂pyz)Ru^{II}(NH₃)₄(2,3-Cl₂pcyd)][ClO₄]**

2,6-Dimethylpyrazine (1 g, 9.52 mmol) was dissolved in 10 mL of water and 1 g (3.29 mmol) of (NH₃)₄Ru(SO₂)Cl₂ was then added. The mixture was stirred and heated at about 40 °C in the dark for 40 min. The mixture was allowed to cool and 12 mL of 1 M HCl were added, followed by 12 mL of 30% H₂O₂. The solution mixture allowed to stir until it turned yellow from red a process which took about 10 min.⁶³ This solution was added in 300 mL of acetone and swirled, and then 300 mL more acetone was added and the mixture was chilled in the freezer for 2 h. The golden brown precipitate was filtered, washed with acetone and diethyl ether before drying it in vacuo for 1 h, yielding 1.1 g of [(2,6-Me₂pyz)Ru(NH₃)₄(SO₄)]Cl. This solid was dissolved in 30 mL water and reduced over 10 g freshly prepared Zn/Hg amalgam for 30 min. The deep red solution was poured into a 200 mL beaker and to this was added a 3 g solution of NaBPh₄ in 20 mL water.

The purple solid that formed was filtered and dried in vacuo for 36 h, yielding 1.70 g $[(2,6\text{-Me}_2\text{pyz})\text{Ru}(\text{NH}_3)_4(\text{OH}_2)][\text{BPh}_4]_2$.

The ligand 2,3- Cl_2Hpcyd (0.5 g, 2.67 mmol) was dissolved in 100 mL acetone and the solution degassed and saturated with argon thrice. An equivalent of $[(2,6\text{-Me}_2\text{pyz})\text{Ru}(\text{NH}_3)_4(\text{OH}_2)][\text{BPh}_4]_2$ (0.85 g) was added into this solution and the reaction mixture was degassed with argon once more. The reaction was allowed to proceed in the dark at room temperature for 48 h in the presence of 3 drops of HPF_6 . Excess TBAB was added into this solution until an orange brown precipitate completely formed. This mixture was chilled in the freezer for 2 h and then filtered. The complex was dissolved in minimum water and charged in a Sephadex column and eluted with basic (pH 8) 0.5 M NaCl. A minor yellowish orange band presumed to be starting the material eluted first, followed by the major, brownish orange band. To this solution was added excess NaBPh_4 and the brown precipitate that formed was filtered and dried in air vacuo overnight, yielding 0.5 g of $[(2,6\text{-Me}_2\text{pyz})\text{Ru}(\text{NH}_3)_4(2,3\text{-Cl}_2\text{pcyd})][\text{BPh}_4]$. This solid was dissolved in 40 mL of acetone and excess TBAB was added. The precipitate that formed was filtered, washed with cold acetone and dried in vacuo for 2 h, yielding 0.2 g of $[(2,6\text{-Me}_2\text{pyz})\text{Ru}(\text{NH}_3)_4(2,3\text{-Cl}_2\text{pcyd})][\text{Br}]$. Metathesis to the perchlorate salt yielded 0.2 g of $[(2,6\text{-Me}_2\text{pyz})\text{Ru}(\text{NH}_3)_4(2,3\text{-Cl}_2\text{pcyd})][\text{ClO}_4]$. This solid was found to be partially oxidized (by observation of a weak LMCT band) and it was dissolved in 20 mL acetone and reduced with polished magnesium strips, filtered under argon and recrystallized by ether diffusion into an acetone solution. The overall approximate yield from the precursor was 0.15 g (30 %). Elemental analysis: Calcd for $\text{C}_{13}\text{N}_8\text{H}_{23}\text{Cl}_3\text{O}_4\text{Ru} + 0.6\text{H}_2\text{O}$: C, 26.34; N, 18.90; H, 4.48; Found: C, 25.97; N, 18.79; H, 3.90.

2.4.5 Preparation of

***Trans*-[(pyz)Ru(NH₃)₄(2,3-Cl₂picyd)][ClO₄]**

Following the method of Kameke,⁶³ this complex was prepared as was the 2,6-dimethylpyrazine complex described above in section 2.4.6 with some modifications. *Trans*-[Ru(NH₃)₄(SO₂)Cl]Cl (0.8 g, 2.63 mmol) and an excess of pyrazine (0.8 g, mmol) were dissolved in water (10 mL) and the pH was adjusted to 7-8 using NaHCO₃ (~0.6 g). The solution turned from orange to deep red. After 15 min stirring in the dark, the solution was acidified with 12 mL of 1.0 M HCl until the CO₂ evolution ceased. About 12 mL of 30 % H₂O₂ was then added with stirring until the solution turned from red to greenish brown. This solution was transferred into 300 mL of acetone and stirred. Then 300 mL more acetone were added, and the solution was chilled in the freezer for 2 h. The yellow precipitate so obtained was filtered out, washed with acetone, and vacuum-dried. It was dissolved in 30 mL of 0.01 M HCl and reduced over 15 g of freshly prepared Zn/Hg amalgam for 30 min. The deep red solution was poured into a 20 mL solution containing 3 g NaPBh₄ and the red precipitate that was formed filtered and dried in vacuo for 48 h. The yield of [(pyz)Ru(NH₃)₄(OH₂)] [BPh₄]₂ was 2.30 g.

The ligand 2,3-Cl₂Hpcyd (0.5 g, 2.67 mmol) was dissolved in 100 mL of acetone containing 10 drops of HPF₆, and the solution was degassed and saturated with argon thrice. This solution was cooled in an ice bath and 0.80 g (1 equiv.) of [(pyz)Ru(NH₃)₄(OH₂)] [BPh₄]₂ was added to this solution. The reaction mixture degassed and saturated with argon once more. The reaction was allowed to proceed in the dark in the ice bath for 16 h. Excess TBAB was added to this solution and the orange brown precipitate that formed was chilled in the freezer for 2 h and then filtered. The complex

was dissolved in minimum water and charged in a Sephadex column and eluted with basic (pH 8) 0.5 M NaCl. A minor yellowish orange band, presumed to be starting the material, eluted first, followed by the major brownish orange band. To this solution was added excess NaBPh₄ and the brown precipitate that formed was filtered and dried in air *vacuo* overnight yielding 0.45 g [(pyz)Ru(NH₃)₄(2,3-Cl₂pcyd)][BPh₄]. This solid was dissolved in 40 mL of acetone containing 5 drops of triethylamine, and 3 g of TBAB were added. The precipitate that formed was filtered, washed with cold acetone and dried in *vacuo* for 2 h yielding 0.20 g [(pyz)Ru(NH₃)₄(2,3-Cl₂pcyd)][Br]. Metathesis to the perchlorate salt in 10 mL basic water (pH 8) yielded 0.22 g of [(pyz)Ru(NH₃)₄(2,3-Cl₂pcyd)][ClO₄]. This solid was dissolved in 20 mL acetone and reduced with polished magnesium strips in the presence of 3 drops of triethylamine, filtered under argon and recrystallized by ether diffusion into acetone solution. The overall approximate yield from the precursor was 0.12 g (25%). Elemental analysis: Calcd for C₁₁N₈H₁₉Cl₃O₄Ru + 0.9(CH₃)₂CO: C, 28.03; N, 19.09; H, 4.19; Found: C, 27.93; N, 18.93; H, 4.04.

2.4.6 Preparation of

***Trans*-[*(Mepyz)Ru*^{II}(NH₃)₄(2,3-Cl₂pcyd)][ClO₄]₂**

Following the method of Ford *et al.*,⁶⁴ solid *trans*-[Ru(NH₃)₄(SO₂)Cl]Cl (3 g, 9.9 mmol) was dissolved in 160 mL of hot 1.5 M HCl. To this solution was added slowly (drop by drop) a solution of 6.5 g (40 mmol) of iodine monochloride in 13 mL 6 M HCl. The yellowish precipitate that formed was allowed to cool to room temperature and then chilled in the freezer for 2 h. The solid product was collected by filtration, washed with ethanol, and air-dried, giving 4.50 g of *trans*-[Ru(NH₃)₄Cl₂][ICl₂]. This solid was then added to a solution of 2.60 g of sodium bisulfite in 10 mL water. Concentrated HCl (2

mL) was then added to this solution and a dark yellow compound precipitated. The solid product was collected by filtration, washed with a mixture of acetone (100 mL) and ethanol (20 mL), then recrystallized from hot 0.02 M HCl. The orange crystals of *trans*-[Ru(NH₃)₄Cl₂][Cl] were separated by filtration, washed with ethanol and air-dried yielding 2.11 g.

Trans-[Ru(NH₃)₄Cl₂][Cl] (1.75 g, 6.36 mmol) was ground with a pestle and mortar and then dissolved in 150 mL of hot water containing 20 drops of CF₃COOH. The solution turned pinkish, yet heating was continued until all of the solid dissolved. This solution was allowed to cool to room temperature and filtered. It was reduced over 20 g of freshly prepared Zn/Hg amalgam for 1 h under argon. An equivalent of Mepyz-tos (1.58 g) was transferred into this solution, and the mixture was degassed once more then saturated with argon. The reaction was allowed to proceed in the dark at room temperature overnight. The deep purple solution was transferred into a 20 mL solution of 5.0 g NaBPh₄ in the dark, chilled for 2 h and filtered. The purple solid was dried in vacuo for 48 h yielding 5.0 g of mostly *trans*-[(mepyz)Ru(NH₃)₄(OH₂)][BPh₄]₃.

A three-molar excess 2,3-Cl₂Hpcyd (1 g, 5.35 mmol) was dissolved in 100 mL acetone containing a trace of HPF₆. To this solution was transferred 1 g of *trans*-[(mepyz)Ru(NH₃)₄(OH₂)][BPh₄]₃ in the dark, and the mixture was degassed and saturated twice with argon. The mixture was allowed to stir at 35 °C for 2 days in the dark. To this solution was added an excess of TBAB and the purple precipitate that formed was filtered and dried in vacuo for 2 h. This was dissolved in a minimum of water and charged in a Sephadex column and eluted with basic (pH 8) 0.5 M NaCl. Two minor bands eluted first, a purple and a pinkish band. The third major band was collected and, to this, was

added excess NaBPh₄. The purple precipitate was filtered and washed with cold water before drying it in *vacuo* overnight. This solid was dissolved in 10 mL of acetone containing 3 drops of triethylamine and then excess TBAB was added. The purple precipitate was filtered and air-dried overnight. This solid was dissolved in a minimum of basic (pH 8) water, excess NaClO₄ was added and the mixture was chilled overnight in the refrigerator. The purple solid was filtered, dried in air and then recrystallized by slow ether diffusion into an acetonitrile solution. After 3 days, purple needles of *trans*-(Mepyz)Ru(NH₃)₄(2,3-Cl₂pcyd)][ClO₄]₂ formed. The overall approximate yield from the precursor was 0.08 g (3 %). Elemental analysis: Calcd for C₁₂N₈H₂₂Cl₄O₄Ru: C, 22.20; N, 17.26; H, 3.42; Found: C, 22.65; N, 16.97; H, 3.77.

2.4.7 Preparation of

***Mer*-(bpy)Ru(NH₃)₃(2,3-Cl₂pcyd)][ClO₄]₂**

The procedure presented here is a slight modification of that of Evans.¹⁷ 2,2'-Dipyridyl (1.0 g, 6.4 mmol) was dissolved in 5 mL of acetone and the volume was made up to 75 mL with water. (NH₃)₄Ru(SO₂)Cl₂ (1.0 g, 3.29 mmol) was added into the solution and the mixture was stirred and heated to about 50 °C for 1.5 h. The mixture was filtered and allowed to cool, and treated with 35 mL of a 1:1 mixture of 0.4 M HCl and 30 % H₂O₂, and stirred for 30 min. The solution was concentrated on a rotary evaporator at 50 °C to 20 mL and then transferred into a 500 mL beaker. About 450 mL of acetone was added to this solution and the reddish oil that formed was chilled overnight in a deep freezer. The supernatant liquid was decanted off and the oil washed several times with acetone and ether before drying it in *vacuo* for 2 h. It was then dissolved in 75 mL of water and reduced over 10 g of freshly made Zn/Hg amalgam for 30 min. The solution

was poured into a 200 mL flask and a 20 mL solution of 3.0 g NaBPh₄ was slowly added. The purple precipitate that formed was filtered and dried in vacuo for 48 hours. The yield of [bpy(NH₃)₃Ru(OH₂)] [BPh₄]₂ was 3.4 g.

The title complex was prepared by the method outlined by DeRosa⁶⁵ with slight modification. The ligand 2,3-dichlorophenylcyanamide (0.2 g, 1.3 mmol) was dissolved in of 100 mL acetone containing 5 drops of HPF₆, degassed and saturated three times with argon gas. Solid [(bpy)(Ru(NH₃)₃(H₂O))] [BPh₄]₂ (1 g, 1.04 mmol) was added and the solution was degassed and saturated with argon one final time. After stirring overnight, the mixture was filtered and to the filtrate was added a slight excess of cerium(IV) ammonium nitrate 0.40 g (0.68 mmol) in 20 mL of water. The mixture was stirred for 6 h and the colour intensified from brownish orange to green-blue. The solution was filtered and 3.0 g of TBAB added to this solution. The precipitated complex, [(bpy)Ru(NH₃)₃(2,3-Cl₂pcyd)]Br₂ was filtered and dried in air. This product was dissolved in 50 mL of distilled water and loaded onto a Sephadex cation-exchange column, and eluted with 0.5 M NaCl. The blue/green product band was preceded by a purple band containing the Ru(II) complex. The desired complex was precipitated by the addition of solid NaClO₄. The solution was filtered and air-dried overnight. The complex was recrystallized by ether diffusion into a concentrated acetonitrile solution. The overall approximate yield from the precursor was 0.3 g (41 %). Elemental analysis: Calcd for C₁₁N₈H₁₉Cl₃O₄Ru : C, 29.45; N, 14.14; H, 2.91; Found: C, 29.63; N, 14.58; H, 3.21.

2.5 SYNTHESIS OF ASYMMETRIC DINUCLEAR COMPLEXES

2.5.1. Preparation of

***Trans*-[(py)Ru(NH₃)₄(dicyd)Ru(NH₃)₅][PF₆]₄**

The precursor, aquotetraaminepyridineruthenium(II) hexafluorophosphate, was prepared as described in section 2.4.3. A freshly prepared batch of this starting material (1.0 g, 1.9 mmol) was dissolved in 150 mL of acetone. The solution was degassed and purged with argon twice. An approximate three fold of dicydH₂ (1.0 g) was added to this solution and the solution was degassed and purged once more. The mixture was allowed to react under argon at 25-30 °C. After 48 h, the mixture was filtered and transferred into an Erlenmeyer flask and stirred overnight for oxidation to take place. Excess TBAB was added and the solution was chilled in the freezer for 2 h. The light green precipitate was filtered, washed with cold acetone and dried in vacuo for 2 h. The green solid was dissolved in a minimum amount of water and charged onto a Sephadex column and eluted with 0.5 M NaCl. A yellow band appeared first and was presumed to be unreacted starting material and/or excess ligand. This was followed by a second blue-greenish band which was the desired product and then a third, blue band presumed to be the symmetric dinuclear complex. To the major mononuclear band was added a 20 ml solution of 4.0 g NaBPh₄ and the chestnut brown precipitate that formed was filtered, washed sparingly with cold water and air-dried overnight, yielding 1.2 g of tetraphenyl borate salt.

The title complex was prepared by dissolving 1.2 g of *trans*-[(py)Ru(NH₃)₄(dicydH)][BPh₄]₂ in 100 mL of acetone containing 5 drops of HPF₆. To this solution was added about 1.0 g of magnesium in strips (polished with emory paper and chopped into 1 cm-long pieces). The solution was degassed and saturated with argon

thrice and the reduction process was allowed to proceed at room temperature. After 2 h, the colour turned from greenish blue to yellowish orange. The solution was transferred under argon into a flask containing freshly prepared 3-fold excess of the $[\text{Ru}(\text{NH}_3)_5(\text{OH}_2)][\text{PF}_6]_2$ complex (3.0 g). The solution was degassed one more time and the reaction was allowed to proceed at room temperature for 24 h. The solution was filtered into a flask containing a 20-fold excess of TBAB and the green precipitate that formed was chilled in the freezer for 2 h, filtered and washed with cold acetone, and the dried in *vacuo* for 2 h. The green solid (1.4 g) was dissolved in a minimum amount of water, stirred for 6 h for complete oxidation and then charged into a Sephadex column. The products were eluted first with 0.5 M NaCl. First to elute was a yellow band presumed to be excess pentaammine precursor, followed by a bluish green band presumed to be unreacted mononuclear intermediate. The third green major band was eluted with 1 M NaCl. To this was added excess NaBPh_4 and the mixture was stirred. A brick-red precipitate formed, it was chilled in the refrigerator for 4 h, filtered and washed sparingly with cold water and finally allowed to air-dry overnight, yielding 0.92 g of tetraphenylborate salt. This product was dissolved in 400 mL of acetone and an excess of TBAB was added. The bromide salt that precipitated was filtered and dried in *vacuo*. Finally, a metathesis to the hexafluorophosphate salt was carried out by dissolving 0.45 g of the bromide salt in 80 mL of water and adding 3.5 g NH_4PF_6 , and chilling the mixture in refrigerator overnight. The brown product was filtered, washed sparingly with cold water and dried in *vacuo*. This product (0.5 g) was dissolved in 100 mL of acetonitrile and recrystallized by slow ether diffusion. After 3 days, microcrystalline product formed which was filtered and and washed with ether. The overall approximate yield from the

precursor was 0.36 g (25%). Elemental Analysis based upon $[(\text{pyridine})\text{Ru}(\text{NH}_3)_4(\text{dicyd})\text{Ru}(\text{NH}_3)_5][\text{PF}_6]_4$. Calcd for $\text{C}_{13}\text{H}_{30}\text{N}_{14}\text{Ru}_2\text{P}_4\text{F}_{24}$: C, 13.34; H, 3.10; N, 16.75. Found: C, 13.39; H, 3.07; N, 16.11.

2.5.2. Preparation of

***Trans*- $[(\text{pyz})\text{Ru}(\text{NH}_3)_4(\text{dicyd})\text{Ru}(\text{NH}_3)_5][\text{PF}_6]_4$**

The precursor, aquotetraaminepyrazineruthenium(II) hexafluorophosphate was prepared as described in section 2.4.5. Excess dicydH₂ (1.0 g) was dissolved in 100 mL of acetone containing 10 drops of HPF₆ and the mixture was degassed and saturated with argon thrice. *Trans*- $[(\text{pyz})\text{Ru}(\text{II})(\text{NH}_3)_4(\text{OH}_2)][\text{BPh}_4]_2$ (1.0 g) was added to this solution and the mixture degassed and saturated with argon. The reaction was allowed to proceed at room temperature in the dark. After 36 h, the purple solution was filtered and excess TBAB was added, followed by 1 mL of triethylamine. The brownish precipitate that formed was chilled in the freezer overnight, filtered and dried in vacuo for 2 hours. The bromide salt was dissolved in 50 mL of water containing 20 drops of 1 M HCl and stirred at 40 °C for 30 min. The solution mixture was filtered, charged into a Sephadex column and eluted with 0.5 M NaCl. The first band was reddish and presumed to be unreacted starting material. The second major band was yellowish-orange followed by a brownish minor band presumed to be the dinuclear complex. To the second band was added excess NaBPh₄ and the yellowish precipitate that formed was filtered and air-dried overnight, yielding 0.6 g of tetraphenylborate salt.

To prevent pyrazine from taking part as bridging ligand, and remaining only as a terminal ligand, the following reaction was carried out in acidic media at low

temperatures. *Trans*-[(pyz)Ru(NH₃)₄(dicydH₂)] [BPh₄]₂ (0.6 g) was dissolved in 100 mL of degassed and argon-saturated acetone containing 10 drops of HPF₆. The solution mixture was degassed and saturated once more with argon and chilled in a liquid nitrogen bath for 1 h. About one equivalent of [Ru(NH₃)₅(OH₂)] [PF₆]₂ (0.4 g) was added to this solution and the mixture degassed and saturated once more with argon. The reaction mixture was then put in an ice bath and the acetone was slowly allowed to thaw with stirring. After reacting overnight in the dark, the solution mixture was filtered and about 1 mL triethylamine was added and the reaction mixture was allowed to stir for 4 h. Excess TBAB was added and the mixture put in the freezer overnight. The precipitate was filtered and dried in vacuo immediately, yielding 0.5 g of bromide salt. This solid was dissolved in a minimum water and stirred for 6 h before charging it into a Sephadex column. Elution first with 0.5 M NaCl produced two minor bands presumed to be unreacted precursor and mononuclear complexes. The third, major band was isolated by adding excess NaBPh₄ and filtering the tetraphenylborate salt immediately. The product formed (0.35 g) was dried in vacuo immediately, and after 5 h it was dry enough for metathesis. It was dissolved in 20 mL of acetonitrile, filtered and treated with 0.65 g of TBAB before chilling it in the freezer overnight. This salt was filtered and washed with cold acetone and dried in vacuo. The bromide salt formed (0.21 g) was dissolved in 20 mL of water, and treated with 1 g NH₄PF₆. The solid that formed as chilled in the fridge overnight and then filtered and washed sparingly with cold water. The hexafluorophosphate salt was finally recrystallized by slow ether diffusion into an acetonitrile solution. The overall approximate yield from the precursor was 0.105 g (15%). Elemental Analysis based upon (pyrazine)Ru(NH₃)₄(dicyd)Ru(NH₃)₅] [PF₆]₄.

Calcd for $C_{12}H_{35}N_{15}Ru_2P_4F_{24} + 0.6H_2O$: C, 12.00; H, 3.22; N, 17.49. Found: C, 12.26; H, 2.97; N, 17.21.

2.5.4. Preparation of

***Mer*-[(bpy)Ru(NH₃)₃(dicyd)Ru(NH₃)₅][PF₆]₄**

The precursor, aquotriammino-2,2'-bipyridineruthenium(II) tetraphenylborate was prepared as described in section 2.4.7. Excess dicydH₂ (1.5 g) was dissolved in 200 mL of acetone containing 5 drops of HPF₆, and the mixture was degassed and saturated with argon thrice. [(bpy)Ru(II)(NH₃)₃(OH₂)] [BPh₄]₂ (3.4 g) was added to this solution and the mixture degassed and saturated with argon once. The reaction was allowed to proceed at room temperature in the dark. After 36 h, the orange solution was filtered and excess TBAB added. The brownish precipitate that formed was chilled in the freezer overnight, filtered and dried in vacuo for 2 h. The bromide salt (1.8 g) was dissolved in 50 mL of water and stirred at 40 °C for 30 min. The solution mixture was filtered, charged into a Sephadex column and eluted with 0.5 M NaCl. The first band was reddish and presumed to be unreacted starting material. The second major band was yellowish-orange followed by a brownish minor band presumed to be the dinuclear complex. To the second band was added excess NaBPh₄ and the yellowish precipitate that formed was filtered and air-dried overnight, yielding 1.8 g of tetraphenylborate salt.

About 1.8 g of [(bpy)Ru(NH₃)₃(DicydH₂)] [BPh₄]₂ was dissolved in 150 mL of degassed and argon-saturated acetone containing 6 drops of HPF₆. The solution mixture was degassed and saturated once more with argon. Freshly prepared excess [Ru(NH₃)₅(OH₂)] [PF₆]₂ complex (2.5 g) was added to this solution and the mixture

degassed and saturated once more with argon. After reacting overnight in the dark, the mixture was filtered and about 1 mL of triethylamine was added and the reaction mixture was allowed to stir for 4 h. An excess of TBAB was added and the mixture put in the freezer overnight, filtered and dried in *vacuo*, yielding 3.4 g of bromide salt. This solid was dissolved in a minimum amount of water and stirred for 6 h before charging it into a Sephadex column. Eluting first with 0.5 M NaCl produced two minor bands presumed to be unreacted precursor and mononuclear complexes. The third, major band was isolated by adding excess NaClO₄ and filtering the perchlorate salt. The product formed (1.35 g) was dried in *vacuo* overnight. A sample (0.5 g) of the product was dissolved in 50 mL of water and 1.0 g of NH₄PF₆ was added. The solid that formed was chilled in the refrigerator overnight and then filtered and washed sparingly with cold water. The hexafluorophosphate salt was finally recrystallized by slow ether diffusion into an acetonitrile solution. The overall approximate yield from the precursor was 0.25 g (35%). Elemental Analysis based upon [(bipyridine)Ru(NH₃)₃(dicyd)Ru(NH₃)₅][PF₆]₄. Calcd for C₁₈H₃₆N₁₄Ru₂P₄F₂₄: C, 17.57; H, 2.95; N, 15.94. Found: C, 17.68; H, 3.08; N, 15.62.

2.6 PHYSICAL MEASUREMENTS

2.6.1 Infrared Spectroscopy

Infrared spectroscopy was performed on a ABB Bomen MB Series IR spectrometer. The data were analyzed using Bomen Grams software. Reference spectra of air were run prior to all measurements on complexes in KBr discs.

2.6.2 Electronic Absorption Spectroscopy

Electronic absorption spectra were taken on a Varian Cary 5 Uv-vis-NIR spectrophotometer at ambient temperature using matched quartz cells (1 cm pathlength) made by Helma (Canada) Limited. A solvent baseline correction was performed before each run. Spectra were obtained at a scan rate of 600 nm/min at intervals of 0.333 nm, with a spectral bandwidth of 2.00 nm and a signal averaging time of 0.033 s. Quantitative spectroscopy on all mononuclear complexes was performed using the solvents described in Section 2.1.7.

2.6.3 Cyclic Voltammetry

Cyclic Voltammetry (CV) was performed by using a BAS-CV-27 Voltammograph online to a BAS X-Y recorder. The electrochemical cell consisted of a double jacketed glass container with an inner volume of approximately 15 mL. The cell temperature was maintained at 25.0 ± 0.1 °C by means of a Haake D8-G refrigerated bath and circulator. The cell was fitted with a Teflon lid through which holes had been drilled to accommodate the electrodes and an argon bubbler. For non-aqueous cyclic voltammetry, the electrodes consisted of platinum disk working and counter electrodes (BAS, 1.6 mm

diameter) and silver wire pseudo-reference electrode. Ferrocene ($E^{\circ} = 0.665$ V vs NHE in acetonitrile) was used as the internal reference. The supporting electrolyte was tetrabutylammonium hexafluorophosphate (TBAH) and was used at concentrations of about 0.1 M. All solvents used the internal reference were as described in Section 2.1.7. In all cases, the solution was deoxygenated by bubbling with argon for about 15 minutes and blanketed with argon prior to each scan.

2.6.4 Spectroelectrochemistry

Spectroelectrochemistry of the mononuclear complexes was performed using an optically transparent thin-layer electrochemical (OTTLE) cell arrangement as designed by Evans *et al.* and shown below¹⁷. The cell had interior dimensions of roughly 1 x 2 cm with path length of 0.2 mm and was fitted with a silver/silver chloride reference electrode. For NIR studies, ITO (indium-titanium oxide)-coated glass served as working and counter electrodes and was purchased from Delta Technologies. Spectra were obtained on a Cary 5 spectrophotometer, as was used for electronic absorption spectroscopy vs appropriate background of solvent and electrolyte at a scan rate of 1800 nm/s. The potentials were controlled as for cyclic voltammetry. During the experiment, the potentials were varied and the system allowed to come to equilibrium after which Uv-vis-NIR spectra were collected at suitable increments. All solvents used were as described in Section 2.1.7.

Figure 2.1: Scheme of the OTTLE cell spacer (left) and the teflon superstructure where **a** is silver reference wire and **b** are platinum working and counter electrodes.

2.6.5 Elemental Analyses

Elemental analyses were performed by Canadian Microanalytical services Ltd. Delta, British Columbia. All complexes were vacuum-dried overnight.

2.7 TECHNIQUES

2.7.1 ITO Preparation and Etching

Etching of the ITO plate for the OTTLE cell was performed as follows. The ITO plate was first cleaned by placing it in a 20% (v/w) solution of ethanolamine in deionized water in an ultrasonic bath for about 20 min. The area of ITO that was to remain intact was first protected using nailpolish and then left to dry overnight. The plate was then placed in a beaker containing an aqueous solution of 20% HCl, 5% HNO₃, and a few drops of liquid detergent. The solution was then heated to between 50 and 60 °C for approximately 5 min. The plate was then rinsed in a 10% aqueous solution of Na₂CO₃. The resistance of the etched portions of the plate was then finally tested for a maximum resistance (20 MΩ) using a multimeter

2.7.2 Ag/AgCl Reference Electrode Preparation

Two strips of silver wire of known diameter and length were twisted together. This was then soaked in 3M HNO₃ for 5 min and rinsed with deionized water. A standard H-cell with working, counter, and reference electrodes was set up using the coiled silver wire as the working electrode and 0.1 M HCl as the electrolyte. The current of the cell was adjusted such that the current density was 0.4 mA/cm² of silver wire, and the cell was left for 30 min. The Ag/AgCl electrode was then rinsed with deionized water and left to dry.

2.8 THEORETICAL CALCULATIONS

2.8.1 Non-linear Curve Fitting

Non-linear curve fitting was performed on a Raven 486 PC equipped with a 80387 coprocessor (v3.0) using Jandel Scientific PeakFit™. With this software, the oscillator strengths of LMCT and MMCT transitions were determined by fitting the band profiles to a set of Gaussian bands. For each band the oscillator strength is given by: $f = 4.61 \times 10^{-9} \left(\sum_n \epsilon_{\max_n} \Delta \nu_{1/2_n} \right)$, where for the n^{th} Gaussian band, $\epsilon_{\max}$ is the maximum extinction coefficient in $\text{M}^{-1}\text{cm}^{-1}$ and $\Delta \nu_{1/2}$ is the bandwidth at one-half $\epsilon_{\max}$ in cm^{-1} . The peak analysis software was also used to deconvolute two mononuclear LMCT transitions from the dinuclear LMCT transition.

CHAPTER 3

RESULTS

3.1 MONONUCLEAR COMPLEXES

3.1.1 Infrared Spectroscopy

Infrared spectroscopy was performed on all seven mononuclear complexes. Data for these complexes are collected in Table 3.1 and representative spectra of ruthenium(II) and ruthenium(III) complexes are given in Figures 3.2 and 3.3. Infrared spectroscopy was used mainly for the early characterization of the complexes where it was found useful in proving that complexation of the ligand to the metal had occurred by virtue of the shift of nitrile stretching.

The Infrared spectra of protonated and tetraphenylarsonium salts of 2,3-dichlorophenylcyanamide have been reported elsewhere.^{59,66} This ligand has sharp and intense $\nu(\text{CN})$ and $\nu(\text{NCN})$ absorption bands located at around 2220 cm^{-1} and 2100 cm^{-1} , respectively. Upon coordination to an electropositive metal ion, the ligand is deprotonated and the $\nu(\text{NCN})$ shifted to an intermediate energy between that of the tetraphenylarsonium salt (i.e. free 2,3-dichlorophenylcyanamide anion) and the neutral protonated ligand. The fact that coordination shifts the cyanamide stretch to higher energies compared to the free ligand can be accounted for by involving an inductive effect between ruthenium ion and the cyanamide nitrile group. The $\nu(\text{NCN})$ due to cyanamide group bound to the ruthenium(III) ion is shifted to lower energies than that of

the analogous ruthenium(II) complex. This shift is due to a greater transfer of electron density to the relatively electron-poor metal, resulting in a net loss of bond order in the NCN moiety.⁶⁷

Figure 3.1: Ruthenium bonding to various resonance forms of phenylcyanamide anion ligand.

The $\nu(\text{NCN})$ values in Table 3.1 do not appear to show a trend when an ammine is substituted with pyridine-based nitrogen heterocycles. The presence of ammine groups in the inner coordination sphere of ruthenium ion is verified in the infrared spectra of the complex. Based on reported values for mononuclear hexaammineruthenium(II) complexes,⁶⁸ the ammine vibrational modes present include the $\nu(\text{N-H})$ in the 3250-3100 cm^{-1} range, and the $\delta(\text{N-H})$ degenerate deformation or bending modes around 1630 cm^{-1} and 1300 cm^{-1} . The presence of perchlorate counter anion which is common to all seven complexes, is verified by a $\nu(\text{Cl-O})$ stretch in the 1080-1105 cm^{-1} range, consistent with previously reported results for ionic perchlorate complexes.⁶⁹

Table 3.1: Infrared Band Positions (cm⁻¹)^a for Selected Characteristic Vibrations of the Mononuclear Complexes.

COMPLEX	$\nu(\text{NCN})$	$\nu(\text{N-H})$	$\delta(\text{N-H})$	$\nu(\text{Cl-O})$
$[(\text{NH}_3)_5\text{Ru}^{\text{III}}(2,3\text{-Cl}_2\text{pcyd})][\text{ClO}_4]_2$	2115	3335, 3269, 3204	1628, 1310	1075
$[(3,5\text{-Me}_2\text{py})(\text{NH}_3)_4\text{Ru}^{\text{III}}(2,3\text{-Cl}_2\text{pcyd})][\text{ClO}_4]_2$	2126	3325, 3264, 3198	1630, 1313	1086
$[(\text{py})(\text{NH}_3)_4\text{Ru}^{\text{III}}(2,3\text{-Cl}_2\text{pcyd})][\text{ClO}_4]_2$	2115	3340, 3234, 3073	1628, 1305	1085
$[(2,6\text{-Me}_2\text{pyz})(\text{NH}_3)_4\text{Ru}^{\text{II}}(2,3\text{-Cl}_2\text{pcyd})][\text{ClO}_4]$	2174	3347, 3233, 3073	1629, 1290	1090
$[(\text{pyz})(\text{NH}_3)_4\text{Ru}^{\text{II}}(2,3\text{-Cl}_2\text{pcyd})][\text{ClO}_4]$	2174	3242, 3230, 3070	1631, 1285	1105
$[(\text{Mepyz})(\text{NH}_3)_4\text{Ru}^{\text{II}}(2,3\text{-Cl}_2\text{pcyd})][\text{ClO}_4]_2$	2172	3329, 3238, 3158	1630, 1301	1087
$[(\text{bpy})(\text{NH}_3)_3\text{Ru}^{\text{III}}(2,3\text{-Cl}_2\text{pcyd})][\text{ClO}_4]_2$	2119	3332, 3252, 3182	1628, 1306	1092

^a performed in KBr discs

Figure 3.2: Infrared spectrum of $[\text{Ru}(\text{NH}_3)_5(2,3\text{-Cl}_2\text{pcyd})][\text{ClO}_4]_2$.

Figure 3.3: Infrared spectrum of $[\text{trans}-(\text{Mepyz})\text{Ru}(\text{II})(\text{NH}_3)_4(2,3\text{-Cl}_2\text{pcyd})][\text{ClO}_4]_2$.

3.1.2 Electronic Absorption Spectroscopy

Quantitative electronic spectra of the seven mononuclear complexes were collected in four solvents spanning a broad range of donor numbers (nitromethane, acetonitrile, acetone and DMSO). All the results are summarized in Tables 3.2–3.14 and in Figures 3.6–3.18, where the spectra of ruthenium(III) complexes display solvent-dependent charge transfer transitions. The characteristic spectral assignments are based on previous spectroscopic studies of mononuclear pentaammineruthenium(III) complexes of anionic phenylcyanamide ligands in which the microsymmetry was assigned to C_{2v} .^{39,59} The following discussion shows how these results can be extended towards asymmetric mononuclear complexes where a nitrogen heterocycle is bound *trans* to the phenylcyanamide ligand in tetraammine and triammineruthenium(III) complexes.

As previously mentioned, the anionic cyanamide group is a resonance-stabilized π system (Figure 3.4A) which, when coordinated to ruthenium(III), should shift the equilibrium towards the Ia resonance form. There are two pairs of π symmetry nonbonding electrons that can delocalize into this three-atom π system, resulting in two orthogonal molecular orbitals, π_{nb1} and π_{nb2} , shown in Figure 3.4B, where the atomic orbital size approximates the magnitude of electron density. Interaction between phenylcyanamide ligand π -molecular orbitals and ruthenium(III) $d\pi$ orbitals give rise to two ligand-to-metal charge transfer (LMCT) transitions in the visible and near IR regions of the complex's electronic absorption spectrum, as shown in Figures 3.4–3.15. The reason for these two LMCT transitions is that π_{nb1} and π_{nb2} are nondegenerate in energy, where π_{nb1} is more stable because it can delocalize into phenyl ring as well as the nitrile group, a result that has been confirmed by theoretical calculations.⁷⁰

Figure 3.4: Resonance-stabilized anionic phenylcyanamide π system (A), showing nonbonding electrons that can delocalize into the π system resulting in orthogonal π_{nb1} and π_{nb2} molecular orbitals (B).

Figure 3.4 illustrates the expected π -bonding interactions and the resulting LMCT transitions of the anionic phenylcyanamide ligand with ruthenium(III) ion. The lower-energy LMCT band has been assigned to an allowed $b_1^* \leftarrow b_1$ ($\pi_1 \rightarrow d\pi^*$) transition between the high-energy π -HOMO of the anionic ligand and a metal-centred πd orbital as the interaction between metal and ligand orbitals is shown in Scheme 3.1. The higher energy LMCT band has been assigned to a symmetry-forbidden $b_1^* \leftarrow b_2$ ($\pi_2 \rightarrow d\pi^*$) transition.

A comparison of the lower energy $b_1^* \leftarrow b_1$ LMCT bands for the mononuclear complexes (Table 3.2–3.14) reveals a trend of decreasing LMCT optical energy as the σ -donor strength of the *trans* nitrogen heterocycle ligand decreases. This trend can be

explained by Figure 3.5B below, by considering that a poor σ -donor ligand stabilizes the metal πd orbitals and this will be discussed in great detail in Chapter 4.

Figure 3.5: A qualitative MO energy level diagram showing the relative energies of the $b_1^* \leftarrow b_1$ LMCT transition for pcyd^- bound to (A) $(\text{NH}_3)_5\text{Ru}^{\text{III}}$ and (B) $L_n(\text{NH}_3)_{5-n}\text{Ru}^{\text{III}}$, where L_n is π -acid substitution of an ammine ligand in the asymmetric ruthenium(III) mononuclear complex. Labeling is appropriate to C_{2v} symmetry.⁵⁹

Scheme 3.1: π -bonding interaction between Ru(III) and cyanamide anionic ligand.

The spectra of the fully reduced ruthenium(II) complexes are dominated by intense high-energy bands which are sensitive to both solvent and the nitrogen

heterocycle bound *trans* to the phenylcyanamide ligand. This phenomenon may be understood in terms of the metal-to-ligand charge transfer (MLCT) transitions between the $d\pi$ orbitals of the metal and the empty π^* antibonding orbitals of the ligand (Figure 3.6). The band shifts with solvent arise largely because the donor-acceptor ability of $\text{Ru}^{\text{III/II}}$ redox couple of ammine complexes is very solvent-sensitive while the acceptor ability of nitrogen heterocycles is not, but it nevertheless affects the stability of metal πd orbitals in a predictable way. These phenomena will be discussed in greater detail in Chapter 4.

Molecular orbital diagrams for $\text{Ru}^{\text{II}}\text{-L}_n$ complexes are given in Figure 3.6 in which the metal-ligand (nitrogen heterocycle) bond is taken as the z-axis (C_{2v} microsymmetry).

Figure 3.6: MO diagram of mononuclear $\text{Ru}^{\text{II}}\text{-L}_n$ complexes showing the MLCT transition, where in (A) L_n is pyridine and in (B) L_n is 2,2'-bipyridine. Labeling is appropriate to C_{2v} symmetry. From reference 71.

Observation of the MLCT spectral data in Figures 3.6–3.18 reveals that, in some complexes, only one MLCT transition band is observable, while for others a split of the bands is observed. For strong π -acceptor nitrogen heterocycles, the π^* orbitals are lower in energy compared to weaker π -acceptor ligands. These lower π^* orbitals (b_2 and a_2) are split by ca. $10\,000\text{ cm}^{-1}$ with b_2 being lower.⁷¹ Since a_2 has nodes on the nitrogen atom while b_2 does not, the $\text{Ru}^{\text{II}}\pi\text{d}-b_2\pi^*$ interaction is expected to be greater, resulting in the splitting of the πd orbitals where $d_{yz}(b_2)$ lies lower in energy as shown in Scheme 3.2.

Scheme 3.2: The $\pi\text{d}-\text{L}\pi^*$ interaction

For weaker π -acceptor ligands, the ground-state HOMO is viewed as largely metal-centred, whereas for stronger π -acceptor ligands, the interactions are qualitatively the same but involve much greater ruthenium(II)- L_n mixing (stronger π -backbonding), as indicated in Figure 3.5B. Provided that the "ruthenium(III)" in the MLCT excited state has the $(d_{xz})^2(d_{xy})^2(d_{yz})^1$ configuration, the most intense MLCT transition will also be the highest energy transition. Thus, transitions arising from excitation of the non-bonding d_{xz} and d_{xy} electrons would occur at lower energy when the visible MLCT bands for these complexes are asymmetric or completely split, with higher intensity on the high energy side.⁷²

Table 3.2: Electronic Absorption Spectroscopy Data for the LMCT Transition of $[(\text{NH}_3)_5\text{Ru}^{\text{III}}(2,3\text{-Cl}_2\text{pcyd})][\text{PF}_6]_2$ as a Function of Solvent.

SOLVENT (DN)	$f_{\text{LMCT}}^{\text{a}}$	$\epsilon_{\text{max}}, \times 10^3$ ($\text{M}^{-1}\text{cm}^{-1}$)	LMCT		
			$\lambda_{\text{max}}(\text{nm})$	$\nu_{\text{max}}(\text{cm}^{-1})$	eV
NM (2.7)	0.18	7.16	730	13700	1.68
AN (14.1)	0.14	6.85	694	14400	1.81
AC (17.0)	0.13	6.56	673	14850	1.80
DMSO (29.8)	0.10	5.12	612	16300	2.03

^a Oscillator strength, f , and molar absorptivity, ϵ_{max} , from ref 73

Figure 3.7: Electronic absorption spectra of $[(\text{NH}_3)_5\text{Ru}^{\text{III}}(2,3\text{-Cl}_2\text{pcyd})][\text{PF}_6]_2$ in NM (a), AN (b), AC (c), and DMSO (d).

Table 3.3: Electronic Absorption Spectroscopy Data for the LMCT Transition of *Trans*-[(3,5-Me₂py)Ru^{III}(NH₃)₄(2,3-Cl₂pcyd)][ClO₄]₂ as a Function of Solvent.

SOLVENT (DN)	f_{LMCT}^a	$\epsilon_{max} \times 10^3$ (M ⁻¹ cm ⁻¹)	LMCT		
			$\lambda_{max}(nm)$	$\nu_{max}(cm^{-1})$	eV
NM (2.7)	0.085	8.55	813	12300	1.53
AN (14.1)	0.071	7.60	782	12800	1.59
AC (17.0)	0.055	6.09	764	13100	1.62
DMSO (29.8)	0.031	3.69	693	14200	1.76

^a Oscillator strength, f , determined using PeakFit software

Figure 3.8: Electronic absorption spectra of [(3,5-Me₂py)Ru^{III}(NH₃)₄(2,3-Cl₂pcyd)][ClO₄]₂ in NM (a), AN (b), AC (c), and DMSO (d).

Table 3.4: Electronic Absorption Spectroscopy Data for the MLCT Transition of *Trans*-[(3,5-Me₂py)Ru^{II}(NH₃)₄(2,3-Cl₂pyd)][ClO₄]₂ as a Function of Solvent.

SOLVENT (DN)	f_{MLCT}^a	$\epsilon_{max} \times 10^4$ (M ⁻¹ cm ⁻¹)	MLCT		
			$\lambda_{max}(nm)$	$\nu_{max}(cm^{-1})$	eV
NM (2.7)	0.11	1.12	418	24000	2.98
AN (14.1)	0.099	1.28	424	23600	2.92
AC (17.0)	0.084	0.90	433	23100	2.86
DMSO (29.8)	0.057	8.53	447	22400	2.78

^a Oscillator strength, f , determined using PeakFit software

Figure 3.9: Electronic absorption spectra of [(3,5-Me₂py)Ru^{II}(NH₃)₄(2,3-Cl₂pyd)][ClO₄]₂ in NM (a), AN (b), AC (c), and DMSO (d).

Table 3.5: Electronic Absorption Spectroscopy Data for the LMCT Transition of *Trans*-[(pyridine)Ru^{III}(NH₃)₄(2,3-Cl₂pcyd)][ClO₄]₂ as a Function of Solvent.

SOLVENT (DN)	f_{LMCT}^a	$\epsilon_{max} \times 10^3$ (M ⁻¹ cm ⁻¹)	LMCT		
			$\lambda_{max}(nm)$	$\nu_{max}(cm^{-1})$	eV
NM (2.7)	0.059	6.54	820	12200	1.51
AN (14.1)	0.063	6.69	789	12700	1.57
AC (17.0)	0.050	5.68	770	13000	1.61
DMSO (29.8)	0.044	5.30	713	14000	1.74

^a Oscillator strength, f , determined using PeakFit software.

Figure 3.10: Electronic absorption spectra of [(py)Ru^{III}(NH₃)₄(2,3-Cl₂pcyd)][ClO₄]₂ in NM (a), AN (b), AC (c), and DMSO (d).

Table 3.6: Electronic Absorption Spectroscopy Data for the MLCT Transition of *Trans*-[(pyridine)Ru^{II}(NH₃)₄(2,3-Cl₂pcyd)][ClO₄]₂ as a Function of Solvent.

SOLVENT (DN)	f_{MLCT}^a	$\epsilon_{max} \times 10^3$ (M ⁻¹ cm ⁻¹)	MLCT		
			$\lambda_{max}(nm)$	$\nu_{max}(cm^{-1})$	eV
NM (2.7)	0.086	8.46	424	23600	2.92
AN (14.1)	0.089	9.93	428	23400	2.90
AC (17.0)	0.077	9.53	437	22900	2.84
DMSO (29.8)	0.090	11.4	455	22000	2.73

^a Oscillator strength, f , determined using PeakFit software.

Figure 3.11: Electronic absorption spectra of [(pyridine)Ru^{II}(NH₃)₄(2,3-Cl₂pcyd)][ClO₄]₂ in NM (a), AN (b), AC (c), and DMSO (d).

Table 3.11: Electronic Absorption Spectroscopy Data for the LMCT Transition of *Trans*-[(2,6-Me₂pyz)Ru^{III}(NH₃)₄(2,3-Cl₂pcyd)][ClO₄] as a Function of Solvent.

SOLVENT (DN)	f_{LMCT}^a	$\epsilon_{max} \times 10^3$ (M ⁻¹ cm ⁻¹)	LMCT		
			$\lambda_{max}(nm)$	$\nu_{max}(cm^{-1})$	eV
NM (2.7)	0.085	7.49	835	12000	1.49
AN (14.1)	0.060	6.91	802	12500	1.55
AC (17.0)	0.065	7.23	773	13000	1.60
DMSO (29.8)	0.050	5.11	717	14000	1.72

^a Oscillator strength, f , determined using PeakFit software.

Figure 3.12: Electronic absorption spectra of [(2,6-Me₂pyz)Ru^{III}(NH₃)₄(2,3-Cl₂pcyd)][ClO₄] in NM (a), AN (b), AC (c), and DMSO (d).

Table 3.8: Electronic Absorption Spectroscopy Data for the MLCT Transition of *Trans*-[(2,6-Me₂pyz)Ru^{II}(NH₃)₄(2,3-Cl₂pcyd)][ClO₄] as a Function of Solvent.

SOLVENT (DN)	f_{MLCT}^a	$\epsilon_{max} \times 10^4$ (M ⁻¹ cm ⁻¹)	MLCT		
			$\lambda_{max}(nm)$	$\nu_{max}(cm^{-1})$	eV
NM (2.7)	0.12	1.55	463	21600	2.68
AN (14.1)	0.12	1.63	470	21300	2.64
AC (17.0)	0.12	1.61	477	21000	2.60
DMSO (29.8)	0.13	1.81	492	20000	2.52

^a Oscillator strength, f , determined using PeakFit software.

Figure 3.13: Electronic absorption spectra of [(2,6-Me₂pyz)Ru^{II}(NH₃)₄(2,3-Cl₂pcyd)][ClO₄] in NM (a), AN (b), AC (c), and DMSO (d).

Table 3.9: Electronic Absorption Spectroscopy Data for the LMCT Transition of *Trans*-[(pyz)Ru^{III}(NH₃)₄(2,3-Cl₂pcyd)][ClO₄] as a Function of Solvent.

SOLVENT (DN)	f_{LMCT}^a	$\epsilon_{max} \times 10^3$ (M ⁻¹ cm ⁻¹)	LMCT		
			$\lambda_{max}(nm)$	$\nu_{max}(cm^{-1})$	eV
NM (2.7)	0.079	8.56	868	11500	1.43
AN (14.1)	0.070	5.05	811	12300	1.53
AC (17.0)	0.059	6.48	799	12500	1.55
DMSO (29.8)	0.046	5.15	725	13800	1.71

^a Oscillator strength, f , determined using PeakFit software.

Figure 3.14: Electronic absorption spectra of [(pyz)Ru^{III}(NH₃)₄(2,3-Cl₂pcyd)][ClO₄] in NM (a), AN (b), AC (c), and DMSO (d).

Table 3.10: Electronic Absorption Spectroscopy Data for the MLCT Transition of *Trans*-[(pyz)Ru^{II}(NH₃)₄(2,3-Cl₂pcyd)][ClO₄] as a Function of Solvent.

SOLVENT (DN)	f_{MLCT}^a	$\epsilon_{max} \times 10^4$ (M ⁻¹ cm ⁻¹)	MLCT		
			$\lambda_{max}(nm)$	$\nu_{max}(cm^{-1})$	eV
NM (2.7)	0.12	1.44	478	209001	2.59
AN (14.1)	0.12	1.69	483	20700	2.57
AC (17.0)	0.12	1.80	490	20400	2.53
DMSO (29.8)	0.11	1.70	507	19700	2.45

^a Oscillator strength, f , determined using PeakFit software.

Figure 3.15: Electronic absorption spectra of [(pyz)Ru^{II}(NH₃)₄(2,3-Cl₂pcyd)][ClO₄] in NM (a), AN (b), AC (c), and DMSO (d).

Table 3.11: Electronic Absorption Spectroscopy Data for the LMCT Transition of *Trans*-[(Mepyz)Ru^{III}(NH₃)₄(2,3-Cl₂pcyd)][ClO₄]₃ as Function of Solvent.

SOLVENT (DN)	f_{LMCT}^a	$\epsilon_{max} \times 10^3$ (M ⁻¹ cm ⁻¹)	LMCT		
			$\lambda_{max}(nm)$	$\nu_{max}(cm^{-1})$	eV
NM (2.7)	0.019	3.52	958	10400	1.29
AN (14.1)	0.058	7.29	904	11100	1.37
AC (17.0)	0.073	10.4	883	11300	1.40
DMSO (29.8)	0.058	7.21	801	12500	1.55

^a Oscillator strength, f , determined using PeakFit software.

Figure 3.16: Electronic absorption spectra of [(Mepyz)Ru^{III}(NH₃)₄(2,3-Cl₂pcyd)][ClO₄]₃ in NM (a), AN (b), AC (c), and DMSO (d). Spectra generated by chemical oxidation of the ruthenium(II) complex with NOBF₄. (The spectroelectrochemical reversibility of the reaction in NM was about 80%).

Table 3.12: Electronic Absorption Spectroscopy Data for the MLCT transition of *Trans*-[(Mepyz)Ru^{II}(NH₃)₄(2,3-Cl₂pcyd)][ClO₄]₂ as Function of Solvent.

SOLVENT	f_{MLCT}^a	$\epsilon_{max} \times 10^4$ (M ⁻¹ cm ⁻¹)	MLCT		
			$\lambda_{max}(nm)$	$\nu_{max}(cm^{-1})$	eV
NM (2.7)	0.13	1.77	579	17300	2.14
AN (14.1)	0.15	1.96	577	17300	2.15
AC (17.0)	0.16	2.09	572	17500	2.17
DMSO (29.8)	0.18	2.31	566	17700	2.19

^a Oscillator strength, f , determined using PeakFit software.

Figure 3.17: Electronic absorption spectra of [(Mepyz)Ru^{II}(NH₃)₄(2,3-Cl₂pcyd)][ClO₄]₂ in NM (a), AN (b), AC (c), and DMSO (d).

Table 3.13: Electronic Absorption Spectroscopy Data for the LMCT Transition of *mer*-[(bpy)Ru^{III}(NH₃)₃(2,3-Cl₂pcyd)][ClO₄]₂ as a Function of Solvent.

SOLVENT	f_{LMCT}^a	$\epsilon_{max} \times 10^3$ (M ⁻¹ cm ⁻¹)	LMCT		
			$\lambda_{max}(nm)$	$\nu_{max}(cm^{-1})$	eV
NM (2.7)	0.078	9.01	880	11400	1.41
AN (14.1)	0.073	8.49	821	12200	1.51
AC (17.0)	0.068	7.81	798	12500	1.56
DMSO (29.8)	0.048	2.73	750	13300	1.65

^a Oscillator strength, f , determined using PeakFit software.

Figure 3.18: Electronic absorption spectra of [(bpy)Ru^{III}(NH₃)₃(2,3-Cl₂pcyd)][ClO₄]₂ in NM (a), AN (b), AC (c), and DMSO (d).

Table 3.14: Electronic Absorption Spectroscopy Data for the MLCT Transition (high- and lower-energy bands) of *Mer*-[(bpy)Ru^{II}(NH₃)₃(2,3-Cl₂pcyd)][ClO₄]₂ as a Function of Solvent.

SOLVENT	f_{MLCT}^a	$\epsilon_{max} \times 10^4$ (M ⁻¹ cm ⁻¹)	MLCT		
			$\lambda_{max}(nm)$	$\nu_{max}(cm^{-1})$	eV
NM (2.7)	0.15	1.11	372	26900	3.33
	0.05	0.65	532	18800	2.33
AN (14.1)	0.12	1.05	377	26500	3.29
	0.04	0.55	540	18500	2.30
AC (17.0)	0.11	1.01	382	26200	3.25
	0.04	0.53	550	18200	2.25
DMSO (29.8)	0.11	1.04	392	25500	3.16
	0.03	0.49	566	17700	2.19

^a Oscillator strength, f , determined using PeakFit software.

Figure 3.19: Electronic absorption spectra of [(bpy)Ru^{II}(NH₃)₃(2,3-Cl₂pcyd)][ClO₄]₂ in NM (a), AN (b), AC (c), and DMSO (d).

3.1.3 Electrochemical Studies

Cyclic voltammetry was performed on all seven complexes in four solvents (nitromethane, acetonitrile, acetone and DMSO). The electrochemical data are presented in Table 3.15 and representative voltammograms for the complexes are shown in Figures 3.18-3.24. The experiments were performed in a manner described in Section 2.6.3. All the spectra presented here were collected at a scan rate of 100 mV/s. Reduction of the complexes showed quasi-reversible behaviour at scanning rates between 50 and 500 mV/s, with potential separation between anodic and cathodic peaks increasing from about 60 to 80 mV with increasing scan rate. The voltammogram of some mononuclear complexes indicated two redox events. The more negative potential is the metal-centred event with ligand centered event being at higher potential. This process is shown by the Scheme 3.1 below. Assignments of the waves was based upon the electrochemistry of free 2,3-dichlorophenylcyanamide and a number of mononuclear complexes.^{39,59,73}

Scheme 3.3: Metal-Centred and Ligand Centred Couples of Mononuclear Complexes.

Table 3.15: Ru(III/II) Reduction Couples ^a and ΔE Values as a Function of Solvent for the Seven Mononuclear Complexes.

Complex	ΔE^b	NM (2.7)	MeCN (14.1)	Acetone (17.0)	DMSO (28.9)
[Ru(NH ₃) ₅ (2,3-Cl ₂ pcyd)][PF ₆] ₂	0.46	0.35	0.20	0.08	-0.11
[(3,5-Me ₂ py)Ru(NH ₃) ₄ (2,3-Cl ₂ pcyd)][ClO ₄] ₂	0.38	0.50	0.40	0.32	0.13
[(pyridine)Ru(NH ₃) ₄ (2,3-Cl ₂ pcyd)][ClO ₄] ₂	0.35	0.59	0.43	0.30	0.23
[(2,6-Me ₂ pyz)Ru(NH ₃) ₄ (2,3-Cl ₂ pcyd)][ClO ₄]	0.35	0.69	0.55	0.35	0.34
[(pyz)Ru(NH ₃) ₄ (2,3-Cl ₂ pcyd)][ClO ₄]	0.31	0.70	0.61	0.48	0.39
[(bpy)Ru(NH ₃) ₃ (2,3-Cl ₂ pcyd)][ClO ₄] ₂	0.28	0.70	0.68	0.54	0.43
[(Mepyz)Ru(NH ₃) ₄ (2,3-Cl ₂ pcyd)][ClO ₄] ₂	0.30	1.11	1.03	0.97	0.80

^a Data reported in V vs NHE.

^b ΔE is the difference between Ru^{III/II} couples of a complex from weakest to strongest donor solvent.

Figure 3.20: Cyclic voltammogram of $[\text{Ru}(\text{NH}_3)_5(2,3\text{-Cl}_2\text{pcyd})][\text{PF}_6]_2$ in DMSO with the internal reference (ferrocene) wave appearing at the more positive potential.

Figure 3.21: Cyclic voltammogram of $[(3,5\text{-Me}_2\text{py})\text{Ru}(\text{NH}_3)_4(2,3\text{-Cl}_2\text{pcyd})][\text{ClO}_4]_2$ in nitromethane with the ligand-centred wave appearing at the more positive potential.

Figure 3.22: Cyclic voltammogram of $[(\text{pyridine})\text{Ru}(\text{NH}_3)_4(2,3\text{-Cl}_2\text{pcyd})][\text{ClO}_4]_2$ in acetonitrile, with the ligand-centred wave appearing at the more positive potential.

Figure 3.23: Cyclic voltammogram of $[(2,6\text{-Me}_2\text{pyz})\text{Ru}(\text{NH}_3)_4(2,3\text{-Cl}_2\text{pcyd})][\text{ClO}_4]$ in acetonitrile.

Figure 3.24: Cyclic voltammogram of $[(\text{pyz})\text{Ru}(\text{NH}_3)_4(2,3\text{-Cl}_2\text{pcyd})][\text{ClO}_4]$ in acetone with the ligand-centred wave appearing at the more positive potential.

Figure 3.25:

Cyclic voltammogram of $[(\text{Mepyz})\text{Ru}(\text{NH}_3)_4(2,3\text{-Cl}_2\text{pcyd})][\text{ClO}_4]_2$ in acetonitrile with the internal reference (ferrocene) wave appearing at the more positive potential.

Figure 3.26:

Cyclic voltammogram of $[(\text{bpy})\text{Ru}(\text{NH}_3)_4(2,3\text{-Cl}_2\text{pcyd})][\text{ClO}_4]_2$ in nitromethane with the ligand-centred wave appearing at the more positive potential.

3.1.4 Spectroelectrochemical Studies

Spectroelectrochemical study of all seven mononuclear complexes was performed in four solvents (nitromethane, acetonitrile, acetone and DMSO). The studies were carried out using the OTTLE cell described in Section 2.6.4. A solution of the complex being evaluated was exposed to an electrical potential, which was varied incrementally about the $\text{Ru}^{\text{III/II}}$ redox couple of the mononuclear complex. At each stepwise change of potential, the electronic absorption spectrum of the complex was monitored and recorded once the system reached equilibrium at that potential. The result is a series of spectra as the oxidation state of the central metal ion was changed. Reduction of ruthenium(III) complexes to ruthenium(II) resulted in a decrease in the intensity of the LMCT band and appearance of a high-energy MLCT band. On the other hand, oxidation of ruthenium(II) complexes resulted in the disappearance of the MLCT transition and simultaneously, a new low-energy band emerged which corresponds to the symmetry-allowed LMCT transition predicted by the qualitative MO scheme (Figure 3.5).⁵⁹ Results of all the complexes evaluated are presented in Figures 3.25 – 3.52.

The main reason for doing this experiment was to determine the chemical reversibility of the ruthenium(III/II) couple in various solvents. To this end, reduction/oxidation of the mononuclear complexes was reversible with regeneration of >95% of the initial complex's spectral intensity and shape in solution in all solvents. However, reversibility of *N'*-methylpyraziniumtetraammine complex in nitromethane was much less reversible resulting in recovery of ~80% of the band intensity and shape. Another justification for these experiments was need to assess the extinction coefficients of the LMCT and MLCT transitions and hence the metal-ligand coupling elements

needed to test the CNS theoretical model. In the preparation of the complexes, some were isolated in the +2 oxidation state and others in the +3 oxidation state. The technique of spectroelectrochemistry allowed the spectra in both oxidation states to be obtained.

Figure 3.27: Spectroelectrochemical data for $[\text{Ru}(\text{NH}_3)_5(2,3\text{-Cl}_2\text{pcyd})][\text{PF}_6]_2$ showing reduction of the Ru^{III} to the Ru^{II} complex in nitromethane.

Figure 3.28: Spectroelectrochemical data for $[\text{Ru}(\text{NH}_3)_5(2,3\text{-Cl}_2\text{pcyd})][\text{PF}_6]_2$ showing reduction of the Ru^{III} to the Ru^{II} complex in acetonitrile.

Figure 3.29: Spectroelectrochemical data $[\text{Ru}(\text{NH}_3)_5(2,3\text{-Cl}_2\text{pcyd})][\text{PF}_6]_2$ showing reduction of the Ru^{III} to the Ru^{II} complex in acetone.

Figure 3.30: Spectroelectrochemical data for $[\text{Ru}(\text{NH}_3)_5(2,3\text{-Cl}_2\text{pcyd})][\text{PF}_6]_2$ showing reduction of the Ru^{III} to the Ru^{II} complex in DMSO.

Figure 3.31: Spectroelectrochemical data for *trans*-[(3,5-Me₂py)Ru(NH₃)₄(2,3-Cl₂pcyd)][ClO₄]₂ showing reduction of the Ru^{III} to the Ru^{II} complex in nitromethane.

Figure 3.32: Spectroelectrochemical data for *trans*-[(3,5-Me₂py)Ru(NH₃)₄(2,3-Cl₂pcyd)][ClO₄]₂ in showing reduction of the Ru^{III} to the Ru^{II} complex in acetonitrile.

Figure 3.33: Spectroelectrochemical data for *trans*-[(3,5-Me₂py)Ru(NH₃)₄(2,3-Cl₂pcyd)][ClO₄]₂ showing reduction of the Ru^{III} to the Ru^{II} complex in acetone.

Figure 3.34: Spectroelectrochemical data for *trans*-[(3,5-Me₂py)Ru(NH₃)₄(2,3-Cl₂pcyd)][ClO₄]₂ showing reduction of the Ru^{III} to the Ru^{II} complex in DMSO.

Figure 3.35: Spectroelectrochemical data for *trans*-[(py)Ru(NH₃)₄(2,3-Cl₂pcyd)][ClO₄]₂ showing reduction of the Ru^{III} to the Ru^{II} complex in nitromethane.

Figure 3.36: Spectroelectrochemical data for *trans*-[(py)Ru(NH₃)₄(2,3-Cl₂pcyd)][ClO₄]₂ showing reduction of the Ru^{III} to the Ru^{II} complex in acetonitrile.

Figure 3.37: Spectroelectrochemical data for *trans*-[(py)Ru(NH₃)₄(2,3-Cl₂pcyd)][ClO₄]₂ showing reduction of the Ru^{III} to the Ru^{II} complex in acetone.

Figure 3.38: Spectroelectrochemical data for *trans*-[(py)Ru(NH₃)₄(2,3-Cl₂pcyd)][ClO₄]₂ showing reduction of the Ru^{III} to the Ru^{II} complex in DMSO.

Figure 3.39: Spectroelectrochemical data for *trans*-[(2,6-Me₂pyz)Ru(II)(NH₃)₄(2,3-Cl₂pcyd)][ClO₄] showing oxidation of the Ru^{II} to the Ru^{III} complex in nitromethane.

Figure 3.40: Spectroelectrochemical data for *trans*-[(2,6-Me₂pyz)Ru(II)(NH₃)₄(2,3-Cl₂pcyd)][ClO₄] showing oxidation of the Ru^{II} to the Ru^{III} complex in acetonitrile.

Figure 3.41: Spectroelectrochemical data for *trans*-[(2,6-Me₂pyz)Ru(II)(NH₃)₄(2,3-Cl₂pcyd)][ClO₄] showing oxidation of the Ru^{II} to the Ru^{III} complex in acetone.

Figure 3.42: Spectroelectrochemical data for *trans*-[(2,6-Me₂pyz)Ru(II)(NH₃)₄(2,3-Cl₂pcyd)][ClO₄] showing oxidation of the Ru^{II} to the Ru^{III} complex in DMSO.

Figure 3.43: Spectroelectrochemical data for *trans*-[(pyz)Ru(II)(NH₃)₄(2,3-Cl₂pcyd)][ClO₄] showing oxidation of the Ru^{II} to the Ru^{III} complex in nitromethane.

Figure 3.44: Spectroelectrochemical data for *trans*-[(pyz)Ru(II)(NH₃)₄(2,3-Cl₂pcyd)][ClO₄] showing oxidation of the Ru^{II} to the Ru^{III} complex in acetonitrile.

Figure 3.45: Spectroelectrochemical data for *trans*-[(pyz)Ru(II)(NH₃)₄(2,3-Cl₂pcyd)][ClO₄] showing oxidation of the Ru^{II} to the Ru^{III} complex in acetone.

Figure 3.46: Spectroelectrochemical data for *trans*-[(pyz)Ru(II)(NH₃)₄(2,3-Cl₂pcyd)][ClO₄] showing oxidation of the Ru^{II} to the Ru^{III} complex in DMSO.

Figure 3.47: Spectroelectrochemical data for *trans*-[(Mepyz)Ru(NH₃)₄(2,3-Cl₂pcyd)][ClO₄]₂ showing oxidation of the Ru^{II} to the Ru^{III} complex in nitromethane.

Figure 3.48: Spectroelectrochemical data for *trans*-[(Mepyz)Ru(NH₃)₄(2,3-Cl₂pcyd)][ClO₄]₂ showing oxidation of the Ru^{II} to the Ru^{III} complex in acetonitrile.

Figure 3.49: Spectroelectrochemical data for *trans*-[(Mepyz)Ru(NH₃)₄(2,3-Cl₂pcyd)][ClO₄]₂ showing oxidation of the Ru^{II} to the Ru^{III} complex in acetone.

Figure 3.50: Spectroelectrochemical data for *trans*-[(Mepyz)Ru(NH₃)₄(2,3-Cl₂pcyd)][ClO₄]₂ showing oxidation of the Ru^{II} to the Ru^{III} complex in DMSO.

Figure 3.51: Spectroelectrochemical data for *mer*-[(bpy)Ru(NH₃)₃(2,3-Cl₂pcyd)][ClO₄]₂ showing reduction of the Ru^{III} to the Ru^{II} complex in nitromethane.

Figure 3.52: Spectroelectrochemical data for *mer*-[(bpy)Ru(NH₃)₃(2,3-Cl₂pcyd)][ClO₄]₂ in showing reduction of the Ru^{III} to the Ru^{II} complex in acetonitrile.

Figure 3.53: Spectroelectrochemical data for *mer*-[(bpy)Ru(NH₃)₃(2,3-Cl₂pcyd)][ClO₄]₂ in showing reduction of the Ru^{III} to the Ru^{II} complex in acetone.

Figure 3.54: Spectroelectrochemical data for *mer*-[(bpy)Ru(NH₃)₃(2,3-Cl₂pcyd)][ClO₄]₂ showing reduction of the Ru^{III} to the Ru^{II} complex in DMSO.

3.2 DINUCLEAR COMPLEXES

Asymmetric Ru_a(III)-Ru_b(III) Complexes of 1,4-dicyanamidobenzene Dianion

Symmetric dinuclear ruthenium complexes of 1,4-dicyanamidobenzene dianion incorporating pentaammine, tetraammines and triammine ruthenium centres have previously been prepared and characterized by IR, electron absorption spectroscopy, solution magnetic susceptibility measurements and aqueous and non-aqueous cyclic voltammetry.^{16,17} In further investigating these types of complexes, the following results section goes further to demonstrate and attempt to explain the solvent dependency of the electronic, electrochemical and magnetic properties of a new class of asymmetric dinuclear ruthenium complexes bridged by 1,4-dicyanamidobenzene dianion. In this regard, the probes used include ¹H NMR, electronic absorption spectroscopy, cyclic voltammetry and solution magnetic measurements. In addition to this, the solvent dependency of the electrochemical properties of the mixed-valence systems formed spectroelectrochemically will be analysed. Antiferromagnetic exchange effects in solvents of varying donor number also will be investigated.

3.2.1 Synthesis

The general synthesis of dinuclear asymmetric complexes of 1,4-dicyanamidobenzene dianion is outlined below.

Scheme 3.4: Reaction scheme for synthesis of asymmetric dinuclear complexes

$n = 1$ and 2 for monodentate and bidentate L_n ligands respectively

Oxidation of SO_2 to SO_4^{2-} allowed an aqueous solution of the complex to be reduced over zinc amalgam where the sulphate ion ‘pops’ out and is substituted by a water molecule. The complex so generated is precipitated as a tetraphenylborate salt which is soluble in non-aqueous solvents. In this complex, the water molecule is

substitutionally labile and a π -donor ligand can easily be bound to the metal. The cyanamide complex generated is purified via cation exchange chromatography where the isolated band of the complex is quantitatively precipitated from aqueous solution by using the bulky tetraphenylborate counter-anion. Though the complex is soluble in most non-aqueous solvents, necessary studies like electrochemistry and ^1H -NMR are obscured by this counter-anion. Metathesis of the salt to hexafluorophosphate or perchlorate was therefore effected. This was achieved by dissolving the tetraphenylborate salt in acetonitrile, and precipitating the bromide complex salt by the addition of excess tetrabutylammonium bromide. The bromide salt was dissolved in minimum water and excess addition of ammonium hexafluorophosphate or sodium perchlorate salts precipitated out the desired complex salt. Recrystallization was effected by slow ether diffusion into an acetonitrile solution of the product. Typical yields were less than 30% and this was primarily due to the formation of more than one product in the course of the reaction.

The structure of the complexes could not be established by X-ray crystallography but can be inferred by previous studies of the Crutchley group. The crystal structure of $[\{(\text{NH}_3)_4\text{Ru}(\text{py})\}_2(\mu\text{-dicyd})]^{4+}$,⁵⁰ shows a coordination geometry where the pyridine ligand is *trans* to the dicyd²⁻ ligand. The synthetic route used for this complex is same as one used for all the monodentate complexes of this study and thus it is reasonable to conclude that their geometry will be similar. Similarly, the complex $[\{(\text{NH}_3)_3\text{Ru}(\text{bpy})\}_2(\mu\text{-dicyd})]^{4+}$ was shown to have a *mer* geometry by a crystal structure determination.¹⁷ Again similarity of the synthetic routes used lead to a suggestion that the complexes of this study which incorporate 2,2'-bipyridine bidentate ligand are of *mer*

geometry. For the dinuclear $[\text{bpy}(\text{NH}_3)_3\text{Ru}(\text{dicyd})\text{Ru}(\text{NH}_3)_5]^{4+}$ complex, ^1H -NMR spectroscopy confirmed this geometry. In the assignment of proton signals, two environments of ammine bound to the substituted end are identifiable, i.e. axial and equatorial, see Figure 3.106.

3.2.2 Synthetic Strategies

All asymmetric $\text{Ru}_a(\text{III})$ - $\text{Ru}_b(\text{III})$ dinuclear complexes have different synthetic routes. Our research group had previously synthesized and isolated (1,4-dicyanamidobenzene)pentaammineruthenium(III) salt, $[(\text{NH}_3)_5\text{Ru}^{\text{III}}(\text{dicydH})]^{3+}$,³⁷ and this was thought to be a good starting material for the synthesis of asymmetric dinuclear complexes. Treating this complex with a pyridine containing precursor, i.e. $[\text{py}(\text{NH}_3)_4\text{Ru}^{\text{II}}(\text{OH}_2)]^{2+}$, gave very low yields after many trials, even after various controls were put in place, for example using an inert atmosphere or warming-up the reaction mixture. Another route was devised whereby this mononuclear was reduced to $[(\text{NH}_3)_5\text{Ru}^{\text{II}}(\text{dicydH})]^{2+}$ and then treated with the pyridine containing precursor at 20-30 °C above room temperature. This method gave about three-fold better yields than the previous method. For analysis and studies proposed for this complex, the yields were still low. Substitution of a water molecule was thought to be a limiting step in the synthesis and a newer route was explored.

The starting material was now prepared as $[\text{py}(\text{NH}_3)_4\text{Ru}^{\text{II}}(\text{dicydH})]^{3+}$ which could be made in higher yield of about 60%. This complex was reduced in trace acid to keep the 1,4-dicyanamidobenzene ligand protonated, i.e as a monoanion and then reacted with $[(\text{NH}_3)_5\text{Ru}^{\text{II}}(\text{OH}_2)]^{2+}$. Note that the nitrile end of the dicydH ligand is a better π -acceptor and can bind to ruthenium(II) and stabilize this oxidation state better than the cyanamide

end, which is a good π -donor. The reaction was carried out at room temperature under argon and the complex oxidized by stirring in air. The yield of the asymmetric complex was more than 10-fold higher than by previous synthetic route. Note that the water molecule in the sixth coordination site of the pentaammine is more substitutionally labile than in pyridinetetraammine precursor.

This new synthetic route was applied to the preparation of the bipyridine-containing asymmetric complex, starting with $[\text{bpy}(\text{NH}_3)_3\text{Ru}^{\text{II}}(\text{dicydH})]^{2+}$ and $[(\text{NH}_3)_5\text{Ru}^{\text{II}}(\text{OH}_2)]^{2+}$, but the yields were dismal. Infrared analysis led to speculation that the products being generated could mostly be the mixed-valent complex, i.e. $[\text{bpy}(\text{NH}_3)_3\text{Ru}^{\text{II}}(\text{Hdicyd})\text{Ru}^{\text{III}}(\text{NH}_3)_5]^{3+}$. Chemical oxidation of this product with a salt of Ce^{IV} indeed gave the desired $\text{Ru}_a(\text{III})\text{-Ru}_b(\text{III})$ product. This synthetic strategy was reviewed in order to reduce the number of steps involved in the synthesis of the final product. After reacting the starting material and the precursor in acidic media, the protonated end of the bridging ligand, dicydH, was deprotonated by adding a base, triethylamine. Stirring the reaction mixture in air oxidized the metal centre and the desired product was isolated in decent yield. This method did not require chemical oxidation with a salt of Ce^{IV} salt as aerial oxidation was sufficient to generate the $\text{Ru}_a(\text{III})\text{-Ru}_b(\text{III})$ species.

The synthesis of the pyrazine-containing asymmetric complex required a different route from those for the previous complexes. Replicating the synthetic route used to generate the bipyridine-containing asymmetric complex gave mixed product and the desired product yields was very low. It was found that the starting material, $[\text{pyz}(\text{NH}_3)_4\text{Ru}^{\text{II}}(\text{dicydH})]^{2+}$, could be binding to the precursor complex,

$[(\text{NH}_3)_5\text{Ru}^{\text{II}}(\text{OH}_2)]^{2+}$, either via the pyrazine or the dicyd²⁻, hence generating two different products. Another drawback was suggested to be favourable substitution of the water molecule by the π -acceptor pyrazine ligand compared to a π -donor dicyd²⁻ ligand. To possibly slow this process, the reaction was carried out in acidic media at very low temperature. Protonation of the pyrazine ligand made it difficult for it to bind ruthenium(II) ion while, on the other hand, this allowed the dicydH⁻ ligand to bind favourably via the π -acceptor nitrile end.

3.2.3 Infrared Spectroscopy

Solid state (KBr mull) infrared spectroscopy was performed upon these complexes. Data for the ligand have been previously published^{39,59,66,73} and those of the asymmetric complexes are collected in Table 3.16. A representative spectrum of *trans*-[(pyridine)Ru(NH₃)₄-dicyd-Ru(NH₃)₅][PF₆]₄ is shown in Figures 3.55.

The Infrared spectroscopic technique was generally used in the early characterization of the complexes, where it is useful in proving the complexation of the ligand to the metal had occurred. In all cases, the characteristic cyanamide band, $\nu(\text{NCN})$ is evident in the 2085-2110 cm^{-1} range. Data for the three asymmetric complexes are similar (in terms of both the vibrational energies and the peak intensities) to the spectra of symmetric pentaammine Ru(III)-Ru(III) dinuclear complexes.³⁷ The presence of ammine groups in the inner coordination sphere of Ru(III) is verified in the infrared spectra of the complex. The ammine vibrational modes present include the $\nu(\text{N-H})$ band in the 3150-3350 cm^{-1} range and the $\delta(\text{N-H})$ band near 1625 cm^{-1} . The presence of hexafluorophosphate is verified by the occurrence of a $\nu(\text{P-F})$ band at 830 cm^{-1} .⁶⁹

Table 3.16: Infrared Band positions (in cm^{-1}) for Selected Characteristic Vibrations of the Asymmetric $\text{Ru}_a(\text{III})$ - $\text{Ru}_b(\text{III})$ Dinuclear Complexes Bridged by dicyd²⁻.

Complex	$\nu(\text{NCN})$	$\nu(\text{N-H})$	$\delta(\text{N-H})$
$[\text{Ru}(\text{NH}_3)_5\text{-dicyd-Ru}(\text{NH}_3)_5][\text{PF}_6]_4$ ^a	2105	3332, 3266	1627
<i>trans</i> -[(pyridine) $\text{Ru}(\text{NH}_3)_4\text{-dicyd-Ru}(\text{NH}_3)_5][\text{PF}_6]_4$	2098	3287, 3366	1626
<i>trans</i> [(pyrazine) $\text{Ru}(\text{NH}_3)_4\text{-dicyd-Ru}(\text{NH}_3)_5][\text{PF}_6]_4$	2098	3289, 3336	1625
<i>mer</i> - [(bipyridine) $\text{Ru}(\text{NH}_3)_3\text{-dicyd-Ru}(\text{NH}_3)_5][\text{PF}_6]_4$	2104	3288, 3360	1625

^a from reference 37.

Figure 3.55: Infrared spectrum of *trans*-[pyRu(NH₃)₄-dicyd-Ru(NH₃)₅][PF₆]₄.

With strongly coupled systems, questions arise as to the formal oxidation state of the ruthenium centres and of particular significance is the oxidation state of the ligand. If the ligand is behaving non-innocently, it may significantly alter the behaviour of the system.¹⁷ The oxidation states of both metal centres and the ligand may be deduced via IR spectroscopy of the complex. The response of metal-metal coupling in a series of pentaammine complexes to inner- and outer-sphere perturbations is consistent with hole-transfer superexchange.¹⁶ Support of the ligands' oxidation state are the cyanamide stretching frequencies, $\nu(\text{NCN})$, which occur over the range of 2098-2105 cm^{-1} for the four complexes, and are consistent with the dianionic form of the ligand. The related vibrations for the fully oxidized form of the ligand occurs at 2170 cm^{-1} ,³⁷ which is much closer to the nitrile-like $\nu(\text{NCN})$ band of the protonated ligand.

3.2.4 Electronic Absorption Spectroscopy

$\text{Ru}_a(\text{III})\text{-Ru}_b(\text{III})$ Complexes

Quantitative Uv-Vis-NIR spectra of the fully oxidized $\text{Ru}_a(\text{III})\text{-Ru}_b(\text{III})$ dinuclear complexes have been collected for all four complexes using four solvents (nitromethane, acetonitrile, acetone, and DMSO). Data for the symmetric dinuclear pentaammine analogue in these solvents, obtained by Evans *et al.*, have been previously reported and discussed,^{16,17} and are reproduced here to facilitate comparisons. This section expands on these results by demonstrating outer-sphere dependency of the electronic absorption spectral features for the asymmetric dinuclear complexes in a range of given solvents. In addition, the inner-sphere (i.e. asymmetric variation of the σ -donor (π -acceptor) strength of ancillary ligands) dependency of these absorption bands in given solvents will be examined.

Electronic absorption data for the complexes are compiled in Tables 3.17-3.20 and the spectra of asymmetric $\text{Ru}_a(\text{III})\text{-Ru}_b(\text{III})$ dinuclear complexes are shown in Figures 3.58-3.61. The solvent dependency of these transitions are also summed up in these tables. Note that, due to the solvent cut-off at 370 nm for nitromethane and at 330 nm for acetone, the ligand-centred $\pi\text{-}\pi^*$ transitions were not observed in these solvents. As well, the solvent cut-off of 275 nm in DMSO prevented the observation of the highest-energy $\pi^* \leftarrow \pi$ transitions.

For all the complexes, the spectra of the fully oxidized species was dominated by an intense low-energy band in the NIR region and a less intense band in the visible region assigned as ligand-to-metal charge transfer (LMCT) transitions^{39,59,70,73} between the high-

energy π -HOMO of the dianion ligand and the metal-centred πd orbital, or a LCAO of both metals' orbitals. In a spectroscopic analysis of the mononuclear complexes' ruthenium(III)-cyanamide chromophore,⁵⁹ such transitions were assigned in C_{2v} microsymmetry (Figure 3.5). The analysis showed that they arise from two non-degenerate pairs of non-bonding electrons that are delocalized over the cyanamide moiety.

The LMCT bands observed in the mononuclear complexes showed that their energy was being shifted to lower energy as the *trans* L_n ligand became a poorer σ -donor. In the asymmetric dinuclear complexes, there are two inequivalent ruthenium(III) centers and each spectrum is expected to demonstrate two ruthenium(III)-cyanamide chromophores. Infact, unlike the spectra of mononuclear complexes, the spectra of these asymmetric dinuclear complexes show splitting of the low-energy LMCT band. As previously discussed in the case of mononuclear ruthenium(III) complexes, LMCT transitions are singly degenerate and the splitting could therefore be regarded as evidence that the band is made up of two low-energy $b_1^* \leftarrow b_1$ LMCT transitions. These are defined here as $Ru_a^{III} - NCN$ and $Ru_b^{III} - NCN$ chromophores, as shown in Figure 3.56.

Figure 3.56: A qualitative MO scheme for the orbitals resulting from π -interaction that show the origins of Ru_a-NCN and Ru_b-NCN LMCT bands.

Parameters for electronic absorption spectra are required for modelling the system via the CNS model, and calculations for the coupling elements must be effected directly from the experimental oscillator strengths. The LMCT band for each Ru-NCN chromophore has therefore to be deconvoluted from the band envelope of the Ru_a(III)-Ru_b(III) complex. For each complex, the two LMCT transition chromophores were modelled by fitting the asymmetric dinuclear LMCT band with two Gaussian bands using the peak-fitting protocol discussed in Section 2.8. It was assumed that the LMCT band profiles of the mononuclear Ru-NCN chromophores were maintained in the asymmetric dinuclear complex. The oscillator strengths of the two fitted bands were individually determined according to $f = 4.6 \times 10^{-9} (\epsilon_{\max} \Delta \nu_{1/2})$ where $\nu_{\max}$, $\epsilon_{\max}$ and $\Delta \nu_{1/2}$ values of the two Gaussian bands fitted the profile of the asymmetric dinuclear complex.

Figure 3.57: Electronic absorption spectra of $[\text{Ru}(\text{NH}_3)_5(\text{dicyd})\text{Ru}(\text{NH}_3)_5][\text{PF}_6]_4$ in (a) nitromethane, (b) acetonitrile, (c) acetone, and (d) DMSO, reproduced from reference 17.

Figure 3.58: Electronic absorption spectra of *trans*- $[(\text{pyridine})\text{Ru}(\text{NH}_3)_4(\text{dicyd})\text{Ru}(\text{NH}_3)_5][\text{PF}_6]_4$ in (a) nitromethane, (b) acetonitrile, (c) acetone, and (d) DMSO.

Figure 3.59: Electronic absorption spectra of $\text{trans-}[(\text{pyrazine})\text{Ru}(\text{NH}_3)_4(\text{dicyd})\text{Ru}(\text{NH}_3)_5][\text{PF}_6]_4$ in (a) nitromethane, (b) acetonitrile, (c) acetone, and (d) DMSO.

Figure 3.60: Electronic absorption spectra of $\text{mer-}[(\text{bipyridine})\text{Ru}(\text{NH}_3)_3(\text{dicyd})\text{Ru}(\text{NH}_3)_5][\text{PF}_6]_4$ in (a) nitromethane, (b) acetonitrile, (c) acetone, and (d) DMSO.

Figure 3.61: Two-Gaussian-band fit of the LMCT profile of *trans*-[(py)Ru(NH₃)₄(dicyd)Ru(NH₃)₅][PF₆]₄ in nitromethane showing (1) (NH₃)₅Ru^{III}-NCN and (2) (pyridine)(NH₃)₄Ru^{III}-NCN chromophores.

Figure 3.62: Two-Gaussian-band fit of the LMCT profile of *trans*-[(py)Ru(NH₃)₄(dicyd)Ru(NH₃)₅][PF₆]₄ in acetonitrile, showing (1) (NH₃)₅Ru^{III}-NCN and (2) (pyridine)(NH₃)₄Ru^{III}-NCN chromophores.

Figure 3.63: Two-Gaussian-band fit of the LMCT profile of *trans*-[(py)Ru(NH₃)₄(dicyd)Ru(NH₃)₅][PF₆]₄ in acetone, showing (1) (NH₃)₅Ru^{III}-NCN and (2) (pyridine)(NH₃)₄Ru^{III}-NCN chromophores.

Figure 3.64: Two-Gaussian-band fit of the LMCT profile of *trans*-[(pyridine)Ru(NH₃)₄(dicyd)Ru(NH₃)₅][PF₆]₄ in DMSO, showing (1) (NH₃)₅Ru^{III}-NCN and (2) (pyridine)(NH₃)₄Ru^{III}-NCN chromophores.

Figure 3.65: Two-Gaussian-band fit of the LMCT profile of *trans*-[(pyz)Ru(NH₃)₄(dicyd)Ru(NH₃)₅][PF₆]₄ in nitromethane, showing (1) (NH₃)₅Ru^{III}-NCN and (2) (pyrazine)(NH₃)₄Ru^{III}-NCN chromophores.

Figure 3.66: Two-Gaussian-band fit of the LMCT profile of *trans*-[(pyz)Ru(NH₃)₄(dicyd)Ru(NH₃)₅][PF₆]₄ in acetonitrile, showing (1) (NH₃)₅Ru^{III}-NCN and (2) (pyrazine)(NH₃)₄Ru^{III}-NCN chromophores.

Figure 3.67: Two-Gaussian-band fit of the LMCT profile of *trans*-[(pyz)Ru(NH₃)₄(dicyd)Ru(NH₃)₅][PF₆]₄ in acetone, showing (1) (NH₃)₅Ru^{III}-NCN and (2) (pyrazine)(NH₃)₄Ru^{III}-NCN chromophores.

Figure 3.68: Two-Gaussian-band fit of the LMCT profile of *trans*-[(pyrazine)Ru(NH₃)₄(dicyd)Ru(NH₃)₅][PF₆]₄ in DMSO, showing (1) (NH₃)₅Ru^{III}-NCN and (2) (pyrazine)(NH₃)₄Ru^{III}-NCN chromophores.

Figure 3.69: Two-Gaussian-band fit of the LMCT profile of *mer*-[(bpy)Ru(NH₃)₃(dicyd)Ru(NH₃)₅][PF₆]₄ in nitromethane, showing (1) (NH₃)₅Ru^{III}-NCN and (2) (bpy)(NH₃)₃Ru^{III}-NCN chromophores.

Figure 3.70: Two-Gaussian-band fit of the LMCT profile of *mer*-[(bpy)Ru(NH₃)₃(dicyd)Ru(NH₃)₅][PF₆]₄ in acetonitrile, showing (1) (NH₃)₅Ru^{III}-NCN and (2) (bpy)(NH₃)₃Ru^{III}-NCN chromophores.

Figure 3.71: Two-Gaussian-band fit of the LMCT profile of *mer*-[(bpy)Ru(NH₃)₃(dicyd)Ru(NH₃)₅][PF₆]₄ in acetone, showing (1) (NH₃)₅Ru^{III}-NCN and (2) (bpy)(NH₃)₃Ru^{III}-NCN chromophores.

Figure 3.72: Two-Gaussian-band fit of the LMCT profile of *mer*-[(bpy)Ru(NH₃)₃(dicyd)Ru(NH₃)₅][PF₆]₄ in DMSO, showing (1) (NH₃)₅Ru^{III}-NCN and (2) (bpy)(NH₃)₃Ru^{III}-NCN chromophores.

Table 3.17: Electronic Absorption Spectroscopy Data for the LMCT Transition of $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-dicyd})][\text{PF}_6]_4$ and averaged sum of oscillator strengths of this complex, with analogous $[\{\text{pyRu}(\text{NH}_3)_4\}_2(\mu\text{-dicyd})][\text{PF}_6]_4$ and $[\{\text{bpyRu}(\text{NH}_3)_5\}_2(\mu\text{-dicyd})][\text{PF}_6]_4$ symmetric dinuclear complexes as a function of solvent.

Solvent (DN)	$\epsilon_{\text{max}}^{\text{a}}$ ($\times 10^4$)	ν_{max} (cm^{-1})	f^{b}	f_{py}^{c}	$f_{\text{bpy}}^{\text{c}}$
NM (2.7)	6.31	9030	0.68	0.74	0.78
AN (14.1)	4.57	9140	0.61	0.69	0.75
AC (17.0)	2.95	9200	0.50	0.56	0.63
DMSO (29.8)	1.41	11100	0.35	0.46	0.57

^a ϵ_{max} has units of ($\text{mol}^{-1}\text{cm}^{-1}$)

^b Oscillator strength calculated from $4.61 \times 10^{-9} \epsilon_{\text{max}} \Delta\nu_{1/2}$.

^c Averaged sum of f from symmetric tetraamminepyridine or triamminebipyridine complexes. Data reproduced from reference 16 and 17

Table 3.18: Deconvoluted ^a Electronic Absorption Spectroscopy Data for the LMCT Transition of *Trans*-[(pyridine)Ru(NH₃)₄(dicyd)Ru(NH₃)₅][PF₆]₄ in Various Solvents.

Solvent (DN)	LMCT	$\nu_{\max}^b$	$\Delta\nu_{1/2}^b$	$\epsilon_{\max}^c$	f^d	f_{total}
NM	Ru _a -NCN	10100	1690	20300	0.16	0.30
	Ru _b -NCN	8900	626	50300	0.14	
AN	Ru _a -NCN	10300	1750	19900	0.16	0.30
	Ru _b -NCN	8800	589	52400	0.14	
AC	Ru _a -NCN	10400	1810	18700	0.16	0.28
	Ru _b -NCN	8700	589	43300	0.12	
DMSO	Ru _a -NCN	10800	2500	9480	0.11	0.15
	Ru _b -NCN	8400	781	13400	0.05	

^a Determined using PeakFit software.

^b The LMCT energy and bandwidth at half-height have units of cm^{-1}

^c $\epsilon_{\max}$ has units of $\text{mol}^{-1}\text{cm}^{-1}$.

^d Oscillator strength calculated from $4.61 \times 10^{-9} \epsilon_{\max} \Delta\nu_{1/2}$.

Table 3.19: Deconvoluted ^a Electronic Absorption Spectroscopy Data for the LMCT Transition of *Trans*-[(pyrazine)Ru(NH₃)₄(dicyd)Ru(NH₃)₅][PF₆]₄ in Various Solvents.

Solvent (DN)	LMCT	$\nu_{\max}^b$	$\Delta\nu_{1/2}^b$	$\epsilon_{\max}^c$	f^d	f_{total}
NM	Ru _a -NCN	10500	1930	20100	0.18	0.30
	Ru _b -NCN	9300	693	38700	0.12	
AN	Ru _a -NCN	10400	1960	17900	0.16	0.29
	Ru _b -NCN	9000	654	41200	0.13	
AC	Ru _a -NCN	10500	2030	17100	0.16	0.28
	Ru _b -NCN	8900	642	39700	0.12	
DMSO	Ru _a -NCN	11000	2150	17600	0.17	0.25
	Ru _b -NCN	8400	650	28100	0.08	

^a Determined using PeakFit software.

^b The LMCT energy and bandwidth at half-height have units of cm^{-1}

^c $\epsilon_{\max}$ has units of $\text{mol}^{-1}\text{cm}^{-1}$.

^d Oscillator strength calculated from $4.61 \times 10^{-9} \epsilon_{\max} \Delta\nu_{1/2}$.

Table 3.20: Deconvoluted ^a Electronic Absorption Spectroscopy Data for the LMCT Transition of *Trans*-[(bipyridine)Ru(NH₃)₃(dicyd)Ru(NH₃)₅][PF₆]₄ in Various Solvents.

Solvent (DN)	LMCT	$\nu_{\max}^b$	$\Delta\nu_{1/2}^b$	$\epsilon_{\max}^c$	f^d	f_{total}
NM	Ru _a -NCN	10500	2040	21600	0.20	0.33
	Ru _b -NCN	9300	708	39600	0.13	
AN	Ru _a -NCN	10400	2030	20300	0.19	0.32
	Ru _b -NCN	9100	689	41000	0.13	
AC	Ru _a -NCN	10400	2120	17200	0.17	0.27
	Ru _b -NCN	9000	686	31100	0.10	
DMSO	Ru _a -NCN	10800	2530	12700	0.15	0.23
	Ru _b -NCN	8300	619	28500	0.08	

^a Determined using PeakFit software.

^b The LMCT energy and bandwidth at half-height have units of cm^{-1}

^c $\epsilon_{\max}$ has units of $\text{mol}^{-1}\text{cm}^{-1}$.

^d Oscillator strength calculated from $4.61 \times 10^{-9} \epsilon_{\max} \Delta\nu_{1/2}$.

3.2.5 Cyclic Voltammetry

Cyclic voltammetry data for $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-dicyd})][\text{PF}_6]_4$ in four solvents (nitromethane, acetonitrile, acetone and DMSO) spanning a broad range of solvent donor number have been previously reported.^{16,17} These data are reproduced in Table 3.21 to facilitate comparisons. This section will expand on these results by demonstrating the outer-sphere dependency of the redox couples for the asymmetric $[\text{Ru}_a(\text{III})\text{-Ru}_b(\text{III})]$ dinuclear complexes in the same solvents. In addition, the inner-sphere (asymmetric variation of σ -donor strength of auxiliary ligands) dependence of the redox couples, in a given solvent, will be examined. Importantly, these data will allow an examination of both the outer- and inner-sphere dependence of metal-metal coupling in asymmetric $[\text{Ru}_a(\text{III})\text{-Ru}_b(\text{III})]$ dinuclear complexes.

Cyclic voltammograms of all the complexes are shown in Figures 3.73-3.84. In most cases, the voltammograms spectra of each of the dinuclear complexes indicated four redox events, as shown in Scheme 3.5 below.

Scheme 3.5: Electrochemical Processes for Metal-Centred and Ligand Centered Events in Dinuclear Systems.

At most negative potentials are the two consecutive one-electron Ru(III/II) reduction couples, with the two couples at higher potentials being formally assigned as the ligand-centred events $\text{L}^{0/-}$ and $\text{L}^{-/2-}$. Note that the assignment of the $\text{L}^{-/2-}$ couple may actually correspond to a Ru(IV/III) couple on the basis of spectroelectrochemical oxidation studies of the $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Me}_2\text{dicyd})][\text{PF}_6]_4$ complex.^{74,75} A specific assignment has been reported to be difficult because of the increased covalent character of the Ru-NCN bond in $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Me}_2\text{dicyd})]^{5+}$. Since this issue has no impact on treatment of the data in this work, it will not be further considered.

The assignments of these bands for the family of the three complexes was based upon electrochemical study of the free dicyd²⁻ ligand^{37,43} and of a number of mononuclear

complexes discussed in section 3.1. The spectra presented here were collected according to the procedure outlined in Section 2.6.3 and were obtained at scan rates of 100 mV/s with electrochemical reversibility being tested over the scan-rate range from 50-500 mV/s.

Although the Ru(III/II) couples were separated sufficiently to enable the determination of the $E_{1/2}$ values, they were insufficiently separated from each other to permit proper measurements of the peak currents by standard methods.⁷⁶⁻⁷⁸ In most cases, the anodic and cathodic current ratios at the scan rate of 100 mV/s were close to unity, $i_{pc}:i_{pa}$. This is a good indication of chemical reversibility. The metal-centred, E_M^o , and ligand-centred $L^{-/2-}$ waves for all the dinuclear complexes in all non-aqueous solvents appeared to be reversible, with separations of between 60 and 80 mV at scan rates of between 50 – 500 mV/s. The $L^{0/-}$ couples occurred close to the solvent limit, and were not in most cases sufficiently resolved for such characterization to be made, but where they were resolvable, the separation was >100 mV and were generally characterized as irreversible.

The E^o values of the various couples were taken as the average of E_{pa} (anodic peak) and E_{pc} (cathodic peak) for all couples in which the voltammogram peaks were fully resolved. This method actually yields $E_{1/2}$ values which are related to E^o .⁷⁹ As long as all the species associated with the couples remain in solution, and their diffusion and activity coefficients have been shown to be similar, it is reasonable to take $E^o = E_{1/2}$ within the reading error of the voltammogram.

Table 3.21: Redox Couples and Compropotionation Constants as a Function of Solvent for $[\text{Ru}(\text{NH}_3)_5\text{-dicyd-Ru}(\text{NH}_3)_5][\text{PF}_6]_4$.^a

Solvent (DN)	$\text{L}^{0/-}$	L^{-2-}	$\text{E}^{\circ}_{\text{Mb}}$	$\text{E}^{\circ}_{\text{Ma}}$	$\Delta\text{E}^{\text{b}}$	K_c^{c}	$\Delta\text{G}_c^{\text{d}}$
NM (2.7)	1.41	0.97	0.25	-0.06	310	2.0×10^5	2520
AN (14.1)	1.29	0.83	0.13	-0.16	290	6.9×10^4	2310
AC (17.0)	1.26	0.77	0.01	-0.23	250	1.4×10^4	1980
DMSO (29.8)	1.07	0.62	-0.14	-0.31	170	6.7×10^2	1350

^a All couples are reported vs NHE in V; data was obtained at a scan rate of 100 mV/s at 25 °C, reproduced from reference 17.

^b ΔE in mV is calculated as the potential difference between $\text{E}^{\circ}_{\text{Ma}}$ and $\text{E}^{\circ}_{\text{Mb}}$.

^c Comproportionation constant calculated from $\text{K}_c = 10^{16.91\Delta\text{E}}$ for ΔE in V.

^d Free energy of comproportionation calculated according to $\Delta\text{G}_c = \text{RTln}(\text{K}_c)$ in cm^{-1} .

Table 3.22: Redox Couples and Comproportionation Constants as a Function of Solvent for [(pyridine)Ru(NH₃)₄-dicyd-Ru(NH₃)₅][PF₆]₄.^a

Solvent	L ^{0/-}	L ^{-1/2-}	E ^o _{Mb}	E ^o _{Ma}	ΔE ^b	K _c ^c	ΔG _c ^d
NM (2.7)	1.45	1.07	0.40	0.0 2	390	5.8 x 10 ⁶	3120
AN (14.1)	1.34	0.93	0.27	-0.12	390	5.8 x 10 ⁶	3120
AC (17.0)	1.22	0.80	0.20	-0.20	410	1.0 x 10 ⁷	3240
DMSO (29.8)		0.67	0.12	-0.33	450	4.1 x 10 ⁷	3590

^a All couples are reported vs NHE in V; data was obtained at a scan rate of 100 mV/s at 25 °C.

^b ΔE in mV is calculated from potential difference between E^o_{Ma} and E^o_{Mb}.

^c Comproportionation constant calculated from $K_c = 10^{16.91\Delta E}$ for ΔE in V.

^d Free energy of comproportionation calculated according to $\Delta G_c = RT\ln(K_c)$ in cm⁻¹.

Table 3.23: Redox Couples and Compropotionation Constants as a Function of Solvent for [(pyrazine)Ru(NH₃)₄-dicyd-Ru(NH₃)₅][PF₆]₄.^a

Solvent	L ^{0/-}	L ^{-1/2-}	E ^o _{Mb}	E ^o _{Ma}	ΔE ^b	K _c ^c	ΔG _c ^d
NM (2.7)	1.49	1.13	0.45	0.02	430	1.5 x 10 ⁷	3470
AN (14.1)	1.37	0.99	0.37	-0.12	450	4.1 x 10 ⁷	3630
AC (17.0)	1.22	0.84	0.25	-0.21	460	1.1 x 10 ⁸	3830
DMSO (29.8)		0.74	0.20	-0.34	540	2.0 x 10 ⁹	4440

^a All couples are reported vs NHE in V; data was obtained at a scan rate of 100 mV/s at 25 °C.

^b ΔE in mV is calculated from potential difference between E^o_{Ma} and E^o_{Mb}.

^c Comproportionation constant calculated from $K_c = 10^{16.91\Delta E}$ for ΔE in V.

^d Free energy of compropotionation calculated according to $\Delta G_c = RT\ln(K_c)$ in cm⁻¹.

Table 3.24: Redox Couples and Compropotionation Constants as a Function of Solvent for [(bipyridine)Ru(NH₃)₃-dicyd-Ru(NH₃)₅][PF₆]₄.^a

Solvent	L ^{0/-}	L ^{-1/2-}	E ^o _{Mb}	E ^o _{Ma}	ΔE ^b	K _c ^c	ΔG _c ^d
NM (2.7)	1.49	1.15	0.49	0.02	470	4.1 x 10 ⁷	3790
AN (14.1)	1.37	1.00	0.37	-0.12	490	6.0 x 10 ⁷	3830
AC (17.0)	1.28	0.90	0.30	-0.21	510	2.9 x 10 ⁸	4070
DMSO (29.8)		0.77	0.26	-0.34	600	1.4 x 10 ¹⁰	4800

^a All couples are reported vs NHE in V; data was obtained at a scan rate of 100 mV/s at 25 °C.

^b ΔE in mV is calculated from potential difference between E^o_{Ma} and E^o_{Mb}.

^c Comproportionation constant calculated from $K_c = 10^{16.91\Delta E}$ for ΔE in V.

^d Free energy of compropotionation calculated according to $\Delta G_c = RT\ln(K_c)$ in cm⁻¹.

Figure 3.73: Cyclic voltammogram of *trans*-[(pyridine)Ru(NH₃)₄-dicyd-Ru(NH₃)₅][PF₆]₄ in nitromethane.

Figure 3.74: Cyclic voltammogram of *trans*-[(pyridine)Ru(NH₃)₄-dicyd-Ru(NH₃)₅][PF₆]₄ in acetonitrile.

Figure 3.75:

Cyclic voltammogram of *trans*-[(pyridine)Ru(NH₃)₄-dicyd-Ru(NH₃)₅][PF₆]₄ in acetone.

Figure 3.76:

Cyclic voltammogram of *trans*-[(pyridine)Ru(NH₃)₄-dicyd-Ru(NH₃)₅][PF₆]₄ in DMSO.

Figure 3.77: Cyclic voltammogram of *trans*-[(pyrazine)Ru(NH₃)₄-dicyd-Ru(NH₃)₅][PF₆]₄ in nitromethane.

Figure 3.78: Cyclic voltammogram of *trans*-[(pyrazine)Ru(NH₃)₄-dicyd-Ru(NH₃)₅][PF₆]₄ in acetonitrile.

Figure 3.79: Cyclic voltammogram of *trans*-[(pyrazine)Ru(NH₃)₄-dicyd-Ru(NH₃)₅][PF₆]₄ in acetone.

Figure 3.80: Cyclic voltammogram of *trans*-[(pyrazine)Ru(NH₃)₄-dicyd-Ru(NH₃)₅][PF₆]₄ in DMSO. Note the redox couple of pyrazine at -1.70 V.

Figure 3.81:

Cyclic voltammogram of *mer*-[(bipyridine)Ru(NH₃)₃-dicyd-Ru(NH₃)₅][PF₆]₄ in nitromethane.

Figure 3.82:

Cyclic voltammogram of *mer*-[(bipyridine)Ru(NH₃)₃-dicyd-Ru(NH₃)₅][PF₆]₄ in acetonitrile.

Figure 3.83: Cyclic voltammogram of *mer*-[(bipyridine)Ru(NH₃)₃-dicyd-Ru(NH₃)₅][PF₆]₄ in acetone.

Figure 3.84: Cyclic voltammogram of *mer*-[(bipyridine)Ru(NH₃)₃-dicyd-Ru(NH₃)₅][PF₆]₄ in DMSO. Note the redox couple of bipyridine at -1.48 V.

3.2.6 Spectroelectrochemistry

A spectroelectrochemical study of the symmetric dinuclear complexes in the four solvents (nitromethane, acetonitrile, acetone and DMSO) was performed using the OTTLE cell described in Section 2.6.4. Results for the complex $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-dicyd})][\text{PF}_6]_4$ has previously been published¹⁷ and are reported here for comparison. A one-electron reduction of the more electropositive ruthenium center, Ru_b , of the asymmetric dinuclear complex, $\text{Ru}_a(\text{III})\text{-Ru}_b(\text{III})$, results in a steady decrease in the intensity of the LMCT absorption band and a concomitant growth of a NIR absorption band. The new band is assigned to be a metal-to-metal charge transfer (MMCT) transition band (commonly called an intervalence transition (IT) band).^{37,80,81} Re-oxidation of the mixed-valence system resulted in the regeneration of the $\text{Ru}_a(\text{III})\text{-Ru}_b(\text{III})$ dinuclear complex with >95% of the initial intensity. Figures 3.85-3.96 illustrate the electronic absorption spectra during a progressive reduction of the electropositive end of the asymmetric dinuclear complexes under study to the mixed-valence form.

Owing to the fact that LMCT and IT transitions displayed by the asymmetric $\text{Ru}_a(\text{III})\text{-Ru}_b(\text{II})$ dinuclear complexes are overlapping, a Hush model treatment of the IT band properties cannot be performed. A previous analysis of analogous symmetrical systems via the Hush model required parameterization of the IT band,^{16,17} where the IT and LMCT transitions were normally deconvoluted from the band envelope of the mixed-valence complex, by using a non-linear curve-fitting analysis. In this curve-fitting protocol, two main assumptions were made; firstly, the IT transition is described by a single Gaussian band, a condition that is not always observed experimentally,¹⁶ secondly,

the energy and band shape of the $b_1^* \leftarrow b_1$ LMCT transition does not change when one of the Ru(III)-cyanamide chromophores is reduced. While this technique worked exceptionally well for the weakly coupled symmetric system,^{16,17} the discrepancies for fitting the high-energy tail of the band were more prominent for strongly coupled symmetric systems. This is because the technique only allows the low-energy side of the mixed-valence complex to be well modelled and the fitting for the high-energy side gets poorer and becomes progressively worse as the modelled system become more strongly coupled. Even when successfully deconvoluted, the IT band predicts bandwidths for weakly coupled systems using only the Mulliken–Hush theoretical expression. With the CNS Model,²⁴ the determination of the coupling element does not require knowledge of the oscillator strength and of the bandwidths at half-height of the IT band. These parameters being poorly determined in these systems by the curve-fitting protocol, allow a better prediction of the coupling element using only an estimate of the energy of the IT band, as shown in Equations 1.16 and 1.17 in Section 1.2.3.

For the sole purpose of determining the energy of the IT band was the spectroelectrochemical study performed and to a first approximation, the energy of the NIR band can be assumed to be that of the IT band. The Ru_a(III)-Ru_b(II) band was deconvoluted and the low-energy band assigned as the IT band. The IT band data for the mixed-valence complexes are summarized in Table 3.25 and Figures 3.85-3.96. The reduction of these complexes was reversible, as evidenced by the maintenance of isosbestic points and the regeneration of the Ru_a(III)-Ru_b(III) spectra upon oxidation. Further reduction of the Ru_a(III)-Ru_b(II) complex to the Ru_a(II)-Ru_b(II) complex proved irreversible in most cases, with only partial recovery of the absorption spectrum of the

Ru_a(III)-Ru_b(II) complexes after reoxidation. This can be explained to be due to lability of this state to ligand exchange. Nevertheless, it was apparent that the Ru_a(II)-Ru_b(II) complexes do not absorb significantly at wavelengths greater than 600 nm (Figure 3.92).

Table 3.25: Estimated Energy ^a of the IT band, E_{IT}^{est} , of the Asymmetric Complexes from Spectrochemical Measurement^b in Various Solvents.

Complex	Nitromethane	Acetonitrile	Acetone	DMSO
[Ru(NH ₃) ₅ -dicyd-Ru(NH ₃) ₅][PF ₆] ₄ ^c	6980	6890	6750	7500
[(py)Ru(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅][PF ₆] ₄	7600	7550	7550	8300
[(pyz)Ru(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅][PF ₆] ₄	8860	7990	8300	8700
[(bpy)Ru(NH ₃) ₃ -dicyd-Ru(NH ₃) ₅][PF ₆] ₄	7770	8000	8050	8800

^a Data in units of cm⁻¹.

^b Deconvoluted using Peakfit software.

^c Data from reference 16.

Figure 3.85: Spectroelectrochemical data for *trans*-[(pyridine)Ru(NH₃)₄-dicyd-Ru(NH₃)₅][PF₆]₄ in nitromethane, showing reduction of the Ru_a(III)-Ru_b(III) complex to the mixed-valent Ru_a(III)-Ru_b(II) complex.

Figure 3.86: Spectroelectrochemical data for *trans*-[(pyridine)Ru(NH₃)₄-dicyd-Ru(NH₃)₅][PF₆]₄ in acetonitrile, showing reduction of the Ru_a(III)-Ru_b(III) complex to the mixed-valent Ru_a(III)-Ru_b(II) complex.

Figure 3.87: Spectroelectrochemical data for *trans*-[(pyridine)Ru(NH₃)₄-dicyd-Ru(NH₃)₅][PF₆]₄ in acetone, showing reduction of the Ru_a(III)-Ru_b(III) complex to the mixed-valent Ru_a(III)-Ru_b(II) complex.

Figure 3.88: Spectroelectrochemical data for *trans*-[(pyridine)Ru(NH₃)₄-dicyd-Ru(NH₃)₅][PF₆]₄ in DMSO, showing reduction of the Ru_a(III)-Ru_b(III) complex to the mixed-valent Ru_a(III)-Ru_b(II) complex.

Figure 3.89: Spectroelectrochemical data for *trans*-[(pyrazine)Ru(NH₃)₄-dicyd-Ru(NH₃)₅][PF₆]₄ in nitromethane, showing reduction of the Ru_a(III)-Ru_b(III) complex to the mixed-valent Ru_a(III)-Ru_b(II) complex.

Figure 3.90: Spectroelectrochemical data for *trans*-[(pyrazine)Ru(NH₃)₄-dicyd-Ru(NH₃)₅][PF₆]₄ in acetonitrile, showing reduction of the Ru_a(III)-Ru_b(III) complex to the mixed-valent Ru_a(III)-Ru_b(II) complex.

Figure 3.91: Spectroelectrochemical data for *trans*-[(pyrazine)Ru(NH₃)₄-dicyd-Ru(NH₃)₅][PF₆]₄ in acetone, showing reduction of the Ru_a(III)-Ru_b(III) complex to the mixed-valent Ru_a(III)-Ru_b(II) complex.

Figure 3.92: Spectroelectrochemical data for *trans*-[(pyrazine)Ru(NH₃)₄-dicyd-Ru(NH₃)₅][PF₆]₄ in DMSO, showing reduction of the Ru_a(III)-Ru_b(III) complex to the mixed-valent Ru_a(III)-Ru_b(II) complex and the spectrum of the fully reduced Ru(II)-Ru(II) complex.

Figure 3.93: Spectroelectrochemical data for *mer*-[(bipyridine)Ru(NH₃)₃-dicyd-Ru(NH₃)₅][PF₆]₄ in nitromethane, showing reduction of the Ru_a(III)-Ru_b(III) complex to the mixed-valent Ru_a(III)-Ru_b(II) complex.

Figure 3.94: Spectroelectrochemical data for *mer*-[(bipyridine)Ru(NH₃)₃-dicyd-Ru(NH₃)₅][PF₆]₄ in acetonitrile, showing reduction of the Ru_a(III)-Ru_b(III) complex to the mixed-valent Ru_a(III)-Ru_b(II) complex.

Figure 3.95: Spectroelectrochemical data for *mer*-[(bipyridine)Ru(NH₃)₃-dicyd-Ru(NH₃)₅][PF₆]₄ in acetone, showing reduction of the Ru_a(III)-Ru_b(III) complex to the mixed-valent Ru_a(III)-Ru_b(II) complex.

Figure 3.96: Spectroelectrochemical data for *mer*-[(bipyridine)Ru(NH₃)₃-dicyd-Ru(NH₃)₅][PF₆]₄ in DMSO, showing reduction of the Ru_a(III)-Ru_b(III) complex to the mixed-valent Ru_a(III)-Ru_b(II) complex.

3.2.7 Solution Magnetic Susceptibility Measurements

Quantitative determinations of paramagnetism were performed via Evans method in a range of deuterated solvents that included nitromethane, acetonitrile, acetone and DMSO. The experiments were performed on a AMX 400 MHz FT-NMR spectrometer in which a coaxial capillary containing only the solvent and reference (TMS) was inserted into the sample tube containing the reference also. If the sample is paramagnetic, there will be a shift of the reference peak for the reference in the sample, but not for the reference in the capillary tube. Two reference peaks thus seen have a splitting, Δf , between them dependent upon the level of paramagnetism of the sample in the solvent.

This study examines the outer-sphere (solvent variation) dependency of the magnetic susceptibility, and hence the effective moment per Ru(III) ion for the asymmetric Ru_a(III)-Ru_b(III) dinuclear complexes in the range of deuterated solvents. In addition to this, the inner-sphere (asymmetric variation of the σ -donor strength of the auxiliary ligand) dependence of the magnetic susceptibility and the effective moment in a given solvent will also be examined. These results are important as they allow an examination of both the outer- and inner-sphere dependency of antiferromagnetic metal-metal coupling of the asymmetric complexes. Results with the symmetric pentaammine Ru(III)-Ru(III) dinuclear complex previously published^{37,47} are included to facilitate comparisons.

The induced isotropic shifts Δf of the TMS ^1H resonance measured for the complexes allow the net molar susceptibility χ_M (at 300 K) to be calculated using Equation 1.32. The corrected molar susceptibility χ'_M can be calculated using Equation 1.33. The effective moment per Ru(III) (μ_{eff}) and the number of unpaired electrons n per

Ru(III) can be calculated assuming a spin-only mode using Equation 1.35 and 1.36 respectively.

Tables 3.26-3.30 summarize the Δf , χ'_M , $\mu_{\text{eff}}/\text{Ru(III)}$ and $n/\text{Ru(III)}$ values obtained. In all cases, the lowest levels of paramagnetism were obtained in nitromethane. Near diamagnetic behaviour in this solvent at room temperature can also be shown on the observation of the ^1H NMR spectra, Figures 3.97-3.110. Indeed, all of the complexes displayed varying levels of paramagnetism in nitromethane, as reflected in their ^1H NMR spectra.

Table 3.26: Magnetic Data of $[\text{Ru}(\text{NH}_3)_5\text{-dicyd-Ru}(\text{NH}_3)_5][\text{PF}_6]_4$ in Various Deuterated Solvents ^a

Solvents (DN)		$\Delta f/\text{Hz}$ ^b	μ_{eff} ($\mu_{\text{B}}/\text{Ru}^{3+}$) ^c	n/Ru^{3+} ^d
NM	(2.7)	2.50	0.64	0.19
AN	(14.1)	9.20	0.79	0.28
AC	(17.0)	13.71	0.88	0.33
DMSO	(29.8)	37.80	1.25	0.60
D ₂ O	(18)	49.07	1.35	0.68

^a The complex concentration was 11 mM, except in nitromethane where it was 1.8 mM, reproduced from reference 37.

^b Isotropic shift (in Hz) of the TMS signal from Evans method.

^c Spin-only effective magnetic moment (in μ_{B}), calculated from $\mu_{\text{eff}} = 2.83(\chi_{\text{M}}T)^{1/2}$.

^d Number of unpaired electrons, calculated from $\mu_{\text{eff}} = [n(n+2)]^{1/2}$.

Table 3.27: Magnetic Data of *Trans*-[(pyridine)Ru(NH₃)₄-dicyd-Ru(NH₃)₅][PF₆]₄ in Various Deuterated Solvents.

Solvents (DN)	Conc. (mg/mL)	$\Delta f/\text{Hz}$ ^a	χ'_m ^b	μ_{eff} (μ_B/Ru^{3+}) ^c	n/Ru^{3+} ^d
NM (2.7)	8.80	1.06	6.59×10^{-4}	0.63	0.18
AN (14.1)	14.42	5.54	8.44×10^{-4}	0.71	0.23
AC (17.0)	13.00	5.64	8.78×10^{-4}	0.72	0.23
DMSO (29.8)	13.01	20.9	1.70×10^{-3}	1.01	0.42
D ₂ O (18)	2.30	7.72	2.92×10^{-3}	1.32	0.66

^a Isotropic shift (in Hz) of of TMS signal from Evans method.

^b $\chi'_M = \chi_m - \chi_d$.

^c Spin-only effective magnetic moment (in μ_B), calculated from $\mu_{\text{eff}} = 2.83(\chi'_M T)^{1/2}$.

^d Number of unpaired electrons, calculated form $\mu_{\text{eff}} = [n(n+2)]^{1/2}$.

Table 3.28: Magnetic Data of *Trans*-[(pyrazine)Ru(NH₃)₄-dicyd-Ru(NH₃)₅][PF₆]₄ in Various Deuterated Solvents

Solvents (DN)	Conc. (mg/mL)	$\Delta f/\text{Hz}$ ^a	χ'_m ^b	μ_{eff} (μ_B/Ru^{3+}) ^c	n/Ru^{3+} ^d
NM (2.7)	11.20	0.907	6.29×10^{-4}	0.61	0.17
AC (17.0)	10.60	2.31	7.25×10^{-4}	0.66	0.20
DMSO (29.8)	11.46	19.2	1.74×10^{-3}	1.02	0.43
D ₂ O (18)	3.20	2.67	1.16×10^{-3}	0.83	0.30

^a Isotropic shift (in Hz) of TMS signal from Evans method.

^b $\chi'_M = \chi_m - \chi_d$.

^c Spin-only effective magnetic moment (in μ_B), calculated from $\mu_{\text{eff}} = 2.83(\chi'_M T)^{1/2}$.

^d Number of unpaired electrons, calculated from $\mu_{\text{eff}} = [n(n+2)]^{1/2}$.

Table 3.29: Magnetic Data of *Mer*-[(bipyridine)Ru(NH₃)₃-dicyd-Ru(NH₃)₅][PF₆]₄ in Various Deuterated Solvents

Solvents (DN)	Conc. (mg/mL)	$\Delta f/\text{Hz}$ ^a	χ'_m ^b	μ_{eff} (μ_B/Ru^{3+}) ^c	n/Ru^{3+} ^d
NM (2.7)	14.8	1.38	6.74×10^{-4}	0.65	0.06
AC (17.0)	11.5	2.35	7.55×10^{-4}	0.67	0.20
DMSO (29.8)	10.3	11.3	1.41×10^{-3}	0.92	0.36
D ₂ O (18)	4.0	3.24	1.20×10^{-3}	0.84	0.31

^a Isotropic shift (in Hz) of TMS signal from Evans method.

^b $\chi'_M = \chi_m - \chi_d$.

^c Spin-only effective magnetic moment (in μ_B), calculated from $\mu_{\text{eff}} = 2.83(\chi'_M T)^{1/2}$.

^d Number of unpaired electrons, calculated from $\mu_{\text{eff}} = [n(n+2)]^{1/2}$.

Table 3.30: Effective Magnetic Moments ^a and Estimated Antiferromagnetic Exchange constants ^b for Symmetric and Asymmetric Complexes in Various Deuterated Solvents

Complexes	NM		AC		DMSO		D ₂ O	
	μ_{eff}	$-2J_{\text{est}}$	μ_{eff}	$-2J_{\text{est}}$	μ_{eff}	$-2J_{\text{est}}$	μ_{eff}	$-2J_{\text{est}}$
$[(\text{NH}_3)_5\text{Ru}^{\text{III}}\text{-dicyd-Ru}^{\text{III}}(\text{NH}_3)_5][\text{PF}_6]_4$ ^c	0.64	720	0.88	570	1.25	380	1.35	330
<i>trans</i> -[py(NH ₃) ₄ Ru ^{III} -dicyd-Ru ^{III} (NH ₃) ₅][PF ₆] ₄	0.63	730	0.72	670	1.01	500	1.32	350
<i>trans</i> -[pyz(NH ₃) ₄ Ru ^{III} -dicyd-Ru ^{III} (NH ₃) ₅][PF ₆] ₄	0.61	740	0.65	710	1.02	500	0.81	600
<i>mer</i> -[bpy(NH ₃) ₃ Ru ^{III} -dicyd-Ru ^{III} (NH ₃) ₅][PF ₆] ₄	0.63	730	0.67	700	0.91	550	0.84	590

^a Per Ru^{III} ion in Bohr magnetons.

^b In cm⁻¹, calculated according to Equation 1.32. Equivalent to ΔG_{ex} .

^c Data from reference 37.

The Evans method experiments^{51,52} suggest very strong antiferromagnetic coupling for dicyd²⁻-bridged complexes. These results imply diamagnetism in the least donating solvent (NM). The significance of various chemical shifts will not be covered, since they do not pertain to the main thrust of this thesis and it is also not easy to deconvolute contact from pseudocontact shifts. It is believed that the nitromethane ¹H NMR spectrum of [bpy(NH₃)₅Ru^{III}-dicyd-Ru^{III}(NH₃)₅][PF₆]₄, showing eight distinct resonances for the protons of bipyridine bound to ruthenium(III) yet effectively in an apparent diamagnetic environment, is unique in the literature. The use of ‘apparent’ to describe the diamagnetism is necessary, since the Evans methods experiments only show the absence of paramagnetism to a certain threshold, and not the presence of diamagnetism. That the complexes are diamagnetic, however, is supported by their 1-D and 2-D NMR spectra (Figures 3.97, 3.101, and 3.106).

3.2.8 ^1H -NMR Spectroscopy of the Asymmetric Complexes

Magnetic resonance experiments were run on the asymmetric complexes in deuterated nitromethane, acetonitrile, acetone and DMSO. Note that in the case of the symmetric dinuclear pentammine, the ^1H -NMR spectra in these deuterated solvents have previously been reported^{37,47} The COSY 2-D technique in nitromethane was used on these complexes to elucidate through-bond coupling. Through-space (T1 relaxation) interactions^{16,82} for the asymmetric [(bpy)Ru(NH₃)₃-dicyd-Ru(NH₃)₅][PF₆]₄ complex was examined via the NOESY 2-D technique in deuterated nitromethane. Solvents of recrystallization are noticeable in some complexes and are highlighted accordingly. The 1-D spectra were obtained over the chemical shift range of +250 ppm to -250 ppm in order to detect any paramagnetically shifted peaks. A summary of the ^1H -NMR chemical shift data for each of the asymmetric Ru_a(III)-Ru_b(III) dinuclear complexes in each of the deuterated solvents of this study is given in Tables 3.31-3.34. In this study, on the basis of comparison with the spectrum of the least paramagnetic dinuclear complex (the spectrum of asymmetric complexes in nitromethane), the integration ratio and the rough expectation of shift, permitted the assignment of all peaks.

Figure 3.97: 400 MHz ^1H NMR spectrum of *trans*-[pyRu(NH₃)₄-dicyd-Ru(NH₃)₅][PF₆]₄ in nitromethane- d_3 (at 300 K).

Figure 3.98: 400 MHz ^1H NMR spectrum of *trans*-[pyRu(NH₃)₄-dicyd-Ru(NH₃)₅][PF₆]₄ in nitromethane- d_3 (at 300 K), showing the pyridine and dicyd²⁻ hydrogen resonances.

Figure 3.99 : 400 MHz COSY of *trans*-[pyRu(NH₃)₄-dicyd-Ru(NH₃)₅][PF₆]₄ in nitromethane-d₃ (at 300 K), showing the pyridine and dicyd²⁻ hydrogen resonances.

Figure 3.100: 400 MHz ^1H NMR spectrum of *trans*-[pyRu(NH₃)₄-dicyd-Ru(NH₃)₅][PF₆]₄ in acetone-d₆ (at 300 K), showing the pyridine hydrogen resonances.

Figure 3.101: 400 MHz ^1H NMR spectrum of *trans*-[pyzRu(NH₃)₄-dicyd-Ru(NH₃)₅][PF₆]₄ in nitromethane-d₃ (at 300 K), showing the pyrazine hydrogen resonances.

Figure 3.102: 400 MHz ^1H -NMR spectrum of *trans*-[pyzRu(NH₃)₄-dicyd-Ru(NH₃)₅][PF₆]₄ in nitromethane-d₃ (at 300 K), showing the pyridine and dicyd²⁻ hydrogen resonances.

Figure 3.103

400 MHz ^1H -NMR spectrum of *trans*-[pyzRu(NH₃)₄-dicyd-Ru(NH₃)₅][PF₆]₄ in nitromethane- d_3 (at 300 K), showing the pyrazine hydrogen resonances.

Figure 3.104: 400 MHz ^1H -NMR spectrum of *trans*-[pyzRu(NH₃)₄-dicyd-Ru(NH₃)₅][PF₆]₄ in acetone- d_6 (at 300 K), showing the pyrazine hydrogen resonances.

Figure 3.105: 400 MHz ^1H -NMR spectrum of *trans*-[pyzRu(NH₃)₄-dicyd-Ru(NH₃)₅][PF₆]₄ in DMSO- d_6 (at 300 K), showing the pyrazine hydrogen resonances.

Figure 3.106: 400 MHz ^1H -NMR spectrum of *trans*-[bpyRu(NH₃)₃-dicyd-Ru(NH₃)₅][PF₆]₄ in nitromethane- d_3 (at 300 K), showing the hydrogen resonances.

Figure 3.107: 400 MHz ^1H -NMR spectrum of *mer*-[bpyRu(NH₃)₃-dicyd-Ru(NH₃)₅][PF₆]₄ in nitromethane- d_3 (at 300 K) showing the hydrogen resonances.

Figure 3.108: 400 MHz COSY (A) and NOESY (B) of *mer*-[bpyRu(NH₃)₃-dicyd-Ru(NH₃)₅][PF₆]₄ in nitromethane-*d*₃ (at 300 K), showing the bipyridine and dicyd²⁻ hydrogen resonances.

Figure 3.109: 400 MHz ^1H -NMR spectrum of *mer*-[bpyRu(NH₃)₃-dicyd-Ru(NH₃)₅][PF₆]₄ in acetone- d_6 (at 300 K), showing the hydrogen resonances.

Figure 3.110: 400 MHz ^1H -NMR spectrum of *mer*-[bpyRu(NH₃)₃-dicyd-Ru(NH₃)₅][PF₆]₄ in DMSO- d_6 (at 300 K), showing the hydrogen resonances.

Table 3.31: Solvent –Dependent ^1H -NMR Chemical Shift Data of $[\text{Ru}(\text{NH}_3)_5\text{-dicyd-Ru}(\text{NH}_3)_5][\text{PF}_6]_4$.^a

Solvent(DN)	Trans-NH ₃ ^b	Cis-NH ₃ ^b	Phenyl ^b
NM (2.7)	18.24	4.90	6.12
AN (14.0)	50.53	11.74	1.72
AC (17.0)	76.49	18.12	-1.18
DMSO (29.8)	201.72	52.18	-8.99

^a All chemical shifts gave integrations consistent with the the assignment; the complex concentrations in mg/mL are indicated in Table 3.26.

^b Values in ppm are referenced to TMS (0.00 ppm), reproduced from Naklicki, M.

Table 3.32: Solvent –Dependent ^1H -NMR Chemical Shift Data of *Trans*-[(pyridine)Ru(NH₃)₄-dicyd-Ru(NH₃)₅][PF₆]₄.^a

Solvent(DN)	Trans-NH ₃	Cis-NH ₃ ^b		Phenyl ^b		pyridine ^b		
		A ¹ _{cs.}	A ² _{cs.}			o	m	p
NM (2.7)	11.25	3.62	2.97	8.18	6.92	8.55	7.96	8.09
AC (17.0)	38.64	9.88	7.85	4.77	3.61	9.14	7.01	6.60
DMSO (29.8)	121.8	41.58		-4.41	-14.7	14.6	-2.53	-1.44

^a All chemical shifts gave integrations consistent with the the assignment; the complex concentrations in mg/mL are indicated in Table 3.27.

^b Values in ppm are referenced to TMS (0.00 ppm)

Table 3.33: Solvent –Dependent ^1H -NMR Chemical Shift Data of *Trans*-[(pyrazine)Ru(NH₃)₄-dicyd-Ru(NH₃)₅][PF₆]₄.^a

Solvent(DN)	Trans-NH ₃	Cis-NH ₃ ^b		phenyl ^b		Pyrazine ^b	
		A ¹ _{cs.}	A ² _{cs.}			o	m
NM (2.7)	9.83	3.43	2.49	9.06	7.01	8.73	
AC (17.0)	21.72	6.81	4.07	7.70	6.36	9.04	8.62
DMSO (29.8)	114.62	32.26	26.40	-13.0		12.86	

^a All chemical shifts gave integrations consistent with the the assignment; the complex concentrations in mg/mL are indicated in Table 3.28.

^b Values in ppm are referenced to TMS (0.00 ppm)

Table 3.34: Solvent –Dependent ^1H -NMR Chemical Shift Data of *mer*-[(bipyridine)Ru(NH₃)₃-dicyd-Ru(NH₃)₅][PF₆]₄.^a

Solvent(DN)	Trans-NH ₃ ^b	Cis-NH ₃ ^b	phenyl ^b	
NM (2.7)	9.80	3.41	9.11	7.06
AC (17.0)	19.90	4.26	8.4	
DMSO (29.8)	88.15	26.28	4.1	

^a All chemical shifts gave integrations consistent with the the assignment; the complex concentrations in mg/mL are indicated in Table 3.29.

^b Values in ppm are referenced to TMS (0.00 ppm)

Unambiguous assignment of the pyridine protons was possible for the asymmetric $[\text{pyRu}(\text{NH}_3)_4\text{-dicyd-Ru}(\text{NH}_3)_5][\text{PF}_6]_4$ complex in nitromethane. This became a basis for the assignments in other solvents. The chemical shift data for all the 1-D experiments have been placed in Tables 3.31-3.34 and the spectra themselves are presented in Figures 3.97-3.100. The COSY 2-D technique was also used on this complex to elucidate through-bond coupling (Figures 3.99).

An examination of the protons on the pyridine ring show a well separated ABC pattern with intensity ratios of 2 (doublet, H_3), 2 (triplet, H_4) and 1 (triplet, H_5). The phenyl ring protons appear as 2 doublets, H_1 and H_2 and their assignment is made possible by their similar splitting and intensity. The pyridine and phenyl ring hydrogens are also unambiguously assignable in the nitromethane spectrum in which the COSY spectrum indicates coupling of the protons. Figure 3.97 provides the numbering scheme for the pyridine and phenyl ring hydrogens.

The *trans* ($\text{A}_{\text{tr.}}$) and *cis* ($\text{A}_{\text{cs.}}$) amines were assigned on basis of their relative 1:4 integration ratios and the absolute integration ratio of 3:2 between the *trans*-amine and the phenyl protons. A downfield shift of the ammine proton signals in acetone and DMSO is observed as the magnetic moment in the dinuclear complex increases. An upfield shift of the phenyl resonances in the same solvents is observed and this is also because of increased paramagnetism.

In the case of $[\text{pyzRu}(\text{NH}_3)_4\text{-dicyd-Ru}(\text{NH}_3)_5][\text{PF}_6]_4$, an unambiguous assignment of the pyrazine and phenyl protons was possible in nitromethane. Figure 3.101 provides the numbering scheme for the pyrazine and phenyl ring hydrogens. The hydrogens were readily assigned from the coupling patterns in the COSY spectrum (Figures 3.103). The

pyrazine signals were weakly split, as is typical, though expected as a result of asymmetry! The phenyl ring protons appear as two doublets, H₁ and H₂ and their assignment is made possible by their similar splitting and intensity.

The assignment of the *trans* (A_{tr.}) and *cis* (A_{cs.}) amines was made on basis of their 1:4 relative integration ratio, and 3:2 absolute integration ratio between the *trans* and ammine peak and phenyl hydrogen peaks. The assignment for this complex in acetone were made by direct analogy with the nitromethane results with the same complex. The pyrazine peaks were split in acetone now, as deduced from their integration. However each peak was not a doublet, as expected and as seen with the phenyl protons. As expected, the ammine peaks were shifted downfield due to increased paramagnetism of the complex in acetone. The phenyl peaks were shifted upfield, as were the pyrazine signals. In DMSO, the ammine peaks were shifted further downfield, as there was an increased paramagnetism in this solvent. A summary of the ¹H-NMR chemical shift data in each of the deuterated solvents of this study is given in Table 3.33.

Table 3.34 shows the chemical shift data for all the 1-D experiments of the asymmetric [bpyRu(NH₃)₃-dicyd-Ru(NH₃)₅][PF₆]₄ complex. The COSY and NOESY results for the aromatic region in nitromethane is presented in Figures 3.106-3.110. Assignments of the bipyridine signals was possible for the complex in nitromethane. Figure 3.106 provides the numbering scheme for the ring hydrogens, and Figures 3.107 shows well separated resonances of the eight bpy hydrogens. The expected shifting of peaks is diminished, with the 3 and 3' and 6 and 6' protons being doublets and the 4 and 4' and 5 and 5' protons being pseudo-triplets. From Figure 3.108, strong through-space interactions of the 3 and 3' protons are apparent with the NOESY spectrum and provides

a starting point from which the remainder of the signals may be readily assigned from the coupling patterns in the COSY spectrum. The NOESY spectrum also indicated a through-space interaction between the H at the 6-position and the equatorial ammine. Differentiation of the 6 and 6' hydrogens allows each proton of bipyridine to be assigned not only to a position on the ring, but to a specific ring.

The acetone spectrum of the bipyridine complex (Figure 3.109) is similar to that in nitromethane. The splittings of many peaks are now no longer resolved. There is no splitting of peak 6 and peak 3 has little splitting also. Assignments were made by analogy with the nitromethane spectrum. In DMSO, there is increased shielding as the system becomes less strongly coupled. The assignment of peaks in this solvent are subject to error, as the possible reduction of the complex by the solvent may introduce a trace of paramagnetism to the experiment.

In all cases, the assignments of the *trans* ($A_{tr.}$), *cis* ($A_{cs.}$), axial ($A_{ax.}$) and equatorial ($A_{eq.}$) amines was made on the basis of their 1:1:2:1 relative integration ratios, and the 3:1 absolute integration ratio between the single equatorial ammine peak and the bipyridine hydrogen peaks. Note that this did not work as expected in acetone and DMSO. The phenyl group hydrogens were unambiguously assignable in the nitromethane spectrum in which the COSY spectrum indicated coupling of protons. The assignment was also made on the basis of integration in nitromethane (through there was overlap of the phenyl and 6' protons).

DISCUSSION

CHAPTER 4

4.1. MONONUCLEAR COMPLEXES

4.1.1 Electronic Absorption Spectroscopy

Solvent and π -acid Ligand Effects on Charge Transfer Energies and Coupling Elements

The dependence of charge-transfer energy on the nature of the solvent is a well known phenomenon.^{40,83} Figure 4.1 and Tables 3.2-3.14 reveal the dependence of the electronic LMCT transition energy (E_{LMCT}) on the solvent donor strength. The data give clear evidence that specific solvent-ammine interactions play a major role in accounting for the E_{LMCT} behaviour of the ruthenium(III)-phenylcyanamide complexes. Careful inspection of this data also reveals that the sensitivity of the LMCT energy increases as the number of ammine ligands in the inner coordination sphere increases.

E_{LMCT} shifts to higher energies as the solvent donor strength is increased and both bands assigned to LMCT transitions are indeed solvent-sensitive. For the ruthenium(III) ion, as the solvent donor strength increases, the electron density on the metal centre increases thus raising the energy of the πd orbitals. This increases the energy gap between the metal πd and the ligand π -HOMO orbitals, as shown in Figure 3.5.

Replacing an ammine ligand (a strong σ -donor) with a π -acid ligand (a weaker σ -donor) stabilizes the ruthenium(III) πd orbitals, relative to the nonbonding orbitals of the phenylcyanamide ligand. This decreases the LMCT energy, and thus, the weaker the σ -donor ligand, the lower the E_{LMCT} (Figure 3.5B).

Figure 4.1: Plot of $b_1^* \leftarrow b_1$ LMCT transition energy versus solvent donor number for $[L_nRu^{III}(NH_3)_{5-n}-2,3Cl_2-pcyd]^m+$ complexes where $n = 1$ for ammine (solid circles), 3,5-Me₂pyridine (solid squares), pyridine (open squares), 2,6-Me₂pyrazine (solid diamonds), pyrazine (open diamonds), methylpyrazinium (solid rectangles) and $n = 2$ for 2,2'-bipyridine (solid triangles) *trans* to phenylcyanamide moiety. $m = 2$ for all complexes except the methylpyrazinium-bound one, where $m = 3$. The data are from Tables 3.2-3.14.

The same argument used to understand the solvent dependence of the ruthenium(III) LMCT energies can be applied to the ruthenium(II) MLCT cases. The ground-state spectra of mononuclear ruthenium(II) complexes are dominated by an intense, visible MLCT band whose energy is sensitive to both the solvent and the nature of the π -acid ligand *trans* to the phenylcyanamide ligand (Figure 4.2).

Figure 4.2: Plot of $\pi^* \leftarrow d\pi$ MLCT energy versus solvent donor number for $[L_nRu^{II}(NH_3)_{5-n}-2,3Cl_2-pcyd]^{m+}$ complexes where $n = 1$ for 3,5-Me₂pyridine (solid squares), pyridine (open squares), 2,6-Me₂pyrazine (solid diamonds), pyrazine (open diamonds), methylpyrazinium (solid rectangles) and $n = 2$ for 2,2'-bipyridine (solid triangles) *trans* to the phenylcyanamide moiety. $m = 1$ for all complexes, except for the methylpyrazinium-bound one, where $m = 2$. The data are from Tables 3.2-3.14.

The energy of the MLCTband (E_{MLCT}) decreases as the donor ability of the solvent increases. This is opposite the trend seen for the LMCT transition energy (Figure 4.1), where the energy of the optical transition increases with the donor ability of the solvent. Using a familiar argument, the electron-deficient hydrogens on the amines can bind to the electron-rich solvent functionalities, and this leads to an increase of electron density at the ruthenium(II) centre. This destabilizes the πd orbitals relative to the π^* orbitals of the π -acid ligand, and thus reduces the energy gap progressively as the solvent donor strength increases, as shown in Figure 4.2 above.

However, for the *trans*-[(mepyz)Ru^{II}(NH₃)₄(2,3Cl₂-pcyd)]²⁺ complex, the variations of (E_{MLCT}) versus solvent donor strength is not similar. The trend shows a slight increase with donor number, similar to the effect on LMCT energies in the ruthenium(III) complexes where. This can be explained by noting that methylpyrazinium cation bound to ruthenium(II) is a very strong π -acceptor ligand. In a series of mononuclear complexes studied by Wishart and Taube,⁸⁴ the length of the ruthenium(II)-N(methylpyrazinium) bond is 1.950 Å. By way of comparison, the Ru-N(pyrazine) distance was found to be 2.006 Å in [(pyz)Ru^{II}(NH₃)₅]²⁺ and Ru-N(isonicotinamide) distance was 2.072 Å in [(isn)₂Ru^{II}(NH₃)₄]²⁺. The shorter bondlength is due to strong back-bonding interactions, whence the electron density is pulled toward the ligand, making ruthenium(II) very electropositive.

An interaction between the ruthenium(II)-methylpyrazinium π -bond and NH₃ is suggested to occur by the mechanism shown in Scheme 4.1 below. In the yz plane, electron density associated with occupied metal πd orbitals of the *trans*-[(mepyz)Ru^{II}(NH₃)₄(2,3Cl₂-pcyd)]²⁺ complex can interact in a π fashion with the NH₃ sp² hybridized σ orbital (which is involved in σ -bonding with a H 1s orbital) via a hyperconjugation mechanism. This interaction can set up a three-center π bonding network in the yz plane, in which the ruthenium(II)-mepyz π bond polarizes the ammine electron density toward itself.

Scheme 4.1: Interaction between ruthenium(II)-methylpyrazinium π -bond and NH_3 .

Because of a high effective nuclear charge and more acidic NH_3 groups, this effect increases as solvent donor number increases and thus the MLCT energy dependence on solvent shows an optical transition energy that increases with the donor ability of the solvent, very much like in ruthenium(III) complexes.

For this complex, the energy difference between πd and the ligand π^* orbitals is smaller, compared to that in the other mononuclear complexes and the ensuing orbital mixing is greater. As a result of the expected stronger π -interactions, the charge-transfer character of these transitions is greatly reduced and this is reflected in the solvent insensitivity of the band, compared to that in the other complexes (Figure 4.2).

For all ruthenium(II) mononuclear complexes, the MLCT transition was incrementally shifted to lower energy as the nitrogen heterocycles became better π -acceptors (poorer σ -donors), compared to the ammine ligand. The decrease in MLCT transition energy as the ligand was varied from 3,5-dimethylpyridine to the strongest π -acceptor, methylpyrazinium, is an indication of the acceptor ability of the nitrogen heterocycle and their influence on the ruthenium(II) ion stability. This has been

comprehensively quantified for many ligands by Levers' ligand electrochemical series,^{40,83} (Figure 4.3).

Figure 4.3: MO scheme showing the MLCT transitions in mononuclear complexes under study.

Observation of the spectra of the mononuclear complexes shows that the MLCT chromophore for the 2,2'-bipyridine-containing mononuclear complex is more complicated than that of the other ruthenium(II) complexes. In the case of *mer*-[(bpy)Ru^{II}(NH₃)₄(2,3Cl₂-pcyd)]⁺, two bands are observed which are assigned as two MLCT transitions. The broad absorption band centered at 372-392 nm was thought to be ligand-field in origin. However, the intensity, solvent dependence and energy of the absorption suggest a more accurate assignment may be as a metal-to-ligand charge transfer transition. Magnuson and Taube have noted and interpreted the occurrence of two low-energy bands for [Os(NH₃)₄Cl(pyzH)]⁺.⁸⁵ They proposed that two transitions originating from the π 'bonding' orbitals and 'nonbonding' orbitals were being observed.

Orbital diagrams for ruthenium(II) complexes of this kind are given in Figure 3.6, whereby the interactions between ruthenium(II) πd and ligands' π^* orbitals result in splitting of the πd orbitals. For weak π -acids, the ground-state HOMO is viewed as largely metal-centred, whereas for the stronger π -accepting 2,2'-bipyridine ligand, the interactions are such that much stronger π -backbonding enhances greater ruthenium-mixing, i.e. the energy gap between π^* and πd non-bonding electrons is smaller. Charge-transfer transitions from any of the πd set to π^* orbitals are allowed, and two transitions are expected (assigned as ν_1 and ν_2) when a strong π -acceptor ligand is bound to ruthenium(II). This reflects a higher extent of π -back bonding in the 2,2'-bipyridine-containing complex, compared to a weaker π -acceptor, pyridine-containing complex. Within this model, the high-energy band arises through excitation from a π -bonding orbital and the lower-energy band through excitation from a non-bonding orbital. MLCT assignments for these bands are suggested by their shape and their solvent sensitivity and, as is generally found in similar complexes, the band shifts to lower energy on going from weak to strong donor solvents. These observations are consistent with the ground-state orbital diagram shown in Figure 3.6 and with the interpretation by Magnuson and Taube.

One of the aims of this thesis is to determine the metal-metal coupling in asymmetric dinuclear complexes. For a series of similar transition-metal dinuclear complexes, the energies of the charge transfer transitions are not expected to vary appreciably and the largest influence on metal-metal coupling is the metal-ligand and/or ligand-metal coupling element, $h_{d\pi}$. These values may be determined from experimental charge transfer band properties using Equation 1.15, where the expression is assumed to be applicable to weakly coupled mixed-valence systems. Creutz, Newton and Sutin

(CNS) have shown²⁴ that for a metal-ligand charge transfer transition in strongly coupled systems, this equation is exact in the two-state model, provided overlap can be neglected and the charge transfer transition is polarized along donor-acceptor axis.

The cyanamide group is coordinated to ruthenium(III) via the nitrile nitrogen and when the two lone pairs of non-bonding electrons of the anion interact with the π -symmetric d orbitals on ruthenium(III), they give rise to two LMCT transitions in the visible region as has been shown previously. The low-energy LMCT transition band ($b_1^* \leftarrow b_1$) is completely separated from the other absorption band and this allows for a reasonable experimental determination of the band's oscillator strength, using the expression, $f = (4.61 \times 10^{-9}) \epsilon_{\max} \Delta\nu_{1/2}$, where the oscillator strength f can be determined experimentally by assuming a Gaussian band shape according to this equation, $\epsilon_{\max}$ is the extinction coefficient at maximum band wavelength and $\Delta\nu_{1/2}$ is the bandwidth at half $\epsilon_{\max}$.

For the ruthenium(III) ammine complexes of the phenylcyanamide ligand, a plot of $b_1^* \leftarrow b_1$ oscillator strength versus the energy of the LMCT band shows a largely negative correlation as seen in Figure 4.4. Oscillator strengths can theoretically be calculated by using Equation 4.1.³⁹

$$f = (1.085 \times 10^{11}) G \nu M^2 \dots\dots\dots 4.1$$

where G refers to the degree of degeneracy of the states concerned. For these complexes, the $b_1^* \leftarrow b_1$ transition is unidimensional and G is taken to be 1, where ν is the energy of charge transfer (in cm^{-1}) at $\epsilon_{\max}$, and M is the transition moment for the dielectric dipole-allowed transitions. This equation predicts that the oscillator strength should increase

with increasing LMCT transition energy. Figure 4.4 shows a plot of oscillator strength versus the energy of this transition for the complexes of this study, as a function of solvent.

Figure 4.4: Plot of oscillator strength versus LMCT transition energy as a function of solvent for $[L_nRu^{III}(NH_3)_{5-n}-2,3Cl_2-pcyd]^m+$ complexes where $n = 1$ for 3,5-Me₂pyridine (solid squares), pyridine (open squares), 2,6-Me₂pyrazine (solid diamonds), pyrazine (open diamonds), methylpyrazinium (solid rectangles) and $n = 2$ for 2,2'-bipyridine (solid triangles) *trans* ligands. $m = 2$ for all complexes except the methylpyrazinium-bound one where $m = 3$ Data from Tables 3.2-3.14.

For all the mononuclear complexes, except $[(mepyz)Ru^{III}(NH_3)_4-2,3Cl_2-pcyd]^{2+}$, the trend in oscillator strength does not follow the expected dependence on ν , the energy of transition according to Equation 4.1 and in fact the trend is opposite for these complexes. This problem can be solved by recognizing that Equation 4.1 is leaving out an important factor. For there to be an allowed transition between ground and excited charge transfer states, there must be an overlap between donor and acceptor. Crutchley *et al.*³⁹ have

observed similar phenomena where the basicity of the cyanamide was varied. They expressed the transition moment in terms of overlap integral developed from Mulliken expression and generated Equation 4.2.

$$f \approx (1.085 \times 10^{-5}) G \nu S^2 R^2 \dots\dots\dots 4.2$$

where G and ν are the same as in Equation 4.1, R is the transition dipole length, which can be approximated as the separation between donor and acceptor wave functions, in angstroms, and S is the overlap integral. From Figure 3.4, the contribution of the terminal nitrogen to the π_{nb1} molecular orbital is determined by the magnitude of its electron density coefficient C_n and therefore the form of the π overlap integral associated with the $b_1^* \leftarrow b_1$ transition can be shown to be

$$S = C_n S_l \dots\dots\dots 4.3$$

where S_l is the optimum π overlap that can occur between anionic nitrogen 2p and ruthenium(III) 4d orbitals at a given separation. The trend in oscillator strength in Figure 4.4 can now be explained by changes in π overlap resulting from variations of the solvent donor strength and σ -donicity of the π -acid ligands. Note that Equation 4.2 is a simplified derivation from hydrogen atomic wavefunctions. For many-electron system, the transition moment is equal to the vector sum of all the changes in dipole moment experienced by the system which includes both inner- and outer- coordination sphere electrons. For these complexes, the value of the transition dipole moment length, R , is expected to be approximately constant. The trend can therefore be understood in terms of an increase in the degree of π -overlap between the cyanamide anion and ruthenium(III) as the solvent donor strength decreases.

This is probably not the case with *trans*-[(mepyz)Ru^{III}(NH₃)₄(2,3Cl₂-pcyd)]³⁺. In this mononuclear complex, the overlap integral *S* is so large that *R* is no longer constant, in fact it is decreasing. The trend can therefore be understood in terms of decrease in the transition dipole moment length, *R* of the ruthenium(III)-cyanamide bond as the solvent donor strength decreases. This result agrees with the theoretical data calculated using the CNS model and this will be discussed below.

The data for the solvent dependence of the ligand-metal coupling element can be extracted from Tables 3.2-3.14 and plots of *H_{LM}* versus donor number are given in Figure 4.5. These trends can be explained by an outer-sphere effect, i.e. a decrease in π overlap between the cyanamide group and ruthenium(III) as the solvent donor number increases. The phenylcyanamide anion bound to ruthenium(III) is a resonance stabilized π -system which is dominated by the $Ph - N = C = N^-$ resonance structure, a strong π -donor. On the other hand, the effect of hydrogen-bonding between solvent and ammine protons gives 'amido' character to the NH₃ ligands, and NH₂⁻ is also a strong π -donor. This set up a 'competition' with the phenylcyanamide anion for the π d orbitals of ruthenium(III), weakening the ability of ruthenium(III) to polarize the cyanamide π electron density to itself and thus increasing the contribution of the $Ph - N^- - C \equiv N$ resonance form to the nonbonding molecular orbital (Figure 3.4). The magnitude of electron density at the terminal nitrogen and hence the overlap for the associated π -bonding interactions is therefore expected to decrease with increasing solvent donor number.

Again from Figure 4.5, the sole exception from the expected trend of ligand-metal coupling element as a function of solvent donor strength perturbations is that of *trans*-[(mepyz)Ru^{III}(NH₃)₄(2,3Cl₂-pcyd)]³⁺. The assumption of the equation used to derive the

H_{LM} values is that bonding in these complexes is predominantly 'ionic'. However, decreasing the energy gap between metal $d\pi$ and ligands π -HOMO orbitals increases their interaction and hence H_{LM} . Up to a certain extent however, a further decrease of this energy gap allows significant overlap and hence a breakdown of Equation 1.15. Therefore this seemingly unexpected result can be attributed to an increasing degree of covalency in the ruthenium-cyanamide bond.

Figure 4.5: Plot of H_{LM} coupling element versus solvent donor number for $[L_nRu^{III}(NH_3)_{5-n}-2,3Cl_2-pcyd]^{m+}$ complexes where $n = 1$ for 3,5-Me₂pyridine (solid squares), pyridine (open squares), 2,6-Me₂pyrazine (solid diamonds), pyrazine (open diamonds), methylpyrazinium (solid rectangles) and $n = 2$ for 2,2'-bipyridine (solid triangles) ligands *trans* to cyanamide moiety. $m = 2$ for all complexes except methylpyrazinium bound one where $m = 3$. Data from Tables 3.2-3.14.

A plot of oscillator strength versus MLCT energy shows two types of trends (Figures 4.6). First, there is a trend among three family of complexes of π -acids i.e. 3,5-Me₂pyridine and pyridine, 2,6-Me₂pyrazine and pyrazine and methylpyrazinium⁺ ligands *trans* to the phenylcyanamide ligand. Generally as ' π -acidity' increases, oscillator

strength increases and this can be explained by Equation 4.2. There is stronger π -backbonding in the methylpyrazinium⁺ ligand bound complex and therefore the π overlap between the metal $d\pi$ and ligand π^* orbitals is higher than in the 3,5-Me₂pyridine and pyridine complexes, where obviously the π -backbonding is not as great. Pyrazine and 2,6-Me₂pyrazine complexes are expected to have intermediate properties, since their π -backbonding properties lie between the above two classes.

Figure 4.6: Plot of oscillator strength versus MLCT energy as a function of solvent for $[L_nRu^{II}(NH_3)_{5-n}-2,3Cl_2-pcyd]^{m+}$ complexes, where $n = 1$ for 3,5-Me₂pyridine (solid squares), pyridine (open squares), 2,6-Me₂pyrazine (solid diamonds), pyrazine (open diamonds), methylpyrazinium (solid rectangles) ligands *trans* to cyanamide moiety. $m = 1$ for all complexes except the methylpyrazinium case where $m = 2$. The data are from Tables 3.2-3.14.

The second trend is the solvent dependence of oscillator strength for each complex of study. As the solvent donor strength increases in the methylpyrazinium⁺ complex, the oscillator strength is seen to increase with MLCT energy.

Methylpyrazinium⁺ ligand, being a strong ' π -acid', polarizes the electron density from the NH₃ ligands, as shown in Scheme 4.1, and this is enhanced by strong donor solvent as shown by this mechanism. Therefore as the solvent donor strength increases, there should be better overlap S between the metal πd orbitals and the methylpyrazinium⁺ π^* orbitals, and greater covalency.

The behaviour of the methylpyrazinium⁺ complex is exactly opposite that by the 3,5-Me₂pyridine and pyridine complexes where the oscillator strength now decreases with increasing solvent donor strength. If the bonding is more ionic in character, the total bonding between donor ruthenium(III) ion and acceptor ligand S will be smaller but R will be larger. The increase in R , together with the increase in MLCT energy, may account for the trend in oscillator strength that is seen for these two complexes.

For pyrazine and 2,6-Me₂pyrazine complexes, the two factors, overlap integral S and transition dipole length R seem to be balancing out, and hence, the complexes' oscillator strength do not significantly vary with solvent, unlike those of methylpyrazinium⁺ and 3,5-me₂pyridine and pyridine ligand bound complexes.

Theoretical calculations agrees with the above observations because the oscillator strength is proportional to H_{LM} (Equation 1.15). This can be easily seen in a plot of H_{LM} versus solvent donor strength (Figure 4.7).

Figure 4.7: Plot of the H_{ML} coupling element versus the solvent donor number for tetraammine $[L_nRu^{II}(NH_3)_{5-n}-2,3Cl_2-pcyd]^m+$ complexes where $n = 1$ for 3,5-Me₂pyridine (solid squares), pyridine (open squares), 2,6-Me₂pyrazine (solid diamonds), pyrazine (open diamonds), and methylpyrazinium (solid rectangles) ligands *trans* to the cyanamide moiety. $m = 1$ for all complexes except the methylpyrazinium case where $m = 2$. The data are from Tables 3.2-3.14.

4.1.2 Electrochemistry

Solvent and π -acid Ligand Effects

The ruthenium(III/II) $E_{1/2}$ couple of the mononuclear complexes shifts to more positive potentials according to the following order: $NH_3 < 3,5-dmpy < py < 2,6-dmpyz < pyz < 2,2'-bpy < Mepyz^+$. This is attributed to the combination of the increasing π -acceptor and poorer σ -donor character of the nitrogen heterocycle along this series, which destabilizes the +3 oxidation state relative to the +2 oxidation state. Previous studies^{40,83} have also shown that π -acid ligands lead to substantially more positive reduction potentials for ruthenium(III/II) couples than when the ligand is a σ -donor

ammine and this is because of their π -accepting ability (π back-bonding). Note that in the complexes of this study, the low spin, d^6 ruthenium(II) centre does not participate in significant π -back bonding with the pseudohalide phenylcyanamide ligand.

All ruthenium(III/II) couples are sensitive to solvent, but some couples may be more sensitive than others. The net effect of a hydrogen bonding interaction between the solvent and ammine protons is transfer of electron density from the partially deprotonated ammine to the ruthenium ion, as has previously been discussed. An 'amido' ligand being a strong π -donor interacts strongly with a low spin, d^5 ruthenium(III) centre which is a good π -acceptor. Thus it becomes easier to oxidize ruthenium(II) as the solvent donor number increases. Since the solvent sensitivity of ruthenium(III/II) redox couple is associated with the ammine ligands, this may mean that the higher the number of ammine ligands bound to ruthenium ion, the greater the sensitivity to solvent donicity. The solvent sensitivity of ruthenium(III/II) redox couples is greatest in the pentaammine complex, compared to the tetraammine which is greater in comparison to the triammine. In these systems, the pentaammine complex is the most easily oxidized in the strongest donor solvent, DMSO, as seen in Figure 4.8.

Figure 4.8: Redox potential as a function of solvent donor number for the $[L_nRu^{II}(NH_3)_{5-n}-2,3Cl_2-pcyd]^{m+}$ complexes where $n = 1$ for ammine (solid circles), 3,5-Me₂pyridine (solid squares), pyridine (open squares), 2,6-Me₂pyrazine (solid diamonds), pyrazine (open diamonds), methylpyrazinium (solid rectangles) and $n = 2$ for 2,2'-bipyridine (solid triangles) ligands *trans* to the phenylcyanamide moiety ligands *trans* to cyanamide moiety. $m = 1$ for all complexes except the methylpyrazinium case where $m = 2$. The data are from Tables 3.15.

From Figure 4.8, one can note that the methylpyrazinium⁺ complex appears to be less sensitive to solvent, compared to the other tetraammine complexes. A more realistic measure of solvent sensitivity is ΔE . This is the difference in the $E_{1/2}$ reduction couple for a given complex from most strongly donating (DMSO) to least donating (NM) solvent, see Table 3.15. The magnitude of ΔE , varies as the *trans* ammine is substituted with different π -acid ligands. A measure of ' π -acidity' for these ligands is however, required. Recognizing that these ligands are poor donors, their pK_a values can be used to reflect their σ -bonding strength between.

Figure 4.9: Variation of ruthenium(III/II) reduction couples of $[L_nRu^{II}(NH_3)_{5-n}-2,3Cl_2-pcyd]^{m+}$ complexes from most to least donating solvent with π -acid strength measured by pKa values, where $n = 1$ for ammine (solid circles), 3,5-Me₂pyridine (solid squares), pyridine (open squares), 2,6-Me₂pyrazine (solid diamonds), pyrazine (open diamonds), methylpyrazinium (solid rectangles) and $n = 2$ for 2,2'-bipyridine (solid triangles). $m = 1$ for all complexes except the methylpyrazinium case where $m = 2$. The data are from Table 3.15.

A plot of ΔE versus pKa is shown in Figure 4.9. For the pentaammine, $[Ru^{III}(NH_3)_5-2,3Cl_2-pcyd]^{2+}$, ΔE is high since only in the complexes' +3 oxidation state is there solvent-ammine donor-acceptor interaction. For $[mepyzRu^{II}(NH_3)_4-2,3Cl_2-pcyd]^{2+}$, the ΔE value is smallest because in the +2 and +3 oxidation states, the methylpyrazinium cationic ligand makes the metal ion very electropositive and this polarizes the ammine electron density toward itself which increases with solvent–ammine interaction (Scheme 4.1). Because donor-acceptor interactions occurs in both +2 and +3 oxidation states, the value of ΔE is smaller. Solvent effects therefore partially cancel.

4.2. ASYMMETRIC DINUCLEAR COMPLEXES

Certain aspects of outer- and inner-sphere perturbations to metal-metal coupling in symmetric dinuclear complexes have previously been examined in our group.^{16,17,37,50} To study inner-sphere effects, complexes incorporating the dicyd²⁻ family of bridging ligands allowed probing of the superexchange pathway. Inner-sphere perturbations of the metal πd orbitals were also investigated via the complexes' ancillary ligands, where substituting a strong σ -donor ammine with weaker σ -donors (pyridine moieties), caused the metal's πd orbital energy to be lowered. Outer-sphere perturbations of metal-metal coupling in these symmetric systems have been studied also by varying the solvent's donor strength.

Building on the above studies, the syntheses of a new family of asymmetric dinuclear complexes, $[L_n Ru(NH_3)_{5-n} \text{-dicyd-Ru}(NH_3)_5][PF_6]_4$ (where $L_n = 1$ (monodentate) or 2 (bidentate)) allowed both inner- and outer-sphere perturbations of the mixed-valence properties to be addressed. The data under consideration herein are for three new asymmetric complexes and for the previously published symmetric pentaammine complex, $[\{Ru(NH_3)_5\}_2(\mu\text{-dicyd})][PF_6]_4$. The emphasis of this discussion will be based on the following techniques: electronic absorption spectroscopy, NMR spectrometry, cyclic voltammetry, and the spectroelectrochemical study of the complexes. These techniques give great insight into metal-metal coupling and allow for its quantification. In conjunction with the CNS model of metal-metal coupling, these techniques will also provide insight into the nature of the complexes' mixed-valence $Ru_a^{III} - Ru_b^{II}$ states. ¹H-NMR results will be used to probe the degree of coupling in the $Ru_a^{III} - Ru_b^{III}$ state by sampling the paramagnetism via Evans method experiments.^{51,52}

Any description of superexchange metal-metal coupling in transition metal complexes must consider the entire set of bridging ligand molecular orbitals to take into account both electron- and hole-transfer superexchange mechanisms. An optimization of the hole-transfer mechanism occurs where there is both an energy and symmetry match between the metal orbitals and the commonly shared *occupied* bridging ligand orbital. For the complexes of this study, metal-metal coupling occurs via hole transfer superexchange involving the π_{nb} HOMO of the dicyd²⁻ ligand. Extended Huckel calculations of the ligand π -HOMO, assuming ideal planar geometry with cyanamide groups in *anti*⁷⁵ conformations produced the picture shown in Figure 1.5. The HOMO spans the entire bridging ligand and is therefore able to interact simultaneously with the πd orbitals of both ruthenium ions.

Elemental analyses, NMR spectrometry, Uv-Vis-NIR and IR spectroscopy were applied to the three complexes of the asymmetric family to fully characterize them. The reported crystal structures of analogous $[\{(\text{NH}_3)_5\text{Ru}\}_2(\mu\text{-dicyd})][\text{OTs}]_4$ ³⁸ and $[\{(\text{NH}_3)_3\text{Ru}(\text{bpy})\}_2(\mu\text{-dicyd})][\text{ClO}_4]_4$,⁸⁸ in which the NCN moieties of the ligand were in an *anti* conformation, are quite similar with the Ru-Ru through space separation being 13.1 Å. Although the crystal structure of the related tetraammine complex, $[\{(\text{NH}_3)_4\text{Ru}(\text{py})\}_2(\mu\text{-dicyd})][\text{PF}_6]_4$, showed the NCN moieties to be in a *syn* arrangement, modelling of the ligand suggests a low barrier to rotation.⁷⁵ For all theoretical modeling reported hereafter, it has been assumed that, in solution the through-space Ru-Ru separation in all the complexes is 13 Å.

4.2.1 Electronic Absorption Spectroscopy

Solvent and *trans* π -acid Ligand Effects on Charge Transfer Energies

Electronic absorption spectroscopy provides insight into the nature of metal-metal coupling and metal-ligand interactions through the response of the electronic absorption spectra to outer- and inner-sphere electronic perturbations. The electronic absorption band assignments for the asymmetric $Ru_a^{III} - Ru_b^{III}$ dinuclear complexes are similar to what has previously been discussed for mononuclear ruthenium(III) complexes of anionic phenylcyanamide ligands. The spectra are dominated by an intense low-energy band in the near-IR region and a less intense high-energy band in the visible region which are assigned as ligand-to-metal charge transfer (LMCT) transitions. With regards to the indicated band properties, some differences exist between asymmetric dinuclear and mononuclear complexes. The most obvious difference pertains to the splitting of the low-energy band. The fact that a cyanamide moiety is bound to two differently coordinated ruthenium(III) centers results in two ruthenium(III)-cyanamide chromophores. The splitting of these bands seems to increase with solvent donor number, so that, in DMSO, there are two bands clearly observed (Figures 3.58-3.73 and Tables 3.17-3.20).

An examination of the data for the symmetric pentammine dinuclear complex reveals that as the solvents donor number increases, the energy of the LMCT band, E_{LMCT} , increases (Table 3.17). A similar trend is reported for mononuclear ruthenium(III) complexes of anionic phenylcyanamide ligands, and this is a consequence of the previously discussed solvent-amine donor-acceptor interactions.

For the asymmetric complexes, the data of the deconvoluted Ru_a^{III} – cyanamide chromophore shows the same solvent-dependent E_{LMCT} as that for symmetric pentaammine complexes (Tables 3.18-3.20). However, examination of the Ru_b^{III} – cyanamide chromophore data shows a different pattern. The expected trend in E_{LMCT} – lowest in nitromethane and highest in DMSO – is reversed. When the bonding in the complex is predominantly ‘ionic’, as in the pentaammine case, a decreasing solvent donor number decreases the energy gap between metal and ligand orbitals and, thus, a decrease in E_{LMCT} is observed. At some threshold, however, significant overlap and, thus, an increase in covalency will manifest itself in the metal-ligand bonding. Henceforth from that point, decreasing the energy gap between metal and ligand orbitals will indeed increase their overlap, but this will result in increased splitting of the resultant bonding and antibonding orbitals (Figure 4.10) and thus an increase in, E_{LMCT} . This phenomenon has been observed for some symmetric Ru^{III} – Ru^{III} complexes.¹⁶

Figure 4.10: A qualitative MO diagram for LMCT in a symmetric Ru^{III} - Ru^{III} complex bridged by a π -HOMO ligand (A). At some threshold, decreasing the energy gap between the π -HOMO and πd orbitals (B) causes an increase in E_{LMCT} due to increasing covalency of the metal-bridge bond.

Figure 4.11 shows the effects of stabilizing the metal π d orbitals by weak donor solvent or replacing a strong σ -donor ammine ligand with strong π -acceptor ligand. This decreases the π d- π -HOMO energy gap and causes an increase in E_{LMCT} due to increasing covalency of the metal-bridge bond. The analogous mononuclear complexes show this phenomenon when the *trans* ammine is replaced with a strong π -acceptor ligand like methylpyrazinium⁺ (Figure 4.4).

Figure 4.11: Plot of E_{LMCT} transition energy of the Ru_b^{III} -NCN chromophore versus solvent donor strength for asymmetric complexes when *trans*-ammine in $[\{Ru(NH_3)_5\}_2(\mu\text{-dicyd})][PF_6]_4$ is asymmetrically substituted with stronger π -acceptor pyridine in *trans*-[pyRu(NH₃)₄-dicyd-Ru(NH₃)₅][PF₆]₄ (squares), pyrazine in *trans*-[pyzRu(NH₃)₄-dicyd-Ru(NH₃)₅][PF₆]₄ (diamonds) and bipyridine in *mer*-[bpyRu(NH₃)₃-dicyd-Ru(NH₃)₅][PF₆]₄ (triangles). The data may be found in Tables 3.21-3.24.

Solvent and *trans* π -acid Ligand Effects on Oscillator Strength

The decrease in oscillator strength of the two Ru^{III} –cyanamide chromophores is dependent on the solvent donor strength (Tables 3.18-3.20). The decrease in LMCT band oscillator strength results from the decoupling of ruthenium(III) ions from the cyanamide groups because of the outer-sphere donor-acceptor interaction between the solvent's non-bonding electron pairs and the protons of the ammine ligands. If the ruthenium(III) ions are decoupled from the cyanamide groups, it follows that they are decoupled from the superexchange pathway and, as such the oscillator strength will be attenuated with an increase in solvent donor strength. In this regard, the oscillator strength for the LMCT transitions serves as a means of probing the magnitude of metal-metal coupling in these systems.

By replacing a σ -donor ammine ligand with a π -acceptor (pyridine, pyrazine or bipyridine) ligand allows the metal and ligand orbitals to be close in energy. This is expected to increase the oscillator strength of asymmetric complexes compared to the symmetric case (Figure 4.12A).

Figure 4.12: Schematic representation of how (A) coordinated π -acceptor ligands, and (B) donor-acceptor interaction between coordinated amines and solvent, perturbs the metal d π energy in relation to the bridging ligand π -HOMO.

However Tables 3.17-3.20 show that the oscillator strengths of the asymmetric complexes are significantly lower, compared to the symmetric analogs, in all solvents. Previous studies in our group have shown the same observation in a similar complex where the asymmetry was generated from the bridging ligand.¹⁶ The solvation of the complex is expected to be asymmetric due to asymmetry caused by the terminal π -acid ligands. This may permit significant solvent trapping of the valence electron on one metal centre relative to the other and consequently disrupt the charge transfer interactions. This has been found to lower the oscillator strength of an intervalence charge transfer band, in going from a strong to a weak coupling case, an observation made and discussed by Solomon *et al.*⁴⁴

4.2.2 Cyclic Voltammetry

The four redox events of the asymmetric complexes of this study, i.e. $L^{0/-}$, $L^{-/2-}$, E_{Ma}^o , and E_{Mb}^o were investigated as a function of solvent and/or ancillary ligands. Herein, the redox couple of the pentaammine end of the dimer will be referred to as $Ru_a^{III/II}$ and that of the substituted end as $Ru_b^{III/II}$.

Previous studies on analogous symmetric pentaammine complexes showed that as the electron density on the metal centre increases as a function of its ancillary ligands, the bridging ligands or the solvent, the metal-centred couples occur at increasingly positive potentials.¹⁷ The couples assigned as being ligand-centered occurred at less positive potentials as the ligand became more polarizable. Generally speaking, these anticipated trends in redox potential are observable in the experimental data (Tables 3.21-3.24).

Since we have two differently coordinated ruthenium ions, the two couples $Ru_a^{III/II}$ and $Ru_b^{III/II}$ are analyzed distinctly in this thesis.

Figure 4.13 demonstrates the effect of outer-sphere donor-acceptor interactions between nonbonding electron pairs of the solvent and the protons of ammine ligands coordinated to the $Ru_b^{III/II}$ end of the dimer. As this interaction increases by increasing the solvent donor strength, the πd orbitals of the metal ion become increasingly destabilized, making reduction of ruthenium(III) more difficult and this is true for all the complexes. The slope with the symmetric pentaammine complex appears to be more steep compared to the one for the asymmetric complexes. The slope indicates a reduced sensitivity of the $Ru_b^{III/II}$ couples to the solvent donor strength and, as such, the sensitivity is lowest for $[bpyRu(NH_3)_3-dicyd-Ru(NH_3)_5][PF_6]_4$ the complex with the fewest ammine ligands.

Figure 4.13: Solvent-dependent $Ru_b^{III/II}$ redox couples of the dimer for $[\{Ru(NH_3)_5\}_2(\mu-dicyd)][PF_6]_4$ (circles), *trans*- $[pyRu(NH_3)_4-dicyd-Ru(NH_3)_5][PF_6]_4$ (squares), *trans*- $[pyzRu(NH_3)_4-dicyd-Ru(NH_3)_5][PF_6]_4$ (diamonds) and *mer*- $[bpyRu(NH_3)_3-dicyd-Ru(NH_3)_5][PF_6]_4$ (triangles) complexes. The data are from Tables 3.21-3.24.

As the σ -donor strength decreases by substituting an ammine ligand with pyridine, pyrazine, or bipyridine π -acceptor ligands, the $Ru_a^{III/II}$ redox couples increasingly shift to more positive potentials. These trends have also been seen in the study of mononuclear ruthenium(III) complexes of phenylcyanamide (Section 3.1.2) when the ligand *trans* to phenylcyanamide became a weaker σ -donor.

Figure 4.14: Solvent-dependent $Ru_a^{III/II}$ redox couples of the dimer for [$\{Ru(NH_3)_5\}_2(\mu$ -dicyd)][PF₆]₄ (circles), *trans*-[pyRu(NH₃)₄-dicyd-Ru(NH₃)₅][PF₆]₄ (squares), *trans*-[pyzRu(NH₃)₄-dicyd-Ru(NH₃)₅][PF₆]₄ (diamonds) and *mer*-[bpyRu(NH₃)₃-dicyd-Ru(NH₃)₅][PF₆]₄ (triangles) complexes. The data are from Tables 3.21-3.24.

The $Ru_a^{III/II}$ redox couple of the dimer end was also investigated as a function of solvent (Figure 4.14). The variations as a function of solvent between the $Ru_a^{III/II}$ redox couples among the complexes are small, compared to the $Ru_b^{III/II}$ redox couples already discussed. In fact, the slope indicates that the sensitivity in the case of all $Ru^{III/II}(NH_3)_5$ moieties is approximately the same in all the asymmetric complexes of this study.

However, the trend of the $Ru_a^{III/II}$ couples in DMSO is the reverse of that seen in the other solvents. This phenomenon can be explained in Figure 4.15 below.

Figure 4.15: Polarization of the dicyd²⁻ bridging ligand in the absence (A) of solvent-ammine interactions, and in the presence (B) of solvent-ammine interactions, in an asymmetric complex.

The effect of polarization known also as the inductive effect is most obviously seen in the $Ru_a^{III/II}$ couples. In the strongly donating DMSO solvent, it is more difficult to reduce the $Ru^{III}(NH_3)_5$ end of the asymmetric complex than that of the symmetric pentaammine complex because the $LRu^{II}(NH_3)_4$ or $L_2Ru^{II}(NH_3)_3$ end is hydrogen bonding with the solvent more strongly than the $Ru^{II}(NH_3)_5$ end. This causes the electron density in the bridging ligand to shift towards the $Ru^{III}(NH_3)_5$ end, stabilizing the ruthenium(III) oxidation state. In weaker donor solvents, the ruthenium(II) end, i.e. $LRu^{II}(NH_3)_4$ or $L_2Ru^{II}(NH_3)_3$ of the asymmetric complexes, is able to polarize the ligand electron density towards itself and this makes it easier to reduce the $Ru^{III}(NH_3)_5$ end. The same effects are not seen in the symmetric case because $Ru^{II}(NH_3)_5$ does not hydrogen-bond significantly with the solvent.

Figure 4.16 shows the solvent- and complex-dependence of the $L^{-/2-}$ couple. Since the dicyd²⁻ bridging ligand has no functionalities that can interact with solvent molecules, there is no expectation of solvent-induced variations as such. However, the variations of the couples within a given solvent is consistent with the electron-withdrawing power of the substituted $LRu^{II}(NH_3)_4$ or $L_2Ru^{II}(NH_3)_3$ ends of the dimer. In addition, the electron-withdrawing power of the ruthenium(III) ions is considerably perturbed by the solvent-ammine donor interactions. Therefore, the variation that is seen is due to the fact that the dicyd²⁻ bridging ligand's HOMO is bonding with the πd orbitals of ruthenium ion.

Figure 4.16: Variation of the $L^{-/2-}$ redox potential with solvent donor properties when *trans*-ammine (solid circles) in $[\{Ru(NH_3)_5\}_2(\mu\text{-dicyd})][PF_6]_4$ is asymmetrically substituted with stronger π -acceptor pyridine in *trans*- $pyRu(NH_3)_4\text{-dicyd-Ru}(NH_3)_5][PF_6]_4$ (squares), pyrazine in *trans*- $[pyzRu(NH_3)_4\text{-dicyd-Ru}(NH_3)_5][PF_6]_4$ (diamonds) and bipyridine in *mer*- $[bpyRu(NH_3)_3\text{-dicyd-Ru}(NH_3)_5][PF_6]_4$ (triangles). The data are from Tables 3.21-3.24.

Previous studies on symmetric ruthenium pentaammine mixed-valence complexes have shown that the free energy of comproportionation decreases with increasing solvent donor strength. The decrease in ΔG_c with solvent donor strength was rationalized by the solvent ammine interactions discussed in Section 1.6, whereby strong donor solvents decouple the ruthenium πd orbitals from the π -HOMO of the bridging ligand and hence result in a smaller ΔG_r contribution to ΔG_c . This is illustrated by Figure 4.17, where the ΔG_c of $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-dicyd})][\text{PF}_6]_4$ is plotted versus solvent donor strength. In contrast, the asymmetric dinuclear complexes in Figure 4.17 show the opposite behaviour with increasing ΔG_c as solvent donor strength increases. Because the solvent is still expected to cause the decoupling of the ruthenium πd orbitals from the superexchange pathway, ΔG_r should decrease. The increase in ΔG_c with solvent donor strength must be ascribed the solvent-dependent polarization, referred to here by an inductive term, ΔG_i of the dicyd²⁻ ligand that perturbs the potentials of the $\text{Ru}_a^{\text{III/II}}$ and $\text{Ru}_b^{\text{III/II}}$ redox couples.

Figure 4.17: Plot of ΔG_c versus solvent donor strength for dinuclear complexes when *trans*-ammine (solid circles) in $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-dicyd})][\text{PF}_6]_4$ is asymmetrically substituted with stronger π -acceptor pyridine in $[\text{pyRu}(\text{NH}_3)_4\text{-dicyd-Ru}(\text{NH}_3)_5][\text{PF}_6]_4$ (squares), pyrazine in $[\text{pyzRu}(\text{NH}_3)_4\text{-dicyd-Ru}(\text{NH}_3)_5][\text{PF}_6]_4$ (diamonds) and bipyridine in $[\text{bpyRu}(\text{NH}_3)_3\text{-dicyd-Ru}(\text{NH}_3)_5][\text{PF}_6]_4$ (triangles). The data are from Tables 3.21-3.24.

In order to derive a quantitative measure of ΔG_i , several assumptions will be made. If we assume that solvent effects are equal to zero in the solvent with the smallest donor number, nitromethane, the difference in the free energy of comproportionation between the symmetric pentaammine complex and the asymmetric complexes, $\Delta\Delta G_c$ is due to change in ΔG_r , ΔG_{ex} , and ΔE_{asy} , (Equation 4.4)

$$\Delta\Delta G_c = (\Delta G_c)_{asy} - (\Delta G_c)_{sym} = \Delta\Delta G_{ex} + \Delta\Delta G_r + \Delta E_{asy} \dots \dots \dots 4.4$$

The antiferromagnetic exchange contribution to $\Delta\Delta G_c$, which is one-half the separation between the singlet ground state and the triplet excited state is small, and in fact it ranges from 5-10 cm⁻¹ in nitromethane (Table 3.30). This suggests that the resonance exchange contribution $\Delta\Delta G_r$ is also small and can be approximated to be equal

to zero. It can therefore be concluded that the difference in free energy of comproportionation seen, $\Delta\Delta G_c$, is largely due to ΔE_{asy} in nitromethane. These values for the asymmetric complexes are shown in Table 4.1.

Table 4.1: ΔE_{asy} Values^a for the Asymmetric Dinuclear Complexes

Complex	ΔE_{asy}
[pyRu(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅][PF ₆] ₄	600
[pyzRu(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅][PF ₆] ₄	950
[bpyRu(NH ₃) ₃ -dicyd-Ru(NH ₃) ₅][PF ₆] ₄	1270

In cm⁻¹. The data are from Tables 3.21-3.24, calculated as
 $\Delta E_{asy} = (\Delta G_c)_{asy} - (\Delta G_c)_{sym}$

If we assume that this difference will be maintained in all other solvents, the apparent increase in the value of ΔG_c for the asymmetric complexes compared to the symmetric pentaammine complex can now be ascribed to the solvent-dependent inductive term, ΔG_i , shown in Table 4.2. These values show how the electron density within the complex shifts as a function of solvent.

Table 4.2: Solvent-Dependent ΔG_i Values^a for the Asymmetric Dinuclear Complexes

Complex	AN	AC	DMSO
[pyRu(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅] ³⁺	210	660	1640
[pyzRu(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅] ³⁺	370	900	2140
[bpyRu(NH ₃) ₃ -dicyd-Ru(NH ₃) ₅] ³⁺	250	820	2180

^a In cm⁻¹. The data are from Tables 3.21-3.24 and Table 4.1. Calculated as
 $\Delta G_i = (\Delta G_c)_{asy} - \Delta E_{asy}$

4.2.3 Spectroelectrochemistry

Because the intervalence transition (IT) and the ruthenium(III)-cyanamide chromophore transition occur at approximately the same energy, the IT bands for each of the complexes had to be deconvoluted. In this procedure, it was assumed that the LMCT band profile of the $Ru_a^{III} - NCN$ chromophore was maintained upon one electron reduction of the $Ru_a^{III} - Ru_b^{III}$ complex. The fitting of the IT band assume a Gaussian band shape and followed a similar procedure as that developed for the symmetric pentaammine complexes.^{37,80} However, as these systems became more strongly coupled, the fits obtained became less reasonable. The breakdown normally occurs on the high-energy side of the band envelope.

Parameters obtained for the IT bands of the asymmetric dinuclear complexes are shown in Table 3.25. These data reflect the approximate nature of the fitting protocol as there is an absence of consistent trends. These results will be used for modelling the complexes using the CNS model.

4.2.4 Testing the CNS Model

To test the predictive abilities of the CNS model, the resonance exchange free energies of symmetric pentaammine complexes predicted from optical properties (Equation 1.18) will be compared with those of asymmetric complexes. Data for the various terms of the model have been placed in Tables 4.3-4.6.

The CNS model approaches the question of metal-metal coupling in dinuclear complexes from the perspective of the superexchange mechanism. Thus, since the metals interact with each other via the dicyd²⁻ ligand, it is their individual interactions with the ligand which ultimately governs the magnitude of their effective coupling. In the asymmetric cases under study, superexchange occurs via hole-transfer and thus LMCT data are used to determine the effective coupling element $H_{MM'}$.

The metal-ligand coupling element, H_{LM} , for a given Ru^{III}-NCN, is determined from the LMCT oscillator strength of an asymmetric $Ru_a^{III} - Ru_b^{III}$ dinuclear complex. Since the LMCT band shapes are non-Gaussian, the calculations of the coupling elements were effected directly from oscillator strengths determined from each spectrum by modeling the LMCT band envelope with two Gaussian bands representing the inequivalent Ru(III)-NCN chromophores in the asymmetric dinuclear complexes. The oscillator strength of the fitted bands were individually determined according to $f = 4.61 \times 10^{-9}(\epsilon_{\max}\Delta\nu_{1/2})$ and Equation 1.15 was used to solve for the two H_{LM} values, where $r = 6.5 \Delta$ is taken as the distance between Ru(III) and the centre of the dicyd²⁻ bridging ligand.⁴⁷

When asymmetry is introduced in the system, predictions of ΔE_{LM}^{eff} from Equation 1.19 give unreasonable values. In some instances, the values of E_{IT} were greater than E_{LMCT} making the second term of the reduced energy gap equation indeterminable. A reasonable estimate of ΔE_{LM}^{eff} can be determined from the analogous symmetric pentaammine, tetraammine and triammine complexes studied previously.^{16,17} This can be done by calculating an averaged value in all solvents under study, giving a measure of 3000 cm⁻¹. This value will be used in estimates of $H_{MM'}$.

Table 4.3: Effective Coupling of the Metal-Centers $H_{MM'}^a$ and Metal-Ligand Coupling Elements H_{LM}^b Values for the Complexes in Nitromethane.

Solvent	H_{LM}^b	H_{LM}^a	$H_{MM'}$	$H_{MM'}^2/E_{IT}$
$[\text{Ru}(\text{NH}_3)_5\text{-dicyd-Ru}(\text{NH}_3)_5]^{3+}$	2570	2570	2000	560
$[\text{pyRu}(\text{NH}_3)_4\text{-dicyd-Ru}(\text{NH}_3)_5]^{3+}$	1870	1680	1400	144
$[\text{pyzRu}(\text{NH}_3)_4\text{-dicyd-Ru}(\text{NH}_3)_5]^{3+}$	2030	1620	1200	160
$[\text{bpyRu}(\text{NH}_3)_3\text{-dicyd-Ru}(\text{NH}_3)_5]^{3+}$	2150	1620	1300	180

^a Values calculated as $H_{MM'} = \frac{H_{LM}^a H_{LM}^b}{\Delta E_{LM}^{\text{eff}}}$ from Equation 1.17.

^b Values calculated from Equation 1.15 using data from Tables 3.18-3.20.

Table 4.4: Effective Coupling of the Metal-Centers $H_{MM'}^a$ and Metal-Ligand Coupling Elements H_{LM}^b Values for the Complexes in Acetonitrile.

Solvent	H_{LM}^b	H_{LM}^a	$H_{MM'}$	$H_{MM'}^2/E_{IT}$
$[\text{Ru}(\text{NH}_3)_5\text{-dicyd-Ru}(\text{NH}_3)_5]^{3+}$	2460	2460	1700	410
$[\text{pyRu}(\text{NH}_3)_4\text{-dicyd-Ru}(\text{NH}_3)_5]^{3+}$	1890	1640	1500	137
$[\text{pyzRu}(\text{NH}_3)_4\text{-dicyd-Ru}(\text{NH}_3)_5]^{3+}$	1910	1600	1600	133
$[\text{bpyRu}(\text{NH}_3)_3\text{-dicyd-Ru}(\text{NH}_3)_5]^{3+}$	2070	1610	1700	158

^a Values calculated as $H_{MM'} = \frac{H_{LM}^a H_{LM}^b}{\Delta E_{LM}^{\text{eff}}}$ from Equation 1.17.

^b Values calculated from Equation 1.15 using data from Tables 3.18-3.20.

Table 4.5: Effective Coupling of the Metal-Centers $H_{MM'}^a$ and Metal-Ligand Coupling Elements H_{LM}^b Values for the Complexes in Acetone.

Solvent	H_{LM}^b	H_{LM}^a	$H_{MM'}$	$H_{MM'}^2/E_{IT}$
$[\text{Ru}(\text{NH}_3)_5\text{-dicyd-Ru}(\text{NH}_3)_5]^{3+}$	2180	2180	1200	220
$[\text{pyRu}(\text{NH}_3)_4\text{-dicyd-Ru}(\text{NH}_3)_5]^{3+}$	1900	1510	1300	116
$[\text{pyzRu}(\text{NH}_3)_4\text{-dicyd-Ru}(\text{NH}_3)_5]^{3+}$	1910	1520	2600	119
$[\text{bpyRu}(\text{NH}_3)_3\text{-dicyd-Ru}(\text{NH}_3)_5]^{3+}$	1960	1400	1600	106

^a Values calculated as $H_{MM'} = \frac{H_{LM}^a H_{LM}^b}{\Delta E_{LM}^{\text{eff}}}$ from Equation 1.17.

^b Values calculated from Equation 1.15 using data from Tables 3.18-3.20.

Table 4.6: Effective Coupling of the Metal-Centers $H_{MM'}^a$ and Metal-Ligand Coupling Elements H_{LM}^b Values for the Complexes in in DMSO.

Solvent	H_{LM}^b	H_{LM}^a	$H_{MM'}$	$H_{MM'}^2/E_{IT}$
$[\text{Ru}(\text{NH}_3)_5\text{-dicyd-Ru}(\text{NH}_3)_5]^{3+}$	2050	2050	780	80
$[\text{pyRu}(\text{NH}_3)_4\text{-dicyd-Ru}(\text{NH}_3)_5]^{3+}$	1610	960	515	33
$[\text{pyzRu}(\text{NH}_3)_4\text{-dicyd-Ru}(\text{NH}_3)_5]^{3+}$	2040	1240	843	88
$[\text{bpyRu}(\text{NH}_3)_3\text{-dicyd-Ru}(\text{NH}_3)_5]^{3+}$	1880	1220	764	77

^a Values calculated as $H_{MM'} = \frac{H_{LM}^a H_{LM}^b}{\Delta E_{LM}^{\text{eff}}}$ from Equation 1.17.

^b Values calculated from Equation 1.15 using data from Tables 3.18-3.20.

The CNS model has successfully predicted metal-metal coupling for the symmetric $Ru^{III} - Ru^{III}$ pentaammine complexes as shown by the good correlation between theoretical and experimental values (Figure 1.9). An examination Tables 4.3-4.6 shows that, when asymmetry is introduced, predictions of the metal-metal coupling element $H_{MM'}$ are underestimated, compared to the symmetric pentaammine case. Creutz, Newton and Sutin (CNS) have estimated $H_{MM'}$ using H_{LM} values derived from mononuclear complexes.²⁴ Similarly, taking the data from Tables 3.2-3.14, $H_{MM'}$ values were generated and the resultant $H_{MM'}^2/E_{IT}$ values compiled (Appendix 1). The trend in this data is essentially identical to that of Tables 4.3-4.6, and this implies that the underestimation of $H_{MM'}$ in the asymmetric systems is due to the calculated H_{LM} values. The H_{LM} values in both cases associated with pentaammine complexes are higher than those of π -acid substituted complexes. These H_{LM} values in the asymmetric complexes are therefore suggested to be small because of a reduction in the transition dipole moment length as a result of increasing covalency (Equation 1.15).

4.2.5 Solution Magnetic Susceptibility and Antiferromagnetic Exchange Measurements.

The calculated values of H_{LM} in Tables 4.3-4.6 can be used to calculate J_{AF} according to Equation 1.29. These values can be compared to experimental values of J_{est} , calculated using Equation 1.30 and compiled in Table 3.30.

Before the value of J_{AF} is calculated, value of Δ must be determined. Δ is a measure of the energy gap between the metal and ligand orbitals and can be determined

from the energy difference between the ground state and the LMCT excited state associated with $h_{d\pi}$, according to Equation 4.5,

$$v_{\max} = \Delta + \lambda \dots \dots \dots 4.5$$

where $v_{\max}$ is the optical energy at $\epsilon_{\max}$ of the low-energy LMCT band and λ is the energy term which arises from Franck-Condon excitation into excited vibrational levels and is related to inner- and outer-sphere reorganizational energies. Using a method developed for analogous systems,^{47,79} the value of χ and $v_{\max}$ can be determined and the resultant values of Δ are displayed in Table 4.7. It can be seen that the energy gap between the metal πd and the π -HOMO orbitals increases as a function of solvent donor strength for the Ru_a^{III} -cyanamide chromophore but not for Ru_b^{III} -cyanamide chromophore. In the latter case, this is a result of significant covalency, as discussed earlier.

Table 4.7: Energy Difference between Ground State and LMCT Excited State, Δ^a (from $Ru_a^{III} - NCN$) and Δ^b (from $Ru_b^{III} - NCN$) Δ being associated with $h_{d\pi}$ ^a for dicyd²⁻-bridged Asymmetric Complexes.

Solvent	$[pyRuA_4-L-RuA_5]^{+4}$		$[pyzRuA_4-L-RuA_5]^{+4}$		$[bpyRuA_4-L-RuA_5]^{+4}$	
	Δ^a	Δ^b	Δ^a	Δ^b	Δ^a	Δ^b
NM (2.7)	5180	3980	5580	4380	5580	4380
AN (14.1)	5380	3880	5480	4980	5480	4180
AC (17.0)	5480	3780	5580	3980	5480	4080
DMSO (29.8)	5880	3480	6080	3480	5880	3480

^a Data in cm^{-1} , calculated from $v_{\max} = \Delta + \lambda$. A is NH_3 and L is dicyd²⁻.

The values of U from Equation 1.30 were determined from low-energy deconvoluted IT bands shown in Figures 3.86-3.97 and Table 3.25.^{36,47,91} The energy of the double-charge-transfer transition was estimated by assuming that it is the sum of stepwise LMCT transitions (from the two deconvoluted energy values), Σ_{LMCT} , the energy difference between first and second oxidation potential of the dicyd²⁻ ligand, ΔE_L (Tables 3.21-3.24) and the pairing energy term (6000 cm⁻¹) of a Ru(II) $d\pi$ orbital, E_p .^{40,47} These values are tabulated in Appendix 2. The calculated theoretical antiferromagnetic exchange constants for the asymmetric complexes as a function of solvent are shown in Table 4.8.

Table 4.8: Calculated Antiferromagnetic Exchange^a Constants for Ruthenium(III) Dinuclear Complexes as a Function of Solvent.^b

Complex	NM	AN	AC	DMSO
[Ru(NH ₃) ₅ -dicyd-Ru(NH ₃) ₅] ^{+4 a}	290	230	140	50
[pyRu(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅] ⁺⁴	200	190	160	50
[pyzRu(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅] ⁺⁴	180	170	160	120
[bpyRu(NH ₃) ₃ -dicyd-Ru(NH ₃) ₅] ⁺⁴	230	180	150	100

^a Calculated according to Equation 1.30 ^bData have units of cm⁻¹.

The plot of estimated $-2J_{est}$ values versus the calculated antiferromagnetic exchange constant $-J_{AF}$, for the complexes in the solvents used in this study, is shown in Figures 4.18. There seems to be a linear correlation between $-2J_{est}$ and $-J_{AF}$, which breaks down as the system becomes more strongly coupled and, thus, increases in covalency. It

is therefore suggested that for the asymmetric complexes, Equation 1.29 is breaking down as a realistic model. From this figure, Equation 1.29 is underestimating the antiferromagnetic exchange coupling. The estimate of $r = 6.5 \text{ \AA}$ used in Equation 1.15 may be a source of significant error whereby covalency in the Ru(III)-NCN bond would have the effect of decreasing the transition dipole moment length. As discussed before, the breakdown is probably related to an underestimate of J_{AF} , because of low H_{LM} values.

Figure 4.18: Plot of calculated versus estimated antiferromagnetic exchange constants for asymmetric complexes where the *trans*-ammine in $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-dicyd})][\text{PF}_6]_4$ is asymmetrically substituted with the stronger π -acceptor pyridine in *trans*- $[\text{pyRu}(\text{NH}_3)_4\text{-dicyd-Ru}(\text{NH}_3)_5][\text{PF}_6]_4$ (squares), pyrazine in *trans*- $[\text{pyzRu}(\text{NH}_3)_4\text{-dicyd-Ru}(\text{NH}_3)_5][\text{PF}_6]_4$ (diamonds) and bipyridine in *mer*- $[\text{bpyRu}(\text{NH}_3)_3\text{-dicyd-Ru}(\text{NH}_3)_5][\text{PF}_6]_4$ (triangles). The data may be found in Tables 3.30 and 4.12.

4.3 CONCLUSIONS AND FUTURE STUDIES

The research objectives outlined in Section 1.7 have been achieved in this thesis. The ability to synthesize and characterize seven mononuclear complexes of 2,3-dichlorophenylcyanamide monoanion ligand has allowed for an elucidation of ligand- and metal-centred inner-sphere and outer-sphere perturbations. Electronic absorption and electrochemical data demonstrated that the ruthenium(III)-cyanamide π -interactions could be controlled or 'tuned' by varying the basicity of the π -acid ligand *trans* to the 2,3-dichlorophenylcyanamide monoanion ligand as well as by varying the solvent donor strength. These studies were particularly valuable in providing a fundamental understanding of the electronic nature of the ruthenium-cyanamide bond and this understanding could be applied to the interpretation of the asymmetric dinuclear systems.

For the second part of this thesis, the studies were particularly valuable in establishing synthetic protocols for the preparation of $Ru_a^{III} - Ru_b^{III}$ asymmetric dinuclear systems bridged by the 1,4-dicyanamidobenzene dianion ligand. The electronic properties of the metal-to-metal charge transfer bands of these complexes are consistent with strong metal-to-metal coupling. The increase of the energetic matching between metal and ligand orbitals increases their interaction. Coupling was systematically increased upon asymmetric substitution of the *trans*-ammine with π -accepting ligands, i.e. from pyridine to pyrazine to 2,2'-bipyridine. This caused a concurrent increase in the degree of covalency in the bonding at the substituted end compared to the unsubstituted end. Solution magnetic susceptibility and ^1H -NMR data indicated that the paramagnetism of the system could similarly be controlled. It is concluded that the weakening of the

ruthenium(III)-cyanamide π -bond was accompanied by the onset of paramagnetism and this resulted in a reduction of the metal-metal antiferromagnetic superexchange coupling.

For the mixed-valence $Ru_a^{III} - Ru_b^{II}$ complexes, these systems provided an interesting problem for the CNS model. The calculation of H_{MM}' required a determination of three experimental electronic transition values, i.e. from each end of the dimer and from the intervalence charge transfer, unlike in the symmetric systems, which required two. It was found that the onset of asymmetry showed a breakdown of the CNS model as there was an underestimation of H_{MM}' and J_{AF} . This has been rationalized as being due to a reduction of the transition dipole moment length as a result of increasing covalency when an ammine is substituted with a weaker σ -donor. This has the effect of reducing the oscillator strength, making the H_{LM} values relatively smaller.

In Creutz-Taube substituted complexes, $[L-Ru(NH_3)_4-pyz-Ru(NH_3)_5]^{3+}$, coupling decreases when the σ -donor *trans*-ammine is replaced with a π -acceptor ligand, L, a good example of a system that utilizes the electron transfer superexchange mechanism.¹ On the other hand, in our systems bridged by the 1,4-dicyanamidobenzene dianion ligand, we observed a little change in the metal-metal coupling when the *trans*-ammine is asymmetrically replaced with a strong π -acceptor ligand, i.e. $[L-Ru(NH_3)_4-dicyd-Ru(NH_3)_5]^{3+}$. Instead, the polarizability of the bridging ligand, together with the solvent-ammine donor-acceptor interaction resulted in a large free energy of induction, ΔG_i which increased ΔG_c with increasing solvent donor strength.

These results should lead to an investigation of coupling in a trinuclear molecule incorporating π -acceptor pyrazine and π -donor dicyd²⁻ as bridging ligands, i.e.

Evidence for long-range interactions between the remote pentaammine groups utilizing both electron- and hole-transfer superexchange mechanisms should be investigated through electrochemical and spectroelectrochemical studies of the trinuclear complex as well as its constituent fragments.

Appendix

Appendix 1: Metal-Ligand Coupling Elements of Symmetric and Asymmetric Complexes from the Mononuclear Complexes $[\text{Ru}(\text{NH}_3)_5(2,3\text{-Cl}_2\text{pcyd})]^{2+}$ and $[\text{L}_n\text{Ru}(\text{NH}_3)_{5-n}(2,3\text{-Cl}_2\text{pcyd})]^{2+}$ LMCT bands as a Function of Solvent, Where $n = 1$ for pyridine and pyrazine and $n = 2$ for 2,2'-bipyridine ligands.

Complex	Solvent ^b (DN)	$H_{\text{LM}2}$	$H_{\text{LM}1}$	$H_{\text{LM}2}H_{\text{LM}1}$ ($\times 10^6$)	$H_{\text{MM}'}$	$H_{\text{MM}'}^2/E_{\text{IT}}$
$[\text{Ru}(\text{NH}_3)_5\text{-dicyd-Ru}(\text{NH}_3)_5]^{4+}$	NM(2.7)	2310	2310	5.34	1780	450
	AN(14.1)	2110	2110	4.45	1480	320
	AC (17.0)	2020	2020	4.08	1360	270
	DMSO(29.8)	1880	1880	3.53	1180	190
$[\text{pyRu}(\text{NH}_3)_4\text{-dicyd-Ru}(\text{NH}_3)_5]^{4+}$	NM(2.7)	2310	1250	2.89	960	120
	AN(14.1)	2110	1320	2.79	930	110
	AC (17.0)	2020	1190	2.40	800	85
	DMSO(29.8)	1880	1160	2.18	730	60
$[\text{pyzRu}(\text{NH}_3)_4\text{-dicyd-Ru}(\text{NH}_3)_5]^{4+}$	NM(2.7)	2310	1410	3.26	1090	153
	AN(14.1)	2110	1370	2.89	963	118
	AC (17.0)	2020	1270	2.56	853	89
	DMSO(29.8)	1880	1170	2.12	707	60
$[\text{bpyRu}(\text{NH}_3)_3\text{-dicyd-Ru}(\text{NH}_3)_5]^{4+}$	NM(2.7)	2310	1410	3.25	1080	153
	AN(14.1)	2110	1390	2.93	977	120
	AC (17.0)	2020	1360	2.75	917	105
	DMSO(29.8)	1880	1180	2.22	740	62

All data in units of cm^{-1} , calculated from Tables 3.2-3.14.

Appendix 2: Generated Data used to Determine the Antiferromagnetic Exchange Constant $-J_{AF}$

Complex	Solvent	Σ_{LMCT}	ΔE_L	E_p	$2/E_{DCT}$ ($\times 10^{-5}$)	$1/U$ ($\times 10^{-4}$)	$2/E_{DCT}+1/U$ ($\times 10^{-4}$)
[pyRu(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅] ⁴⁺	NM	19060	3020	6000	7.12	1.38	2.09
	AN	19110	3330	6000	7.02	1.32	2.05
	AC	19090	3430	6000	7.01	1.32	2.02
	DMSO	19210	5400	6000	6.53	1.18	1.83
[pyzRu(NH ₃) ₄ -dicyd-Ru(NH ₃) ₅] ⁴⁺	NM	19830	2920	6000	6.96	1.30	2.00
	AN	19470	3020	6000	7.02	1.26	1.96
	AC	19360	3060	6000	7.04	1.32	2.02
	DMSO	19390	5400	6000	6.50	1.17	1.82
[bpyRu(NH ₃) ₃ -dicyd-Ru(NH ₃) ₅] ⁴⁺	NM	19790	2720	6000	7.01	1.29	1.99
	AN	19500	2820	6000	7.06	1.11	1.82
	AC	19360	3020	6000	7.05	1.30	2.00
	DMSO	19140	5400	6000	6.55	1.17	1.822

REFERENCES

- 1) Salameyer, F.; Berhane, S.; Yusof, R.; de la Rosa, R.; Fung, E. Y.; Motamoros, R.; Lau, K. W.; Zheng, Q.; Kober, E. M.; Curtis, J. C. *Inorg. Chem.* **1993**, 32, 3895.
- 2) Sutin, N. *Prog. Inorg. Chem.* **1983**, 30, 441.
- 3) Ward, M.D. *Chem. Soc. Rev.* **1995**, 121.
- 4) Ruminisk, R. R.; Freiheit, D.; Serveiss, D.; Snyder, B.; Johnson, J. E. B. *Inorg. Chim. Acta.* **1994**, 224, 27.
- 5) Bolger, J.; Gourdon, A.; Ishow, E.; Launay, J. P. *Inorg. Chem.* **1996**, 35, 2937.
- 6) Beley, M.; Collin, J. P.; Sauvage, J. P. *Inorg. Chem.* **1993**, 32, 4539.
- 7) a) Creutz, C. *Prog. Inorg. Chem.* **1983**, 30, 1. b) Crutchley, R. J. *Adv. Inorg. Chem.* **1994**, 41, 273.
- 8) Brown, D. M., Ed., D. Reidel: Dordrecht, Holland, 1980.
- 9) Meyer, T. J., Demadis, K. D.; Hartshorn, C. M. *Chem. Rev.* **2001**, 101, 2655.
- 10) Woodward, J. *Philos. Trans. R. Soc. London*, **1724**, 33, 15.
- 11) a) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1969**, 91, 3988. b) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1973**, 95, 1086.
- 12) a) Marcus, R. A. *J. Chem. Phys.* **1956**, 24, 966 b) Marcus, R. A. *J. Chem. Phys.* **1957**, 26, 867 c) Marcus, R. A. *J. Chem. Phys.* **1957**, 26, 872.
- 13) Robin, M. D.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, 10, 247.
- 14) Allen, G. C.; Hush, M. S. *Prog. Inorg. Chem.* **1967**, 8, 357.
- 15) a) Hush, M.S., *Electro. Chim. Acta.* **1968**, 13, 1005. b) Hush, M.S., *Prog Inorg. Chem.* **1967**, 8, 391.

- 16) Evans, C. E. B.; Naklicki, M. L.; Rezvani, A. L.; White, C. A.; Kondratieva, V. V.; Crutchley, R. J. *J. Am. Chem. Soc.* **1998**, 120, 13103.
- 17) a) Evans, C. E. B. Ph.D. Thesis, Carleton University, **1997**. b) Evans, C. E. B.; Yap, G. P. A.; Crutchley, R. J. *Inorg. Chem.* **1998**, 37, 6161.
- 18) Elliot, C. M.; Derr, D. L.; Ferrere, S.; Newton, M.D.; Liu, Y.P. *J. Am. Chem. Soc.*, **1996**, 118, 5221.
- 19) de la Rosa, R.; Chang, P. J.; Salameya, F.; Curtis, J. C. *Inorg. Chem.* **1985**, 24, 4231.
- 20) Lau, K. W.; Hu, A. M.; Yen, M. J.; Fung, E. Y.; Grzybicki, S.; Matamoros, R.; Curtis, J.C. *Inorg. Chim. Acta.* **1994**, 226, 137.
- 21) Sutton, J. E.; Sutton, P. M.; Taube, H. *Inorg. Chem.* **1979**, 18, 1017.
- 22) Richardson, D. E.; Taube, H. *Coord. Chem. Rev.* **1984**, 60, 107.
- 23) a) Wong, K.Y., Schatz, P.N. *Prog. Inorg. Chem.* **1981**, 28, 369. b) Ondrechen, M. J.; Ko, J.; Zhang, L. T. *J. Am. Chem. Soc.* **1987**, 109, 1672.
c) Piepho, S.; Krausz, E. R.; Shatz, P. N. *J. Am. Chem. Soc.* **1978**, 100, 2996.
d) Piepho, S. *J. Am. Chem. Soc.* **1990**, 112, 4197.
- 24) Creutz, C.; Newton, M. D.; Sutin, N. *J. Photochem. Photobiol. A: Chem.* **1994**, 82, 47.
- 25) Mulliken, R. S.; Pearson, W. B. *Molecular Complexes*. ; Wiley: New York, 1969.
- 26) a) Mulliken, R. S. *J. Am. Chem. Soc.* **1952**, 64, 811. b) Mulliken, R. S.; Pearson, W. B. *J. Am. Chem. Soc.* **1969**, 91, 3409.
- 27) Bender, C. J. *Chem. Soc. Rev.* **1986**, 15, 475.
- 28) Reichardt, C. *Angew. Chem. Int. Ed. Engl.*, **1965**, 4, 29 and references therein.

- 29) Gutmann, V. *The Donor-Acceptor Approach to Molecular Interactions*, Plenum. Press, N.Y. **1978**.
- 30) Curtis, J. C.; Sullivan, B. P.; Meyer, T. J. *Inorg Chem.*, **1983**, 22, 224.
- 31) Hupp, J. T.; Neyhart, G. A.; Meyer, T. J. *J. Am. Chem. Soc.* **1986**, 108, 5349.
- 32) Neyhart, G. A., Hupp, J. J., Curtis, J. C., Timpson, C. F, Meyer, T. J. *J. Am. Chem. Soc.* **1996**, 118, 3724.
- 33) a) Neyhart, G. A., Timpson, C. J., Bates, D. W., Meyer, T. J., *J. Am. Chem. Soc.* **1996**, 118, 3730. b) Hupp, J.T., Meyer, T.J. *Inorg. Chem.* 1987, 26, 2332.
c) Brunschwig, B. S.; Ehrenson, S.; Sutin, N; *J. Phys. Chem.* **1986**, 90, 3657.
- 34) Bertrand, P. *Chem. Phys. Lett.* **1985**, 113, 104
- 35) a) Kahn, O.; Briat, B. J. *J. Chem. Soc. Farady II.* **1976**, 268. b) Kahn, O.; *In Magneto- Structural Correlations in Exchange Coupled Systems*. Willet, R. D., Gatteschi, D., Kana, O., Eds; Reidel: Dordrecht, Holland, **1985**.
- 36) Anderson, P.W. *Phys. Rev.* **1959**, 115, 2.
- 37) Nacklicki M. L. Ph.D. Thesis, Carleton University, **1995**.
- 38) Aquino, M. A. S.; Lee, F. L.; Gabe, E. J.; Bensimon, C.; Greeden, J. E.; Crutchely, R. J. *J. Am. Chem. Soc.* **1992**, 114, 5130.
- 39) Crutchley, R. J.; McCaw, K.; Lee, F. L.; Gabe, E.J., *Inorg. Chem.* **1990**, 29, 2576.
- 40) *Inorganic Electronic Spectroscopy*, 2nd ed.; Lever, A.B.P. Ed; Elsevier Publishing Co.; Amsterdam, **1985**.
- 41) Hay, J. P.; Thibault, J. C.; Hoffman, R. *J. Am. Chem. Soc.* **1975**, 97, 4884.
- 42) a) Kahn, O. *Molecular Magnetism*; VCH Publishers. NY, **1993**.
b) Dardey, J.P.; De Loig, P.; Malriev, J.P. In *Magneto-Structural Correlations in*

Exchange Coupled Systems. Willet, R.D., Gatteschi, D., Kana, O., Eds; Reidel: Dordrecht, Holland, **1985**.

- 43) Aquino, M. A. S. Ph.D. Thesis, Carleton University, **1991**.
- 44) Tuczek, F; Solomon, E. T. *Inorg. Chem.* **1993**, 32, 2850.
- 45) Cave, R. J.; Newton, M. D. *Chem. Phys. Lett.* **1996**, 249, 15.
- 46) Thompson, L. K.; Ramaswamy, B. S. *Inorg Chem.* **1986**, 25, 2664.
- 47) Nacklicki, M.L.; White, C. A.; Plante, L. L.; Evans, C. E. B; Crutchley, R. J. *Inorg. Chem.* **1998**, 37, 1880.
- 48) Bleaney, B.; Bowers, K. D. *Proc.Roy.Soc. (London)* **1952**, A214.
- 49) Coffman, R. E.; Buettner, G. R. *J.Phys.Chem.* **1979**, 83, 2387.
- 50) a) Rezvani, A. A. Ph.D. Thesis, Carleton University, **1994**. b) Rezvani, A. A; Bensimon, C; Crompt, B.; Reber, C.; Kondratieva, V. V.; Crutchley, R. J. *Inorg.Chem.* **1997**, 36, 3329.
- 51) Evans, D. F. *J.Chem.Soc.* **1959**, 2003.
- 52) Phillips, W. D.; Poe, M. *Meth.Enzymol.* **1972**, 24, 304.
- 53) Crawford, T.H.; Swanson, J. *J.Chem.Edu.* **1972**, 48, 382
- 54) Drago, R. S., *Physical Methods for Chemists*, Sanders, Ft.Worth, **1992**.
- 55) Figgis, B. N.; Lewis, J. *Prog.Inorg. Chem.* **1964**, 6, 173.
- 56) Riddic, J. A.; Bunger, W. B.; Sakano, T. K. *Techniques of Chemistry*, Vol.II, Organic Solvents: *Physical Properties and Methods of Purifications*, 4th Ed.; Wiley-Interscience : New York, **1986**.
- 57) Clarke, R. E. M.Sc. Thesis, University of California at Santa Barbara, **1978**.
- 58) Vogst, L. H.; Katz, J. L.; Wiberly, S. E., *Inorg.Chem.* **1965**, 8, 1157.

- 59) Crutchley, R. J.; Naklicki, M. L. *Inorg. Chem.* **1989**, 28, 1955.
- 60) Magnuson, H. Ph.D. Thesis, Stanford University, **1973**.
- 61) Callahan, R.W.; Brown, G.M.; Meyer, T. J. *Inorg.Chem*, **1975**, 14, 1443.
- 62) Chang, P. P.; Fung, E.Y.; Curtis, J. F. *Inorg.Chem*, **1986**, 25, 4233.
- 63) a) Von Kameke, A.; Tom, G.M.; Taube, H. *Inorg. Chem.* **1978**, 17, 1790.
b) Milena, S.; Alessandro, F.; Margherita, V.; Paola C.; Cicilia, G.; Gianfranco, D.
Inorg. Chem. 2002, **41**, 1263.
- 64) Ford, P. C.; Clarke, R. E.; Boggs, S. E. *Inorg.Chim. Acta.* **1996**, 247, 129.
- 65) Derosa M. C.; White, C. A.; Evans, C. E. B.; Crutchley, R. J. *J.Am.Chem.Soc.* 2001, 123, 1395.
- 66) Zhang, W.; Bensimon, C.; Crutchley, R. J. *Inorg.Chem.* **1993**, 32, 5808.
- 67) Desjardins, P. M.Sc. Thesis. Carleton Univeristy, **1998**.
- 68) Allen, A.D.; Scenoff, C. V. *Can.J.Chem.* **1967**, 45, 1337.
- 69) *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.,
Nakamoto, K. Ed.; John Wileys & Sons: New York, **1986**.
- 70) Evans, C. E. B.; Ducharme, D.; Crutchley, R. J. *Inorg. Chem.* **1995**, 34, 1350.
- 71) Winkler, J. R.; Netzel, T. L.; Creutz, C.; Sutin, N. *J.Am.Chem.Soc.* **1987**, 109, 2381.
- 72) Dubicki, L.; Ferguson, J.; Krausz, E. R. *J.Am.Chem.Soc.* **1985**, 107, 179.
- 73) Saleh, A. A.; Crutchley, R. J. *Inorg.Chem.* **1990**, 29, 312.
- 74) Naklicki, M. L.; White, C. A.; Kondratiev, V.; Crutchley, R. J. *Inorg.Chim.Acta.*
1996, 242, 63.
- 75) Rezvani, A. A.; Bensimon, C.; Crompton, B.; Reber, C.; Greedan, J.E.; Kondratieev, V.
V.; Crutchley, R. J. *Inorg.Chem.* **1997**, 36, 3322.

- 76) Mabbot, G. A. *J.Chem.Edu.* **1983**, 60, 697
- 77) Kissinger, P.T.; Heineman, W. R. *J.Chem.Edu.* **1983**, 60, 702.
- 78) Harris, D.C. *Quantitative Chemical Analysis*, 2nd Ed., Freeman and Co., NY. **1987**.
- 79) Richardson, D. E.; Taube, H. *Inorg.Chem.* **1981**, 20, 1278.
- 80) Naklicki, M. L.; Crutchley, R. J. *Inorg.Chim.Acta.* **1994**, 225, 123.
- 81) Naklicki, M. L.; Crutchley, R. J. *J.Am.Chem.Soc.* **1994**, 116, 6045.
- 82) Abraham, R. J; Fisher, J.; Loftus, P. *Introduction to NMR Spectroscopy*, John Wiley & Sons Ltd., Chichester, **1991**.
- 83) Lever, A. B. P. *Inorg.Chem.* **1990**, 29, 1271.
- 84) Wishart, J. F.; Bino, A.; Taube, H. *Inorg.Chem.* **1986**, 25, 3318.
- 85) Magnuson, R.; Taube, H. *Inorg.Chem.* **1987**, 26, 2994.