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**INNER AND OUTER SPHERE PERTURBATION OF
THE Ru(III)-CYANAMIDE BOND AND THE CONSEQUENCES TO
METAL-METAL COUPLING**

by

ALIREZA REZVANI, B.Sc., M.Sc.

**A thesis submitted to the
Faculty of Graduate Studies and Research
in partial fulfilment of
the requirements for the degree of
Doctor of Philosophy**

Department of Chemistry

**Carleton University
Ottawa, Ontario
January, 1995**

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THE Ru(III)-CYANAMIDE BOND AND THE CONSEQUENCES TO
METAL-METAL COUPLING”**

submitted by

ALIREZA, REZVANI, B.Sc., M.Sc.

in partial fulfilment of the requirements
for the degree of Doctor of Philosophy

(Chair, Department of Chemistry

Thesis Supervisor

External Examiner

Carleton University

January, 1995

ABSTRACT

To examine the effect of spectator ligands on the electronic perturbation of the Ru-cyanamide chromophore, a series of mononuclear complexes, $\text{cis-}[\text{Ru}(\text{bpy})_2(\text{L})_2]$, where L = monoanions of phenylcyanamide(pcyd), 2-chlorophenylcyanamide (2-Clpcyd), 2,3-dichlorophenylcyanamide (2,3-Cl₂pcyd), 2,4,5-trichlorophenylcyanamide(2,4,5-Cl₃pcyd), 2,3,4,5-tetrachloro phenylcyanamide(2,3,4,5-Cl₄pcyd), and pentachloro phenylcyanamide(Cl₅pcyd), have been synthesized and characterized by elemental analysis, IR, ¹H NMR, and UV-Vis near-IR spectroscopies, and cyclic voltammetry. Oxidation of the complexes by controlled potential electrolysis generated $\text{cis-}[\text{Ru}(\text{bpy})_2(\text{L})_2]^+$. The LMCT spectra and redox chemistry of these complexes have been compared to those for $[(\text{NH}_3)_5\text{Ru}(\text{L})]^{2+}$ and the difference related to a significant increase of Ru(III)-cyanamide π bond covalency.

In order to explore the effect of the spectator ligands on the metal-metal coupling in dinuclear complexes, the $[\{\text{Ru}(\text{bpy})(\text{terpy})\}_2(\mu\text{-dicyd})](\text{PF}_6)_2$ where terpy = 2,2',2''-terpyridine, bpy = 2,2'-bipyridine and dicyd²⁻ = 1,4-dicyanamidobenzene dianion, has been synthesized and fully characterized. The mixed valence ion, $[\{\text{Ru}(\text{bpy})(\text{terpy})\}_2(\mu\text{-}$

$\text{dicyd})]^{3+}$ is strongly coupled with $K_C = 2.75 \times 10^7$ and has an intervalence band at $\lambda = 1090 \text{ nm}$ ($\epsilon_{\text{max}} = 5600 \text{ M}^{-1}\text{cm}^{-1}$, $\nu_{1/2} = 1800 \text{ cm}^{-1}$). The mixed valence properties of this complex were compared to its ammine analogue $[(\text{NH}_3)_5\text{Ru}]_2(\mu\text{-dicyd})]^{3+}$ and the difference rationalized by the effect of the spectator ligands on the interaction of ruthenium ions with the dicyd^{2-} superexchange pathway.

In addition, a series of *trans*- $[(\text{NH}_3)_4\text{RupY}]_2(\mu\text{-L})]^{4+}$ complexes, where L = 1,4-dicyanamidobenzene(dicyd^{2-}) (I), 1,4-dicyanamido-2,5-dimethylbenzene($\text{Me}_2\text{dicyd}^{2-}$) (II), 1,4-dicyanamido-2,5-dichlorobenzene($\text{Cl}_2\text{dicyd}^{2-}$) (III), 1,4-dicyanamido-2,5-tetra chlorobenzene($\text{Cl}_4\text{dicyd}^{2-}$) (IV) were synthesized and characterized using spectroscopic and electrochemical techniques. The crystal structure of the complex (I) has shown that the cyanamide groups are almost planar with the phenyl ring but in a *syn*-configuration.

The electronic properties of the metal to metal charge transfer bands of these complexes are indicative of strong metal-metal coupling i.e. the value of the comproportionation constants for the complex (II) has a $K_C = 5.6 \times 10^6$ in acetonitrile, which is higher than the K_C for the Creutz-Taube ion ($[(\text{NH}_3)_5\text{Ru}]_2(\mu\text{-pyz})]^{5+}$, $K_C = 4 \times 10^6$). However, complex (II) shows considerable solvent dependence and highlights the

inappropriateness of K_C as the sole criteria for a class III assignment.

Variable temperature magnetic susceptibility measurement for these complexes show strong antiferromagnetic behavior ($J \geq 800 \text{ cm}^{-1}$). In solution (Evans' method), the magnetic susceptibility depends on the donor number of solvent. For instance, the complex (II) is diamagnetic in acetonitrile but becomes paramagnetic in DMSO. The origin of this effect is suggested to be a donor-acceptor interaction between the solvent molecule and the proton of the ammine ligand, which weakens Ru(III)-cyanamide bond and in turn weakens the antiferromagnetic superexchange coupling through the 1,4-dicyanamidobenzene bridging ligand.

The replacement of the ammine with the pyridine moiety increases the stability of the ruthenium d -orbitals in both +2 and +3 oxidation states because of pyridine's π -acceptor properties and pyridine's poorer σ donor properties compared to the strong σ donor ammine ligand. The effect this has on the Ru(III) ion can be readily seen by a comparison of the Ru(III/II) reduction couples of $[\{(\text{NH}_3)_5\text{Ru}\}_2(\mu\text{-dicyd})]^{4+}$ which occur at 0.131 and -0.155 V vs NHE with those of $\text{trans-}[\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-dicyd})]^{4+}$ which occur at 0.350 and -0.015 V vs NHE and for $[\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-dicyd})]^{3+}$ which occur at

0.840 and 0.415 V vs NHE in acetonitrile solutions. The increased stability of the Ru(III) *d*-orbitals increases the covalency of its π -interaction with the cyanamide groups of the bridging ligand, which in turn increases metal-metal coupling via the π HOMO superexchange pathway of the bridging ligand.

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Dedication

This Thesis is dedicated to my wife

M. Fazaeli, to my son Sohail

my daughter Setayesh and

to my parents.

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ABBREVIATIONS

Me	methyl
Bu	butyl
Ph	phenyl
OAc	acetate anion
Ots	tosylate anion
pz	pyrazine
py	pyridine
bpy	2,2'-bipyridine
terpy	2,2',2''-terpyridine
phen	1,10-phenanthroline
pycd	phenylcyanamide
dicyd	1,4-dicyanamidobenzene
HOMO	highest occupied molecular orbital
LUMO	lowest unoccupied molecular orbital
SHOMO	second highest occupied molecular orbital
TBAH	tetrabutylammonium hexafluorophosphate

bpii 1,3-bis(2,pyridylimino) isoindolate

CHAPTER 1

INTRODUCTION

1.1 Background.

Much attention has been paid to the intramolecular electron transfer process between metal ions in ligand - bridged di or oligonuclear complexes with regard to the design of photochemical molecular devices[1,2] or mimetic models of the photosynthetic system in biology[3].

Novel molecular materials may be prepared by considering a mixed-valence complex as a molecular building block. Polymerization and retention of electron delocalization between blocks then leads to a long chain molecular wire. Researchers[4] have found varying degrees of conductivity in bisaxially coordinated macrocyclic ruthenium complexes $[(\text{Mac})\text{RuL}]_n$. For example when Mac = phthalocyanine, and L = pyrazine or 1,2,4,5-tetraazine, the conductivity was found to be $10^{-7} \text{ S cm}^{-1}$ [5] and $10^{-1} \text{ S cm}^{-1}$ [6], respectively.

Other researchers have investigated intramolecular energy and electron transfer in supramolecular species based on ruthenium(II) polypyridine systems[7]. These

supramolecular species could perform the same function as light harvesting structures found in the photosynthetic apparatus.

The purposeful construction of a single supermolecule for signal processing is a practical application of mixed-valence complexes and a major synthetic challenge. The control of signal transfer (electron) from one metal site to another obviously depends on control of metal-metal coupling. Theoretical studies have focussed on the effect of photoinduced conformational changes of the bridging ligand on the interaction between metals[8]. The effect on metal-metal coupling must be extreme to be useful because a change in conformation can open new pathways which although not as efficient serve to diminish the effect[9]. The degree of metal-metal coupling is also affected by the nature of its spectator ligands as well as the outer coordination sphere(solvent). This thesis deals with a comprehensive study of these factors which perturb the metal-metal coupling in dinuclear ruthenium complexes bridged by dicyanamidobenzene dianion (dicyd^{-2}) and its derivatives. Dinuclear ruthenium complexes form the largest group by far of any mixed-valence system. Ruthenium is the transition metal of choice to study electron transfer or exchange because it is relatively inexpensive, forms stable Ru(III) and Ru(II) coordination complexes and the synthetic coordination chemistry of

ruthenium is well developed[10]. In addition, dinuclear ruthenium compounds have been the subject of early studies on the properties of mixed-valence compounds[11,12,13] and the theory of intervalence transitions in mixed-valence systems which has been developed in detail by Hush[14].

1. 2 The Theory of Mixed-Valence System.

The systematic study of mixed-valence materials began in 1967-1970 as a result of several parallel developments. In 1967 Allen and Hush[15] and Robin and Day[16] published two reviews on the physical properties of mixed-valence systems. These were followed by Hush who provided a theoretical bridge between the physical properties of mixed-valence complexes in solution and the Marcus theory of intermolecular electron transfer[17]. The case for a symmetric dinuclear mixed-valence complex in which the odd electron is coupled between donor(M) and acceptor(M^+) is illustrated by the classical potential energy versus nuclear configuration diagrams(Figure 1.1)[18]. The left-hand parabola represents the potential energy surface for $(M - L - M^+)$ and the right-hand curve is for $(M^+ - L - M)$. The vertical transition (E_{Op}) is the energy required to photoexcite an electron between states. This is called the intervalence transition (IT) or metal to metal charge transfer

(MMCT). E_{th} is defined as an energy barrier to thermal electron transfer between states. The two curves are split at their intersection by $2H_{ab}$, where H_{ab} is the resonance

Figure 1.1 Potential energy-configuration diagram for a symmetric mixed-valence complex.

energy between the two states and is a measure of the degree of electronic coupling between the two states and hence between M and M^+ . According to the degree of metal-metal coupling, Robin and Day have distinguished three broad classes of mixed-valence complexes[16].

Class I, Completely valence trapped (no coupling between metal ions $H_{ab} = 0$). The odd electron is fully localized on one of the metal ions. These mixed-valence materials only display the properties of the corresponding isolated mononuclear M and

M^+ complexes and the oscillator strength of the *MMCT* transition is essentially zero (Figure 1.2a).

Class II, Valence trapped (weak coupling between metal ions).

A distinct interaction between metal centers is present, leading to an intervalence transition, usually in the 3000 to 20,000 cm^{-1} range. This interaction is, however, not strong. Therefore, such systems largely exhibit the properties of their mononuclear counterparts (albeit perturbed by the interaction between the metal ions, Figure 1. 2b).

Class III, Delocalized valency (strong coupling between metal ions). Here the interaction between the two metal centers is so great that the properties of the individual ions are absent and only the new properties of the $(M - L - M)^+$ unit are observed (Figure 1. 2c). In these systems the odd electron is completely delocalized between the metal ions[19].

For the weak coupling mixed-valence system, Hush derived the following relationships of intervalence band properties. For class I in which there is no electronic coupling between metal ions ($H_{ab} = 0$) the E_{op} is related to the energetic barrier for thermal electron transfer. For symmetric species

$$E_{op} = \lambda = 4E_{th} \quad (1.1)$$

Figure 1.2 Potential energy diagram for a symmetric mixed-valence complex. a)Class I b)Class II c)Class III.

As the interaction is increased in class II, H_{ab} becomes significant and the E_{th} is decreased.

$$E_{th} = \lambda/4 - H_{ab} \quad (1.2)$$

The intervalence transition band width at half intensity $\Delta\nu_{1/2}$ (in cm^{-1}) gives an indication about which type of mixed-valence species has been obtained. The band width can be calculated using equation (1.3).

$$\Delta\nu_{1/2} = [2310 \nu_{\max}]^{1/2} \quad (1.3)$$

Another feature that may be derived from the properties of the IT band is the extent of electronic coupling, H_{ab} which can be evaluated directly from the spectral analysis. Hush showed that the oscillator strength of an intervalence charge transfer (IT) was related to the extent of coupling between donor and acceptor. The oscillator strength(f) of a IT transition is given by the equation derived by Hush,

$$f = 1.085 \times 10^{11} G.H_{ab}^2.R^2/\nu_{\max} \quad (1.4)$$

where G refers to the degeneracy of the states concerned and R is the transition dipole length (the distance through which charge is carried) in centimeters. For a Gaussian band, the oscillator strength can also be determined experimentally[20].

$$f = 4.6 \times 10^{-9} \epsilon_{\max} \cdot \Delta\nu_{1/2} \quad (1.5)$$

Substituting equation (1.5) for f and rearranging gives

$$H_{ab} = [(2.06 \times 10^{-2})/R] \times (\nu_{\max} \times \epsilon_{\max} \times \Delta\nu_{1/2})^{1/2} \quad (1.6)$$

where $\epsilon_{\max}$ is the molar absorptivity ($M^{-1} \text{ cm}^{-1}$) at the band maximum and R is the separation between the metal centers (in Å). In the case of strong coupling (class III complexes), the magnitude of H_{ab} has become so great that $E_{th} = 0$ and a single minimum due to the delocalized $(M - L - M)^+$ is now present (Figure 1.2c). The energy of intervalence transition (E_{op}) is a measure of electronic coupling between donor and acceptor wave function.

$$E_{op} = 2 H_{ab} \quad (1.7)$$

In addition to the method developed by Hush, a measure of electronic coupling can also be obtained experimentally by determining the comproportionation constant (K_C)[21]. For a

dinuclear ruthenium complex in which each ruthenium can have an oxidation state of II or III, the mixed-valence state can be represented as (III, II) and is stabilized with respect to the isovalent state (III, III) and (II, II). The degree of this stabilization is reflected in K_C (ie. the larger K_C is, the greater the electronic coupling). The comproportionation constant (K_C) is determined by the equilibrium for class I and II complexes.

and for class III complexes

K_C is usually deduced from the difference in potential between metal center reduction couples.

$$\log K_C = 16.9 (E_1 - E_2) \quad (1.8)$$

1.3 The Superexchange Mechanism

The mechanism of coupling between two metal centers linked by a ligand is referred to as superexchange and can occur through two pathways: Electron transfer and hole transfer[22]. For dinuclear ruthenium complexes in which the ruthenium ions are six-coordinate, the former mechanism involves the transfer of an electron from the $d\pi$ orbital on the electron-rich metal (M) via the vacant lowest unoccupied molecular orbital (LUMO), usually a π^* orbital of the bridged ligand, to the appropriate $d\pi$ orbital on the electron

Scheme 1

deficient metal (M^+). This pathway will be favoured when the energies of the metal orbital are close to that of the ligand *LUMO* see Scheme 1.

The hole transfer mechanism is favoured when the energies of the metal $d\pi$ orbitals are close enough to the ligand highest occupied molecular orbital (*HOMO*). In this pathway, the positive hole is transferred from the electron deficient metal center (M^+) through the π *HOMO* of the bridging ligand to the electron rich metal center (M) as

Scheme 2

shown in Scheme 2. Depending on the nature of the metal centers and the bridging ligand, either the electron or the hole transfer mechanism may predominate.

The superexchange mechanism in the dinuclear ruthenium complexes requires that the atomic orbitals of the ruthenium ions overlap simultaneously with a single ligand orbital. To overlap effectively, the ruthenium and the bridging ligand orbital must have the same symmetry and be as close in energy to each other as possible.

a. Nature of Ruthenium Ions: The energy of Ru(II) donor and Ru(III) acceptor orbitals and the ability of these orbitals to interact with the bridging ligand can be significantly affected by the nature of spectator ligand (the ligands which make up the coordination sphere). It is well known that the potential of the Ru(III/II) couple becomes increasingly anodic with increasing coordination of π -acceptor ligands. For instance, the $[\text{Ru}(\text{NH}_3)_6]^{3+/2+}$ couple = 0.051 V [23], whereas the $[\text{Ru}(\text{bpy})_3]^{3+/2+}$ couple = 1.272 V vs NHE in aqueous solution[24].

In another study, Curtis and co-workers[25,26] have shown the influence of spectator ligands on the magnitude of metal-metal coupling in a symmetric system. The properties of a class III complex $[(\text{NH}_3)_5\text{Ru}(\mu\text{-pyz})\text{Ru}(\text{NH}_3)_5]^{5+}$, can be converted to class II properties simply by replacing an ammine ligand with a strong π -acceptor ligand. The decrease

Table 1.1. Comproportionation constant and electronic data of IT band for different spectator ligands.

Complex	K_C	$\lambda_{\max}^a$ nm	$\epsilon_{\max}^b$ $M^{-1}cm^{-1}$	$\Delta\nu_{1/2}$ cm^{-1}	Ref.
$[(bpy)_2RuCl(\mu-pyz)Ru(NH_3)_5]^{4+}$	1.2×10^7	1035	1300	5470	25
$[(bpy)_2RuCl(\mu-pyz)Ru(NH_3)_4(py)]^{4+}$	6.1×10^4	1176	1340	5480	25
$[(bpy)_2RuCl(\mu-pyz)Ru(NH_3)_3(bpy)]^{4+}$	510	1313	400	5650	27
$[(bpy)_2RuCl(\mu-pyz)Ru(NH_3)_3(phen)]^{4+}$	330	1310	826	5940	27
$[(bpy)_2RuCl(\mu-pyz)Ru(NH_3)_4(3-Fpy)]^{4+}$	7.1×10^3	1266	918	5440	27
$[(NH_3)_5Ru(\mu-pyz)Ru(NH_3)_4(3-Clpy)]^{5+}$	5.1×10^7	1490	3400	3180	25,27
$[(NH_3)_5Ru(\mu-pyz)Ru(NH_3)_3bpy]^{5+}$	4.7×10^7	1153	1650	4040	25,27
$[(NH_3)_5Ru(\mu-pyz)Ru(NH_3)_4py]^{5+}$	1.9×10^8	1441	2920	3160	26

pyz = pyrazine, bpy = bipyridine, py = pyridine, phen = phenanthroline,

in extinction coefficient (ϵ) and increase in band width at half height ($\Delta\nu_{1/2}$) of a intervalence transition is consistent with this conversion. Table 1.1 shows a series of dinuclear ruthenium complexes with different spectator ligands.

b. Nature of the Bridging Ligand

The magnitude of metal-metal coupling in mixed-valence complexes whether a class II or class III obviously depends a great deal on the nature of bridging ligand. As mentioned earlier, the molecular orbitals of the bridging ligand must be symmetry and energy matched and interact simultaneously with the donor and acceptor orbitals of the ruthenium ions. Theoretical studies show that metal-metal coupling is mediated by the full set of bonding and antibonding orbitals of the bridging ligand[28,29,30]. Depending on the π acceptor or donor behavior of the bridging ligand, one of these π superexchange pathways will be preferred. Table 1.2 shows the electronic coupling data for a series of dinuclear pentaamine ruthenium complexes.

C. The Nature of the Outer Coordination Sphere

Modification of metal-metal coupling is not just restricted to the inner coordination sphere. The outer sphere can also perturb the metal-metal coupling in a mixed-valence complex. Curtis, et al.[31] showed that metal-metal coupling

in dinuclear ammine complexes decreased with increasing donor number of the solvent. This dependency suggested a hydrogen-bonding type of interaction involving the solvent's non-bonding electrons and the N-H bond. The strength of this interaction is greater for an ammine bound to a Ru(III) ion because of the greater acidity of ammine protons compared to those of an ammine bound to Ru(II). The net effect of this interaction is the transfer of electron density from the partially deprotonated ammine to the ruthenium ion. Thus, for asymmetric mixed valence complexes, the Ru(III) oxidation state is stabilized by strong donor solvents and $\Delta E_{1/2}$ increases with increasing donor number [32,33]. This solvent stabilization of the Ru(III) coordination sphere decreases delocalization of the odd electron and the magnitude of metal-metal coupling. The metal-metal coupling in delocalized mixed-valence systems (class III) is less sensitive to the solvent perturbation because the charge is distributed equally on both metal centers and therefore, the solvent stabilization of both metal ions is the same.

Table 1.2 Comproportionation constant and electronic data of IT band in D₂O for pentaammine ruthenium dimers.

Complex	K _C	$\epsilon_{\max}$ M ⁻¹ cm ⁻¹	H _{ab} eV	Class (Ref)
[{(NH ₃) ₅ Ru} ₂ (μ-4,4'-bpy)] ⁵⁺	20	9.2×10 ³	0.048	II, (34)
[{(NH ₃) ₅ Ru} ₂ (μ-Pz)] ⁵⁺	4×10 ⁶	4.8×10 ²	0.39	III, (35)
[{(NH ₃) ₅ Ru} ₂ (N≡C-) ₂] ⁵⁺	>10 ¹³	4.1×10 ²	0.44	III, (36)
[{(NH ₃) ₅ Ru} ₂ (NC-C(tBu)-CN)] ⁵⁺	>10 ¹⁰	1.6×10 ⁴	0.53	III, (37)
[{(NH ₃) ₅ Ru} ₂ (μ-NCPhCN)] ⁵⁺	23.4	507	0.029	II, (38)
[{(NH ₃) ₅ Ru} ₂ (μ-dicyd)] ³⁺	10	-	-	II, (39)
[{(NH ₃) ₅ Ru} ₂ (μ-Me ₂ dicyd)] ³⁺	28	-	-	II, (39)
[{(NH ₃) ₅ Ru} ₂ (μ-Cl ₄ dicyd)] ³⁺	13	575	-	II, (39)
[{(NH ₃) ₅ Ru} ₂ (μ-Cl ₂ dicyd)] ³⁺	21	-	-	II, (39,40)

1.4 Magnetic Properties

The magnetic properties of a substance arise mainly from the electrons in a molecule because the magnetic moment of an electron is about 10^3 times that of the proton[41]. Both diamagnetic and paramagnetic effects contribute to the magnetic susceptibility χ_m of a molecule (the tendency of a molecule to align its magnetic dipoles with an external field).

$$\chi_m = \chi_{dia} + \chi_{para} \quad (1.9)$$

Diamagnetism arises from field-induced electron circulation of paired electrons, which generate a field opposite to applied field. Thus, all molecules have contributions from diamagnetic effects. The molar diamagnetic susceptibility of a compound χ_{dia} can be obtained by summing the diamagnetic contribution from all of the atoms χ_A and from all of the bonds χ_B in functional groups.

$$\chi_{dia} = \sum \chi_A + \sum \chi_B \quad (1.10)$$

The values for χ_A and χ_B are referred as Pascal's constant and can be found in several references. χ_A can be calculated from equation (1.11).

$$\chi_A = -(Ne^2/6mc^2) \sum_n r_i^2 = -2.83 \times 10^{10} \sum_n r_i^2 \quad (1.11)$$

where n is the number of electrons located at a radius r .

The paramagnetic contribution to susceptibility arises from the spin and orbital angular moments of electrons interacting with the external field. The magnetic moment associated with a system containing only one unpaired electron is given by

$$\mu = g \beta S \quad (1.12)$$

where S is the spin angular momentum, g is the g -factor of electron and β is the Bohr magneton of an electron.

The macroscopic magnetic moment, M is the population weighted sum of magnetic moments over the individual states for a mole of compound.

$$M = N \sum_n \mu_n P_n = Ng^2 \beta^2 H / 4kT \quad (1.13)$$

Where N is Avogadro's number, P_n is the individual probability of each state, T is absolute temperature, k is Boltzmann's

constant, g is the electron g -factor, β is the Bohr magneton, S is the spin angular momentum operator.

The molar magnetic susceptibility, χ_m is related to the magnetic moment by

$$\chi_m = M/H = Ng^2\beta^2/4kT \quad (1.14)$$

Equation (1.14) is the so called Curie law and it predicts a straight-line relationship between the susceptibility and the reciprocal of temperature [42]. This type of behavior is the ideal case. Non ideal behavior leads to Curie-Weiss law[43]

$$\chi_m = C/(T - \theta) \quad (1.15)$$

where $C = (Ng^2\beta^2)/4k$ and θ corrects the temperature for the non-zero intercept. A plot of magnetic susceptibility for a system that obeys the Curie-Weiss law yields the straight solid line as shown in Figure 1.3. The intercept of the line with the temperature axis gives both the sign and magnitude of the Weiss constant. A positive value for θ (lower dashed line in Figure 1.3) is caused by ferromagnetic spin interactions, while a negative value (upper dashed line Fig. 1.3) is caused by antiferromagnetic spin interactions[43]. Fig. 1.4 shows the three most common types of magnetic behavior

Figure 1.3 The plot $(1/\chi_m)$ versus temperature, (i) ferromagnetic, (ii) paramagnetic, (iii) antiferromagnetic behavior.

Figure 1.4 Temperature dependence of (i) ferromagnetic, (ii) paramagnetic, and (iii) antiferromagnetic behavior.

namely paramagnetic, ferromagnetic and antiferromagnetic. The temperature at which the maximum occurs for the antiferromagnetic system is called the Neel temperature (T_N) while for ferromagnetic systems the temperature at which the deviation from paramagnetic behavior occurs is called the Curie temperature (T_C). Magnetic susceptibility and magnetic moment are macroscopic properties. For transition metal complexes, it is common to use the microscopic quantity called the effective magnetic moment, μ_{eff} with units of Bohr magnetons (BM) [41].

$$\mu_{eff} = [3k/N\beta^2]^{1/2} (\chi'_m T)^{1/2} = 2.83 (\chi'_m T)^{1/2} \quad (1.16)$$

The susceptibility, χ'_m , used in the expression is the corrected paramagnetic susceptibility.

1.5 Magnetic Electron Exchange in Dinuclear Ruthenium complexes.

Depending on the nature of inner and outer coordination spheres, Ru(III) dinuclear complexes show different magnetic behavior. The Ru(III) ion is a low spin d^5 system with an

unpaired electron in t_{2g} ground state(t_{2g}^5)(e_g^0). Therefore, each Ru(III) has one unpaired electron with spin ($S = 1/2$). The Hamiltonian for the magnetic interaction between the spins of two ruthenium(III) ions can be written[44]

$$H = -2J S_a \cdot S_b \quad (1.17)$$

where the exchange coupling constant J is positive if the spins are parallel and negative if they are paired. If two Ru(III) with $S = 1/2$ are antiferromagnetically coupled, a singlet ground state and excited triplet state that are separated in energy by $-2J$ are created.

Ferromagnetic coupling results in the formation of a triplet ground state and excited singlet state. Whether a singlet or triplet ground state is formed depends on the magnitude of ferromagnetic (J_F) and antiferromagnetic (J_{AF}) terms.

$$2J = J_F - J_{AF} \quad (1.18)$$

Where J_F represents the overall spin pairing energy and J_{AF} is the energy released as a result of the coupling of spin. The magnitude of J_{AF} reflects the extent of electron exchange stabilization.

Bertrand[45] gave the following relationship between J_{AF} and H_{ab} (extent of electronic coupling).

$$J_{AF} = 2/H_{ab} / E_{op}' \quad (1.19)$$

E_{op}' is the charge transfer energy between the initial and final states(shown below).

So any factors (i.e. solvent, spectator and bridging ligand) which perturb H_{ab} , affect J_{AF} the same way.

1.6 Experimental Evaluation of the Electron Exchange Constant J .

J can be experimentally evaluated by variable temperature magnetic susceptibility measurements[44]. The simplest model for the analysis of susceptibility data for $S = 1/2$ spin coupled dimers is the so called Bleaney-Bowers equation[46].

$$\chi_m = (2Ng^2\beta^2/3kT)[1 + 1/3 \exp(-2J/kT)]^{-1} \quad (1.20)$$

Where all the symbols have been previously defined.

Inspection of this equation shows that for negative J (antiferromagnetic), χ_m has a maximum (Figure 1.5). This usually occurs at $J/kT_m \approx -4/5$ (where T_m is the temperature at the maximum χ_m). For positive J (ferromagnetic) the magnetic susceptibility becomes large at lower temperature Figure 1.6.

It appears that the chemical nature of the bridging ligand has a profound effect on the efficiency of magnetic exchange. Coffman and Buettner[47] proposed that while the nature of bridging medium may very well contribute to the efficiency of the propagation of magnetic information, the dominant factor was the separation between metal magnetic

Figure 1.5 A plot of the Bleaney-Bowers equation for an $S = 1/2$ spin coupled dimer with a typical set of parameters, $g = 2.2$ and $2J/k = -30$ K.

Figure 1.6 The Bleaney-Bowers equation (dashed line) for $S = 1$, $g = 2.2$ and $J/k = 30$ K compared with the Curie law (solid line) with $S = 1/2$ per mole and $g = 2.2$.

orbitals. They proposed the following limit function for antiferromagnetic exchange.

$$|2 J_{lim}| = 1.35 \times 10^7 \exp(-1.80 R) \quad (1.21)$$

where J is the antiferromagnetic exchange coupling constant (in cm^{-1}) and R is the distance between metal ions (in $\text{\AA}$).

The above equation predicts negligible coupling, $|J| < 0.5 \text{ cm}^{-1}$ at distances greater than $10 \text{ \AA}$. This relationship has held up fairly well with some exceptions. In a study, Chaudhuri et al, [48] showed the existence of moderately strong antiferromagnetic coupling ($J = -70 \text{ cm}^{-1}$) between Cu(II) ions in a μ -terephthalato complex in which the metal-metal separation was $11.25 \text{ \AA}$. Here equation (1.21) predicts $|2J_{lim}| = 0.02 \text{ cm}^{-1}$.

In another study in Ru(III) complexes, Aquino et.al[39] reported the synthesis of dinuclear Ru(III) complexes bridged by 1,4-dicyanamidobenzene dianion ligand and its derivatives with an internuclear distance of $13.2 \text{ \AA}$. At this separation, equation (21) predicts $|2J_{lim}| = 6.5 \times 10^{-4} \text{ cm}^{-1}$. The experimental values obtained (Table 1.3) are in total disagreement with the predicted value.

The failure of the Coffman and Buettner limit function for Ru(III) complexes arises from the difference in the nature

and properties of the superexchange pathway as compared with Cu(II) complexes. In Cu(II), the unpaired electron occupies a mostly σ symmetry d -orbital and a change would occur via the σ bonding framework of the bridging ligand. The energy gap(>3.0 eV) between Cu(II) magnetic orbitals and σ bonding superexchange pathway is very large and this doesn't favour superexchange coupling.

Table 1.2 Magnetic coupling data for dinuclear ruthenium (III) Complexes.

Complex ^a	M-M(Å)	J(cm ⁻¹)	Ref.
[{LRu} ₂ (μ-O)(μ-OAC) ₂](PF ₆) ₂	3.26	diamg.	49,50
[{Ru(bpy) ₂ NO ₂ } ₂ (μ-O)](PF ₆) ₂	3.69	-87	51,52
[{NH ₃ } ₅ Ru] ₂ (μ-pz)](OTs) ₆	6.8	J<0.2	53,54
[{(NH ₃) ₅ Ru] ₂ (μ-dicyd)](ClO ₄) ₄	>13	diamg.	39
[{(NH ₃) ₅ Ru] ₂ (μ-Me ₂ dicyd)](ClO ₄) ₄	>13	diamg.	39
[{(NH ₃) ₅ Ru] ₂ (μ-Cl ₂ dicyd)](ClO ₄) ₄	>13	-95.9	39
[{(NH ₃) ₅ Ru] ₂ (μ-Cl ₄ dicyd)](ClO ₄) ₄	>13	61.9	39

L = N,N',N''-trimethyl-1,4,7-triazacyclononane.

For the Ru(III) complexes (Table 1.2), the electron exchange pathway occurs a via Ru(III)- $d\pi$ orbital and the π symmetry HOMO of the bridging Dicyd⁻² ligand. The energy gap between Ru(III) $d\pi$ -orbitals and the π HOMO of the dicyd⁻² ligand is significantly smaller(0.48 to 0.94 eV) compared to the Cu(II) dimers of the Coffman-Buettner study and it was suggested that this permitted strong antiferromagnetic coupling at large separation(13 Å) between Ru(III) ions[39,56].

1.7 Magnetic Susceptibility Measurement in Solution (Evans Method) .

In 1959, D. F. Evans[57] outlined a method for determining the paramagnetic susceptibility of a substance in solution utilizing nuclear magnetic resonance spectroscopy(NMR). He related the observed difference in chemical shift(Hz) of a signal from an inert reference material(tetramethylsilane TMS) in the presence and absence of a paramagnetic solute to the mass susceptibility χ_g of the solute with the following equation[58].

$$\chi_g = (3\Delta f/2\pi\nu) + \chi_o + \chi_o(d_o - d_s)/m \quad (1.22)$$

Where χ_g is the mass susceptibility of the sample (cm^3/g), Δf is the separation of the resonance line in the presence and absence of paramagnetic solute (Hz), ν is the probe frequency (frequency of spectrophotometer Hz), χ_o is the mass susceptibility of the pure solvent, m is the concentration of the paramagnetic substance expressed in g/cm^3 , d_o is the density of the solvent (g/cm^3) and d_s is the density of solution (g/cm^3).

Equation (1.22) is limited to Evans method experiments which use NMR spectrometers with a magnetic field perpendicular to the sample. Modern high-field spectrometers produce a magnetic field parallel to the cylindrical sample axis. For their instruments, Live and Chan[59] found the Δf (difference in chemical shift of a reference signal) was twice in magnitude and of the opposite sign from that predicted by equation (1.22). Thus, the Evans equation should be corrected as follows[60].

$$\chi_g = (-3\Delta f/4\pi m\nu) + \chi_o + \chi_o(d_o - d_s)/m \quad (1.23)$$

The term $\chi_o + [\chi_o(d_o - d_s)/m]$ has been found to make only a small correction and in the cases where the paramagnetism is large, this term is negligible[61]. The mass susceptibility

χ_g may be converted into molar susceptibility χ_m by multiplying the χ_g by the molecular weight of the complex.

$$\chi_m = \chi_g \times M \quad (1.24)$$

χ_m must be corrected for inherent diamagnetism of atoms using Pascal's constants. The corrected magnetic susceptibility χ_m' can be related directly to the effective magnetic moment by equation (1.16).

1.8 Nuclear Magnetic Resonance in Paramagnetic systems

The proton magnetic resonance of paramagnetic complexes started first in laboratory of Prof. L. Sacconi in his studies of nickel(II) complexes[62,63]. The observed shifts from the TMS (inert reference) in the presence of a paramagnetic compound are well outside the normal range of proton shift in diamagnetic compound(-2 to 10 ppm)[64]. For a paramagnetic solute, the observed nuclear resonance spectrum arises from both diamagnetic and paramagnetic shift given by

$$(\Delta\nu/\nu)_{\text{observed}} = (\Delta\nu/\nu)_{\text{dia}} + (\Delta\nu/\nu)_{\text{para}} \quad (1.25)$$

where $(\Delta\nu/\nu)$ represents the particular shift in ppm. The last term in the above equation represents the paramagnetic effects that occur as a result of unpaired electron-nucleus interactions. This contribution to the chemical shift is sometimes called the hyperfine or isotropic shift[65]. There are two principal interactions between an unpaired electron and nuclei within a paramagnetic molecule, called the contact shift and the pseudo-contact shift.

$$(\Delta\nu/\nu)_{\text{isotropic}} = (\Delta\nu/\nu)_{\text{contact}} + (\Delta\nu/\nu)_{\text{dipolar}} \quad (1.26)$$

The extent and the type of interaction are determined by the nature of the paramagnetic center, by its coordination geometry and by the nature of its ligands.

The first of these intramolecular interactions is a result of unpaired spin density being transferred off the metal onto the ligand through the chemical bonds(σ or π). Thus, the contact shift relates to the extent of metal-ligand bonding and is given by the following relationship[66],

$$(\Delta\nu/\nu)_{\text{contact}} = A_{\text{con}} \{g\beta S(S+1)\} / (3g_n h k T) \quad (1.27)$$

where A_{con} is the contact hyperfine coupling constant, S is the spin quantum number of a paramagnetic center, g_n is the

magnetogyric ratio of the nucleus and the other symbols have already been defined. A_{con} is proportional to the amount of unpaired spin density at the resonating nucleus as a result of a direct delocalization via chemical bonds. So, different nuclei in a molecule may have different hyperfine coupling constants.

The second term in Eqn. 1.26 represents non-exchange type coupling between electron magnetic moments and nuclear magnetic moments. Dipolar coupling is a through space type of interaction which depends on the relative location of the two magnetic moments (electron and nuclear) which are oriented along the magnetic field. Upon rapid rotation, as occurs in solution, this contribution is averaged and is called the pseudocontact shift. In the point-dipole approximation, i.e. when the unpaired electron or electrons are assumed to be localized on the metal ions, the pseudocontact contribution is given by [67],

$$(\Delta\nu/\nu) = (3 \cos^2 \theta - 1)(g_{\parallel} - g_{\perp}) / 12\pi r^3 \quad (1.28)$$

where r is the metal-nucleus distance, θ is the angle formed by r with the molecular z axis, $g_{\perp}$ and $g_{\parallel}$ are the equatorial and axial components of the g value respectively and the other quantities have been already defined. The $(3 \cos^2 \theta - 1)$ term is

frequently referred to as the geometric factor. The relative direction of the dipolar shift depends on the sign of the magnetic anisotropy, represented by the g factor term and the θ . The above equation suggests that the magnitude of a dipolar shift depends upon the magnitude of g anisotropy, the geometry factor, and the distance of a nucleus from the metal. Thus, the largest dipolar shifts should occur for nuclei that have the largest geometric factor, that are closest to metal, and that have the largest g anisotropy.

If more than one paramagnetic metal ion is present (dinuclear ruthenium complexes) the metal ions can be antiferromagnetically coupled, and this can dramatically affect the NMR chemical shifts [68,70]. As mentioned in Section 1.5, this antiferromagnetic coupling between the electron spin moments of the two paramagnetic centers results in the formation of a singlet ground state and a triplet excited state. The Boltzmann distribution between these two states depends on the magnitude of magnetic exchange coupling. The magnetic moment which is sensed by each individual nucleus, is the average of this spin distribution. Magnetic coupling may be affected by both the outer coordination sphere (solvent) and the inner coordination sphere (bridging and spectator ligands).

1.9 The Chemistry of Metal-Cyanamide Complexes

Phenylcyanamide anion (pcyd^{-2}) ligands are pseudohalides [71] and are stabilized by two resonance forms (Figure 1.7)[72]. Two pairs of non-bonding π electrons are delocalized on the cyanamide group. π_{nb2} is more stable than π_{nb1} because only π_{nb2} has correct symmetry to mix into the bonding σ orbitals of the phenyl ring as shown by extended Huckel calculations [71,72].

In order to explore the coordination chemistry of the cyanamide group, the following complexes, pentaammineruthenium(III) phenylcyanamide [71,73,74], pentaammineruthenium(III) dicyanamidobenzene dinuclear complexes [39,40,75], 1,3-bis(2-pyridylimino)isoindolinateonickel(II) phenylcyanamide [76], (2,2'-bipyridine) copper(II) phenylcyanamide [77], (2,2',2''-terpyridine)palladium(II) phenylcyanamide [78], diethylene-triaminecopper(II), and 1,3-bis(2,pyridylimino)isoindolinate copper(II) phenylcyanamide complexes and their dinuclear complexes [79] have been synthesized and characterized by Crutchley et.al.

The X-ray crystal structure of pentaammineruthenium(III) 2,3-dichlorophenylcyanamide complex shows that the anionic

(a)

(b)

Figure 1.7 (a) Resonance stabilized phenylcyanamide anion ligand. (b) π -symmetry orbitals (π_{nb1} is orthogonal to π_{nb2}) resulting from the delocalization of two bonding electron pairs as in resonance form B. The size of atomic orbitals approximate their contribution to the molecular orbital.

cyanamide and phenyl group are nearly co-planar, indicating that a strong π interaction exists between Ru(III) and the cyanamide moiety. The electronic properties of the Ru(III)-cyanamide LMCT (ligand to metal charge transfer) chromophore have been probed by varying the nature of the cyanamide ligand and by outer coordination sphere perturbation(solvent). A linear correlation was found between the optical energy(E_{op}) of LMCT band and the potential difference between ligand, $L(0/-)$ and $Ru(III/II)$ reduction couples, and showed that the complexes have similar properties with the only variable being the nature of the substituent on the phenyl ring. A linear relationship was also found between the oscillator strength of the LMCT band and the solvent donor numbers as well as the energy of LMCT band (shift to higher energy as the donor number of the solvent is increased) [74].

In another study, Aquino et al. synthesized and characterized a series of bis(pentaammineruthenium(III)) dinuclear complexes bridged by a 1,4-dicyanamidobenzene dianion ($dicyd^{2-}$) derivative ligand [39,40,75]. The X-ray crystal structure of one complex, $[{(NH_3)_5Ru}_2(\mu-dicyd)](CH_3C_6H_4SO_3)_4$, showed that two forms of the dimer (linear and bent) existed in each unit cell. In both forms the bridging ligand ($dicyd^{2-}$) is nearly planar and the cyanamide groups are in an anti-configuration. The electronic coupling for $[Ru(III), Ru(II)]$ and antiferromagnetic coupling

for the [Ru(III), Ru(III)] dinuclear complexes were investigated. Variable temperature magnetic susceptibility measurements of these complexes showed the Ru(III) ions to be strongly antiferromagnetically coupled. The magnitude of magnetic exchange constant $-2J$ (100 to ≥ 800 cm⁻¹) is unprecedented at a separation between Ru(III) ions of 13 Å. In contrast to strong antiferromagnetic coupling in fully oxidized [Ru(III), Ru(III)]dinuclear complexes, the electronic coupling in mixed-valence [Ru(III), Ru(II)] complexes showed only very weak coupling in water. These systems were classified as localized class II (valence-trapped).

In order to explore the properties of the above dinuclear complexes, Naklicki et al. [80,81] studied the effect of the outer coordination sphere on the metal-metal interaction. These studies demonstrated a remarkable sensitivity of metal-metal coupling on the nature of solvent. This effect arises from a preferential solvent donor-acceptor interaction with the pentaammineruthenium(III) moiety, which decouples the Ru(III) ions from the cyanamide groups of the bridging ligands.

1.10 Research Goals and the Aims of Thesis

The ultimate goal of our research group is to build a molecular wire to allow the intramolecular propagation of an electron between a donor and acceptor site through a polymer chain. To achieve this, the symmetry and energy match of the metal $d\pi$ orbital and the bridging ligand's orbitals, should be as close as possible. The electronic properties of the Ru(III)-cyanamide moiety have been probed by varying the nature of the cyanamide ligand and by the outer-coordination sphere perturbation of solvent molecules. It is well known that the nature of the spectator ligands can also play an important role in adjusting the energy and size of metal orbitals and can therefore be used to significantly perturb both electronic and magnetic exchange coupling in dinuclear ruthenium complexes.

The replacement of the ammine ligands(π -donor) with the π -acceptor (pyridine type) ligands is expected to increase the stability of the ruthenium d -orbitals in both +2 and +3 oxidation states because of pyridine's π -acceptor properties and pyridine's poor σ -donor properties compared to the ammine ligand. To examine this perturbation, the following steps are the aims of thesis.

1. Synthesis and characterization of a series of mononuclear complexes, $[\text{Ru}(\text{bpy})_2(\text{Cl}_n\text{-pcyd})_2]$ where bpy = 2,2'-bipyridine, $n = 0, 1, 2, 3, 4, 5$, and pcyd = phenylcyanamide anion ligand. The *LMCT* spectra and redox chemistry of these complexes will be compared to those of their pentaammineruthenium(III) phenylcyanamide analogues.

$\text{Ru}(\text{bpy})_2 (2,3\text{-Cl}_2\text{-pcyd})_2$

2. Synthesis and characterization of $[\{(\text{bpy})(\text{trpy})\text{Ru}\}_2(\mu\text{-dicyd})](\text{PF}_6)_2$.

3. Synthesis and characterization of a series of dinuclear complexes, $\text{trans-}[\{\text{pyRu}(\text{NH}_3)_4\}(\mu\text{-dicyd})](\text{PF}_6)_4$.

- $\text{X}_1=\text{X}_2=\text{H}$
- $\text{X}_1=\text{H} \quad \text{X}_2=\text{CH}_3$
- $\text{X}_1=\text{X}_2=\text{Cl}$
- $\text{X}_1=\text{H} \quad \text{X}_2=\text{Cl}$

4. To investigate the electronic coupling in the mixed valence form of the dinuclear complexes.
5. To investigate magnetic susceptibility in $[\{\text{pyRu}(\text{NH}_3)_4\}(\mu\text{-dicyd})](\text{PF}_6)_4$ complexes both in the solid state by temperature dependent magnetic susceptibility measurements and in solution by the Evans method.
6. Comparison of the results of these studies with the analogous pentaammineruthenium(III) dinuclear complexes.

CHAPTER 2

EXPERIMENTAL

2.1 Starting Materials

2.1.1 Reagents for Ligand Syntheses

Ammonium thiocyanate (reagent grade, Fisher Scientific Co.), benzoyl chloride (99%, reagent grade, Aldrich Chem. Co.), lead acetate trihydrate (reagent grade, Anachemia), sodium hydroxide (lab grade, Anachemia), glacial acetic acid (99.7%, reagent grade, Anachemia), aniline (99%, Aldrich Chem. Co.), iron metal (powder, Fisher Scientific Co.), thallium acetate (99.99%, Aldrich Chem. Co.), triethylamine (TEA, 99%, Aldrich Chem. Co.), pentachloronitrobenzene (96%, Aldrich), hydrochloric acid (36.5-38%, reagent grade, Anachemia), 1,4-phenylenediamine (97%, Aldrich), 2,5-dichloro-1,4-phenylenediamine (Aldrich), 2,5-dimethyl-1,4-phenylenediamine (97%, Aldrich) were used as received. 2,3,5,6-tetrachloro-1,4-phenylenediamine was prepared from 1,4-phenylenediamine and thionyl chloride[82]. The protonated and thallium salts of phenylcyanamide(pcyd) derivatives, 2-chlorophenylcyanamide

(2,Clpcyd), 2,3-dichlorophenylcyanamide (2,3-Cl₂pcyd), 2,4,5-trichlorophenylcyanamide(2,4,5-Cl₃pcyd), 2,3,4,5-trichlorophenylcyanamide(2,3,4,5-Cl₄pcyd), pentachlorophenylcyanamide (Cl₅pcyd) were prepared by literature methods[72,73,74,83,84]. The neutral and the tetraphenylarsonium salts of 1,4-dicyanamidobenzene(dicyd), 1,4-dicyanamido-2,5-dimethylbenzene (Me₂dicyd), 1,4-dicyanamido-2,5-dichlorobenzene (Cl₂dicyd), 1,4-dicyanamido-tetrachlorobenzene (Cl₄dicyd) were prepared by literature methods[40].

2.1.2 Reagents for Metal Complex Syntheses

Ruthenium(III)chloride (Johnson Matthey), 2,2'-bipyridyl (99+%,Aldrich), 2,2'2"-terpyridine (98%,Aldrich), lithium chloride (reagent grade, Mallinckrodt), silver hexafluoro phosphate (98%, Aldrich), ammonium hexafluorophosphate (99.99%, Aldrich), tetraphenylboron sodium (99.5%, reagent grade, Aldrich), hydrochloric acid (36.5-38%, reagent grade, Anachemia), hydrazine monohydrate (98%,Aldrich), tetrabutyl ammonium bromide (99%, Aldrich), sulfur dioxide (gas-Matheson), sodium bisulfite (reagent grade, Fisher Scientific, Co.), pyridine (distilled in glass, Caledon) were used as received. Zinc/Mercury amalagam was prepared by first cleaning zinc metal (mossy, reagent grade, Anachemia) with 1 M

HCl then treating with a saturated solution of mercurous chloride (reagent grade, Anachemia).

Cis-dichlorobis (2,2'-bipyridine)

ruthenium(II) . *cis*-[Ru(II) (bpy)₂ Cl₂] .

This was prepared by a method similar to that of Sullivan et al[85]. A mixture of 6.18 g(29.8 mmol) of RuCl₃, 9.36 g(60 mmol) 2,2'-bipyridine and 8.4 g(0.2 mol) LiCl were heated in 50 ml reagent grade dimethylformamide and refluxed for 8 hours. The reaction was stirred throughout this period. After the reaction mixture was cooled to room temperature, 250 mL of reagent grade acetone was added and the resultant solution cooled at 0 °C overnight. The dark-green black micro crystals were filtered off and washed three times with 25 mL portions of water followed by three 25 ml portions of diethyl ether and dried in vacuo. The yield of *cis*-[Ru(bpy)₂ Cl₂] was 9.35 g (65%).

TriChloro-terpyridineruthenium (III)

655 mg(2.5 mmol)ruthenium trichloride(RuCl₃) and 582.5 mg 2,2',2''-terpyridine were dissolved in 200 ml of absolute ethanol. The mixture was heated at reflux for 3 hour while being stirred vigorously. Upon cooling, the fine brown powder product was precipitated and filtered out. The product was washed with 3 X 30 mL portions of absolute ethanol followed by 3 X 30 mL portions of ether and air dried. The yield of [Ru(terpy)Cl₃] was 1.090 g (79.3%)[86].

Chloro(2,2',2''-terpyridine)(2,2'-bipyridine) ruthenium(II) hexafluorophosphate. [Ru(bpy)(terpy)Cl]PF₆.

[Ru(terpy)(bpy)Cl]PF₆ was prepared by the method of Calvert and et al.[87] with a small modification. A mixture of Ru(terpy)Cl₃ (528 mg, 1.20 mmol) and 2,2'-bipyridine (197 mg, 1.26 mmol) in 150 mL 4:1 (v/v) water/ethanol was heated at reflux for 5 hours, then an excess amount of LiCl(500 mg) was added and the mixture heated for an additional 30 min. 200 mg

NH_4PF_6 was added and the volume of solution reduced by rotary evaporation to about 50 mL and left in fridge overnight. The brown solid product was filtered out. The crude product was purified by column chromatography using grade III alumina type WA-I(Sigma) and a 2:1 mixture of toluene/acetonitrile as eluent. The main deep purple band was collected and the solvents evaporated to dryness by rotary evaporation. The deep-purple powdery residue was recrystallized by the diffusion of ether into a acetone solution of the complex. The yield was 500 mg (63%).

Chloropentaammineruthenium(III)

Chloride. $[(\text{NH}_3)_5\text{RuCl}]\text{Cl}_2$.

This starting material was prepared by a method similar to that of Clarke[88]. 5 g(24 mmol)of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ was slowly added to 125 ml solution of 1:1 hydrazine(64%)/water and stirred overnight. The purple-red solution was then cooled in an ice bath and 125 mL of concentrated HCl(12 M) added very slowly. The resulting mixture was heated at reflux for 2 hours, then allowed to cool in the fridge for 3 hours. The yellow-orange product was filtered off and recrystallized from 0.1 M HCl. The final yield of $[(\text{NH}_3)_5\text{RuCl}]\text{Cl}_2$ was 4.97 g (71%).

**Trans-Chlorotetraamminesulphur dioxide
ruthenium (II) Chloride.**

A mixture of $[(\text{NH}_3)_5\text{Ru}(\text{III})\text{Cl}]\text{Cl}_2$ (5 g, 17 mmol) and NaHSO_3 was dissolved in 200 mL water, then heated at 80 °C for 90 min. A continuous stream of SO_2 gas was bubbled through the solution during this period. Upon cooling in fridge overnight, the pale yellow microcrystals of $\text{trans-}[(\text{NH}_3)_5\text{Ru}(\text{HSO}_3)_2]$ was filtered out and washed with acetone, and dried in vacuo. This material was then heated at reflux for 20 min in 400 mL of 6 M HCl . Upon cooling, the fine orange crystals of product was precipitated and filtered out. The yield of $\text{trans-}[(\text{NH}_3)_4\text{RuSO}_2\text{Cl}]\text{Cl}$ was 2.80 g (60%)[89].

**Trans-Sulphate (pyridine) tetraammine
ruthenium(III) Chloride.**

Trans- $[(\text{NH}_3)_4\text{RuSO}_4\text{py}]\text{Cl}$.

In a typical preparation, 2.8 g (8.4 mmol) of *trans*- $[(\text{NH}_3)_4\text{RuSO}_2\text{Cl}]\text{Cl}$ was dissolved in 140 mL neutral water at 40 °C and five molar excess of pyridine (3.6 mL, 42 mmol), added then the solution stirred until the color changed from orange to yellow was complete. The product *trans*- $[(\text{NH}_3)_4\text{RuSO}_2\text{py}]\text{Cl}_2$ was precipitated by adding 500 mL of acetone, collected by filtration, washed with acetone and ether and dried in vacuo. This solid was then dissolved in a minimum volume of water (120 mL) and filtered out. To this solution was slowly added 84 mL of an oxidizing solution consisting of 1:1 mixture of HCl(2 M)/H₂O₂(30%) and stirred for 10 min to ensure complete reaction. The yellow product, *trans*- $[(\text{NH}_3)_4\text{RuPySO}_4]\text{Cl}$, was precipitated by adding of 2 litres of acetone. The yield was 2.9 g (83%) [90].

**Trans-pyridine (aqua) tetraammine
ruthenium(II) hexafluorophosphate.**

This was prepared in a glove bag under argon, in a similar manner to that of Chang et al.[90] 2.9 g of [(NH₃)₄RupySO₄]Cl was dissolved in 50 mL of water and reduced over a fresh Zn/Hg amalgam for 10 to 15 min. The resulting orange-red solution was transferred to a flask containing a 10 fold molar excess of NH₄PF₆ (12 g) and stirred under argon for 5 min then cooled in fridge. The yellow product was filtered out under argon and washed with ether. The yield was 2.9 g (67%).

2.1.3 Solvents

N,N-Dimethyl formamide (DMF) (reagent and Accusolv grade), Ethanol(absolute, Consolidated Alcohols Ltd.), diethyl ether (anhydrous,Caledon Labs Ltd.), acetone (spectro grade, Caledon Labs Ltd.), acetonitrile (reagent and HPLC grade, Caledon Labs Ltd), acetonitrile (anhydrous, aldrich), toluene (spectra grade, Caledon Labs Ltd.), dichloromethane (reagent grade, Anachemia), methanol (spectra grade, Caledon Labs

Ltd.), dimethylsulphoxide (DMSO, distilled in glass, Anachemia), deuterated acetonitrile (99.9 atom %D, Cambridge isotopes Ltd.), deuterated dimethylsulphoxide (99.5 atom % D, Aldrich) and deuterated nitromethane (99 atm, %D, Aldrich) were used as received. Caledon HPLC grade acetonitrile was distilled over activated alumina and degassed under vacuum prior to use in cyclic voltammetry and electrolysis. Accusolv grade DMF was deoxygenated and stored under argon prior to use in cyclic voltammetry and electrolysis.

2.1.4. Electrolyte and Chromatography.

Tetrabutylammonium hexafluorophosphate (98%, Aldrich) was recrystallized from ethanol twice and dried under vacuum at 110 °C for 18 hours. Alumina, for column chromatography (activity grade 1, type WA-1:acid, Sigma) was deactivated to grade III and I by adding 6% and 15% water, and stirred for two hours. CM-Sephadex C25 cation exchange resin (bead size: 40-125 microns, Sigma) and sodium chloride (99+% reagent grade, Anachemia) were used as received.

2.2 Syntheses of Mononuclear Metal Complexes.

Cis-bis (phenylcyanamide)bis (2,2'-bipyridine) ruthenium(II) .

Cis- [Ru (bpy) ₂ (pcyd) ₂] .

A mixture of deprotonated phenylcyanamide(Tl salt) (321.4 mg, 1 mmol) and cis-[Ru(bpy)₂Cl₂] (242 mg, 0.5 mmol) dissolved in 20 mL of DMF was stirred at reflux temperature for 3 hours. The resulting reaction mixture was allowed to cool to room temperature and then left in a refrigerator overnight . A white solid (TlCl) was filtered off. 500 mL ether was added to deep purple filtrate, and the solution was placed in the refrigerator overnight. The dark brown product which precipitated was filtered off and washed with ether. For further purification, the complex was crystallized by diffusing ether into a DMF solution. The deep purple needle crystals were collected and dried under vacuo overnight. yield: 200 mg (62%). Anal. Calcd.(%) for C₃₄H₂₆N₈Ru: C, 63.06; H, 4.01; N, 17.31. Found: C, 62.41; H, 4.12; N, 17.22[91].

Cis-bis (2-Chlorophenylcyanamide) bis (2,2'-bipyridine) ruthenium (II) .

Cis- [Ru (bpy) ₂ (2-Clpcyd) ₂] .

This complex was prepared in a similar manner to that of *cis*-[Ru(bpy)₂(pcyd)₂] using the following reagent amount: 242 mg (0.5 mmol) and 356 mg Tl(2-Clpcyd). Crystallization was carried out in the same fashion as for the *cis*-[Ru(bpy)₂(pcyd)₂] complex. Yield 200 mg (56%). Anal. Calcd. (%) for C₃₄H₂₄N₈Cl₂Ru: C, 56.98; H, 3.35; N, 15.64. Found: C, 56.81, H, 3.53; N, 15.92.

Cis-bis (2,3-dichlorophenylcyanamide) bis (2,2'-bipyridine) ruthenium (II) .

Cis- [Ru (bpy) ₂ (2,3-Cl₂pcyd) ₂] .

This complex was prepared in a similar way to *cis*-[Ru(bpy)₂(pcyd)₂], however, the following amounts were used: *Cis*-[Ru(bpy)₂Cl₂] (242 mg, 0.5 mmol) and thallium salt of 2,3-dichlorophenylcyanamide (390.4 mg, 1 mmol). Crystallization was done in similar manner to *cis*-[Ru(bpy)₂(pcyd)₂]. Yield was 282.6 mg (72%). Anal. Calcd. (%) for C₃₄H₂₂N₈Cl₄Ru:

C, 52.04; H, 2.80; N, 14.26. Found: C, 52.21; H, 2.97; N, 14.45.

**Cis-bis(2,4,5-trichlorophenylcyanamide)
bis(2,2'-bipyridine) ruthenium(II) .**

Cis-[Ru(bpy)₂(2,4,5-Cl₃pcyd)₂] .

This complex was prepared in a similar way to *cis*-[Ru(bpy)₂(pcyd)₂] with the following starting reagents: *Cis*-[Ru(bpy)₂(pcyd)₂] (242 mg, 0.5 mmol) and Tl(2,4,5-Cl₃pcyd) (426 mg, 1 mmol) and DMF (30 mL). Recrystallization was carried out in a similar fashion to *cis*-[Ru(bpy)₂(pcyd)₂]. The yield was 300 mg (70%). Anal. Calcd.(%) for C₃₄H₂₀N₈Cl₆Ru: C, 47.77; H, 2.34; N, 13.11. Found: C, 48.10; H, 2.50; N, 13.55.

**Cis-bis(2,3,4,5-tetrachlorophenyl
cyanamide)bis(2,2'-bipyridine) ruthenium
(II) . Cis-[Ru(bpy)₂(2,3,4,5-Cl₄pcyd)₂] .**

This complex was prepared in a similar manner to

cis-[Ru(bpy)₂(pcyd)₂] using the following reagent amounts: *Cis*-[Ru(bpy)₂Cl₂] (242 mg, 0.5 mmol), Tl(2,3,4,5-Cl₄pcyd) (470 mg, 1 mmol) and DMF (30 mL). Crystallization was accomplished in a similar way to *cis*-[Ru(bpy)₂(pcyd)₂]. Yield 300 mg (65%). Anal. Calcd.(%) for C₃₄H₁₈N₈Cl₈Ru: C, 44.20; H, 1.95; N, 12.13. Found: C, 44.33; H, 2.25; N, 11.92.

***Cis*-bis(pentachlorophenylcyanamide)**

bis (2,2'-bipyridine) ruthenium (II) .

***Cis*- [Ru (bpy) ₂ (Cl₅pcyd) ₂] .**

This complex was prepared in a similar way to *cis*-[Ru(bpy)₂(pcyd)₂] except for the following starting quantities: *Cis*-[Ru(bpy)₂Cl₂] (242 mg, 0.5 mmol), Tl(Cl₅pcyd) (494 mg, 1 mmol) and DMF (100 mL). To separate the product, more DMF was added and heated to reflux. Recrystallization was performed in the same fashion as *cis*-[Ru(bpy)₂(pcyd)₂]. The yield was 397 mg (80%). Anal. Calcd.(%) for C₃₄H₁₆N₈Cl₁₀Ru: C, 41.12; H, 1.61; N, 11.29. Found: C, 40.70; H, 1.76; N, 11.32.

2.3 Syntheses of Dinuclear Metal Complexes.

Trans-bis (pyridinetetraammineruthenium (III)) (μ -1,4-Dicyanamidobenzene) hexafluorophosphate.

Trans-[{ (NH₃)₄Rupy }₂ (μ -dicyd)] (PF₆)₄.

278 mg (0.5 mmol) of *trans*-[(NH₃)₄Rupy(H₂O)](PF₆)₂ and 39.5 mg (0.25 mmol) of DicydH₂ were placed in two separate 100 mL round bottom flask and purged with argon on a vacuum line. 80 mL of acetone was placed in a separate flask and degassed. The acetone was then transferred to both reactant flasks and stirred under argon to dissolve. The two solutions were mixed and stirred over night under an argon atmosphere with gentle heating (25-30 °C). The orange-red solution slowly turned to green. The solution was then exposed to air for one hour to ensure complete oxidation. To this dark-green solution was then added a solution of 1.5 g tetrabutylammonium bromide in 20 mL acetone and immediate precipitation of the crude dark-

green bromide salt occurred. This was then filtered and washed with 30 mL cold acetone and followed with ether.

For more purification the crude bromide salt was dissolved in a minimum amount of 0.3 M NaCl solution, filtering and loading the solution onto a 3 cm x 40 cm column of CM-Sephadex C25 cation exchange resin. Elution with a 0.3 M NaCl solution separated out a yellow band which was possibly due to unreacted ligand followed by a green-blue band and grass-green band (desired product). Elution with 0.5 M NaCl washed out the green-blue band (a mononuclear species with a charge of +2). The desired product (dinuclear complex with a charge of +4) was eluted with 1 M NaCl solution and crashed out as PF_6^- salt by adding excess amount of NH_4PF_6 . For recrystallization the PF_6^- salt was dissolved in a minimum volume of acetonitrile, filtered and then placing it in a jar containing diethyl ether. The deep grass-green needle crystals were obtained and washed with ether and dried in vacuo. Yield 50 mg (16.20%) based on starting materials. Anal. calcd.(%) for $\text{C}_{18}\text{H}_{38}\text{N}_{14}\text{P}_4\text{F}_{24}\text{Ru}_2\cdot\text{H}_2\text{O}$: C, 17.27; H, 3.19; N, 15.67. Found(%): C, 17.61; H, 2.99; N, 15.20.

The X-ray quality crystals of PF_6^- salt were grown from a dilute acetonitrile solution of the purified dinuclear complex by ether diffusion in a fridge for a week.

***Trans*-(μ -1,4-Dicyanamido-2,5-dimethyl
benzene)bis (pyridinetetraammineruthenium
(III)) hexafluorophosphate.**

***Trans*-[{ (NH₃)₄Rupy }₂ (μ -Me₂dicyd)] (PF₆)₄.**

This complex was prepared in a similar manner to [{ (NH₃)₄Rupy }₂ (μ -dicyd)] (PF₆)₄, with the following reagent amounts: *Trans*-[(NH₃)₄Rupy(H₂O)] (PF₆)₂ (278 mg, 0.5 mmol); Me₂dicydH₂ (46.5 mg, 0.25 mmol) and tetrabutylammonium bromide (1.5 g, 4.5 mmol). Purification was carried out in a similar fashion to that of *trans*-[{ (NH₃)₄Rupy }₂ (μ -dicyd)] (PF₆)₄. The yield was 65 mg (20.6%). Anal. Calcd.(%) for C₂₀H₄₂N₁₄P₄F₂₄Ru₂: C, 19.03; H, 3.33; N, 15.54. Found(%): C, 19.54; H, 3.38; N, 15.08.

(μ -1,4-Dicyanamido-2,5-dichlorobenzene)
 bis-*trans*-(pyridinetetraammineruthenium
 (III)) hexafluorophosphate.

Trans-[{ (NH₃)₄Rupy }₂ (μ -Cl₂dicyd)] (PF₆)₄:

The crude bromide salt of this complex was synthesized in a manner similar to that of *trans*-[{ (NH₃)₄Rupy }₂ (μ -dicyd)](PF₆)₄ with slight differences using the following reagent amounts: *trans*-[(NH₃)₄Rupy(H₂O)](PF₆)₂ (278 mg, 0.5 mmol); [AsPh₄]₂[Cl₂dicyd] (248 mg, 0.25 mmol due to poor solubility of the protonated ligand(Cl₂dicydH₂)) and 500 mL acetone(450 mL for bridging ligand and 50 mL for metal complex). Due to poor solubility of the ligand, the acetone solution had to be heated to 40-50 °C. Then the two solutions were mixed and stirred under argon overnight with gentle heating. The solution was then filtered through a medium glass frit, to remove the precipitated AsPh₄PF₆, and the volume of solution reduced to 50-60 mL and then exposed to air for 3-4 hour to ensure complete oxidation. To this yellow-greenish solution was then added 2 g tetrabutylammonium bromide to immediately precipitate the crude green bromide

salt. This was then filtered and washed with cold acetone. The crude product was dried in vacuo before proceeding.

Purification of this complex was accomplished in a slightly different fashion. The crude product was dissolved in 1 M NaCl solution and eluted through the column CM-Sephadex C25 to separated three bands (grass-green, green-blue and deep green(desired product)). The desired product was washed out by using 2 M NaCl solution and concentrated by rotary-evaporation and allowed to cool in the fridge overnight. The chloride salt which formed was filtered off and converted to PF_6 salt by dissolving in a minimum amount of water in the presence of excess amount of NH_4PF_6 . The PF_6^- salt of dinuclear complex was recrystallized by ether diffusion into an acetonitrile solution. The yield was 50 mg (15.4%). Anal. Calcd.(%) for $\text{C}_{18}\text{H}_{36}\text{N}_{14}\text{Cl}_2\text{P}_4\text{F}_{24}\text{Ru}_2$: C, 16.61; H, 2.79; N, 15.07. Found(%): C, 17.68; H, 2.82; N, 14.81.

(μ -1,4-Dicyanamido-2,3,4,5-tetrachloro
benzene) bis-trans-(pyridinetetraammine
ruthenium(III)) hexafluorophosphate

Trans-[{ (NH₃)₄Ru py }₂ (μ -Cl₄dicyd)] (PF₆)₄:

This complex was prepared in a similar way to that of *trans*-[{ (NH₃)₄Rupy }₂ (μ -Cl₂dicyd)] (PF₆)₄ using the following reagent amounts: *trans*-[(NH₃)₄Rupy(H₂O)] (PF₆)₂ (278 mg, 0.5 mmol); [AsPh₄]₂[Cl₄dicyd] (264.5 mg, 0.25 mmol); 300 mL of acetone and 2 g of tetrabutylammonium bromide. Purification was carried out in the same fashion as for the [{ (NH₃)₄Rupy }₂ (μ -Cl₄-dicyd)] (PF₆)₄ complex. The yield of PF₆⁻ salt was 17 mg (5%). Anal. Calcd.(%) for C₁₈H₃₄N₁₄Cl₄P₄F₂₄Ru₂: C, 15.75; H, 2.48; N, 14.29. Found: C, 16.19; H, 2.59; N, 14.08.

(μ -1,4-dicyanamidobenzene)bis(2,2',2''-terpyridine) (2,2'-bipyridine) ruthenium (II) hexafluorophosphate.

$[\{ \text{Ru}(\text{terpy})(\text{bpy}) \}_2 (\mu\text{-dicyd})] (\text{PF}_6)_2$:

A mixture of $[\text{Ru}(\text{terpy})(\text{bpy})\text{Cl}](\text{PF}_6)$ (224 mg, 0.33 mmol) and AgPF_6 (85 mg, 0.33 mmol) was placed in acetone (50 mL and stirred at reflux for 3 hours. The reaction mixture was then filtered and to the filtrate was added dicydH_2 (27 mg, 0.17 mmol). The solution was vacuum degassed and then stirred with slight heating (25-30 °C) under argon atmosphere overnight. The solvent was removed and the crude product purified by column chromatography by using grade V alumina type WA-1 (Sigma) and a 2:1 mixture of $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ as eluent. Three major bands were eluted in the order: a yellow band (possibly deprotonated ligand), a purple band (a mononuclear $\text{Ru}(\text{II})\text{terpy}$ derivative) and finally a brown band of the dinuclear complex. The product eluent was evaporated to dryness and the product recrystallized by the diffusion of ether into a dimethylformamide solution of the complex. Dark-brown fine crystals of the dinuclear complex were collected and washed with ether and vacuum dried[92]. Yield: 51 mg, 21%. Anal.

Calcd.(%) for $C_{61}H_{49}N_{15}P_2F_{12}Ru_2$: C, 48.83; H, 3.27; N, 14.01.
Found: C, 48.08; H, 3.59, N, 14.33.

2.4 Physical Measurements

2.4.1 Infrared Spectra

Infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR spectrophotometer which was online to a Hewlett-Packard Colorpro Plotter. All samples were prepared as KBr (oven dried at 120 °C) disks. Reference spectra of air were run prior to all sample spectra.

2.4.2 NMR Spectra

All the 1H spectra were recorded on a Bruker AMX-200 or AMX-400 NMR spectrometer at ambient temperature. Normally, 5 mg of samples (vacuum dried) were dissolved in 0.5 ml of d_6 -dimethyl sulphoxide, d_3 -acetonitrile, d_3 -nitromethane and analyzed in a Norell XR-55 NMR tube. Chemical shifts were derived from an internal TMS reference or from residual solvent peak positions.

2.4.3 Electronic Absorption Spectra

Electronic spectra were recorded on a Cary 5 UV-vis near-IR spectrophotometer interfaced with a Raven 386/40 personal computer online to a Hewlett-Packard Laserjet IID printer. All samples were run using matching quartz cells and a background correction was performed before each run.

2.4.4 Cyclic Voltammetry

Cyclic voltammograms were recorded by using a BAS CV-27 apparatus. The electrochemical cell consisted of a double-jacketed glass container with an inner volume of approximately 15 ml. Cell temperature was set at 25 °C by means of a Haake D8-G refrigerated bath and circulator (accuracy ± 0.02 °C). The cell was fitted with a Teflon plug through which holes had been drilled to permit insertion of electrodes and argon gas inlet and outlet tubes. Three electrodes were utilized in this system, a platinum disk working electrode (BAS, 1.6-mm diameter), a platinum wire auxiliary electrode, and a silver wire quasi-reference electrode. The platinum disk working electrode was manually cleaned with 1 mM diamond polish prior to each scan. Ferrocene($E^\circ = 665$ mV vs NHE) was used as an internal reference[93]. Caledon HPLC grade acetonitrile was

2

PM-1 3½" x 4" PHOTOGRAPHIC MICROCOPY TARGET
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distilled over activated alumina and Anachemia Accusolv grade dimethyl formamide (DMF) was used as received. The supporting electrolyte, 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) was recrystallized twice from methanol and vacuum-dried at 110 °C overnight. Acetonitrile and dimethylformamide were degassed under vacuum prior to use in cyclic voltammetry. The solutions were deoxygenated by bubbling with argon for 15 min. and blanketed with argon prior to each scan.

2.4.5. Spectroelectrochemistry

Spectroelectrochemistry was performed in a cell constructed from a 1 cm quartz cuvette with a quartz fritted compartment separating the working and counter-electrode units. The counter electrode was a Pt-wire and the working electrode was a Pt-mesh cylinder mechanically supported by a Pt strip and located just above the quartz cuvette. Stirring was accomplished by bubbling with argon. Both compartments were deoxygenated by bubbling with argon through a teflon needle. A silver wire was used as the reference electrode and was placed in the working electrode compartment isolated from the working electrode. The potential of the cell was controlled by using a BAS CV-27 apparatus. Aldrich anhydrous acetonitrile , Anachemia Accusolv grade dimethylformamide(DMF)

and dimethylsulfoxide(DMSO) were degassed under vacuum prior to use in electrolysis. The supporting electrolyte, 0.1 M tetrabutylammonium hexafluorophosphate(TBAH), was recrystallized twice from ethanol and vacuum-dried at 110 °C overnight.

2.4.6. X-ray Structure Determination

Crystal structure determination was performed at the University of Ottawa. For a plate crystal of *trans*- $[(\text{NH}_3)_4\text{Rupy}]_2(\mu\text{-dicyd})(\text{PF}_6)_{4.1}/2\text{H}_2\text{O}$ complex with dimensions of 0.1 mm x 0.1 mm x 0.35 mm, all of the measurements were made on a Rigaku diffractometer with Mo K_α radiation. The data was collected at -160 °C using the omega 2 θ scan technique to a maximum 2 θ value of 49.9 degrees. The structure was solved by direct methods[94]. All of the atoms were refined anisotropically except the hydrogen. The hydrogen atoms were calculated. All the calculations were performed using the NRCVAX crystallographic software package[95].

2.4.7. Magnetic Susceptibility Measurements

Variable-temperature magnetic susceptibility measurements were performed at the Institute for Materials Research at McMaster University, Hamilton, Ontario, by Prof. J. E. Greedan and C. V. Stager using a Quantum Design Superconducting Quantum Interference Device (SQUID) magnetometer. The magnetic susceptibility measurements in solution were determined by Evans methods[57] on an AMX-400 NMR spectrometer at ambient temperature. In this method, a solution of paramagnetic complex containing an internal standard is added to the inner tube. A solution of the same inert standard, dissolved in the same solvent that was used to dissolve the complex, is placed in the outer tube (capillary tube)

2.4.8. Elemental Analyses

Elemental analyses of all samples were performed by Canadian Microanalytical Services Ltd.

2.4.9 Theoretical Calculation

Extended Huckel Molecular Orbital (EHMO) calculations were performed on the ligands using FORTICON 8[96] obtained through the Quantum Chemistry Program Exchange (QCPE), Indiana University, Dept. of Chemistry. Calculations were performed on a Raven 386 PC equipped with a 80387 coprocessor and using Microsoft Fortran 5.0. Data input files were constructed using bond length and bond angle information obtained from the relevant X-ray crystal structures.

CHAPTER 3

Mononuclear Complexes

Cis-Bis (2,2'-bipyridine) ruthenium (II)

Complexes of Phenylcyanamide

Derivatives: Physical

Characterization and Result.

3. 1 Synthesis

The *cis*-[bis(phenylcyanamide)bis(2,2'-bipyridine) ruthenium(II)] complexes were prepared from the metathesis reaction of *cis*-[Ru(bpy)₂Cl₂] with an excess of the thallium salt of a phenylcyanamide anion derivative[91].

The neutral complexes crystallized as deep purple needles and their solubility in organic solvents decrease with increasing

number of chloro substituents on the phenyl ring. The elemental analyses of the complexes are consistent with their formulation as are the following spectroscopic and the electrochemical characterizations.

3.2. Infrared Spectroscopy

The infrared data of the free phenylcyanamide ligands (Tl salt) have been reported elsewhere[71,74]. The ligands have a sharp and intense absorption band located around 2100 cm^{-1} which is assigned to $\nu(\text{NCN})$. When a phenylcyanamide ligand coordinates to an electropositive transition metal ion, the $\nu(\text{NCN})$ is shifted to higher energies[74,76,77]. A representative IR spectrum of *cis*-[Ru(bpy)₂(2,3-Cl₂pcyd)₂] is shown in Figure 3.1 and the infrared data of the Ru(II) complexes are collected in Table 3.1. The presence of only one sharp and intense absorption band for the cyanamide stretching frequency (Table 3.1) in all the complexes provides evidence that both cyanamide ligands are equivalent in the solid state. When the cyanamide ligands are inequivalent multiple $\nu(\text{NCN})$ are observed[76]. A small positive shift in $\nu(\text{NCN})$ is observed with increasing chloro substitution of the phenyl ring.

Table 3.1. Infrared Spectra Data for *cis*-Bis(bipyridine) Ruthenium(II) Phenylcyanamide Complexes, KBr disk.

Complex	$\nu(\text{NCN}) \text{ cm}^{-1}$
<i>cis</i> -Ru(bpy) ₂ (pcyd) ₂	2168
<i>cis</i> -Ru(bpy) ₂ (2-Clpcyd) ₂	2169
<i>cis</i> -Ru(bpy) ₂ (2,3-Cl ₂ pcyd) ₂	2171
<i>cis</i> -Ru(bpy) ₂ (2,4,5-Cl ₃ pcyd) ₂	2174
<i>cis</i> -Ru(bpy) ₂ (2,3,4,5-Cl ₄ pcyd) ₂	2176
<i>cis</i> -Ru(bpy) ₂ (Cl ₅ pcyd) ₂	2178

Figure 3.1. IR spectrum of $\text{cis-}[\text{Ru}(\text{bpy})_2(2,3\text{-Cl}_2\text{pcyd})_2]$, KBr disk.

3.3. Proton NMR Spectroscopy

The ^1H -NMR data of the Ru(II) complexes are compiled in Table 3.2 and illustrated in Figure 3.2 by representative ^1H -NMR spectra of $\text{Ti}(2,3\text{-Cl}_2\text{pcyd})$ and $\text{cis-}[\text{Ru}(\text{bpy})_2(2,3\text{-Cl}_2\text{pcyd})_2]$. The ^1H -NMR spectrum of the free $2,3\text{-Cl}_2\text{pcyd}$ anion consists of a simple ABC phenyl proton pattern. When two of these ligands are coordinated to the *cis*-bis(bpy)ruthenium(II) moiety, a small upfield shift of a single ABC phenyl proton pattern is observed (Figure 3.2b). The integration of these proton chemical shifts and comparison with those of pyridine suggest that both $2,3\text{-Cl}_2\text{pcyd}$ anion ligands occupy magnetically equivalent coordination environments. The bipyridine ligands in a *cis*-complex have two magnetically inequivalent pyridine moieties and should result in two ABCD pyridine proton patterns for a total of eight chemical shifts. Only seven are observed (Table 3.2) and that is because the chemical shifts of the 3,3' protons are nearly equivalent[97].

Table 3.2. ^1H NMR spectra data for *cis*-bis(bipyridine) ruthenium phenylcyanamide complexes in dimethylsulfoxide- d_6 .

Complex	Phenylcyanamide	Bipyridine
<i>cis</i> -[Ru(bpy) ₂ (pcyd) ₂]	6.40(t), 6.65(d), 6.95(t)	7.29(t), 7.75(d), 7.90(m), 8.23(d), 8.65(d), 8.80(d), 9.52(d)
<i>cis</i> -[Ru(bpy) ₂ (2-Clpcyd) ₂]	6.15(d), 6.40(t), 6.73(t), 7.03(d)	7.29(t), 7.75(d), 7.90(m), 8.23(d), 8.65(d), 8.80(d), 9.52(d)
<i>cis</i> -[Ru(bpy) ₂ (2,3-Cl ₂ pcyd) ₂]	6.28(d), 6.70(m)	7.29(t), 7.75(d), 7.90(m), 8.23(d), 8.65(d), 8.80(d), 9.52(d)
<i>cis</i> -[Ru(bpy) ₂ (2,4,5-Cl ₃ pcyd) ₂]	6.15(s), 7.33(s)	7.29(t), 7.75(d), 7.90(m), 8.23(d), 8.65(d), 8.80(d), 9.52(d)
<i>cis</i> -[Ru(bpy) ₂ (2,3,4,5-Cl ₄ pcyd) ₂]	6.17(s)	7.29(t), 7.75(d), 7.90(m), 8.23(d), 8.65(d), 8.80(d), 9.52(d)
<i>cis</i> -[Ru(bpy) ₂ (Cl ₅ pcyd) ₂]		7.29(t), 7.75(d), 7.90(m), 8.23(d), 8.65(d), 8.80(d), 9.52(d)

Data in ppm vs TMS reference at 0.00 ppm.

Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet

Integrations are consistent with assignment.

Figure 3.2. (A) ^1H -NMR spectra of $\text{Ti}(2,3\text{-dichlorophenylcyanamide})$ with concentration $5.3 \times 10^{-2} \text{ M}$ and (B) $\text{cis-}[\text{Ru}(\text{bpy})_2(2,3\text{-Cl}_2\text{pcyd})]$ with concentration $9.0 \times 10^{-3} \text{ M}$ in dimethylsulfoxide (d_6).

3.4. Electronic Spectra

Electronic spectral data of the Ru(II) complexes in acetonitrile and dimethylformamide are assembled in Table 3 and a representative spectrum of *cis*-[(bpy)₂Ru(2,3-Cl₂pcyd)₂] is shown in Figure 3.3. The absorption bands seen in the UV region are assigned to ligand centered $\pi \rightarrow \pi^*$ transitions[71,83,98]. The two bands centered at approximately 355 and 520 nm are assigned to metal to ligand charge transfer (MLCT) ($d\pi \rightarrow \pi^*$) by analogy to other Ru(II) bipyridine complexes[98,99].

Figure 3.3. Electronic absorption spectrum of *cis*-[Ru(bpy)₂(2,3-Cl₂pcyd)₂] with concentration of 4×10^{-4} M in acetonitrile.

Table 3.3. Electronic Spectroscopy Data^a for Cis-bis(bipyridine)ruthenium phenylcyanamide complexes in acetonitrile.

Complex	$\pi \rightarrow \pi^*$	MLCT
[Ru(bpy) ₂ (pcyd) ₂]	247 (4.49), 285 (4.82), 294 (4.75)	374 (4.04), 535 (3.90)
[Ru(bpy) ₂ (2-Clpcyd) ₂]	246 (4.53), 284 (4.86), 294 (4.80)	371 (4.05), 531 (3.90)
[Ru(bpy) ₂ (2,3-Cl ₂ pcyd) ₂]	245 (4.52), 296 (4.89), 325 (4.23)	365 (4.11), 518 (3.96)
[Ru(bpy) ₂ (2,4,5-Cl ₃ pcyd) ₂]	246 (4.51), 295 (4.90)	343 (4.29), 511 (3.93)
[Ru(bpy) ₂ (2,3,4,5-Cl ₄ pcyd) ₂]	218 (4.81), 295 (4.87)	333 (4.35), 507 (3.94)
[Ru(bpy) ₂ (Cl ₅ pcyd) ₂] ^b	300 (4.86)	347 (4.44), 521 (3.95)

^a in nm (log ϵ).

^b in dimethylformamide(DMF) solution.

3. 5. Cyclic Voltammetry

The electrochemical data of the six complexes are given in Table 3.4 and a representative voltammogram of *cis*-[Ru(bpy)₂(2,3-Cl₂pcyd)₂] is shown in Figure 3.4. Cyclic voltammetry experiments were performed on acetonitrile solutions of the complexes with the exception of *cis*-[Ru(bpy)₂(Cl₅pcyd)₂] which was sufficiently soluble in DMF. The reduction $E_{1/2}$ were determined from the average of the anodic and cathodic peak potentials, where $E_{1/2} = (E_{pa} + E_{pc})/2$ at a scan rate of 100 mV s⁻¹. The electrochemical reactions associated with the labelled cyclic voltammetry waves in Figure 3.4 are given in the general scheme below.

Oxidation Processes

Reduction Processes

Table 3.4. Electrochemical^a Data for *Cis*-[Ru(bpy)₂(L)₂] Complexes.

L	Ru (III/II)	E _{ox1} ^b	E _{ox2} ^b	η ^d	bpy _{red1}	bpy _{red2}
pycd	595	1355	1545	-220	-1.330	-1.580
2-Clpcyd	705	1385	1535	-165	-1.290	-1.515
2,3- Cl₂pcyd	755	1405	1585	-140	-1.270	-1.495
2,4,5- Cl₃pcyd	815	1475	1765	-110	-1.260	-1.485
2,3,4,5- Cl₄-pcyd	935	1545	1965	-50	-1.260	-1.470
Cl₅pcyd	965 ^c	-	-	-35	-1.210	-1.485

^adata mV vs NHE (0.1 M TBAH acetonitrile solution)

^banodic wave only

^cestimated value in acetonitrile. The value in DMF was determined and corrected for solvent shift by using *cis*-[Ru(bpy)₂(2,3,4,5-Cl₄pcyd)₂] as a calibrant.

^dligand additivity value[102]

Table 3.5. Electrochemical Data^a for Pentaammineruthenium (III) Phenylcyanamide Complexes.

Complex	Ru(III/II)	E_{ox}	η^b	$\Delta\eta^c$
$[(NH_3)_5Ru(pycd)]^{2+}$	64	1318	-285	-65
$[(NH_3)_5Ru(2-Clpycd)]^{2+}$	127	1410	-225	-65
$[(NH_3)_5Ru(2,3-Cl_2pycd)]^{2+}$	163	1504	-185	-45
$[(NH_3)_5Ru(2,4,5-Cl_3pycd)]^{2+}$	202	1546	-145	-35
$[(NH_3)_5Ru(2,3,4,5-Cl_4pycd)]^{2+}$	230	1627	-115	-65
$[(NH_3)_5Ru(Cl_5pycd)]^{2+}$	229	1668	-125	-90

^adata from reference[74] and corrected for $E_{1/2}(Fc^+/Fc) = 665$ mV vs NHE.

^bligand additivity value[102]

^cLigand additivity difference between *cis*-[Ru(bpy)₂(L)₂] and $[(NH_3)_5Ru(L)]^{2+}$ complexes.

Figure 3.4. Cyclic voltammetry of *cis*-[Ru(bpy)₂(2,3-Cl₂pcyd)₂] with concentration of 1.1×10^{-4} M in dry acetonitrile (0.1 M TBAH) at a scan rate of 100 mV/S.

The Ru(III/II) couple demonstrates quasi-reversible behavior between scanning rates of 50 and 250 mV/s, with the separation between anodic and cathodic peaks increasing from 60 to 70 mV, respectively. The two irreversible oxidation waves at positive potentials (Figure 3.5) are assigned to the sequential oxidation of the coordinated phenylcyanamide anion ligands, which are shifted positively because of their coordination to Ru(III)[71]. The two reversible reduction waves at negative potential are assigned to the sequential reductions of the two bipyridine ligands by analogy to $[\text{Ru}(\text{bpy})_3]^{2+}$ [100,101]. The electrochemical data of the analogous pentaammine ruthenium(III) phenylcyanamide complexes have been added to Table 3.4 to permit comparison between the ruthenium complexes. The first ligand oxidation couple $L_{\text{ox}1}$ is usually irreversible and appears to be insensitive to whether ammine or bipyridine ligands are coordinated to Ru(III). This is not true for the Ru(III/II) couple which illustrates the stabilization of the Ru(III) oxidation state by π acceptor bipyridine ligands. Lever[102] has developed a ligand additivity relationship for the determination of the potential of Ru(III/II) couples. For each ligand, a single electrochemical value η can be assigned that reflects the ligands' contribution to the total potential of the Ru(III/II) couple. The ligand additivity relationship has been shown to hold true for a large number of complexes with disparate

ligands. The η values for phenylcyanamide ligands have been calculated for each complex and are found in Table 3.4. The η value for a given *pcyd* ligand should remain independent of the other ligands about ruthenium. However, the η of $[\text{Ru}(\text{NH}_3)_5(\text{L})]^{2+}$ complexes are significantly more negative (see $\Delta\eta$ in table 3.5) than those for the corresponding *cis*- $[\text{Ru}(\text{bpy})_2(\text{L})_2]$ complexes. Lever describes this behaviour of the phenylcyanamide anion ligands as "non-innocent" in that the value of η depends on how electron rich the metal center is. No clear trend in $\Delta\eta$ can be resolved in Table 3.4 and more data is necessary before anything definitive can be said concerning the origin of this effect. Nevertheless, we speculate that for *cis*- $[\text{Ru}(\text{bpy})_2(\text{L})_2]^+$ complexes, an increase in covalency of the Ru(III)-cyanamide bond may lower the calculated value of η for these ligands. In the *cis*- $[\text{Ru}(\text{NH}_3)_5(\text{L})]^{2+}$ complexes, the covalency of the Ru(III)-cyanamide bond is less because of the larger energy difference between Ru(III) and cyanamide orbitals (see Table 3.4). The presence of π acceptor bipyridine in the ruthenium coordination sphere may also play a synergistic role. Evidence of the greater covalency of the Ru(III)-NCN bond in the *cis*- $[\text{Ru}(\text{bpy})_2(\text{L})_2]^+$ compared to $[\text{Ru}(\text{NH}_3)_5(\text{L})]^{2+}$ complexes

can be found in an analysis of the complexes' visible absorption spectra.

3.6. Spectroelectrochemistry

Controlled potential electrolysis of $\text{cis-}[\text{Ru}(\text{bpy})_2(\text{L})_2]$ in DMF was used to generate the absorption spectra of the $\text{cis-}[\text{Ru}(\text{bpy})_2(\text{L})_2]^+$ complexes. The UV-vis spectra of aliquots of the electrolysis solution were taken during the course of the experiment. The visible absorption data of $\text{cis-}[\text{Ru}(\text{bpy})_2(\text{L})_2]^+$ together with analogous $[\text{Ru}(\text{NH}_3)_5(\text{L})]^{2+}$ complexes are compiled together with their assignments in Table 3.6. A representative spectrum of $\text{cis-}[\text{Ru}(\text{bpy})_2(2,3\text{-Cl}_2\text{pcyd})_2]^+$ is shown in Figure 3.5.

Reversibility was evaluated by the maintenance of isosbestic points in the absorption spectrum for both forward oxidation and reverse reduction processes which were determined to be one electron processes by coulometry. Both $\text{cis-}[\text{Ru}(\text{bpy})_2(\text{pcyd})_2]^+$ and $\text{cis-}[\text{Ru}(\text{bpy})_2(2\text{-Clpcyd})_2]^+$ decomposed during the oxidation step and so only the position of the absorption bands could be determined with accuracy. The other oxidized complexes proved to be sufficiently stable (for a periodS no longer than 15 min) to allow the determination of accurate molar extinction coefficients.

Figure 3.5. Spectroelectrochemical oxidation results for $[\text{Ru}(\text{bpy})_2(2,3\text{-Cl}_2\text{pcyd})_2]$ in dimethylformamide solution (0.1 M TBAH).

Table 3.6. Electronic Spectral Data (LMCT Band)^a for *Cis*-bis(bipyridine)ruthenium(III)^b and Pentaamineruthenium(III)^c Complexes of Anionic Phenylcyanamide Ligands (L).

<i>cis</i> -[Ru(bpy) ₂ (L) ₂] ⁺			[(NH ₃) ₅ Ru(L)] ²⁺
L	a ₁ → a ₁ [*]	b ₁ → a ₁ [*]	b ₁ → b ₁ [*] ^e
pcyd ^d	811	1067	743 (3.80 0.135)
2-Clpcyd ^d	800	1051	716 (3.86 0.155)
2,3-Cl ₂ pcyd	793 (3.76 0.132)	1023 (3.70 0.052)	699 (3.84 0.147)
2,4,5-Cl ₃ pcyd	803 (3.79 0.144)	1035 (3.75 0.056)	692 (3.85 0.148)
2,3,4,5-Cl ₄ pcyd	789 (3.81 0.138)	1013 (3.72 0.056)	678 (3.78 0.119)
Cl ₅ pcyd	764 (3.79 0.128)	957 (3.67 0.049)	645 (3.76 0.126)

^a All data are in nm(log $\epsilon_{\max}$, f). The oscillator strength f was calculated by using the equation $f = (4.6 \times 10^{-9}) \epsilon_{\max}(\Delta\nu)$, where $\Delta\nu$ in cm^{-1} is the bandwidth at half $\epsilon_{\max}$. ^b In DMF

^c In acetonitrile; from reference[74].

^d Decomposes too rapidly for quantitative data.

^e Assignment is derived in reference[74].

In Figure 3.5, the oxidation of *cis*-[Ru(bpy)₂(2,3-Cl₂pcyd)₂] results in the disappearance of the *MLCT* transitions centered at 518 nm and the appearance of new bands at lower energy. These low energy bands are assigned to ligand to metal charge transfer (*LMCT*) $\pi \rightarrow d\pi^*$ transitions associated with the Ru(III)-cyanamide chromophore. The dependence of charge transfer energy on solvent polarity is a well-known phenomenon[89,103]. For the *cis*-[Ru(bpy)₂(L)₂]⁺ complexes, changing the solvent from acetonitrile to dimethylformamide represents an increase in solvent polarity and causes the low energy *LMCT* bands to shift to higher energy. This behaviour is consistent with ground state stabilization of the complexes' permanent dipole by the solvent.

In an earlier study[71], it was shown that the cyanamide group possesses two non-degenerate π_{nb} pairs of electrons (see Figure 1.7). For the complexes of this study, linear combinations of two sets of two π_{nb} molecular orbitals must be considered[104]. If the coordination sphere about Ru(III) has *C*_{2v} microsymmetry, the interaction between cyanamide π_{nb} orbitals and Ru(III) is suggested to be represented by Figure 3.6. This MO scheme predicts two low energy *LMCT* transition $a_1 \rightarrow a_1^*$ and $b_1 \rightarrow a_1^*$ and a single high energy transition $a_2, b_2 \rightarrow a_1^*$ and forms the basis of the assignments given in

Table 3.5. The lower energy LMCT bands of $\text{cis-}[\text{Ru}(\text{bpy})_2(2,3\text{-Cl}_2\text{pcyd})_2]^+$ were resolved into their components by fitting the band envelope to a two gaussian band model (Figure 3.7). This analysis gave good fits for all the complexes with the square of the coefficients greater than 0.999. The spectra data derived from the analyses are found in Table 3.6.

The gaussian band for the lowest energy LMCT transition $b_1 \rightarrow a_1^*$ has a smaller oscillator strength than that for the $a_1 \rightarrow a_1^*$ transition. This is expected since the $b_1 \rightarrow a_1^*$ LMCT transition is formally forbidden. In addition, the band width for this transition is more than twice as small as that for the $a_1 \rightarrow a_1^*$ transition. A large contribution to band width occurs when there is a large difference in internuclear separation between ground and excited states as is seen in transitions between bonding and anti-bonding orbitals. The b_1 MO is formally non-bonding and so transitions between it and a_1^* would be expected to have a smaller band width compared to transitions between bonding a_1 and antibonding a_1^* π -MO's.

There have been a number of studies in which linear correlations have been found between electrochemical potentials and charge transfer bands of charge transfer complexes[71,89,105], The rationale has been that since the donor and acceptor are oxidized and reduced, respectively,

Figure 3.6 Qualitative MO scheme resulting from the interaction between Ru(III) π_d and phenylcyanamide π_{nb} orbitals in C_{2v} microsymmetry.

Figure 3.7 Assuming two transitions, the best Gaussian fit of the lower energy LMCT band envelope of $[\text{Ru}(\text{bpy})_2(2,3\text{-Cl}_2\text{pcyd})_2]$ (DMF solution spectrum).

in the formation of a charge transfer excited state, the energy difference between charge transfer ground and excited states should be proportional to the difference between the electrochemical reduction and oxidation potentials of the charge transfer complex. This description is an ionic model in which the electron involved in charge transfer is located in the ground state on a ligand orbital and in the excited state on a metal orbital. For a series of similar charge transfer complexes where the differences in solvation energy are small, the entropy differences between various redox components are small and the optical transitions are of the ($0''-0'$) vibrational type, the following expression is expected to hold,

$$E_{op} = \Delta E + C = [E(L_{ox}) - \{E(Ru(III)) + C\}] + \chi \quad (3.1)$$

where C is a constant which takes into account the fact that it is not possible to measure the oxidation of $Ru(II)$ by experiment when the oxidized ligand is bound and χ takes into account the outer and inner sphere reorganizations that occur upon an electronic transition. The above expression predicts that a plot of the difference in energy of a LMCT band E_{op} should give a linear correlation provided C and χ are constant. When the data points for ΔE_{red} vs E_{op} are plotted for both $[Ru(NH_3)_5(L)]^{2+}$ and $cis-[Ru(bpy)_2(L)_2]^+$ complexes (Figure 3.8) linear distributions are seen but with important

differences between the two sets of complexes. The most dramatic observation is the negative slope seen for the *cis*-[Ru(bpy)₂(L)₂]⁺ data points. This behaviour is contrary to a simple ionic model for the bonding between Ru(III) and the cyanamide anion ligand and can be explained if covalency of the Ru(III)-NCN π -bond is invoked. As the energy difference between donor and acceptor π -orbitals gets smaller, the amount of orbital mixing increases and this results in an increase in the interaction energy. The extra stabilization of the ground state and corequisite destabilization of the excited state causes an increase in E_{op} beyond that predicted by the simple ionic model. A modified expression for E_{op} is given by

$$E_{op} = \Delta E + \chi + E_{cov} \quad (3.2)$$

which attempts to take into account the added energy E_{cov} that covalency contributes to the optical transition energy. If the interaction between donor and acceptor orbitals is entirely covalent, $\Delta E = 0$ and the optical energy will depend largely on E_{cov} . The above expression, although simple in form is extremely difficult to solve experimentally because of the interdependence of the terms.

The matching of donor and acceptor orbital energy is a necessary prerequisite to a delocalized system and the ability of such a system to transmit electronic information.

Figure 3.8. Correlation between the optical energy of the LMCT transitions ($b_1 \rightarrow b_1^*$ and $a_1 \rightarrow a_1^*$, respectively) and the difference between L_{ox1} and $Ru(III/II)$ couples for both $[Ru(NH_3)_5(L)]^{2+}$ (O) and $[Ru(bpy)_2(L)_2]^+$ (Δ) complexes using the data in Table 3.4, 3.5 and 3.6.

CHAPTER 4

Dinuclear Metal Complexes

4.1 Bis{ (2,2'-bipyridine) (2,2',2"- terpyridine) ruthenium (II) } (μ - dicyanamidobenzene) hexafluorophosphate: Physical Characterization, and Results.

4.1.1 Synthesis.

In the preparation of $[\{Ru(bpy)(terpy)\}_2(\mu-dicyd)](PF_6)_2$, the mono-nuclear complex $[Ru(bpy)(terpy)Cl]PF_6$ is reacted with the neutral ligand ($dicydH_2$). Since Cl^- is strongly bonded to Ru, it was difficult to substitute by the $dicyd^{2-}$ ligand. The addition of Ag^+ to a solution of $[Ru(bpy)(terpy)Cl]^+$ precipitated $AgCl$ and formed the substitutionally labile complex $[Ru(bpy)(terpy)(S)]^{2+}$ where S

is a solvent molecule. The resulting solution was then reacted with neutral ligand(*dicydH*₂).

S = solvent

The crude product, $\{[\text{Ru}(\text{bpy})(\text{terpy})]_2(\mu\text{-dicydH}_2)\}(\text{PF}_6)_4$ was purified by column chromatography over alumina WA-1 grade V and eluted by a mixture of $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ solvents. The desired eluent(brown band), which was deprotonated during the elution, was evaporated to dryness and crystallized in DMF by ether diffusion. The elemental analysis(Chapter 2), IR and ¹H NMR spectroscopic characterizations of the deep brown microcrystalline form of dinuclear complex were consistent with the formulation of $\{[\text{Ru}(\text{bpy})(\text{terpy})]_2(\mu\text{-dicyd})\}(\text{PF}_6)_2 \cdot \text{DMF}$.

4.1.2 IR and ^1H NMR spectroscopy

The infrared spectrum of the crude product in Figure 4.1 consists of a broad absorption band located around 2250 cm^{-1} which is assigned to protonated cyanamide $\nu(\text{NCN})$ [83]. The complex was deprotonated during the purification as shown by the characteristic anionic cyanamide $\nu(\text{NCN})$ band observed at 2151 cm^{-1} Figure 4.2. Observation of a band at 1669 cm^{-1} indicated the presence of DMF in recrystallized material.

The ^1H NMR spectrum of the dinuclear complex is represented in Figure 4.3. The integration of the ^1H NMR spectrum also confirms the presence of one molecule of DMF associated with complex as it shows the DMF resonances at 2.74 (3 H, singlet), 2.91 (3 H, singlet), 7.95 (1 H, singlet). The integration also shows a singlet equal to 4 proton at 5.50 ppm for the phenyl proton and several resonances equal to 38 H for both bipyridine and terpyridine at 7.13 (2 H, triplet), 7.39 (2 H, doublet), 7.41 (4 H, triplet), 7.65 (4 H, doublet), 7.82 (2 H, triplet), 8.01 (4 H, triplet), 8.10 (2 H, triplet), 8.24 (2 H, triplet), 8.40 (2 H, triplet), 8.67 (4 H, doublet), 8.70 (2 H, doublet), 8.81 (4 H, doublet), 8.94 (2 H, doublet), 9.65 (2 H, doublet).

Figure 4.1. IR Spectrum of the crude dinuclear complex of $[\{\text{Ru}(\text{bpy})(\text{terpy})\}_2(\mu\text{-dicydH}_2)](\text{PF}_6)_4$, KBr disk.

Figure 4.2. IR Spectrum of crystallized $[\{\text{Ru}(\text{bpy})(\text{terpy})\}_2(\mu\text{-dicyd})](\text{PF}_6)_2 + \text{DMF}$, KBr disk.

Figure 4.3. ^1H NMR Spectrum of $[\{\text{Ru}(\text{bpy})(\text{terpy})\}_2(\mu\text{-dicydH}_2)](\text{PF}_6)_4$ in dimethylsulfoxide- d_6 .

4.1.3 Cyclic Voltammetry

The cyclic voltammograms of the mononuclear complex $[\text{Ru}(\text{bpy})(\text{terpy})\text{Cl}]\text{PF}_6$ and the dinuclear complex $[\{\text{Ru}(\text{bpy})(\text{terpy})\}_2(\mu\text{-dicyd})](\text{PF}_6)_2$ in DMF solution are compared in Figure 4.4. The cyanamide anion group is a pseudo halide and is expected to perturb the $\text{Ru}(\text{III}/\text{II})$ couple in much the same way as a chloride anion ligand. Thus, for the dinuclear complex, Figure 4.4B, the $\text{Ru}(\text{III}/\text{II})$ couples occur in approximately the same region as the $\text{Ru}(\text{III}/\text{II})$ couple of $[\text{Ru}(\text{bpy})(\text{terpy})\text{Cl}]\text{PF}_6$ at 1.025 V vs *NHE* (Figure 4.4A) but are split into one-electron waves (at 0.250 and 0.690 V vs *NHE*) because of significant metal-metal coupling. The $\text{Ru}(\text{III}/\text{II})$ reduction couples for both complexes appear quasi-reversible with an average separation between cathodic and anodic waves of 70 mV that is largely independent of scan rate between 50-250 mV/s. From the difference in $\text{Ru}(\text{III}/\text{II})$ couples of the dinuclear complex ($\Delta E = 440$ mV), the comproportionation constant (K_C) for the formation of the $\text{Ru}(\text{III}) - \text{Ru}(\text{II})$ mixed-valence complex was determined (Eqn. 1.8) to be 2.75×10^7 . This comproportionation constant is approximately the same as that found for the Creutz-Taube ion $[\{(\text{NH}_3)_5\text{Ru}\}_2(\mu\text{-pz})]^{5+}$ (pz=pyrazine) ($K_C = 8.54 \times 10^6$ in DMF)[105] and by analogy,

Figure 4.4. Cyclic Voltammograms of: (A) $[Ru(bpy)(terpy)Cl]PF_6$ and (B) $[Ru(bpy)(terpy)]_2(\mu-dicyd)(PF_6)_2$ in dimethylformamide at the scan rate of 100 mV/s.

supports a class III assignment for the $[\{\text{Ru}(\text{bpy})(\text{terpy})\}_2(\mu\text{-dicyd})]^{3+}$ ion[18,106,107].

The PF_6^- salt of the dinuclear complex proved sparingly soluble in all but strong donor solvents and this severely limited studies of solvent dependent properties. Enough complex as the tetraphenylborate salt (BPh_4^-) was dissolved in acetonitrile to permit an examination of the solvent dependence of the $\text{Ru}(\text{III}/\text{II})$ couples. At a scan rate of 100 mV/s and with 0.025 M electrolyte tetrabutylammonium tetraphenylborate (TBAB), two $\text{Ru}(\text{III}/\text{II})$ couples were observed at 0.415 and 0.840 V vs NHE. The small change in separation between $\text{Ru}(\text{III}/\text{II})$ couples in acetonitrile and DMF shows that the magnitude of metal-metal coupling is only slightly perturbed by the nature of the solvent. In contrast, $[\{(\text{NH}_3)_5\text{Ru}\}_2(\mu\text{-Me}_2\text{dicyd})]^{4+}$, shows dramatic solvent perturbation of metal-metal coupling where in nitromethane $\Delta E = 368$ mV while in DMSO $\Delta E = 198$ mV[80]. The solvent dependence of these $\text{Ru}(\text{III}/\text{II})$ couples was suggested to be caused by the donor-acceptor interaction between the solvent molecules and the ammine ligands. Importantly, this effect is absent in $[\{\text{Ru}(\text{bpy})(\text{terpy})\}_2(\mu\text{-dicyd})]^{2+}$.

Three one electron ligand reduction waves are observed between -1.0 V and -2.0 V, in the cyclic voltammogram of $[\text{Ru}(\text{bpy})(\text{terpy})\text{Cl}]^+$, Figure 4.4A. The first reduction wave

probably corresponds to the reduction of the coordinated terpy ligand because of the greater stability of terpy's π^* orbital, compared to that of bpy[87,108],

The above couple occurs at a potential of -1.100 V vs *NHE* with cathodic and anodic peak separation (70 mV) independent of scan rate from 50-250 mV/s. This is followed closely by the irreversible reduction of the coordinated bpy ligand,

The cathodic peak maximum of this couple occurred at -1.320 V vs *NHE* and a weak anodic wave that is associated with this couple is seen at approximately -0.9 V vs *NHE*. This anodic wave doesn't appear unless the potential is swept past -1.320 V. The irreversibility of this reduction step is suggested to be due to the loss of the chloride ligand. The third reduction wave probably corresponds to the second reduction of the terpy ligand.

For the dinuclear complex, Figure 4.4B, ligand reduction couples analogous to those of the mononuclear complex are expected between -1.0 to -2.0 V. The first reduction couple

{terpy(0/-) = -1.250 V vs NHE}, appears reversible with cathodic to anodic peak separation of 70 mV, independent of scan rates between 50-250 mV/s. The second reduction wave {bpy(0/-) = -1.550 V vs NHE} approaches reversibility at scan rates greater than 250 mV/s where the anodic peak current starts to match that of the cathodic peak. It is important to note that the current of these ligand reduction couples is twice that of the Ru(III/II) couples at positive potentials and that this is consistent with one electron ligand reductions at each end of the complex at the same potential. However, the third reduction step, the terpy(-/2-) couple, is split into two one-electron redox waves and strongly suggests intramolecular ligand-ligand coupling in the (terpy²⁻, terpy⁻) complex. It is possible that these couples may be Ru(II/I) couples although previous studies support ligand centered reductions[109]. The first terpy(-/2-) redox wave appears quasi-reversible although its overlap with the bpy redox wave makes this a difficult judgement. The second wave is irreversible with significant loss of anodic current at scan rates less than 100 mV/s. The instability of these reduction products prevented spectroelectrochemical characterization.

Cyclic voltammetry of the free dicyd²⁻ molecule in acetonitrile showed two redox couples corresponding to dicyd(-/2-) = -0.215 and dicyd(0/-) = 0.460 V vs NHE. These couples shift positively when coordinated to Ru(III). For

example, the dicyd(-/2-) and dicyd(0/-) couples occur at 0.830 and 1.292 V vs *NHE* in the cyclic voltammogram of $[(\text{NH}_3)_5\text{Ru}]_2(\mu\text{-dicyd})^{4+}$ in acetonitrile solution. For the complex, *trans*- $[(\text{NH}_3)_4\text{Rupy}]_2(\mu\text{-dicyd})^{4+}$, the replacement of one ammine ligand with pyridine shifted the dicyd(-/2-) and dicyd(0/-) couples to 0.965 and 1.340 V vs *NHE*, respectively.

An even greater anodic shift of these couples can be expected for $[\{\text{Ru}(\text{bpy})(\text{terpy})\}_2(\mu\text{-dicyd})]^{4+}$. Unfortunately, these couples were not observed up to DMF's anodic limit of 1.75 V vs *NHE* and attempts to observe these couples in solvents with greater anodic limits were frustrated by the poor solubility of the complex.

4.1.4 Spectroelectrochemistry

Spectroelectrochemistry of the $[\{\text{Ru}(\text{bpy})(\text{terpy})\}_2(\mu\text{-dicyd})]^{2+}$ and the free dicyd^{2-} ligand were performed in anhydrous DMF and acetonitrile. The absorbance spectrum of the fully oxidized ligand in acetonitrile solution (Figure 4.5) has been obtained and consists of a broad band centered at 330 nm ($\epsilon = 29,500 \text{ M}^{-1}\text{cm}^{-1}$) [110]. Solutions of 1,4-dicyanamidobenzene dianion and its substituted derivatives are very air sensitive and upon oxidation to the radical anion

give blue solutions which show a characteristic three band pattern in the visible region (Figure 4.5). It is important to note that oxidation of $[\{\text{Ru}(\text{bpy})(\text{terpy})\}_2(\mu\text{-dicyd})]^{2+}$ acetonitrile solution to obtain the absorption spectrum of the mixed-valence [3,2] complex (Figure 4.6) and the fully oxidized [3,3] complex (Figure 4.7) does not result in the appearance of the radical anion chromophore and further supports Ru(III/II) couple assignments. Reversibility was indicated by the return of the absorption spectrum of [2,2] upon reduction of [3,3].

The absorption spectrum of the [2,2] complex (Figure 4.6) shows *MLCT* bands at 356 nm that are typical of Ru(II)(terpy)(bpy) chromophores[89,111]. Upon oxidation to the mixed-valence [3,2] complex, a new band grows in centered at approximately 950 nm with a band maximum at 1006 nm ($\epsilon_{\text{max}} \approx 1.2 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$). The asymmetry of this broad band is suggested to arise from the overlap of the Ru(III)-cyanamide *LMCT* chromophore and an intervalence transition (*IT*). A spectroscopic analysis of the Ru(III)-cyanamide *LMCT* chromophore has shown that two *LMCT* transition arise from the interaction of Ru(III) with the two non-degenerate π_{L} molecular orbitals of the cyanamide group[71]. The absorption spectrum of the fully oxidized [3,3] complex (Figure 4.7)

Figure 4.5. Spectroelectrochemical oxidation of [AsPh₄]₂[Dicyd], 4.63×10^{-6} M in acetonitrile solution, forming the radical anion Dicyd^{•-}.

Figure 4.6. Spectroelectrochemical oxidation of $[\{\text{Ru}(\text{bpy})(\text{terpy})\}_2(\mu\text{-dicyd})](\text{PF}_6)_2$ forming the mixed-valence $[3,2]$ complex, 1.0×10^{-5} M in acetonitrile solution.

Figure 4.7. Spectroelectrochemical oxidation of $[\{Ru(bpy)(terpy)\}_2(\mu-dicyd)]^{3+}$ forming the [3,3] complex, 1.0×10^{-5} M in acetonitrile solution.

clearly shows these two LMCT transitions at 443 and 900 nm and also shows that upon oxidation of [3,2] to [3,3], NIR absorbance intensity is lost. This is taken as evidence for the presence of an intervalence transition which was estimated from the absorption spectrum of [3,2] to have λ_{max} at 1090 nm ($\epsilon_{max} = 5600 \text{ M}^{-1}\text{cm}^{-1}$, $\nu_{1/2} = 1800 \text{ cm}^{-1}$).

Spectroelectrochemistry of the dinuclear complex was also performed on DMF solutions and the growth of the [3,2] complex spectrum was essentially identical to that obtained in Figure 4.6 (isosbestic points in acetonitrile solutions, 356, 475, 641 nm compared to those in DMF, 357, 490, 649 nm). There is also a slight red shift of the IT band maximum to 1066 nm ($\epsilon_{max} = 1.2 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$). Unfortunately, incomplete reversibility in DMF solutions was noted when regeneration of [2,2] from [3,3] showed significant loss of absorption intensity.

Previous studies show that the magnitude of metal-metal coupling in the mixed-valence complex, $\{[(\text{NH}_3)_5\text{Ru}]_2(\mu\text{-dicyd})\}^{3+}$, was strongly dependent on the donor and acceptor properties of the solvent[80,81]. The comproportionation constant of this complex was shown to increase from 10 to 68,400 in aqueous and acetonitrile solutions, respectively. In addition, the IT band properties of this complex in aqueous solution, were consistent with a weakly coupled class II

system but in acetonitrile solution, the *IT* band properties ($\lambda_{\max} = 1447 \text{ nm}$, $\epsilon_{\max} = 20100 \text{ M}^{-1}\text{cm}^{-1}$, $\nu_{1/2} = 26400 \text{ cm}^{-1}$), do not fit Hush model predictions and suggest that the complex is borderline between class II and III systems in acetonitrile solution. If we compare the *IT* band properties of this complex in acetonitrile solution with those of the class III mixed-valence complex of this study, $[\{\text{Ru}(\text{bpy})(\text{terpy})\}_2(\mu\text{-dicyd})]^{3+}$ ($\lambda_{\max} = 1090 \text{ nm}$, $\epsilon_{\max} = 5600 \text{ M}^{-1} \text{ cm}^{-1}$, $\nu_{1/2} = 1800 \text{ cm}^{-1}$), an obvious difference in intervalence transition, energies, intensities and band widths is apparent and can be explained by a transition from valence localized to delocalized mixed-valence systems.

The energy of the *IT* band of a class II system arises from inner and outer sphere reorganizational energies. On the other hand, the *IT* band energy of a class III ion reflects the magnitude of metal-metal coupling and is estimated to be twice the resonance exchange integral H_{ab} . For $[\{\text{Ru}(\text{bpy})(\text{terpy})\}_2(\mu\text{-dicyd})]^{3+}$, H_{ab} [18] is estimated to be 0.57 eV.

The oscillator strength, f of an electronic transition is given by the expression [103],

$$f = (1.085 \times 10^{11}) G \nu M^2 \quad (4.4)$$

where G refers to the degeneracy of the states concerned, ν is the energy of the transition in cm^{-1} and M is the transition moment. Experimentally, oscillator strength is evaluated from band properties by equation 1.5.

In the case of a weakly coupled class II system, Hush[17] approximated the transition moment of an intervalence transition by the expression,

$$M \approx e \alpha R \quad (4.5)$$

where R represents the transition dipole moment length, e is the electronic charge and α is the mixing coefficient of donor and acceptor wavefunctions. The increase in oscillator strength for the intervalence band of $[(\text{NH}_3)_5\text{Ru}]_2(\mu\text{-dicyd})^{3+}$ in going from aqueous to acetonitrile solutions can therefore be ascribed to an enhanced mixing of donor and acceptor wavefunctions since R remains the same[81]. In addition, the magnitude of metal-metal coupling increases with intervalence oscillator strength[17].

For a strongly coupled class III system, the approximations used to derive equation (4.5) are no longer valid and the transition dipole moment is more appropriately given by[73,74,112]

$$M \approx e S_{ad} R \quad (4.6)$$

where S_{ad} is the overlap integral between donor and acceptor wavefunctions. Studies of $[(\text{NH}_3)_5\text{Ru}(\text{L})]^{2+}$, where L is a phenylcyanamide anion derivative, have shown that variations in the ligand to metal charge transfer (LMCT) oscillator strength may be rationalized in terms of the overlap integral between $\text{Ru(III)} \pi d$ orbitals and the π HOMO of the cyanamide ligand. For the IT band of $[\{\text{Ru}(\text{bpy})(\text{terpy})\}_2(\mu\text{-dicyd})]^{3+}$, the contribution of S_{ad} to the oscillator strength is unknown. However, what can be said with confidence is that a class III complex will have greater charge delocalization in both ground and excited states and that this would result in a smaller change in electron distribution upon IT excitation. Therefore, R is smaller for a class III complex compared to a class II complex and this accounts to a significant degree for the difference in the IT oscillator strength that is observed for $[\{\text{Ru}(\text{bpy})(\text{terpy})\}_2(\mu\text{-dicyd})]^{3+}$ and $[\{(\text{NH}_3)_5\text{Ru}\}_2(\mu\text{-dicyd})]^{3+}$ complexes.

The variation in intervalence oscillator strength f_{it} that is observed for other mixed-valence complexes can now be understood within the context of this study. For example, the mixed-valence complex $[\{(\text{NH}_3)_4\text{Ru}\}_2(\mu\text{-bptz})]^{5+}$ where bptz is 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine, has a large K_c (10^{15})

but only a small $\epsilon_{\max}(IT) = 500 \text{ M}^{-1}\text{cm}^{-1}$ [113,114]. This is probably a class III system in which the delocalization of the odd electron in both ground and excited states results in R being small for the intervalence transition. The f_{it} of this complex is significantly smaller than other class III system [15,113] and this may be explained variations in S_{ad} . The mixed-valence complex, $[(\text{tterpy})\text{Ru}]_2(\mu\text{-tpbp})]^{3+}$ where tterpy is 4'-p-toly-2,2',6,6',2''-terpyridine and tpbp is the tetrapyridinebiphenyl dianion, has a relatively small K_c (600) but large $\epsilon_{\max}(IT) = 27,000 \text{ M}^{-1}\text{cm}^{-1}$ [115]. This is a class II system in which the combination of a large R and a large α result in an unusually large intervalence $\epsilon_{\max}$.

The importance of the overlap integral S_{ad} in equation (4.6) to the f_{it} of class III ions requires further investigation.

**4.2 Trans-bis{ (pyridine) tetraammine
ruthenium (III) } Dicyanamidobenzene
Hexafluorophosphate:**

Physical Characterization and discussion:

4.2.1. Synthesis:

Both *trans*-[$\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-dicyd})\}(\text{PF}_6)_4$ and *trans*-[$\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-Me}_2\text{dicyd})\}(\text{PF}_6)_4$ complexes were prepared by reacting a 2:1 mole ratio of *trans*-[$(\text{NH}_3)_4\text{Rupy}(\text{H}_2\text{O})\}(\text{PF}_6)_2$ and the neutral bridging ligand in acetone solution under an argon atmosphere. The reaction mixtures were air oxidized and the crude bromide salts isolated. The crude products were purified by cation-exchange chromatography and precipitated as PF_6^- salts.

Due to the poor solubility of the neutral ligand, the tetraphenylarsonium salts of 2,5-dichlorophenyldicyanamide $[\text{Ph}_4\text{As}]_2(\text{Cl}_2\text{dicyd})$ and tetrachlorophenyldicyanamide $[\text{Ph}_4\text{As}]_2(\text{Cl}_4\text{dicyd})$ were reacted with the *trans*- $[(\text{NH}_3)_4\text{RupY}(\text{H}_2\text{O})](\text{PF}_6)_2$.

All of the dinuclear complexes were recrystallized by ether diffusion into an acetonitrile solution of a complex. The yields were quite low (<20%) due to the fact that several different products were formed, the lability of the second ruthenium coordination side and the loss of material precipitating on the top of column resin.

Precipitation on the column appeared to be a large problem for the chloro-substituted complexes, *trans*-

$[(\text{NH}_3)_4\text{Rupy}]_2(\mu\text{-Cl}_2\text{dicyd})]^{4+}$ and *trans*- $[(\text{NH}_3)_4\text{Rupy}]_2(\mu\text{-Cl}_4\text{dicyd})]^{4+}$. These complexes generally moved down the column more slowly than the others and a more concentrated electrolyte solution was required for elution. This and the problem of precipitation resulted in very low yields of these dinuclear complexes. By analogy to the pentaammine dinuclear complexes, which were sensitive to heat, the *trans*- $[(\text{NH}_3)_4\text{Rupy}]_2(\mu\text{-L})(\text{PF}_6)_4$ complexes were stored in the fridge.

4.2.2. Infrared Spectroscopy

IR spectra of the four dinuclear complexes are exhibited in Figure 4.8-4.11. They all show the characteristic strong $\nu(\text{NCN})$ stretching bands in the range $2086\text{-}2110\text{ cm}^{-1}$. The $\nu(\text{NCN})$ of the complexes are shifted very slightly to lower energies with respect to the free ligands.

No significant changes are observed in $\nu(\text{NCN})$ in comparison to the pentaammineruthenium(III) analogues. As the electron withdrawing ability of the substituents on the phenyl rings increases (from CH_3 to Cl) the $\nu(\text{NCN})$ is shifted to higher energy. The IR spectra data of all dinuclear complexes are collected in Table 4.1.

Table 4.1. Characteristic IR bands for four dinuclear complexes (cm^{-1}) KBr disk.

Complex	$\nu(\text{NCN})$
<i>trans</i> -[$\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-Me}_2\text{dicyd})\}(\text{PF}_6)_4$	2084
<i>trans</i> -[$\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-dicyd})\}(\text{PF}_6)_4$	2086
<i>trans</i> -[$\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-Cl}_2\text{dicyd})\}(\text{PF}_6)_4$	2099
<i>trans</i> -[$\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-Cl}_4\text{dicyd})\}(\text{PF}_6)_4$	2110

Figure 4.8 IR spectrum of *trans*-[$\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-dicyd})\}(\text{PF}_6)_4$ (KBr disk)

Figure 4.9 IR spectrum of *trans*-[$\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-Me}_2\text{dicyd})\}(\text{PF}_6)_4$ (KBr disk)

Figure 4.10 IR spectrum of $\text{trans}-[(\text{NH}_3)_4\text{Rupy}]_2(\mu\text{-Cl}_2\text{dicyd})](\text{PF}_6)_4$ (KBr disk).

Figure 4.11 IR spectrum of $\text{trans}-[(\text{NH}_3)_4\text{Rupy}]_2(\mu\text{-Cl}_4\text{-dicyd})](\text{PF}_6)_4$ (KBr disk).

4.2.3. Electronic Spectra

The UV-Vis near IR spectra for the four dinuclear complexes are displayed in Figures 4.12-4.15 and the respective assignments of the absorptions are compiled in Table 4.2. Two absorption peaks observed in the UV-region are assigned as ligand centered transitions ($\pi \rightarrow \pi^*$) from the bridging ligand and the pyridine rings, respectively. The strong absorption peak in the near IR region (1068-1176 cm^{-1}) and the one in visible region (380-400 cm^{-1}) are assigned as ligand to metal charge transfer LMCT ($\pi \rightarrow d\pi^*$) transitions associated with the Ru(III)-cyanamide chromophore. Previous studies[72-73] have shown that the cyanamide group possesses two non-degenerate π_{nb} pairs of electrons. The combination of these orthogonal π_{nb} orbitals with the appropriate Ru(III) orbitals ($d\pi^*$) results in two LMCT transitions described above.

The low energy band does not appear gaussian and may even be resolvable into two separate features (Figures 4.12-4.15). This transition is monodegenerate and in the absence of vibronic structure should only show one feature. The intensity of the low energy side of this LMCT band appears to be decreasing relative to the high energy side with increasing electron withdrawing properties of the substituents on the dicyd²⁻ ligand. The effect of the electron withdrawing

substituent is to weaken the interaction between the cyanamide group and Ru(III). A similar transformation in the low energy LMCT band of $[(\text{NH}_3)_5\text{Ru}]_2(\mu\text{-Me}_2\text{dicyd})^{4+}$ was observed when this complex was placed in solvents with large differences in solvent donor properties [80-81]. In strong donor solvents, electron density is placed on the Ru(III) ion and this weakens the Ru(III)-NCN bond. It is also important to note that some mononuclear complexes also show evidence of splitting of the low energy LMCT band. It was suggested[115] that because the cyanamide ligand is not rigid, a number of conformations are possible when this ligand is bound to Ru(III). These conformers could result in a range of LMCT transition energies and what is observed is the average spectrum. The Boltzmann distribution of conformers in solution could well be dependent on the strength of the interaction between Ru(III) and the cyanamide group and this is a possible explanation for the changes in the shape of the low energy LMCT band observed with solvent for the Ru(III) dimers.

Table 4.2. Electronic Spectroscopy Data^a for the Dinuclear Metal Complexes in CH₃CN.

Complex	($\pi \rightarrow \pi^*$)	LMCT
<i>trans</i> -[{ (NH ₃) ₄ Rupy } ₂ (μ-Me ₂ dicyd)] (PF ₆) ₄	244 (4.16) 290 (4.01)	378 (4.18) 1126 (4.88)
<i>trans</i> -[{ (NH ₃) ₄ Rupy } ₂ (μ-dicyd)] (PF ₆) ₄	250 (4.27) 274 (4.25)	379 (4.08) 1163 (4.73)
<i>trans</i> -[{ (NH ₃) ₄ Rupy } ₂ (μ-Cl ₂ dicyd)] (PF ₆) ₄	248 (4.36) 280 (4.34)	392 (4.02) 1176 (4.73)
<i>trans</i> -[{ (NH ₃) ₄ Rupy } ₂ (μ-Cl ₄ dicyd)] (PF ₆) ₄	225 (4.09) 297 (4.34)	407 (3.91) 1069 (4.42)

^a in nm (log ε in parentheses)

Figure 4.12 UV-Vis-NIR absorption spectrum of *trans*- $[(\text{NH}_3)_4\text{Rupy}]_2(\mu\text{-dicyd})](\text{PF}_6)_4$ in CH_3CN (conc. = $2.35 \times 10^{-5} \text{ M}$).

Figure 4.13 UV-Vis-NIR absorption spectrum of *trans*- $[(\text{NH}_3)_4\text{Rupy}]_2(\mu\text{-Me}_2\text{dicyd})](\text{PF}_6)_4$ in CH_3CN (conc. = $2.28 \times 10^{-5} \text{ M}$).

Figure 4.14 UV-Vis-NIR absorption spectrum of *trans*- $[(\text{NH}_3)_4\text{Rupy}]_2(\mu\text{-Cl}_2\text{dicyd})](\text{PF}_6)_4$ in CH_3CN (conc. = $1.26 \times 10^{-5}\text{M}$).

Figure 4.15 UV-Vis-NIR absorption spectrum of *trans*- $[(\text{NH}_3)_4\text{Rupy}]_2(\mu\text{-Cl}_4\text{dicyd})](\text{PF}_6)_4$ in CH_3CN (conc. = $1.47 \times 10^{-5}\text{M}$).

4.2.4 X-ray Crystallography.

The X-ray crystallography data of *trans*-[$\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-dicyd})\](\text{PF}_6)_4$ and the data collection parameters are listed in Table 4.3. ORTEP diagrams with atomic labelling, without and with counter ions, are shown in Figures 4.16 and 4.17, respectively. A stereoview of the unit cell is displayed in Figure 4.18. Selected bond lengths and angles as well as atomic positional parameters are summarized in Tables 4.4 and 4.5. The refinement of this crystal structure is slightly high with the unweighted residual (R_f) for the significant reflection being 8.0%. This may be because of crystal disorder due to the counterion (PF_6^-).

In the crystal structure of *trans*-[$\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-dicyd})\](\text{PF}_6)_4$, the two cyanamide groups of the bridging ligand are in a *syn*-configuration. This is in contrast to the crystal structure of [$\{(\text{NH}_3)_5\text{Ru}\}_2(\mu\text{-dicyd})\](\text{CH}_3\text{PhSO}_3)_4$ where the cyanamides are in an *anti*-configuration.

The overall planarity of the dinuclear complex with respect to the free dicyd^{2-} ligand appears reasonably well maintained. One of the cyanamide planes formed by {N(9)-C(11)-N(13)} is slightly tilted by only 9 degrees with respect to the plane of the phenyl ring formed by {C(12)-C(13)-C(14)-C(15)-C(16)-C(17)}. Another cyanamide plane formed by {N(5)-

Table 4.3 Crystallographic Data for *Trans*-[$\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-dicyd})\}(\text{PF}_6)_4 \cdot 1/2\text{H}_2\text{O}$

Parameter	Value ^a
Empirical Formula	$\text{Ru}_2\text{P}_4\text{F}_{24}\text{N}_{14}\text{C}_{18}\text{H}_{38} + 1/2 \text{H}_2\text{O}$
Formula Weight	1240.58
Crystal Dimensions(mm)	0.1 X 0.2 X 0.35
Space Group	P 21 Monoclinic
a, (Å)	7.826(3)
b, (Å)	20.445(7)
c, (Å)	14.428(5)
β (deg)	95.76(3)
Z, (molecules/cell)	2
F(000), (electrons)	1219.94
$d_{\text{calc.}}$, (g/cm ³)	1.794
2 θ (max), (deg.)	49.9
# of Reflcs. Measd.	4038
# of Unique Reflcs.	3717
# of Reflcs with $I_{\text{net}} > 2.5\sigma(I_{\text{net}})$	3292
Transmission Factor Range	0.4491 - 0.5827
Last Least Squares Cycle Calcd.	101 atm, 563 param, 3291 ref
R_f (sig. refl.) ^b	0.080
R_w (sig. refl.) ^c	0.075
Goodness of Fit ^d	6.13
R_f (all refl.)	0.092
R_w (all refl.)	0.075
Max. Shift/a	0.110
Last D- map:	
Deepest Hole, (e/ Å ³)	1.490
Highest Peak, (e/ Å ³)	-1.320

^aESD's are in parentheses and refer to the last digit printed.

^b $R_f = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^c $R_w = [\sum W(|F_o| - |F_c|)^2 / \sum (W|F_o|)^2]^{1/2}$.

^dGoodness of fit = $[\sum W(|F_o| - |F_c|)^2 / (\text{No. of refl.} - \text{No. of parameter})]^{1/2}$

Figure 4.16 ORTEP drawing for the complex *trans*- $[(\text{NH}_3)_4\text{Rupy}]_2(\mu\text{-dicyd})(\text{PF}_6)_4 \cdot 1/2\text{H}_2\text{O}$. The PF_6^- and H_2O has not been shown for clarity.

Figure 4.17 A whole view of the dinuclear complex labelling scheme including hydrogen.

Figure 4.18 Stereoview of the unit cell for the *Trans*- $[(\text{NH}_3)_4\text{Rupy}]_2(\text{u-dicyd})(\text{PF}_6)_4 \cdot 1/2 \text{H}_2\text{O}$.

Table 4.4 Selected Bond Lengths(Å) and Angles(deg.) for *Trans*-[{ (NH₃)₄Rupy }₂(μ-dicyd)] (PF₆)₄·1/2 H₂O.

Bond	Distance	Angle	Deg.
Ru(1)-N(1)	2.127(17)	N(1)-Ru(1)-N(2)	87.5(8)
Ru(1)-N(2)	2.143(18)	N(1)-Ru(1)-N(3)	178.8(7)
Ru(1)-N(3)	2.147(18)	N(2)-Ru(1)-N(4)	177.4(8)
Ru(1)-N(4)	2.176(16)	N(3)-Ru(1)-N(6)	89.6(7)
Ru(1)-N(5)	1.912(20)	N(4)-Ru(1)-N(5)	89.0(7)
Ru(1)-N(6)	2.081(17)	N(5)-Ru(1)-N(6)	178.5(7)
Ru(2)-N(7)	2.164(19)	N(7)-Ru(2)-N(10)	179.19(7)
Ru(2)-N(8)	2.133(17)	N(7)-Ru(2)-N(12)	88.5(8)
Ru(2)-N(9)	1.989(20)	N(8)-Ru(2)-N(11)	177.3(8)
Ru(2)-N(1)	2.109(18)	N(8)-Ru(2)-N(9)	89.6(7)
Ru(2)-N(11)	2.132(17)	N(9)-Ru(2)-N(12)	176.5(7)
Ru(2)-N(12)	2.041(20)	N(10)-Ru(2)-N(11)	88.4(70)
N(5)-C(18)	1.25(3)	N(5)-C(18)-N(14)	175.9(25)
N(9)-C(11)	1.12(3)	N(13)-C(11)-N(9)	168(3)
N(13)-C(11)	1.30(3)	C(1)-N(6)-Ru(1)	122.6(14)
N(13)-C(12)	1.32(3)	C(5)-N(6)-Ru(1)	121.3(15)
N(14)-C(15)	1.40(3)	C(18)-N(5)-Ru(1)	174.9(18)
N(14)-C(18)	1.25(3)	C(6)-N(12)-Ru(2)	126.6(20)
C(12)-C(13)	1.41(3)	C(10)-N(12)-Ru(2)	120.3(16)
C(13)-C(14)	1.39(3)	C(11)-N(9)-Ru(2)	174.6(15)
C(14)-C(15)	1.43(3)	C(12)-N(13)-C(11)	121.3(15)
C(15)-C(16)	1.36(3)	C(15)-N(14)-C(18)	119.1(21)
C(16)-C(17)	1.38(4)		
C(17)-C(12)	1.44(3)		

**Table 4.5 Atomic Parameters x, y, z and B_{iso}^a for Trans-
[$(NH_3)_4Rupy)_2(\mu-dicyd)](PF_6)_4 \cdot 1/2 H_2O$.**

	X	Y	Z	B_{iso}
Ru(1)	0.32208(21)	0.59172	0.20818(10)	3.12(6)
Ru(2)	0.17184(20)	1.11850(11)	0.31169(10)	3.06(6)
N(1)	0.294(30)	0.6439(11)	0.0800(11)	4.0(9)
N(2)	0.5362(24)	0.5426(10)	0.1578(14)	3.9(8)
N(3)	0.3445(23)	0.5394(10)	0.3379(11)	3.4(8)
N(4)	0.1084(20)	0.6457(10)	0.2565(11)	3.0(8)
N(5)	0.4754(23)	0.6564(10)	0.2646(10)	3.5(8)
N(6)	0.1565(22)	0.5198(9)	0.1499(10)	2.8(7)
N(7)	0.3740(23)	1.1776(12)	0.2629(10)	3.9(10)
N(8)	0.1528(21)	1.0681(110)	0.1816(11)	3.3(8)
N(9)	0.3512(22)	1.0555(10)	0.3620(12)	3.5(8)
N(10)	-0.0248(24)	1.0599(10)	0.3575(12)	3.5(8)
N(11)	0.1963(24)	1.1648(10)	0.4447(13)	3.5(8)
N(12)	-0.0017(23)	1.1856(12)	0.2552(11)	3.9(10)
N(13)	0.5912(24)	0.9880(10)	0.4195(12)	3.4(8)
N(14)	0.6990(23)	0.7296(11)	0.3453(14)	3.9(9)
C(1)	0.195(3)	0.4577(12)	0.1535(12)	3.2(9)
C(2)	0.112(5)	0.4050(17)	0.111(3)	7.6(19)
C(3)	-0.041(3)	0.4256(13)	0.0620(14)	4.2(11)
C(4)	-0.089(3)	0.4880(14)	0.0519(16)	4.1(11)
C(5)	0.0035(24)	0.5362(13)	0.0934(13)	3.0(10)
C(6)	-0.138(3)	1.1737(15)	0.1976(15)	4.7(12)
C(7)	-0.263(3)	1.2166(20)	0.1572(15)	6.0(18)
C(8)	-0.240(5)	1.2775(25)	0.1814(24)	9.4(24)
C(9)	-0.117(6)	1.3001(15)	0.2371(20)	7.8(20)
C(10)	0.015(4)	1.2538(16)	0.2817(17)	5.1(13)
C(11)	0.457(3)	1.0198(12)	0.3837(12)	3.0(9)
C(12)	0.612(3)	0.9254(12)	0.4018(14)	3.2(10)
C(13)	0.770(3)	0.8960(13)	0.4333(17)	3.8(10)
C(14)	0.798(3)	0.8309(13)	0.4130(17)	3.9(10)
C(15)	0.665(3)	0.7956(13)	0.3601(15)	3.6(10)
C(16)	0.519(3)	0.8272(14)	0.3249(16)	4.1(11)
C(17)	0.483(3)	0.8220(14)	0.3413(15)	3.8(11)
C(18)	0.585(3)	0.6947(12)	0.3033(12)	2.9(9)

^a B_{iso} is the mean of the principal axes of the thermal ellipsoid.

Note: Estimated standard deviations (ESD'S) are in brackets and refer to the last digit printed.

C(18)-N(14)} is tilted out of the phenyl ring plane by 29 degrees. The data in Table 4.4 show that there are two types of Ru-N(cyanamide) bonds, Ru(1)-N(5) = 1.912(20) Å and Ru(2)-N(9) = 1.989(20) Å. The difference in Ru-N(cyanamide) bond lengths and the distortion of the $dicyd^{2-}$ ligand from ideal planar geometry are probably due to crystal packing forces. The shortest Ru(1)-Ru(2) through bond distance is 15.7 Å and through space is 10.9 Å which is considerably smaller than the through space distance (13.1 Å) found for the pentaammine ruthenium analogue(anti-configuration).

4.2.5 Extended Huckel Molecular Orbital Calculation

As mentioned in Chapter one, the metal-metal coupling is mediated by the full set of bonding and antibonding orbitals of the bridging ligand. Therefore the nature of the bridging ligand determines to a great extent, the magnitude of metal-metal coupling. Ru(III) and Ru(II) ions in octahedral or pseudo-octahedral environments, with respective low spin d^5 and d^6 electron configurations, have highest occupied π -symmetry d -orbitals. Therefore, effective electron exchange between two ruthenium ions requires that there be a continuous π symmetry bridging ligand MO that can interact simultaneously

with both ruthenium ions. The crystal structure of *trans*- $[\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-dicyd})](\text{PF}_6)_4$ shows that the bridging ligand binds to the ruthenium ions in a *syn*-configuration, in contrast to $[\{(\text{NH}_3)_5\text{Ru}\}_2(\mu\text{-dicyd})](\text{PF}_6)_4$ where the bridging ligand binds to ruthenium ions in an *anti*-configuration. To compare the energy of the frontier orbitals of the bridging ligand in both configurations, Extended Huckel Molecular Orbital (EHMO) calculations have been carried out on both *syn* and *anti* configurations of the dicyanamidobenzene dianion. The EHMO program, FORTICON 8 was used to perform the calculations and the data files are given in Appendix I. These files were constructed by using the crystal structure data of *trans*- $[\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-dicyd})](\text{PF}_6)_4$.

The energies for the LUMO, HOMO, and SHOMO (2nd HOMO) for both *syn* and *anti* configurations are collected in Table 4.6 and show that energies are almost the same. The overall one electron stabilization energy for *syn*- dicyd^{2-} and *anti*- dicyd^{2-} are practically the same being -1046.988 eV and -1046.991 eV, respectively. The reason why the X-ray structure of free dicyd^{2-} ligands[112] and the pentaammine ruthenium dimers[39] show only an *anti* configuration is therefore unclear. It could be that crystal packing forces prefer the *anti*-configuration or it is possible that the level of theory

used(EHMO) is unable to distinguish a real energy difference between the conformers.

Table 4.6. The energy(eV) for LUMO, HOMO, and SHOMO(2nd HOMO) For both *syn* and *anti-dicyd*²⁻.

Ligand	LUMO	HOMO	SHOMO(2nd HOMO)
<i>Syn-dicyd</i> ²⁻	-8.887	-11.821	-12.554
<i>Anti-dicyd</i> ²⁻	-8.889	-11.821	-12.554

HOMO Superexchange Pathway

Figure 4.19 Frontier orbitals(HOMO) of *dicyd*²⁻ from EHMO calculations, the most likely pathway for superexchange.

4.2.6 Cyclic Voltammetry

Cyclic voltammetry of the four dinuclear complexes was performed in acetonitrile and dimethyl sulfoxide (DMSO) using a platinum working and auxiliary electrodes and a silver wire as a reference electrode. The $E_{1/2}$ potential of the redox couples were corrected vs NHE by using ferrocene as the internal reference [$E_{1/2}(\text{Fc}^+/\text{Fc}) = 665 \text{ mV vs NHE}$][95]. All the cyclic voltammograms in both solvents are shown in Figures 4.20 to 4.23. In acetonitrile solution, they all show a similar pattern of four one electron redox processes. These can be assigned to two consecutive one electron redox processes centered at the ruthenium [$\text{Ru(III,III/III,II)}$, and Ru(III,II/II,II)] followed by two redox couples of the ligand [i.e. $\text{L}(-/2-)$, and $\text{L}(0/-)$]. The electrochemical reactions associated with the couples are given in Scheme 4.1 and the redox potentials are collected in Table 4.6. The cyclic voltammograms in DMSO also show the same pattern except for *trans*-[$\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-Cl, dicyd})\}(\text{PF}_6)_4$, where the second redox couple of the ligand disappeared due to the solvent limit. The electrochemical data in DMSO are summarized in Table 4.8.

In most cases, the anodic to cathodic current ratios at the scan rate of 100 mV/S are close to unity. This is indicative of chemical reversibility.

Scheme 4.1

The metal based waves for all the dinuclear complexes in both solvents appear reversible with an average separation between cathodic and anodic waves of 60 mV that is independent of scan rate between 50-500 mV/S. This is also true for the first ligand redox couple ($\text{L}^{-/2-}$) in all the complexes and the second couple in *trans*-[$\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-dicyd})\}(\text{PF}_6)_4$ and *trans*-[$\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-Me}_2\text{dicyd})\}(\text{PF}_6)_4$ in both solvents. Only an anodic peak is observed for the second ligand redox couple in both *trans*-[$\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-Cl}_2\text{dicyd})\}(\text{PF}_6)_4$ and *trans*-[$\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-Cl}_4\text{dicyd})\}(\text{PF}_6)_4$ as shown by Figures 4.21 and 4.22.

The comproportionation constant K_C is related to the separation between two ruthenium centered reduction couples in

Figure 4.20 Cyclic voltammogram of $\text{trans}-\{[(\text{NH}_3)_4\text{Rupy}]_2(\mu\text{-dicyd})(\text{PF}_6)_4$ (A) in acetonitrile and (B) in DMSO (0.1 M TBAH) at a scan rate of 100 mV/s.

Figure 4.21 Cyclic voltammogram of $\text{trans}-[(\text{NH}_3)_4\text{Rupy}]_2(\mu\text{-Me}_2\text{dicyd})](\text{PF}_6)_4$ (A) in acetonitrile and (B) in DMSO (0.1 M TBAH) at a scan rate of 100 mV/s.

Figure 4.22 Cyclic voltammogram of $\text{trans}-\{[(\text{NH}_3)_4\text{Rupy}]_2(\mu\text{-Cl}_2\text{dicyd})\}(\text{PF}_6)_4$ (A) in acetonitrile and (B) in DMSO (0.1 M TBAH) at a scan rate of 100 mV/s.

Figure 4.23 Cyclic voltammogram of $\text{trans}-[(\text{NH}_3)_4\text{Rupy}]_2(\mu\text{-Cl}_4\text{ dicyd})](\text{PF}_6)_4$ (A) in acetonitrile and (B) in DMSO (0.1 M TBAH) at a scan rate of 100 mV/s.

dinuclear complexes (Eqn. 1.8). The value of K_c reflects the stabilization of the mixed valence complex in solution. The larger K_c is, the greater the electronic coupling. For *trans*-[$\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-L})\}(\text{PF}_6)_4$ complexes, as the nature of substituent on the phenyl group of the bridging ligand is changed from CH_3 to Cl (Table 4.9), the value of K_c decreases from 5.75×10^6 for *trans*-[$\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-Me}_2\text{dicyd})\}(\text{PF}_6)_4$ to 1.10×10^3 for *trans*-[$\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-Cl}_4\text{dicyd})\}(\text{PF}_6)_4$. This is explained by the reduction of metal-metal coupling due to the increasing the energy gap between the Ru $d\pi$ orbitals and the HOMO of the bridging ligand as the electron withdrawing ability of the substituents on the phenyl ring increase. Importantly, the *trans*-[$\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-Me}_2\text{dicyd})\}(\text{PF}_6)_4$ complex has a $K_c = 5.6 \times 10^6$ in acetonitrile which is higher than the K_c for the Creutz-Taube ion ($[\{(\text{NH}_3)_5\text{Ru}\}_2\text{pz}]^{5+}$, $K_c = 4 \times 10^6$). Numerous studies[116-117], among them solvent independence of the IT band and K_c , have indicated that the Creutz-Taube ion is a class III delocalized system. However, the *trans*-[$\{\text{py}(\text{NH}_3)_4\text{Ru}\}_2(\mu\text{-Me}_2\text{dicyd})\}(\text{PF}_6)_4$ shows considerable solvent dependence (see Table 4.6 and 4.8) even though the magnitude of the K_c might lead one to predict class III solvent independence. The results of this thesis bring into question the importance of K_c as a bench mark for class III behavior

Table 4.7 Electrochemical Data(Volt vs NHE) for Dinuclear Complexes $\text{trans}-\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-L})(\text{PF}_6)_4$ in Acetonitrile Solution(0.1 M TBAH).

L	E_{M1}	E_{M2}	K_c	L(-/2-)	L(0/-)
Me ₂ dicyd	0.315	-0.085	5.75×10^6	0.935	1.265
dicyd	0.350	-0.015	1.5×10^6	0.965	1.340
Cl ₂ dicyd	0.410	1.165	1.4×10^4	1.045	1.455
Cl ₄ dicyd	0.435	0.255	1.1×10^3	1.170	1.595

Table 4.8 Electrochemical Data^a (Volt vs NHE) for Dinuclear Complexes $\{(\text{NH}_3)_5\text{Ru}\}_2(\mu\text{-L})(\text{PF}_6)_4$ in Acetonitrile Solution(0.1 M TBAH).

L	E_{M1}	E_{M2}	K_c	L(-/2-)	L(0/-)
Me ₂ dicyd	0.089	-0.251	5.6×10^5	0.767	1.205
dicyd	0.131	-0.155	6.8×10^4	0.830	1.292
Cl ₂ dicyd	0.192	-0.020	3.8×10^3	1.000	1.455
Cl ₄ dicyd	0.200	0.051	330	1.112	1.563

^aData taken from the ref.[120]

Table 4.9 Electrochemical Data (Volt vs NHE) for Dinuclear Complexes $\text{trans}-\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-L})\}(\text{PF}_6)_4$ in Dimethyl sulfoxide.

L	E_{M1}	E_{M2}	K_c	L(-/2-)	L(0/-)
Me_2dicyd	0.110	-0.170	5.4×10^4	0.660	1.055
dicyd	0.070	-0.160	7.7×10^3	0.530	1.120
Cl_2dicyd	0.155	0.005	343	0.865	1.275 ^a
Cl_4dicyd	0.175	0.065	72	1.020	-

^acathodic peak only.

Table 4.10 Electrochemical Data^a (Volt vs NHE) for Dinuclear Complexes $\{(\text{NH}_3)_5\text{Ru}\}_2(\mu\text{-L})\}(\text{PF}_6)_4$ in Dimethylsulfoxide.

L	E_{M1}	E_{M2}	K_c	L(-/2-)	L(0/-)
Me_2dicyd	-0.163	-0.361	2.2×10^3	0.582	1.050
dicyd	-0.144	-0.311	664	0.622	1.068
Cl_2dicyd	-0.180	-0.310	157	0.828	-
Cl_4dicyd	-0.154	-0.269	88	0.966	-

^aData is taken from ref.[120]

and support the suggestion that the Creutz-Taube ion is only borderline class III.

The electrochemical data of the *trans*- $[\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-L})](\text{PF}_6)_4$ complexes (Table 4.6) indicate that both ruthenium and ligand centered redox couples are shifted to more positive potentials and that the value of K_c is increased approximately by a factor of 10 in comparison to the data for the analogous $[\{(\text{NH}_3)_5\text{Ru}\}_2(\mu\text{-L})](\text{PF}_6)_4$ complexes. These changes are due to the replacement of a strong σ donor ligand (NH_3) with a poor σ donor ligand (pyridine), which stabilizes the Ru(III) $d\pi$ orbitals and reduces the energy gap between the ruthenium $d\pi$ and the HOMO of the bridging ligand. Consequently, metal-metal superexchange coupling is enhanced.

Curtis et al, (Chapter 1) [31] showed that metal-metal coupling in dinuclear amine complexes decreased with increasing donor number of the solvent. This dependency suggested a hydrogen-bonding type of interaction involving the solvent's nonbonding electrons and the N-H bond. The net effect of this interaction is the transfer of electron density from the partially deprotonated ammine to the ruthenium ion. Solvent dependency of the redox couples for the *trans*- $[\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-L})](\text{PF}_6)_4$ can be observed by comparison of the metal redox couples in both solvents. As the donor number of the solvent increases from CH_3CN to DMSO , the coupling

between the two ruthenium ions decreases i.e. the value of K_c decreases from 5.75×10^6 for *trans*-[$\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-Me}_2\text{dicyd})\}(\text{PF}_6)_4$ in acetonitrile (Table 4.6) to 5.39×10^4 in dimethyl sulfoxide (Table 4.8). Extra electron density from the ammine ligands destabilized the Ru(III)-NCN π bond which results in an overall reduction in metal-metal coupling via the π superexchange pathway.

4.2.7 Mixed-Valence Charge Transfer and Electronic Coupling

The absorption spectra of the mixed-valence [3,2] complexes in acetonitrile solutions were obtained by spectroelectrochemical methods. Application of a potential slightly negative of the first ruthenium reduction couple (E_{M1}^0) resulted in a steady decrease in the intensity of the LMCT absorption band and a concomitant growth of a near IR absorption tail. Figures 4.24 to 4.27 illustrate the electronic absorption spectra of progressive reduction of *trans*-[$\{\text{py}(\text{NH}_3)_4\text{Ru}\}_2(\mu\text{-dicyd})(\text{PF}_6)_4$ and *trans*-[$\{\text{py}(\text{NH}_3)_4\text{Ru}\}_2(\mu\text{-Me}_2\text{dicyd})(\text{PF}_6)_4$ to the mixed-valence form. Since this peak is absent in both [3,3] and [2,2] dinuclear complexes the new band is assigned as metal to metal charge transfer (intervalence transition, *IT*). Reoxidation of mixed-valence complexes[3,2] in solution results in the complete regeneration of fully oxidized [3,3] complex. Reversibility was evaluated by the maintenance of isosbestic points in the absorption spectra for both reduction and oxidation processes, which were determined to be one-electron processes by coulometry. The asymmetry of the mixed-valence low energy band is suggested to arise from the overlap of Ru(III)-

Figure 4.24 Spectroelectrochemical reduction results for $\text{trans}-[(\text{NH}_3)_4\text{Rupy}]_2(\mu\text{-dicyd})(\text{PF}_6)_4$ in CH_3CN solution (0.1 M TBAH) .

Figure 4.25 Spectroelectrochemical reduction results for $\text{trans}-[(\text{NH}_3)_4\text{Rupy}]_2(\mu\text{-Me}_2\text{dicyd})(\text{PF}_6)_4$ in CH_3CN solution (0.1 M TBAH) .

Figure 4.26 Spectroelectrochemical reduction results for *trans*-[$\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-Cl}_2\text{dicyd})\}(\text{PF}_6)_4$ in CH_3CN solution (0.1 M TBAH) .

Figure 4.27 Spectroelectrochemical reduction results for *trans*-[$\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-Cl}_4\text{dicyd})\}(\text{PF}_6)_4$ in CH_3CN solution (0.1 M TBAH) .

cyanamide *LMCT* and intervalence transition (*IT*) bands. Non-linear curve fitting (Peakfit) software was used to deconvolute the *IT* band from the *LMCT* transition. The deconvolution is attained with two assumptions: 1) description of the *IT* transition by a single Gaussian band, a condition that is not always seen experimentally [118], and 2) the energy and the shape of the *LMCT* transition band doesn't change upon reduction of one of the Ru(III)-cyanamide chromophores (for instance, the shape of *LMCT* band in the mixed metal $[(\text{NH}_3)_5\text{Ru}(\mu\text{-dicyd})\text{Cu}(\text{bpil})]^{3+}$ [119] is almost the same as $[(\text{NH}_3)_5\text{Ru}(\mu\text{-dicyd})\text{Ru}(\text{NH}_3)_5]^{3+}$). Figure 4.28 shows a multiple Gaussian fit of the mixed-valence complex. This fitting (three Gaussian bands for *LMCT* and one additional band for the *IT* transition) was used to model the band profile of the mixed valence complex in acetonitrile.

The electronic properties of the metal to metal charge transfer bands for the dinuclear complexes are collected in Table 4.10. As mentioned in Chapter 1, the oscillator strength(*f*) of an *IT* transition for a class II system in a mixed valence complex is related to the extent of coupling between donor and acceptor as well as to *R* (the distance through which charge is carried) (Eqn. 1.4) where $f_{IT} \propto H_{ab}^2 R^2$. In a class II system where *R* is constant (view the electron transition as between metal ions) variations in f_{IT}

Figure 4.28 Multiple gaussian fit of the (A) LMCT and (B) LMCT+IT bands of *trans*-[$\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-Me}_2\text{dicyd})](\text{PF}_6)_4$.

Table 4.11 The Electronic Data of the IT Band Derived from Least Squares Fitting using Peakfit Software for $\text{trans-}[(\text{NH}_3)_4\text{Rupy}]_2(\mu\text{-L})]^{3+}$ in Acetonitrile.

L	b_R^2	$\nu_{\max}$ cm^{-1}	$\epsilon_{\max}$ $\text{M}^{-1}\text{cm}^{-1}$	$\Delta\nu_{1/2}$ cm^{-1}	f_{IT}	$^a\Delta\nu_{1/2}$ cm^{-1}
Me₂dicyd	0.9764	7406	2.23×10^4	1641	0.168	4136
dicyd	0.9521	7132	2.55×10^4	1902	0.224	4059
Cl₂dicyd	0.9979	6627	2.18×10^4	2562	0.257	3913
Cl₄dicyd	0.9943	6520	1.79×10^4	3202	0.264	3881

Table 4.12 The Electronic Data^c of the IT Band Derived from the Least Squares Fitting using Peakfit Software for $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-L})]^{3+}$ in Acetonitrile.

L	b_R^2	$\nu_{\max}$ cm^{-1}	$\epsilon_{\max}$ $\text{M}^{-1}\text{cm}^{-1}$	$\Delta\nu_{1/2}$ cm^{-1}	f_{IT}	$^a\Delta\nu_{1/2}$ cm^{-1}
Me₂dicyd	0.993	7115	2.02×10^4	2341	0.218	44054
dicyd	0.996	6912	1.94×10^4	2635	0.235	3995
Cl₂dicyd	0.993	6751	163×10^4	3227	0.242	3949
Cl₄dicyd	0.976	6392	8.15×10^3	4025	0.151	3842

^a $\Delta\nu_{1/2}$ is calculated from equation $\Delta\nu_{1/2} = [2310 \nu_{\max}]^{1/2}$

^b R^2 =Square of the correlation coefficient. ^cData from ref.[120]

can be related to variation in H_{ab} . The larger the metal-metal coupling is, the larger the f_{IT} . For a mixed valence complex which approaches class III behavior, R is much smaller than the separation between metal ions and depends upon the extent of odd electron delocalization. Therefore, the larger odd electron delocalization the smaller the f_{IT} . In Table 4.10, the f_{IT} value increases from 0.168 for *trans*- $[\{py(NH_3)_4Ru\}_2(\mu-Me_2dicyd)](PF_6)_4$ to 0.264 for *trans*- $[\{py(NH_3)_4Ru\}_2(\mu-Cl_4dicyd)](PF_6)_4$, whereas for the same series of complexes the comproportionation constant decreases (Table 4.8). This trend is opposite to what is predicted for a class II system and is another indication of strong metal-metal coupling in *trans*- $[\{py(NH_3)_4Ru\}_2(\mu-L)](PF_6)_4$ complexes.

The electronic data of the intervalence charge transfer band for $[(NH_3)_5Ru]^{3+}$ analogue complexes in acetonitrile solution are put in Table 4.11 to facilitate the comparison between the two systems. The stronger metal-metal coupling of the *trans*-pyridine complexes is also reflected by the difference between the Hush theory predicted band width at half-peak height ($\Delta\nu_{1/2}$) of the IT band with the curve fitted value of $\Delta\nu_{1/2}$ for *trans*- $[\{py(NH_3)_4Ru\}_2(\mu-L)](PF_6)_4$. The disagreement between theory and curve fitting $\Delta\nu_{1/2}$ values of the *trans*- $[\{py(NH_3)_4Ru\}_2(\mu-L)]^{3+}$ complexes is significantly

greater than that observed for the $[(\text{NH}_3)_5\text{Ru}_2\text{L}]^{3+}$ complexes. Of the complexes in Tables 4.11 and 4.12, only the IT band properties of $[(\text{NH}_3)_5\text{Ru}_2(\mu\text{-Cl}_4\text{dicyd})]^{3+}$ appear to obey Hush theory (class II).

4.2.8 Magnetic Susceptibility Measurement.

A. Variable Temperature Magnetic Susceptibility

Magnetic susceptibility measurements of all of the complexes were made over the temperature range 5-300 K using a superconducting quantum interference device (SQUID) magnetometer. The measurements were made at McMaster University, Hamilton, by Professor John E. Greeden using 50 mg of the complex in pellet form. The fitted plots of molar magnetic susceptibility versus temperature(K) are displayed in Figures 4.29-4.32.

The raw data was fitted using a Curie-Weiss equation(eq.10) for $S = 1/2$ spin-coupled dimers mentioned in the introduction. The data received showed that all the dinuclear complexes displayed diamagnetic behavior at room temperature. However, very small amounts of paramagnetic impurity, which in the present case is most likely due to the presence of mononuclear complex, caused the curve to rise sharply at low temperature.

Figure 4.29. Molar magnetic susceptibility from 5 to 300 K in a 1.0 T field for *trans*-[$\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-dicyd})\}(\text{PF}_6)_4$.

Figure 4.30. Molar magnetic susceptibility from 5 to 300 K in a 1.0 T field for $\text{trans}-\{[(\text{NH}_3)_4\text{Rupy}]_2(\mu\text{-Me}_2\text{dicyd})\}(\text{PF}_6)_4$. The solid line is a fit to equation (1.15).

Figure 4.31. Molar magnetic susceptibility from 5 to 300 K in a 1.0 T field for *trans*- $[(\text{NH}_3)_4\text{Rupy}]_2(\mu\text{-Cl}_2\text{dicyd})](\text{PF}_6)_4$. The solid line is a fit to equation (1.15).

Figure 4.32. Molar magnetic susceptibility from 5 to 300 K in a 1.0 T field for *trans*- $[(\text{NH}_3)_4\text{Rupy}]_2(\mu\text{-Cl}_4\text{dicyd})](\text{PF}_6)_4$. The solid line is a fit to equation (15).

The magnetic data are consistent with singlet state occupancy up to 300 K for all of the $\text{trans}-[\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-L})](\text{PF}_6)_4$ complexes. Because the triplet state is not populated to a significant extent in the temperature range studied, the magnetic exchange constant can only be approximated to be $-2J \geq 800 \text{ cm}^{-1}$. Nevertheless, the magnitude of J is significantly greater than that observed for the $[\{(\text{NH}_3)_5\text{Ru}\}_2(\mu\text{-L})]^{4+}$ complexes (where $\text{L} = \text{Cl}_2\text{dicyd}^{2-}$ and $\text{Cl}_4\text{dicyd}^{2-}$ and $-2J = 192$ to 124 cm^{-1} respectively)[39]. It is also clear that the *syn* configuration of the bridging ligand does not appear to interfere with metal-metal exchange as expected from the results of the Extended Huckel calculation (section 4.2.5).

The explanation for the enhanced metal-metal exchange is much the same as that given to explain the enhanced metal-metal coupling which was observed for the mixed valence complexes. Namely, replacement of a strong σ donor ligand (NH_3) with weak σ donor ligand (pyridine) stabilizes the Ru(III) d -orbitals and increases the $\pi d-\pi_{nb}$ interaction between Ru(III) and the cyanamide groups. This in turn, increases the interaction of the Ru(III) πd magnetic orbital with the superexchange pathway (*HOMO* of the dicyd^{2-} ligand) and results in strong antiferromagnetic coupling.

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B. Magnetic Susceptibility Measurement in Solution (Evans Method)

The Evans Method experiments of the four dinuclear complexes in both acetonitrile and dimethyl sulfoxide (DMSO) were performed on the AMX 400 MHz FT-NMR spectrometer and the data are collected in Tables 4.13 and 4.14. The Δf (the frequency separation of the inert reference TMS, in presence and absence of paramagnetic compound) were measured and the molar susceptibility (χ_M) calculated using equations (1.23, 1.24). The χ_M must be corrected for the diamagnetic contribution from the ligands and counter ion atoms. This was done by simply summing the diamagnetic contribution of each ligand atom and group of atoms and adding the sum to the susceptibility of the complex to give the corrected molar susceptibility χ_M . For instance, the calculation for diamagnetic contribution using the Pascal's constants for $\text{trans}-[(\text{NH}_3)_4\text{RuPy}]_2(\mu\text{-dicyd})(\text{PF}_6)_4$ are as follows:

$$\chi_{dia} = 2 \times \chi(\text{Ru}^{3+}) + 8 \times \chi(\text{NH}_3) + 2 \times \chi(\text{py}) + 1 \times \chi(\text{dicyd}^{2-}) + 4 \times \chi(\text{PF}_6^-)$$

The diamagnetic contribution of each ligand or group of atoms can be found in various reference books[121-122] or calculated by adding the contribution of each atom in the ligand. The corrected molar magnetic susceptibility is related to the effective magnetic moment by the equation (1.16).

The solution magnetic susceptibility data in Tables 4.13 and 4.14 indicate that the Ru(III) dinuclear complexes are more paramagnetic in dimethyl sulfoxide than in acetonitrile solution. The solvent dependent magnetic properties arise from an outer-sphere donor-acceptor interaction between the solvent's non-bonding electron pairs and the protons of ammine ligands which transfers electron density to Ru(III). This weakens the magnitude of antiferromagnetic coupling, reducing $-J$ and resulting in the population of the triplet state.

The effective magnetic moment (μ_{eff}) of the analogous pentaammine ruthenium dimers[120] are included in Tables 4.13 and 4.14. In comparison, the *trans*- $[\{\text{py}(\text{NH}_3)_4\text{Ru}\}_2(\mu\text{-L})]^{4+}$ complexes show smaller magnetic susceptibility values, which again reflects the stronger antiferromagnetic exchange that is seen for these complexes.

The nature of the substituents on the phenyl group of the bridging ligand also perturbs metal-metal antiferromagnetic coupling. The magnetic susceptibility increases when going

Table 4.13 The Evans Experiment Data for *Trans*-
 $[(\text{NH}_3)_4\text{Rupy}]_2(\mu\text{-L})(\text{PF}_6)_4$ in Acetonitrile(d_3).

L	Δf (Hz)	χ_M (g.mol)	χ_{dia} (g.mol)	μ_{eff} (BM)	$^a\mu_{eff}$ (BM)
Me₂dicyd	0.98	6.73×10^{-5}	-6.24×10^{-4}	0.644	0.725
dicyd	1.30	8.80×10^{-5}	-6.01×10^{-4}	0.694	0.794
Cl₂dicyd	24.60	1.29×10^{-3}	-6.29×10^{-4}	1.072	1.105
Cl₄dicyd	31.02	1.74×10^{-3}	-6.57×10^{-4}	1.199	1.296

^a μ_{eff} of $[(\text{NH}_3)_5\text{Ru}]_2(\mu\text{-L})(\text{PF}_6)_4$ in acetonitrile(d_3) [120].

Table 4.14 The Evans Experiment Data for *Trans*-
 $[(\text{NH}_3)_4\text{Rupy}]_2(\mu\text{-L})(\text{PF}_6)_4$ in Dimethyl Sulfoxide(d_6).

L	Δf (Hz)	χ_M (g.mol)	χ_{dia} (g.mol)	μ_{eff} (BM)	$^a\mu_{eff}$ (BM)
Me₂dicyd	8.02	4.08×10^{-4}	-6.24×10^{-4}	0.787	1.115
dicyd	18.05	1.27×10^{-3}	-6.01×10^{-4}	1.065	1.250
Cl₂dicyd	38.02	1.98×10^{-3}	-6.29×10^{-4}	1.252	1.375
Cl₄dicyd	44.93	2.42×10^{-3}	-6.57×10^{-4}	1.359	1.423

^a μ_{eff} of $[(\text{NH}_3)_5\text{Ru}]_2(\mu\text{-L})(\text{PF}_6)_4$ in DMSO(d_6) [120].

from $\text{trans}-\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-Me}_2\text{dicyd})(\text{PF}_6)_4$ to $\text{trans}-\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-Cl}_4\text{dicyd})(\text{PF}_6)_4$ due to stabilization of HOMO of the bridging ligand and decoupling of the Ru(III) ions from the HOMO of the dicyd^{2-} ligand.

C. Nuclear Magnetic Resonance

^1H NMR spectra of some dinuclear ruthenium complexes in acetonitrile, dimethyl sulfoxide and nitromethane are displayed in Figures 4.33 to 4.36. The assignment of each resonance line for all dinuclear complexes are collected in Tables 4.15 and 4.16.

In paramagnetic dinuclear complexes, each peak can be dramatically shifted either down or upfield from their normal diamagnetic peak position. These chemical shifts can be described by two processes, namely contact shift and pseudo-contact shift. The former is a result of unpaired electron spin density being transferred off the metal onto the ligands and depends on the magnitude of ligand character in the half-filled molecular orbital. Different protons experience different magnitudes of contact shift because the delocalization of spin density is not evenly distributed. The second process is called pseudo-contact shift and arises from the through space interaction between electron and nuclear

Figure 4.33 ^1H NMR spectra of $\text{trans}-\{[(\text{NH}_3)_4\text{Rupy}]_2(\mu\text{-dicyd})\}(\text{PF}_6)_4$ in nitromethane(d_3).

Figure 4.34 ^1H NMR spectra of $\text{trans}-[\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-Me}_2\text{dicyd})](\text{PF}_6)_4$ (A) in acetonitrile(d_3) and (B) in DMSO(d_6).

Figure 4.35 ^1H NMR spectra of *trans*- $[\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-Cl}_2\text{dicyd})](\text{PF}_6)_4$ (A) in acetonitrile(d_3) and (B) in DMSO(d_6).

Figure 4.36 ^1H NMR spectra of $\text{trans}-[\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-Cl}_4\text{dicyd})](\text{PF}_6)_4$ (A) in acetonitrile(d_3) and (B) in DMSO(d_6).

magnetic moments. The magnitude and the sign of this shift depends on distance, the relative geometry(angles) of each proton from the metal center and the anisotropy of magnetic susceptibility. This shift usually has a negative sign and shifts the proton chemical shifts upfield. Depending on their position, each particular proton experiences a combination of these two types of shift and this can be seen in the NMR spectra of the dinuclear complexes given in Figures 4.33 to 4.36 and the data in Tables 4.15 and 4.16.

For the dinuclear ruthenium [3,3] complexes, in addition to electron spin-nuclear spin interactions, the electron spin moments of the two ruthenium ions also can be magnetically coupled through a diamagnetic bridging ligand. As explained earlier, the magnitude of metal-metal antiferromagnetic exchange can be perturbed by both outer-sphere(solvent) and inner-sphere (spectator and bridging ligand) effects. Thus, the magnitude of contact and pseudocontact shifts depend on the degree of coupling between the two metal centers.

The assignment of the NMR spectra of paramagnetic species has always been a difficult task as the chemical shift values cannot be easily predicted[65,123]. The isotropic shift is the sum of the two contributions which can be opposite in sign and which are determined by many factors.

In this study, on the basis of comparison with the spectrum of a diamagnetic dinuclear complex (the spectrum of

Table 4.15 ^1H NMR Data of *Trans*- $\{[(\text{NH}_3)_4\text{Rupy}]_2(\mu\text{-L})\}(\text{PF}_6)_4$ in Acetonitrile(d_3) Solution.

L	$^a\text{NH}_3$	NH_3	Me	Phenyl	Pyridine		
					(O)	(P)	(M)
Me ₂ dicyd	5.60	2.60		7.20	8.40	8.04	7.80
dicyd	11.70	4.10			8.85	8.83	8.50
Cl ₂ dicyd	34.50	16.40		-0.28	11.09	3.45	3.41
Cl ₄ dicyd	48.50	34.50			16.90	-4.10	-4.23

^athe cis-amine proton of $\{[(\text{NH}_3)_5\text{Ru}]_2(\mu\text{-L})\}(\text{PF}_6)_4$ in acetonitrile(d_3) solution[120].

Table 4.16 ^1H NMR Data of *Trans*- $\{[(\text{NH}_3)_4\text{Rupy}]_2(\mu\text{-L})\}(\text{PF}_6)_4$ in Dimethyl Sulfoxide(d_6) Solution.

L	$^a\text{NH}_3$	NH_3	Me	Phenyl	b Pyridine		
					(O)	(P)	(M)
Me ₂ dicyd	43.81	13.82	6.65	1.90	9.78	5.30	4.90
dicyd	52.18	26.31		-3.60	12.30	1.70	0.40
Cl ₂ dicyd	67.13	57.80		-10.80	16.58	- 5.89	-9.04
Cl ₄ dicyd	72.87	72.55			20.05	-11.30	-13.12

^a the cis-amine proton of $\{[(\text{NH}_3)_5\text{Ru}]_2(\mu\text{-L})\}(\text{PF}_6)_4$ in dimethyl sulfoxide(d_6) solution[120].

^b (O)Ortho, (P)Para, (M)Meta

trans-[$\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-dicyd})(\text{PF}_6)_4$ in nitromethane), the ratio of integration and the rough expectation of shift, permitted the assignment of all peaks. All the ammine protons are equivalent and appear as a singlet peak in the NMR spectrum. Because the amines are directly bound to Ru(III), the ammine peak can be shifted down field by contact shift. The NMR spectra data in Tables 4.15 and 4.16 confirmed these changes i.e. the ammine protons peak shifts from 2.60 ppm for *trans*-[$\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-Me}_2\text{dicyd})(\text{PF}_6)_4$ in acetonitrile to 13.82 ppm in dimethyl sulfoxide and to 34.50 ppm in *trans*-[$\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-Cl}_4\text{dicyd})(\text{PF}_6)_4$ in acetonitrile.

As expected, the protons on the pyridine ring show an ABC pattern with intensity ratio of 2(doublet), 2(triplet) and 1(triplet). This pattern is seen in the diamagnetic spectra of *trans*-[$\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-dicyd})(\text{PF}_6)_4$ in nitromethane(Figure 4.33) and *trans*-[$\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-Me}_2\text{dicyd})(\text{PF}_6)_4$ in acetonitrile. But as the magnetic moment in the dinuclear complexes increases, on decreasing the metal-metal magnetic coupling by outer and inner-sphere perturbations, these protons experience different shifts. The ortho hydrogens of pyridine which are closest to Ru(III), are again affected mostly by contact shift and are shifted downfield. On the other hand, the meta and para hydrogens are shifted upfield largely because of pseudo-contact shift. The contribution of

contact shift for these protons is small because of their distance from Ru(III). The nature of both solvent and bridging ligand can change the magnitude of shift of these protons, i.e. the ortho protons shifted from 8.40 ppm for *trans*- $[\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-Me}_2\text{dicyd})](\text{PF}_6)_4$ in acetonitrile to 9.78 ppm in dimethyl sulfoxide and 20.50 ppm for *trans*- $[\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-Cl}_4\text{dicyd})](\text{PF}_6)_4$ in DMSO. The para and meta protons shifted from 8.04 and 7.80 ppm for *trans*- $[\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-Me}_2\text{dicyd})](\text{PF}_6)_4$ in acetonitrile to 5.30, and 4.90 ppm in DMSO, and -11.30 and -13.12 ppm, respectively for *trans*- $[\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-Cl}_4\text{dicyd})](\text{PF}_6)_4$ in DMSO.

Depending on the nature of the solvent and the bridging ligand, the phenyl protons appear as a broad singlet peak shifted upfield because of a dominant contribution by pseudo-contact shift. For instance, the phenyl protons shift from 7.20 ppm for *trans*- $[\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-Me}_2\text{dicyd})](\text{PF}_6)_4$ in acetonitrile to 1.90 ppm in DMSO and -10.80 ppm for *trans*- $[\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-Cl}_2\text{dicyd})](\text{PF}_6)_4$ in DMSO.

The chemical shifts of the *cis*-ammines for the pentaammine ruthenium dinuclear analogue complexes are added to Tables 4.15 and 4.16 to facilitate a comparison between these two systems. As can be seen from the data, the amines' chemical shift in $[\{(\text{NH}_3)_5\text{Ru}\}_2(\mu\text{-L})](\text{PF}_6)_4$ is shifted

downfield compared to those for *trans*- $[(\text{NH}_3)_4\text{Rupy}]_2(\text{L})(\text{PF}_6)_4$. These results are a consequence of the replacement of an ammine with pyridine which increases the antiferromagnetic coupling between the two Ru(III) ions and reduces the overall magnetic moment of the complex. Therefore, the magnitude of contact and pseudo contact contribution to the isotropic shift is less. The chemical shift difference between the two systems is reduced by adding electron withdrawing substituents to the bridging ligand and by increasing the electron donor properties of the solvent (Tables 4.15 and 4.16). The greater sensitivity of the ammine chemical shift of the *trans*- $[(\text{NH}_3)_4\text{Rupy}]_2(\text{L})(\text{PF}_6)_4$ to those factors can be illustrated graphically.

If it is assumed that the dominant contributor to the isotropic shift is contact shift, there is predicted a linear relationship between the magnitude of contact shift and the amount of shift in Evans method (Δf) (the observed difference in chemical shifts of a inert reference peak in the presence and absence of a paramagnetic solute).

$$(\Delta\nu/\nu)_{\text{contact}} = A_{\text{con}} \{g\beta S(S+1)\} / (3g_n\beta_n kT) \quad (1.27)$$

Now,

$$\mu_{eff} = g[S(S+1)]^{1/2} = 2.83 (\chi'_m T)^{1/2} \quad (1.16)$$

$$\therefore S(S+1) = 8(\chi'_m T)/g^2 \quad (4.7)$$

substitution of (4.7) into (1.27)

$$(\Delta v/v)_{contact} = 8A_{con}\{\beta\chi'_m\}/(3g_n\beta_nkg) \quad (4.8)$$

since:

$$\chi_m = \chi_g \cdot M = (3M\delta f/4\pi m v)$$

$$\therefore (\Delta v/v)_{contact} = 8A_{con}(\beta 3M\Delta f/4\pi m v)/(3g_n\beta_nkg) \quad (4.9)$$

$$\Delta v_{contact} = (2A_{con}\beta M/\pi m g_n\beta_nkg) \Delta f \quad (4.10)$$

Because the concentration of the complexes were slightly different, the Δf 's were normalized to the trans-
 $[(\text{NH}_3)_4\text{Rupy}]_2(\mu\text{-Cl}_2\text{dicyd})]^{4+}$ concentration of 11.09 mM,

$$\Delta v_{contact} = N (2A_{con}\beta M/\pi m g_n\beta_nkg) \Delta f \quad (4.11)$$

where, N = the ratio of concentration of *trans*- $[\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-Cl}_2\text{dicyd})]^{4+}$ in DMSO to the concentration of each individual complexes in both solvent.

$$\Delta\nu_{\text{contact}} = (2A_{\text{con}}\beta_M/\pi mg_n\beta_n kg) \Delta f' \quad (4.12)$$

Therefore a plot of $\Delta\nu$ vs $\Delta f'$ gives a straight line with slope $(2A_{\text{con}}\beta_M/\pi mg_n\beta_n kg)$. Figure 4.35 shows this relationship for the chemical shift of the *cis*-ammines for all the complexes in both solvents. There are exceptions for the *trans*- $[\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-Cl}_2\text{dicyd})](\text{PF}_6)_4$ and *trans*- $[\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-Cl}_4\text{dicyd})](\text{PF}_6)_4$ in acetonitrile which may be from experimental error and require further investigation. From the slope of the line, a value for (A_c/h) was determined to be 1.36 Mhz. This is slightly greater than the hyperfine coupling constant determined for the *cis* ammines in the $[\{(\text{NH}_3)_5\text{Ru}\}_2(\mu\text{-dicyd})]^{4+}$ complexes $[(A_c/h) = 1.16 \text{ Mhz}]$, and suggests a slightly stronger interaction between Ru(III) and the *cis* ammines in the *trans*- $[\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-L})](\text{PF}_6)_4$ complexes.

Figure 4.37 Plot of $\Delta \nu$ (Hz) vs $\Delta f'$ (Hz) for the *trans*- $[(\text{NH}_3)_4\text{Rupy}]_2(\mu\text{-L})(\text{PF}_6)_4$ complexes in both acetonitrile and DMSO.

CHAPTER 5

Summary and Future Work

Previous studies[80-81] have shown that the mixed valence $[(\text{NH}_3)_5\text{Ru}]_2(\mu\text{-dicyd})^{3+}$ complexes are class II systems in which the odd electron is localized on one of the ruthenium ions. To get delocalization which is needed in the design of conducting coordination polymers, it is necessary to decrease the energy difference between the ruthenium d -orbitals and the π HOMO of the dicyd bridging ligand. One way of accomplishing this objective is to replace an ammine ligand with a poor σ donor ligand. To test this hypothesis, a series of mononuclear complexes, $\text{cis-}[\text{Ru}(\text{bpy})_2(\text{Cl}_n\text{pcyd})_2]$ were synthesized and characterized. The physical properties of these complexes are consistent with increased covalency of the Ru(III)-cyanamide bond compared to their $[(\text{NH}_3)_5\text{Ru}(\text{pcyd})]^{2+}$ analogues and showed that replacement of a strong σ donor ligand (NH_3) by pyridine moieties stabilized the ruthenium $d\pi$ orbitals (see Figure 3.8).

In response to these results, the mixed valence complex, $[\{\text{Ru}(\text{bpy})(\text{terpy})\}_2(\mu\text{-dicyd})]^{3+}$ was synthesized and

characterized. Its electronic properties show strong metal-metal coupling with only slight solvent dependence. Therefore, on the basis of the Robin and Day classification of mixed-valence complexes, this complex was classified as a class III system with comproportionation constant, $K_C = 2.75 \times 10^7$ and an intervalence band at $\lambda = 1090$ nm ($\epsilon_{\max} = 5600$ M⁻¹cm⁻¹).

A series of *trans*-[$\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-dicyd})\}^{4+}$ complexes were synthesized and characterized by spectroscopic and electrochemical techniques. The physical properties of these complexes are just as interesting as those found for the dinuclear pentaammine ruthenium complexes.

The crystal structure of the *trans*-[$\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-dicyd})\}(\text{PF}_6)_4$ complex has shown the cyanamide groups to be approximately planar with the phenyl ring but in a *syn* configuration. This was not expected since previous crystal structures of a dinuclear pentaammineruthenium complex and free *dicyd*²⁻ ligands showed that the *anti* configuration was preferred. An extended Huckel molecular orbital calculation didn't show a significant energy difference between these two configurations. In addition the appearance of the HOMO (electron density coefficients) appeared to be the same for both *syn* and *anti* configurations

The electronic properties of the metal to metal charge transfer bands of these complexes are consistent with strong metal-metal coupling. The predicted band width at half-peak height ($\Delta\nu_{1/2}$) of the intervalence band by Hush model for weakly coupled system (class II), is significantly greater than found by curve fitting analysis and this is characteristic of strongly coupled mixed valence systems. Comproportionation constants of these complexes are significantly higher than that observed for class II systems ($<10^3$). Importantly, the *trans*-[$\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-Me}_2\text{dicyd})\](\text{PF}_6)_4$ complex has a $K_C = 5.6 \times 10^6$ in acetonitrile and is higher than the K_C for Creutz-Taube ion ($\{[(\text{NH}_3)_5\text{Ru}]_2(\mu\text{-pz})\}^{5+}$, $K_C = 4 \times 10^6$). However, the *trans*-[$\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-Me}_2\text{dicyd})\](\text{PF}_6)_4$ complex shows considerable solvent dependence (Tables 4.8 and 4.10) even though the magnitude of K_C might suggest class III solvent independence.

The variable temperature magnetic susceptibility measurements of the *trans*-[$\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-L})\](\text{PF}_6)_4$ complexes indicated that all of the complexes are strongly antiferromagnetically coupled and show diamagnetic behavior up to room temperature. The magnetic susceptibility measurements of these complexes in solution (Evans method) show diamagnetic behavior in poor donor solvents (CH_3NO_2 ,

CH₃CN) , but as the donor number of the solvent increases from acetonitrile to dimethyl sulfoxide, the magnetic exchange coupling between two ruthenium(III) ions decreased. The ¹H NMR spectra show that the magnitude of contact and pseudocontact shifts of proton resonances depends on the magnetic susceptibility of the complex which increases as the donor number of the solvents increases. The solvent dependent magnetic properties arise from an outer-sphere donor-acceptor interaction between the solvent's non-bonding electron pairs and the protons of the ammine ligands which transfers electron density to Ru(III). This weakens the magnitude of antiferromagnetic coupling, reducing -J and resulting in the population of the triplet state. More studies need to be carried out in a range of solvents, to fully explore the solvent dependence of metal-metal coupling in these complexes.

The replacement of the ammine with the pyridine moiety increases the stability of the ruthenium d-orbitals in both +2 and +3 oxidation state because of pyridine's π -acceptor properties and pyridine's poorer σ donor properties compared to the strong σ donor ammine ligand. The effect this has on the Ru(III) ion can be readily seen by a comparison of the Ru(III/II) reduction couples of $[\{(\text{NH}_3)_5\text{Ru}\}_2(\mu\text{-dicyd})]^{4+}$, which occur at 0.131 and -0.155 V vs NHE, with those of $\text{trans-}[\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-dicyd})]^{4+}$, which occur at 0.350 and -0.015 V

vs *NHE* and for $[\{\text{Ru}(\text{bpy})(\text{terpy})\}_2(\mu\text{-dicyd})]^{3+}$, which occur at 0.840 and 0.415 V vs *NHE*, in acetonitrile solutions. The increased stability of the Ru(III) *d*-orbitals increases the covalency of its π -interaction with the cyanamide groups of the bridging ligand, which in turn increases metal-metal coupling via the π *HOMO* superexchange pathway of the bridging ligand.

To further explore the effect of inner sphere perturbations on the metal-metal coupling, future systems to be synthesized are those in which the ammine ligands in $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-dicyd})]^{4+}$ are progressively replaced by pyridine are *cis*- $[\{(\text{NH}_3)_4\text{Rupy}\}_2(\mu\text{-dicyd})]^{4+}$, $[\{(\text{NH}_3)_3\text{Ru}(\text{bpy})\}_2(\mu\text{-dicyd})]^{4+}$ and $[\{(\text{NH}_3)_2\text{Ru}(\text{terpy})\}_2(\mu\text{-dicyd})]^{4+}$.

APPENDIX

Ligand Input Data Files for EHMO Calculation

NOTE: The first row in each data set contains four numbers which represent the number of hydrogen atoms, the number of heavy atoms, the charge on the compound and the method used (0,1,2 or 3), respectively. The total number of atoms can not exceed 50. This is followed by the x,y and z coordinates of each atom (hydrogens must be listed first) and a last line indicating the heavy atoms in the order they appear in the coordinate list. The atom labels correspond to those of the crystal structure in 4.2.4.

*Syn-dicyd*²⁻

4 12 -2 0			
Atom	X	Y	Z
H	1.350	2.100	0.000
H	-1.250	2.150	0.000
H	-1.300	-2.200	0.000
H	1.100	-2.150	0.000
C	1.400	0.000	0.000
C	0.750	1.200	0.000
C	3.370	-1.150	0.000
C	0.750	-1.200	0.000
C	-0.750	1.200	0.000
C	-0.750	-1.200	0.000
C	-1.400	0.000	0.000
C	-3.500	-1.100	0.000
N	2.720	0.000	0.000
N	3.920	-2.150	0.000
N	-2.800	0.000	0.000
N	-4.100	-2.100	0.000
C C C C C C C C N N N N			

*Anti-dicyd²⁻***4 12 -2 0**

Atom	X	Y	Z
H	1.350	2.100	0.000
H	-1.250	2.150	0.000
H	-1.300	-2.200	0.000
H	1.100	-2.150	0.000
C	1.400	0.000	0.000
C	0.750	1.200	0.000
C	3.370	-1.150	0.000
C	0.750	-1.200	0.000
C	-0.750	1.200	0.000
C	-0.750	-1.200	0.000
C	-1.400	0.000	0.000
C	-3.500	1.100	0.000
N	2.720	0.000	0.000
N	3.920	-2.150	0.000
N	-2.800	0.000	0.000
N	-4.100	2.100	0.000
C C C C C C C C N N N N			

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