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RUTHENIUM-CYANAMIDE BOND IN MONONUCLEAR AND
DINUCLEAR PENTAAMMINERUTHENIUM COMPLEXES OF
1,4-DICYANAMIDOBENZENE LIGANDS

by

MARK L. NAKLICKI, B.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

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RUTHENIUM-CYANAMIDE BOND IN MONONUCLEAR AND
DINUCLEAR PENTAAMMINERUTHENIUM COMPLEXES OF
1,4-DICYANAMIDOBENZENE LIGANDS"

submitted by

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

Chair, Department of Chemistry

Thesis Supervisor

External Examiner

Carleton University

March, 1995

Abstract

Three mononuclear pentaammineruthenium(III) complexes of the 1,4-dicyanamidobenzene monoanion ligands ($[(\text{NH}_3)_5\text{Ru}(\text{LH})]^{2+}$, where $\text{LH} = 2,5\text{-Me}_2\text{DicydH}^-$, DicydH^- and $2,5\text{-Cl}_2\text{DicydH}^-$) have been synthesized and characterized. Their singly deprotonated dianion bound counterparts, $[(\text{NH}_3)_5\text{Ru}(\text{L})]^+$, have been reversibly generated in aqueous solution as verified by the formation of characteristic UV-vis-NIR spectral profiles and cyclic voltammograms. Based on differences in the optical energy E_{op} and the oscillator strength of the $b_1^* \leftarrow b_1$ LMCT transition and on differences in the potential of the Ru(III/II) reduction couple, it was concluded that deprotonation strengthens the Ru(III)-cyanamide π interaction as the 1,4-dicyanamidobenzene dianion ligands are stronger π donors than their monoanion counterparts. In addition, whether protonated or not, the Ru(III)-cyanamide π interaction was shown to be dependent on the π donor strength of the cyanamide ligand with methyl substitution strengthening the interaction and chloro substitution weakening it. Via the chemical oxidation of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{DicydH})]^{2+}$, the pentaammineruthenium(IV) complex, $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})]^{2+}$, has been synthesized and characterized. Most notable are the ^1H NMR results, which strongly support a diamagnetic complex designation. From a comparison of E_{op} and the oscillator strength of the $b_1^* \leftarrow b_1$ LMCT transition, it was concluded that the ruthenium-cyanamide π interaction is strengthened upon oxidation of Ru(III) to Ru(IV). For the series of previously prepared (refer to Refs. 3-7) dinuclear pentaammineruthenium(III) complexes of the 1,4-dicyanamidobenzene dianion ligands ($[\mu\text{-(L)}\text{-(NH}_3)_5\text{Ru}]_2]^{4+}$ or $[\text{Ru(III), Ru(III)}]$: where $\text{L} = 2\text{-MeODicyd}^{2-}$ (1), $2,5\text{-Me}_2\text{Dicyd}^{2-}$ (2), 2-MeDicyd^{2-} (3), Dicyd^{2-} (4), $2,5\text{-Cl}_2\text{Dicyd}^{2-}$ (5) and $2,3,4,5\text{-Cl}_4\text{Dicyd}^{2-}$ (6)), trends in E_{op} and the oscillator strength of the $b_1^* \leftarrow b_1$ LMCT transition and trends in redox data, demonstrate that the strength of the Ru(III)-cyanamide π interaction and hence the extent of superexchange metal-metal coupling in the $[\text{Ru(III), Ru(III)}]$ systems are dependent on both solvent (an

outer-sphere perturbation) and on the π donor strength of the bridging cyanamide ligand (an inner-sphere perturbation). The results demonstrated that for a given [Ru(III), Ru(III)] complex, the strength of the Ru(III)-cyanamide π interaction followed the order: **nitromethane (NM) > acetonitrile (AN) > acetone (AC) > water (H₂O) > dimethyl sulfoxide (DMSO)**, whereas in a given solvent, the strength of the interaction followed the order: **1 > 2 > 3 > 4 > 5 > 6**. Similarly, solution magnetic susceptibility and ¹H NMR results demonstrated that for a given [Ru(III), Ru(III)] complex, paramagnetism increased in the order: **NM < AN < AC < DMSO < H₂O**, whereas in a given solvent, paramagnetism increased in the order: **1 < 2 < 3 < 4 < 5 < 6**.

6. For both perturbations, the onset of paramagnetism was the result of a reduction in metal-metal antiferromagnetic coupling. Cyclic voltammetry studies have shown that metal-metal coupling in the mixed-valence [Ru(III), Ru(II)] complexes is also dependent on solvent and on the π donor strength of the bridging cyanamide ligand. For a given [Ru(III), Ru(III)] complex, the separation between Ru(III/II) couples ΔE and hence the comproportionation constant K_c followed the order: **NM > AN > AC > DMSO > H₂O**, whereas in a given solvent, ΔE and K_c followed the order: **1 > 2 > 3 > 4 > 5 > 6**.

6. Such a dependence of K_c on solvent and π donor strength of the bridging cyanamide ligand is consistent with a transformation from weakly coupled Class II properties in high donor number solvents and for weakly π donating cyanamides, respectively, to borderline Class II/Class III properties in low donor number solvents and for strongly π donating cyanamides, respectively. The near-IR absorption spectra, showing the intervalence (IT) transition of the mixed-valence [Ru(III), Ru(II)] complex of the Dicyd²⁻ bridging ligand, have been obtained by spectroelectrochemical methods in aqueous and acetonitrile solution. A Hush treatment of the IT band properties showed that despite the limited solvent range, the resonance exchange integral H_{ad} and hence metal-metal coupling in $[\mu\text{-(Dicyd)}\text{-(NH}_3)_5\text{Ru}]_2^{3+}$ demonstrated a solvent dependency with weakly coupled Class II behaviour being approached in aqueous solution and borderline Class II/Class III

behaviour being attained in acetonitrile. Spectroelectrochemical studies in acetonitrile only, have generated the IT band for all six mixed-valence [Ru(III), Ru(II)] complexes. In this case, a Hush analysis demonstrated a dependency of H_{ad} on the π donor strength of the bridging cyanamide ligand that followed the order: $1 > 2 > 3 \gg 4 > 5 \gg 6$. Such a dependence of H_{ad} is consistent with a transformation from weakly coupled Class II properties in the case of weakly π donating cyanamides to borderline Class II/Class III properties for strongly π donating cyanamides. Finally, via the chemical oxidation of $[\mu-(2,5\text{-Me}_2\text{Dicyd})\text{-}(\text{NH}_3)_5\text{Ru}]_2^{4+}$, the mixed-valence [Ru(IV), Ru(III)] complex, $[\mu-(2,5\text{-Me}_2\text{Dicyd})\text{-}(\text{NH}_3)_5\text{Ru}]_2^{5+}$, has been synthesized and characterized. ^1H NMR and solution magnetic susceptibility results suggest that the odd electron is delocalized on the NMR time scale, such that each ruthenium ion contributes 1/2 of an electron spin. However, the UV-vis-NIR spectral profile of the mixed-valence [Ru(IV), Ru(III)] complex is reflective of a localized environment as the $b_1^* \leftarrow b_1$ and $b_1^* \leftarrow b_2$ LMCT transitions associated with both the Ru(III)- and Ru(IV)-cyanamide chromophores are observed. The experimental observation of an IT band has not been possible as the intense low energy LMCT bands are believed to obscure it.

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**This work is dedicated to my wife, Barbara,
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List of Abbreviations

bpbim	2,2'-bis(2-pyridyl)bibenzimidazole dianion
bpy	bipyridine
CM	carboxymethyl
DCNQI	<i>N,N'</i> -dicyanoquinone diimine
DSS	2,2-dimethyl-2-silapentane-5-sulfonate, sodium salt
HOMO	highest occupied molecular orbital
imid	imidazole
LUMO	lowest unoccupied molecular orbital
Mac	macrocyclic ligand
Me	methyl
MeO	methoxy
MPD	1-methyl-2-pyrrolidinone
OTs	tosylate anion
phen	1,10-phenanthroline
py	pyridine
pyz	pyrazine
SHOMO	second highest occupied molecular orbital
SP	sulfopropyl
TBAB	tetrabutylammonium bromide
TBAH	tetrabutylammonium hexafluorophosphate
TCNE	tetracyanoethylene
TEAC	tetraethylammonium chloride
terpy	terpyridine
TMS	tetramethylsilane

CHAPTER 1

Introduction

1.1 Background

The study of electron exchange and electron transfer in polymetallic complexes, in which coupling between metals is propagated via a polarizable bridging molecule, has clear application to the design of novel magnetic and electronic solid-state materials.¹ Another important application concerns the design of analogue systems that model the active sites of metalloproteins and attempt to elucidate the fundamental role of polymetallic centers in biological processes.²⁻⁴

1.1.1 Magnetic and Electronic Molecular Materials

The design and synthesis of novel magnetic or electronic solid-state materials that are based on polymetallic complexes, requires that the fundamental molecular properties of the unit building blocks, that make up the crystal lattice, be fully understood. Examples of molecular building blocks include metal donor-organic ligand acceptor (D^+-A^-) charge-transfer complexes, or dinuclear mixed-valence ($M-L-M^+$) complexes bridged by a polarizable organic ligand. The idea is to custom design the molecular properties of each unit building block, such that upon assembly, the desired cooperative property is expressed. An example of such a strategy as applied to the construction of a magnetic material is demonstrated by the charge-transfer salt of decamethylferrocene with tetracyanoethylene, $[Fe^{III}(C_5Me_5)_2]^{+}[TCNE]^{-}$.⁵ This molecular organic solid, comprised of linear chains of alternating $S = 1/2$ metallocenium donors D and cyanocarbon acceptors A, $(-D^{+}A^{-})_n$, exhibits cooperative bulk ferromagnetic behaviour below the Curie temperature of 4.8 K. Replacement of Fe(III) with Cr(III), Ni(III) and Fe(II) leads to complexes with antiferromagnetic coupling, ferrimagnetic behaviour and almost no

magnetic interaction, respectively. A particularly important class of electronic solid-state materials that display high electrical conductivities, are the charge-transfer complexes of the *N,N'*-dicyanoquinone diimine (DCNQI) acceptors, having the stoichiometry $M(\text{DCNQI})_2$.⁶ Remarkably, the copper salt of the radical anion form of 2,5-dimethyl-*N,N'*-dicyanoquinone, $\text{Cu}(\text{Me}_2\text{DCNQI})_2$, exhibited metallic conductivity down to 3.5 K with $\sigma = 5 \times 10^5 \text{ S cm}^{-1}$.^{6f} Crystal structure data^{6f,7} indicate that the Me_2DCNQI ligands are arranged in stacks linked together by tetrahedrally coordinated copper ions. The primary mechanism of conduction was suggested to occur via the π stacks of Me_2DCNQI molecules with an additional transverse contribution occurring via the NCN-Cu-NCN bridges between the individual stacks. Note that high conductivity along π acceptor stacks has been demonstrated by other organic charge-transfer molecular metals, in which each π acceptor molecule possesses a partial negative charge.⁸ The implication is that electrons can move within a π stack without a Coulombic barrier. In the case of the $\text{Cu}(\text{Me}_2\text{DCNQI})_2$ molecular metals, for such a conduction mechanism to be operative, copper must exist in a mixed-valence state. Indeed, X-ray photoelectron spectroscopy^{6b} and low-temperature X-ray diffraction^{7b} studies indicate an average Cu oxidation state of 1.3. Such a delocalization was proposed to arise from the direct mixing of copper $d\pi$ orbitals with radical anion Me_2DCNQI $p\pi$ orbitals.⁶

Dinuclear mixed-valence complexes, particularly those of ruthenium, have demonstrated an important viability in terms of their application to the construction of molecular electronic devices and molecular materials.⁹ For example, the design of molecular electronic devices for signal processing is a practical application of mixed-valence complexes, however, the idea poses a major synthetic challenge.¹⁰ The control of signal transfer from one metal site to another depends on control of metal-metal coupling, which should be highly sensitive to modest external stimuli without resulting in decomposition. Protonation of the bridging ligand¹¹⁻¹⁴ or outer-sphere coordination of crown ethers¹⁵ are two chemical approaches

that demonstrate this principle. For example, in the dinuclear mixed-valence complexes, $[M(L)_2(bpbim)M(L)_2]^{3+}$ ($M = Ru, Os$; $L = bpy, phen$; $bpbim = 2,2'$ -bis(2-pyridyl)bibenzimidazole dianion), metal-metal coupling (as measured by the resonance exchange integral H_{ad} from the intervalence transition) is 4-6 times larger than that of the protonated $bpbimH_2$ bridged complexes. The suggestion is that proton transfer on the bridging ligand can be used to serve as a trigger signal for controlling (ie. switching on and off) the metal-metal interaction. Unfortunately though, chemical approaches such as this are not practically useful for reasons of being too slow and technically difficult to incorporate into a molecular electronic device. As an alternative, $[(1,5\text{-dithiacyclooctane } 1\text{-oxide})\{(NH_3)_5Ru\}_2]^{5+}$ undergoes a linkage isomerization upon oxidation.¹⁶ The reversible process is an example of molecular hysteresis, with a potential application to high density memory storage. In the construction of novel molecular materials, a mixed-valence complex ($M-L-M^+$) can be considered as a molecular unit building block. Polymerization and the retention of electronic delocalization between unit building blocks could lead to potentially conducting linear mixed valency oligomers, $(-M-L-)_n$, also known as long-chain molecular wires.^{17,18} Bisaxially coordinated macrocyclic ruthenium complexes, $[(Mac)RuL]_n$, have demonstrated varying degrees of conductivity.¹⁹ For example, when Mac is phthalocyanine and L is pyrazine²⁰ or 1,2,4,5-tetraazine²¹, the conductivity was found to be 10^{-7} and $10^{-1} \text{ S cm}^{-1}$, respectively.

1.1.2 Polymetallic Sites in Biology

The active sites of numerous metalloproteins contain polymetallic centers whose metal ions are linked or bridged together by various chemical groups. Interestingly, nature has selected such elaborated polymetallic sites to accomplish redox chemistry, oxygen fixation, chemical transformation of substrates and to act as electron carriers. Some examples of bridged dinuclear metal sites (shown in parenthesis) that are found in metalloproteins include: oxidized two-iron ferredoxin,²² an electron carrier, whose active site contains two

Fe(III) ions bridged by two S^{2-} anions (Fe_2S_2); hemerythrin,²³ involved in oxygen fixation, whose active site contains two Fe(III) ions bridged by one oxo and two carboxylato groups to form the core ($Fe_2O(RCO_2)_2$); manganese catalase,²⁴⁻²⁶ which catalyzes the reaction $H_2O_2 \rightarrow H_2O + 1/2O_2$, the active site of which is believed to be similar to that of hemerythrin with Fe(III) being replaced by Mn(III), ($Mn_2O(RCO_2)_2$); and superoxide dismutase,²⁷ which catalyzes the reaction $2O_2^{\cdot-} \rightarrow O_2 + O_2^{2-}$, and whose active site contains Cu(II) and Zn(II) metal ions bridged by an imidazole molecule ($N_3Cu-imad-ZnN_3$). Dinuclear metal centers found in the active sites of metalloproteins can form bridged species as a result of their function. Some examples include: hemocyanin,²⁸ involved in oxygen fixation, whose active site is believed to be comprised of a coupled dinuclear Cu(II) center that reversibly binds oxygen as peroxide to form oxy-hemocyanin ($N_3Cu-O_2-CuN_3$); and cytochrome *c* oxidase,^{29,30} which catalyzes the reduction of O_2 to H_2O in the reaction $O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$, whose active site for O_2 binding is thought to contain a dinuclear Fe(III)-Cu(II) center (Fe-heme-Cu). Importantly, magnetic exchange studies of the native metalloproteins have shown the metal ions of the dinuclear sites to be antiferromagnetically coupled to a significant extent yielding coupling constants, $-J$ (where $\mathcal{H} = -J\mathbf{S}_a \cdot \mathbf{S}_b$), of 268 cm^{-1} for hemerythrin;³¹ 366 cm^{-1} for two-iron ferredoxin;³² and a lower limit of 625 cm^{-1} for oxy-hemocyanin.³³ Clearly, the study of metal-metal interactions in model systems will greatly aid in the understanding of the fundamental chemistry underlying the biological reactions of metalloproteins with polymetallic active sites.

1.1.3 Scope of Thesis Research

The focus of this thesis is concerned with electron exchange (superexchange) interactions in dinuclear pentaammineruthenium ($[Ru(III), Ru(III)]$) complexes bridged by 1,4-dicyanamidobenzene dianion ligands. Somewhat minor focuses pertain to metal-metal coupling and intervalence charge transfer in mixed-valence $[Ru(III), Ru(II)]$ and $[Ru(IV),$

Ru(III)] complexes, also bridged by 1,4-dicyanamidobenzene dianion ligands. For the [Ru(III), Ru(III)] and mixed-valence [Ru(III), Ru(II)] systems, both outer- and inner-sphere perturbations of the Ru(III)-cyanamide bond will be conducted with the intent of demonstrating controlled metal-metal coupling. However, in order to obtain a fundamental understanding of the electronic nature of the ruthenium-cyanamide interaction in the dinuclear complexes, and as well to provide a clear synthetic pathway to their preparations, the mononuclear pentammineruthenium(III) and (IV) complexes of the 1,4-dicyanamidobenzene anionic ligand had to be synthesized and characterized first. It should be noted that the choice of ruthenium as a transition metal to study electron exchange and intervalence charge transfer is for reasons of it being relatively inexpensive and its ability to form stable Ru(IV), Ru(III) and Ru(II) coordination complexes. Furthermore, the synthetic coordination chemistry of ruthenium is well developed.³⁴

Prior to considering the mononuclear and dinuclear ruthenium systems that form the subject of this thesis, a detailed discussion regarding electron exchange interactions in dinuclear systems, the solution behaviour of paramagnetic complexes, and intervalence transfer in mixed-valence complexes will be given. Of course, throughout the introduction, a focus will be placed on ruthenium ammine complexes.

1.2 Electron Exchange

1.2.1 Magnetic Electron Exchange

For a system composed of metal A with spin S_a and metal B with spin S_b , bridged by an organic molecule L,

the isotropic Hamiltonian for the intramolecular magnetic interaction between spins can be written as

$$\mathcal{H} = -2J\mathbf{S}_a \cdot \mathbf{S}_b \quad (1.1)$$

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

Ferromagnetic coupling results in the formation of a triplet ground state and an excited singlet state:

The formation of a singlet or triplet ground state will depend on the relative magnitude of ferromagnetic (J_F) and antiferromagnetic (J_{AF}) terms:

$$2J = J_F - J_{AF} \quad (1.2)$$

where J_F represents the overall spin pairing energy and J_{AF} is the energy released when the spins are coupled. For large metal-metal separations, the value of J_F is usually believed to be small relative to J_{AF} . Indeed, as metal-metal separation increases, both second order antiferromagnetic contributions and the ferromagnetic term become less important, such that the former cancels out the latter.³⁵

1.2.2 The Charge Transfer Model for Antiferromagnetic Exchange

Examining the extent of overlap between coupled metal magnetic orbitals³⁶ or by using parameters that reflect the extent of electron exchange stabilization^{35,37-39} are two strategies that have been employed to explain the magnitude of J_{AF} . The following approach has as its basis the same ideas used to develop Marcus electron-transfer theory and the Hush model for intervalence transitions.

The electron exchange interaction can be described³⁷ as being the result of the mixing of the charge transfer state F with the initial state I as shown in Scheme 1.1:

Scheme 1.1

where the requirement for mixing is that the spins in state I be antiparallel and result in the stabilization energy J_{AF} . Figure 1.1 shows the potential energy-configuration diagram that represents the initial and final states in which E_o (the energy separation between states) is not large. In the diagram, E_{op} is the metal to metal charge transfer (MMCT) energy

between initial and final states that are at the same nuclear configuration. H_{ab} is the resonance exchange energy between the two states, which really represents the stabilization energy that results from the delocalization of electron density. Importantly, when E'_o (the energy difference between initial and final states) is large, a poor mixing of states and hence a very weak antiferromagnetic interaction will result.

Figure 1.1 The potential energy-configuration diagram representing initial I and final F states in the charge transfer model for antiferromagnetic exchange.

An expression for the antiferromagnetic exchange term J_{AF} that ignores second order contributions has been derived by Bertrand.^{35b}

$$J_{AF} = 2|H_{ab}|^2/E'_{op} \quad (1.3)$$

Although the result is an approximation, it still serves as a valuable guide in the design of exchange coupled systems. For example, as previously mentioned, for dinuclear complexes in which the metal-metal separation is large, the ferromagnetic term J_F is likely to be cancelled out by second-order antiferromagnetic contributions. With reference to Eq.

1.2, the antiferromagnetic term J_{AF} is now a direct measure of the exchange coupling constant $-2J$, thus allowing the resonance exchange energy H_{ab} to be estimated from Eq. 1.3 if the coupling constant and MMCT energy have been experimentally determined.

The fact that the predicted MMCT transition of an antiferromagnetically coupled dinuclear system has not been observed experimentally is believed to be due to the bridging ligand giving rise to an intense ligand to metal charge transfer (LMCT) transition in the visible region which overlaps and obscures the MMCT transition. If this is the case, the application of electroabsorption spectroscopy to MMCT transitions⁴⁰⁻⁴² as a means of deconvoluting LMCT and MMCT bands may be useful.

1.2.3 Bridging Ligand Mediated Electron Exchange: Superexchange

Electron exchange between two metals that is mediated by the bridging ligand is known as superexchange. The mechanism is analogous to the hole-transfer superexchange mechanism that accounts for electron transfer in mixed-valence complexes (refer to Section 1.4). In terms of electron exchange, understanding the nature of the bridging ligand and the manner in which it interacts with the magnetic orbitals of the metal ions is crucial to determining the magnitude of H_{ab} and hence J_{AF} . For the 1,4-dicyanamidobenzene dianion ligand bridged dinuclear pentaammineruthenium(III) complexes, $[Ru(III), Ru(III)]$,⁴³⁻⁴⁵ the metal-metal separation is too large for the Ru(III) ions to interact directly as shown in Scheme 1.1. The implication is that for metal-metal coupling to occur, the bridging ligand orbitals must be intimately involved. Scheme 1.2 demonstrates the involvement of LMCT excited states in the superexchange mechanism.

Scheme 1.2

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

In order for superexchange to be optimized, the magnetic orbitals of both metal ions must overlap simultaneously with a single bridging ligand molecular orbital. In the case of hole-transfer type superexchange, it is the highest occupied molecular orbital (HOMO) of the bridging ligand that is expected to serve as the dominant superexchange pathway. For effective overlap, the metal magnetic orbitals and the HOMO of the bridging ligand must be closely matched in terms of symmetry and energy. Also important in the optimization of metal-metal antiferromagnetic superexchange coupling is the requirement that the HOMO or superexchange pathway be continuous and span the entire bridging ligand. In this regard, the absolute planarity of the bridging ligand is a necessity. The interaction between metal and bridging ligand will produce a LMCT transition whose energy is a measure of the energy gap between metal magnetic orbitals and the HOMO superexchange pathway.⁴³ Furthermore, the oscillator strength of the LMCT band is a measure of the electronic interaction between the metal ion and the bridging ligand.^{46,47} The energy gap ΔE between the metal magnetic orbitals and the HOMO of the bridging ligand can be estimated by^{46,48}

$$\Delta E = E_{op} - \lambda \quad (1.4)$$

where E_{op} is the energy of the LMCT transition and λ is a correction term that compensates for the change in inner and outer coordination sphere configurations that result from a transition into an excited vibrational level of the excited state.

1.2.4 Experimental Evaluation of the Exchange Coupling Constant Based on Solid-State Measurements

For an antiferromagnetically coupled dinuclear complex in the solid-state, the molar magnetic susceptibility χ_m is determined by the thermal population distribution of singlet ground and triplet excited states using the modified Bleaney-Bowers expression:⁴⁹

$$\chi_m = C/(T - \theta) + (2N_A g_{av}^2 \beta^2 / 3kT) [1 + (1/3)\exp(-2J/kT)]^{-1} + \chi_p \quad (1.5)$$

where g_{av} is the powder average g value for the complex, $C/(T - \theta)$ is a Curie-Weiss term that corrects for any paramagnetic impurity at low temperatures, and χ_p is a correction term for any background paramagnetism (note that N_A is the Avogadro constant, β is the Bohr magneton and k is the Boltzmann constant).

Although for Ru(II), its orbital angular momentum may make a contribution to the measured molar susceptibility, a good estimate of the exchange coupling constant for Ru(III) dinuclear complexes can be obtained using the spin-only treatment of Eq. 1.5, if it is assumed that the $S = 1/2$ spins are isotropically coupled. The reader is referred to Section 1.3.1 for a more complete discussion of spin-only paramagnetic behaviour in transition metal complexes.

1.2.5 Experimental Evaluation of the Exchange Coupling Constant Based on Solution Measurements

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

Cotton *et al.* have shown that the singlet-triplet energy separation or $-2J$ (where $\mathcal{H} = -2J\mathbf{S}_a \cdot \mathbf{S}_b$) can be obtained from solution samples of both molybdenum⁵⁰ and chromium⁵¹ dimers by NMR spectroscopy. On the basis of a negligible pseudocontact contribution, the temperature dependence of the chemical shift of the nucleus in question can be used to calculate $-2J$ and the hyperfine coupling constant A_c (arising from contact contributions) from the expression for the paramagnetically induced isotropic shift:

$$\nu_{\text{obsd}} = \nu_{\text{diam}} + [2A_c g_{\text{av}} \beta \nu_0 / (\gamma_N / 2\pi) kT] [3 + e^{2J/kT}]^{-1} \quad (1.6)$$

where ν_{obsd} is frequency of the nuclei resonance of the complex being measured, ν_{diam} is the frequency the same nucleus would have in a diamagnetic environment, T is the absolute temperature, g_{av} is the rotationally averaged g value for the complex in solution, ν_0 is the probe frequency, γ_N is the nuclear magnetogyric ratio and the remaining terms have been previously defined. In all cases, the chemical shift of the nucleus in question experiences a downfield shift as the temperature increases. The reader is referred to Sections 1.3.3 and 1.3.4 for a complete discussion of paramagnetically induced isotropic shifts.

Another interesting treatment, developed by Thompson *et al.*,⁵² demonstrates that for a series of monohydroxo-bridged dinuclear copper(II) complexes in the solid-state, a calibration curve can be constructed that relates the effective room temperature magnetic moment μ_{eff} and the exchange coupling constant $-J$ (determined from fitting temperature dependent molar susceptibility data). It should be possible to construct a similar calibration

curve for any series of dinuclear complexes that relates $-J$ values determined in the solid state to room temperature values of μ_{eff} determined in solution. Such a treatment will at the very least provide an estimate of the exchange coupling constant in solution.

Owing to the sensitive nature of the interaction between the metal magnetic orbitals and the superexchange pathway (ie. the HOMO of the bridging ligand), metal-metal antiferromagnetic coupling can be selectively perturbed by both inner-sphere and outer-sphere manipulations. A notable example of the latter concerns the outer-sphere perturbation of the Ru(III)-cyanamide bond in a series of mononuclear pentaammineruthenium(III) complexes of anionic phenylcyanamide ligands.⁴⁷ In this study, the dependence of the LMCT energy and oscillator strength on the solvent's donor number was rationalized in terms of a donor-acceptor interaction (refer below to Scheme 1.3) involving the solvent's nonbonding electrons and the protons of the ammine ligands coordinated to Ru(III). The net effect of this interaction is the transfer of electron density from the partially deprotonated ammine to the Ru(III) ion, thereby destabilizing its $d\pi$ acceptor orbitals and leading to a weakening of the Ru(III)-cyanamide π bond. In essence, the outer-sphere perturbation caused the Ru(III) ion to become decoupled from the cyanamide (NCN) group of the phenylcyanamide ligand, thereby inducing fluxionality in the Ru(III)-cyanamide nitrile nitrogen bond.

Scheme 1.3

Extended to dinuclear pentaammineruthenium(III) complexes bridged by 1,4-dicyanamidobenzene dianion ligands, [Ru(III), Ru(III)], such an outer-sphere perturbation would be expected to have significant ramifications with regards to metal-metal antiferromagnetic coupling. Clearly, complex fluxionality would lead to a randomized geometry and hence a disruption of the rigid dimeric framework that is necessary for electron exchange. As a result, the experimental evaluation of solution antiferromagnetic coupling in the [Ru(III), Ru(III)] systems will necessitate that complications associated with complex fluxionality be dealt with.

1.3 Nuclear Magnetic Resonance of Paramagnetic Complexes in Solution

Prior to the discussion of the NMR behaviour of paramagnetic complexes (with emphasis on Ru(III) complexes) in solution, a brief account of paramagnetism under the spin-only approximation will be given.⁵³

1.3.1 Paramagnetism: Spin-Only Treatment

The paramagnetic contribution to the magnetic susceptibility comes from the spin and orbital angular momenta of the electrons that are interacting with the applied field. In a spin-only treatment, the contribution of orbital angular momentum is not considered.

The temperature dependence of the molar susceptibility χ_m (in $\text{cm}^3 \text{g}^{-1}$) of a paramagnetic species is given by the Curie law:

$$\chi_m = N_A g^2 \beta^2 / 4kT \quad (1.7)$$

where T is the absolute temperature (in Kelvin, K), g is the electron g -factor (g_e) and the remaining terms have been previously defined. Eq. 1.7 predicts a straight-line relation

between χ_m and $1/T$, giving a zero intercept. However, this type of behaviour is usually not observed experimentally. Straight-line plots are obtained for many systems, but the intercept is non-zero. To account for deviations from ideal Curie law behaviour, the Curie-Weiss law (Eq 1.8) is typically employed.

$$\chi_m = C/(T - \theta) \quad (1.8)$$

In Eq. 1.8, $C = N_A g^2 \beta^2 / 4k$ and θ (in K) corrects the temperature for the non-zero intercept.

For the case of molecules with no orbital angular momentum, the Curie law is commonly written as

$$\chi_m = N_A g^2 \beta^2 S(S + 1) / 3kT \quad (\text{in } \mu_B) \quad (1.9)$$

where S is the total spin quantum number of the system. Eq. 1.9 yields the spin-only molar susceptibilities of complexes containing different numbers of unpaired electrons. For $S = 1/2$, it reduces to Eq. 1.7.

The effective magnetic moment μ_{eff} is a microscopic quantity that is commonly used to describe the magnetic properties of transition metal complexes. By replacing $g^2[S(S + 1)]$ in Eq. 1.9 with μ_{eff}^2 and solving for μ_{eff} , one obtains

$$\mu_{\text{eff}} = (3k/N_A \beta^2)^{1/2} (\chi'_m T)^{1/2} = 2.828(\chi'_m T)^{1/2} \quad (\text{in } \mu_B) \quad (1.10)$$

where χ'_m is the true paramagnetic molar susceptibility that has been corrected for diamagnetic contributions (refer below).

It is important to realize that for transition metal complexes, it is only possible to measure (or observe) the net molar susceptibility $\chi_{m(\text{obsd})}$, which is the sum of the paramagnetic χ'_m and diamagnetic $\chi_{m(\text{diam})}$ contributions. χ'_m is then given by:

$$\chi'_m = \chi_{m(\text{obsd})} - \chi_{m(\text{diam})} \quad (1.11)$$

The molar diamagnetic susceptibility $\chi_{m(\text{diam})}$ of a complex ion can be approximated by summing the molar diamagnetic contributions (Pascal's constants) from all of the atoms, $\chi_{m(A)}$, and from all of the bonds in functional groups, $\chi_{m(B)}$.

$$\chi_{m(\text{diam})} = \sum_i \chi_{m(A)_i} + \sum_j \chi_{m(B)_j} \quad (1.12)$$

The spin-only magnetic moments of transition metal complexes can also be calculated for various values of S :

$$\mu_{\text{eff}} = g[S(S + 1)]^{1/2} \quad (\text{in } \mu_B) \quad (1.13)$$

where $g = 2.0023$ (≈ 2.0) for an electron with no orbital angular momentum.

In the spin-only approximation, the number of unpaired electrons n is related to S by

$$S = n/2 \quad (1.14)$$

Substituting Eq. 1.14 for S and 2.0 for g in Eq. 1.13 produces

$$\mu_{\text{eff}} = [n(n + 2)]^{1/2} \quad (\text{in } \mu_B) \quad (1.15)$$

Eq. 1.15 is very useful as it allows one to calculate the number of unpaired electrons in a transition metal system, if the effective moment has been previously evaluated experimentally.

For low spin Ru(III) complexes, experimental values of μ_{eff} range from 1.90 to 2.07 μ_{B} ,⁵⁴ suggesting that a close to spin only treatment is sufficient with only a small contribution from orbital angular momentum.

1.3.2 Experimental Determination of Magnetic Susceptibility

A common method used to determine the mass susceptibility of paramagnetic solutions at the microscale level is the NMR method originally developed by Evans⁵⁵ for use with conventional NMR spectrometers, and later modified by Phillips and Poe⁵⁶ to utilize with high-field NMR spectrometers that contain superconducting magnets. In the Evans method, a solution of the paramagnetic complex containing an internal reference (ie. TMS or DSS) is added to the outer of two coaxial NMR tubes. A solution of the same inert reference, dissolved in the same solvent containing the dissolved complex, is placed in the inner of the two coaxial tubes. Two separate resonance lines corresponding to the reference are observed, with the line from the paramagnetic solution lying at lower frequencies (ie. upfield from 0.00 ppm). The mass susceptibility χ_g (in $\text{cm}^3 \text{g}^{-1}$) of the dissolved complex is then given by

$$\chi_g = -3\Delta f/4\pi\nu m + [\chi_o + \chi_o(d_o - d_s)/m] \quad (1.16)$$

where Δf is the observed frequency shift (in Hz) of the reference resonance; ν is the fixed probe frequency (in Hz) of the NMR spectrometer; χ_o is the mass susceptibility (in $\text{cm}^3 \text{g}^{-1}$) of the solvent; m is the mass (in g) of the complex per cm^3 of solution; d_o and d_s are the densities (in g cm^{-3}) of the solvent and solution, respectively. It should be noted that the

negative sign in Eq. 1.16 is a convention that distinguishes between upfield and downfield shifts of the reference resonance obtained with high-field and conventional NMR spectrometers, respectively. The square-bracketed term in Eq. 1.16 represents a correction to the solvent mass susceptibility for any changes in solution density. At a fixed NMR probe temperature, the solution density d_s remains constant and can be approximated by $d_0 + m$, thus giving for the molar susceptibility χ_m (in $\text{cm}^3 \text{mol}^{-1}$):

$$\chi_m = \chi_g M = -3\Delta f M / 4\pi \nu m \quad (1.17)$$

where M is the molecular weight (in g mol^{-1}) of the complex. Once the molar susceptibility has been determined in this manner, the corrected molar susceptibility χ'_m , the effective magnetic moment μ_{eff} (in μ_B , Bohr magnetons) and the number of unpaired electrons n can be calculated using the previously outlined spin-only expressions (refer to Eq. 1.11, 1.10 and 1.15, respectively, in Section 1.3.1).

1.3.3 The Isotropic NMR Shift

Unpaired electrons reside in molecular orbitals (formed between metal ions and their surrounding ligands), and as such are delocalized over the entire molecule. An unpaired electron in one molecular orbital can also spin polarize an electron pair in a doubly occupied molecular orbital. At every point in the framework of the molecule, there are contributions from the direct delocalization (except at a node) and spin polarization mechanisms. Thus, a nucleus in a paramagnetic molecule, containing one or more unpaired electrons, may experience spin density at its point in space and/or feel spin density that is nearby. If molecular orbitals are referred to as being comprised of atomic orbitals, net spin density exists at the nucleus of the atom under investigation only through its atomic s orbitals. This is the case since only the wave functions for s orbitals have a finite value at the nucleus, whereas, a node exists at the nucleus in all other types of orbitals. It must be realized that

only a fractional amount of unpaired electron density resides in orbitals other than s in the atom of interest and on neighbouring atoms.

In a paramagnetic molecule, the interaction or coupling of magnetic nuclei with unpaired electrons gives rise to a chemical shift contribution in the NMR spectrum, the magnitude of which is proportional to the nature and extent of coupling. The magnitude of the shift may be anisotropic depending on the molecule's orientation with respect to the external magnetic field. In solution, rapid molecular rotation results in an average value of the shift anisotropy, consequently, giving rise to an isotropic shift. This isotropic shift can be determined experimentally by measuring the difference in shift of a given atom in a paramagnetic compound (observed) and that of the same atom in an analogous diamagnetic compound.

$$(\Delta\nu/\nu)_{\text{isotropic}} = (\Delta\nu/\nu)_{\text{observed}} - (\Delta\nu/\nu)_{\text{diamagnetic}} \quad (1.18)$$

The term $(\Delta\nu/\nu)$ represents the particular shift in ppm, where $\Delta\nu$ is the frequency difference between the resonance of interest and the frequency of an internal reference whereas ν is the absolute frequency of the NMR probe.

The interaction between magnetic nuclei and unpaired electrons to give molecular paramagnetism can be formally divided into two contributions:^{53,57} i) the through-bond contact coupling term, which arises from the presence of spin density at the resonating nucleus; and ii) the through-space pseudocontact coupling term, which arises from the presence of spin density in the rest of the molecule. Accordingly, the isotropic shift can be expressed as a sum of contact shift and pseudocontact shift contributions:

$$(\Delta\nu/\nu)_{\text{isotropic}} = (\Delta\nu/\nu)_{\text{contact}} - (\Delta\nu/\nu)_{\text{pseudocontact}} \quad (1.19)$$

1.3.3a The Contact Shift Term

As mentioned, a contact shift (or Fermi contact shift) results from the presence of spin density at the resonating nucleus, and as such, the magnitude of the shift is proportional to the amount of spin density at that nucleus. Furthermore, the shift is scalar in nature as it is independent of molecular rotation. The spin-only expression commonly used to obtain the contact shift term from the isotropic NMR shift is given by Eq. 1.20 in SI units.

$$(\Delta\nu/\nu)_c = (A_c)_i g_{av} \beta_S (S + 1) / g_N \beta_N 3kT \quad (1.20)$$

In this expression, A_c is the contact hyperfine coupling constant (in Joules, J), g_N is the nuclear g -factor, β_N is nuclear magneton and the remaining terms have been previously defined. By convention, a positive $(\Delta\nu/\nu)_c$ value and hence a downfield shift in the resonance of the nucleus in question favours a dominant direct delocalization mechanism, whereby unpaired spin density is transferred from the paramagnetic metal onto neighbouring ligands containing the resonating nucleus. Conversely, a negative $(\Delta\nu/\nu)_c$ value and hence an upfield shift in the resonance of the nucleus in question favours a dominant spin polarization mechanism, whereby spin density is induced in the resonating nucleus.

Simply stated, the contact hyperfine coupling constant A_c describes the coupling between an electron and a particular nucleus. $(A_c)_i$ is defined as:

$$(A_c)_i = (8\pi/6S) g_{av} \beta_S g_N \beta_N |\Psi^i(0)|^2 \quad (1.21)$$

where $|\Psi^i(0)|^2$ represents the square of a wavefunction for the i^{th} nucleus, evaluated at that nucleus (ie. zero distance from the nucleus). Therefore, $(A_c)_i$ expresses the probability of finding spin density at the particular nucleus. From quantum mechanics,⁵⁸ in order for

$(A_c)^i$ to be nonzero, net spin density must appear in an orbital with s character, since only for s -type orbitals is $|\Psi^i(0)|^2$ nonzero when evaluated at the nucleus. This raises an important question. If unpaired spin density originates in metal ion d orbitals, how can it show up in a ligand s orbital? The answer lies in the molecular orbital treatments of the direct delocalization and spin polarization contributions to the contact interaction. The reader is referred to Section 1.3.4 for further discussion.

Finally, with reference to Eq. 1.20, if the temperature dependence of the contact shift is evaluated, a plot of $\Delta\nu_c$ vs. $1/T$ should produce a straight line with a slope proportional to A_c for systems exhibiting Curie law behaviour. The departure from Curie behaviour in some systems indicates the oversimplification of Eq. 1.20, and the need to incorporate second-order contributions into the description. Importantly, Eq. 1.20 is valid in solution as long as one considers an average value of g for the paramagnetic compound.

1.3.3b The Pseudocontact Shift Term

The pseudocontact shift (or dipolar shift) is the result of a through-space non-exchange coupling interaction between the nuclear magnetic moment and the electron magnetic moments, that result from spin density at points all over the molecule (except that at the resonating nucleus). Therefore, the pseudocontact shift unlike the contact shift, is sensitive to the spin density cloud in the rest of the molecule as opposed to the spin density at the resonating nucleus. It is customary to further divide the pseudocontact interaction into metal-centered and ligand-centered terms. The former considers the unpaired electrons to be localized on the metal center while the latter considers the unpaired electron density to be delocalized on the ligand.

The complete evaluation of the pseudocontact shift requires that the spin density distribution over the entire molecule be known. Unfortunately, such information is usually not available. Based on the metal-centered term, where unpaired electrons are assumed to

be localized only on the metal ion, a point dipole model leads to an expression for evaluating the pseudocontact contribution to the isotropic shift. For an axially symmetric system, the spin-only expression for the pseudocontact shift term is given by:

$$(\Delta\nu/\nu)_{\text{pc}}^{\text{i}} = [\beta^2 S(S+1)/9kT][(1 - 3\cos^2\theta_i)/r_i^3][g_{\parallel}^2 - g_{\perp}^2] \quad (1.22)$$

where θ is the angle between the principal symmetry axis of the complex and the vector between the metal ion center and the nucleus whose NMR is being observed, r is the distance between the metal ion and the nucleus, $g_{\parallel}$ and $g_{\perp}$ represent the g anisotropy of the system in the direction parallel and perpendicular to, respectively, the principle symmetry axis of the complex, and the remaining terms have been previously defined. Figure 1.2 defines the factors in the pseudocontact shift equation for an axially symmetric molecule.

Figure 1.2 Definition of the factors in Eq. 1.22 for an axially symmetric paramagnetic molecule, using metal centered Cartesian coordinates. M represents the metal and N represents a remote nucleus.

In Eq. 1.22, the $(1 - 3\cos^2\theta)/r^3$ term is referred to as the geometric factor. When $\theta = 54.7^\circ$, $(1 - 3\cos^2\theta) = 0$ and nuclei lying anywhere on the spatial cones described by this angle experience no pseudocontact shift (refer to Figure 1.3).

Figure 1.3 Spatial cones (described by $\theta = 54.7^\circ$) for an axially symmetric molecule in which the molecule-centered z axis is the principal axis.

Furthermore, pseudocontact shifts are of opposite signs for identical nuclei lying on opposite sides of the cone. For example, if a proton lying outside the cone experiences a downfield pseudocontact shift (positive $(\Delta\nu/\nu)_{pc}$), a proton lying inside the cone experiences an upfield shift (negative $(\Delta\nu/\nu)_{pc}$), and vice versa. The relative directions of these shifts will obviously depend upon the sign of the g anisotropy term, represented by $(g_{||}^2 - g_{\perp}^2)$ in Eq. 1.22.

The form of Eq. 1.22 suggests that the magnitude of a pseudocontact shift depends upon the magnitudes of the geometric factor, the g anisotropy term and the distance of the nucleus in question from the metal (expressed as $1/r^3$). On this basis, the largest pseudocontact shifts should occur for those nuclei that have the largest geometric factor, that are closest to the metal, and that have the largest g anisotropy.

Finally, similar to the contact shift, Eq. 1.22 predicts that the pseudocontact shift will be dependent on temperature. Therefore, a plot of $\Delta\nu_{pc}$ vs. $1/T$ should be linear for systems exhibiting Curie law behaviour. Again, the departure from Curie behaviour in some systems indicates the oversimplification of Eq. 1.22, and the need to incorporate second-order contributions into the description. Importantly, Eq. 1.22 is only valid when the

nucleus in question feels the unpaired electron density as a point dipole (ie. when delocalization can be neglected and the nucleus is relatively far from the metal).⁵⁹ Any significant delocalization of electron density, at least within the inner coordination sphere, may prevent the quantitative use of Eq. 1.22 for donor atom nuclei or for nuclei close to other donor atoms.⁶⁰

1.3.4 The Contact Interaction and Spin Density

If the contact contribution dominates the isotropic shift or if the pseudocontact shift has been factored out,^{61,62} a measure of the contact hyperfine coupling constant A_c is available. Recall that the contact contribution as measured by A_c is related to the actual spin density on the resonating nucleus (evaluated by calculating $|\Psi(0)|^2$ at that nucleus) through Eq. 1.21. As previously mentioned, the presence of spin density at the resonating nucleus arises from the direct delocalization and spin polarization mechanisms, contributions from which can be calculated through a molecular orbital treatment. The direct delocalization contribution A_d (in MHz, after dividing by the Planck constant h) can be obtained by:⁶³

$$A_d/h = K\rho/2S \quad (1.23)$$

where K is the isotropic hyperfine coupling due to a full electron on an atom⁶⁴ and $\rho/2S$ is the spin density at the nucleus in question (normalized to one electron). If the nucleus in question is hydrogen ($K = 1420$ MHz) and the paramagnetic system contains one unpaired electron ($S = 1/2$), ρ can be expressed as

$$\rho = (1/1420)A_d/h \quad (1.24)$$

The early work of Drago *et al.*,⁶⁵ in which the direct delocalization contribution on hydrogen nuclei was evaluated through extended Hückel calculations, showed that

unpaired spin density originating on the metal delocalizes onto neighbouring ligands through the highest occupied molecular orbital. In simple terms, for paramagnetic transition metal complexes, unpaired spin density originating in metal orbitals can be transferred onto the ligand by both σ and π bonding interactions (either empty or full π ligand molecular orbitals can be involved in the latter). In all cases, it is the HOMO (of metal character) that serves as the pathway for spin density transfer. Of course, a bonding interaction will be precluded when metal orbitals and ligand molecular orbitals do not have the correct symmetry to overlap effectively. Under these circumstances, the spin polarization mechanism can induce spin density on the ligand.

1.3.5 Experimental Evaluation of the Contact Hyperfine Coupling Constant

For a paramagnetic transition metal complex, the extent of the contact interaction can be determined through an experimental evaluation of the contact hyperfine coupling constant A_c . Only for systems where the contact term dominates the isotropic shift or the pseudocontact shift has been factored out, will A_c be a good measure of the contact interaction.

As mentioned in Section 1.3.3a, determining the temperature dependence of the contact shift is one experimental strategy that can be used to evaluate A_c . A plot of $\Delta\nu_c$ vs. $1/T$ should be linear, with the slope being proportional to A_c for systems exhibiting Curie law behaviour. However, what about systems that for whatever reason do not follow Curie law behaviour?

Another experimental strategy involves evaluating the direct dependence of the contact shift $\Delta\nu_c$ on the molar susceptibility χ_m of the transition metal complex under the conditions of constant temperature and constant concentration. Using the solution NMR Evans method, the molar susceptibility, expressed as Δf (refer to Section 1.3.2), of the system can be

determined. As the paramagnetism of the system increases, the trends in $\Delta\nu_c$ and $|\Delta f|$ are expected to parallel each other. A spin-only derivation follows, the final result of which shows the relationship between $\Delta\nu_c$, Δf and A_c .

Begin by equating Eq. 1.10 to Eq. 1.13 and recognizing that $\chi'_m = \chi_m - \chi_{m(\text{diam})}$ (from Eq. 1.11). Then solving for $S(S + 1)$ gives

$$S(S + 1) = [8T/g^2][\chi_m - \chi_{m(\text{diam})}] \quad (1.25)$$

Substituting Eq. 1.25 for $S(S + 1)$ into Eq. 1.20 produces

$$(\Delta\nu)_c/\nu = [8A_c\beta/3gg_N\beta_Nk][\chi_m - \chi_{m(\text{diam})}] \quad (1.26)$$

Substituting Eq. 1.17 for χ_m into Eq. 1.26 yields the final result in SI units:

$$(\Delta\nu)_c = -A_cZ [(3M/4\pi m)\Delta f + \nu\chi_{m(\text{diam})}] \quad (\text{in Hz}) \quad (1.27)$$

where the prefactor Z has the form:

$$Z = 1 \times 10^7 [8\beta/3gg_N\beta_Nk] \quad (\text{in mol cm}^{-3} \text{ J}^{-1}) \quad (1.28)$$

A linear plot of $\Delta\nu_c$ vs. $-\Delta f$ yields a slope and y-intercept from which A_c and $\chi_{m(\text{diam})}$ can be evaluated:

$$A_c = [\text{slope}/Z][4\pi m/3M] \quad (\text{in J}) \quad (1.29)$$

$$\chi_{m(\text{diam})} = \text{y-intercept}/\nu A_c Z \quad (\text{in cm}^3\text{mol}^{-1}) \quad (1.30)$$

where A_c should be divided by the Planck constant h (A_c/h expressed in MHz) when the value of g_{av} for the system is unknown and therefore approximated by g_e .⁶⁶

Eq. 1.27 predicts that an increase in the paramagnetism of the system will be characterized by an increasingly larger downfield contact shift (positive $\Delta\nu_c$) of the nucleus in question as $|\Delta f|$ for the system increases. Such behaviour is consistent with the direct delocalization contribution to the contact interaction being dominant over the spin polarization contribution. Therefore, A_d rather than A_c can be evaluated from Eq. 1.29.

1.4 Intervalence Charge Transfer in Mixed-Valence Complexes

For a mixed-valence system consisting of two metal ions M_A and M_B^+ linked together by a bridging ligand L,

intervalence charge transfer between the metal centers is said to proceed via either an electron transfer superexchange mechanism or a hole-transfer superexchange mechanism, with the dominance of one over the other being determined by the nature of the bridging system. An examination of the dependence of metal-metal coupling on the nature of the bridging ligand, in strongly coupled mixed-valence [Ru(III), Ru(II)] complexes,^{9,67} illustrates this point. For example, when π accepting nitrogen donor atom heterocyclic ligands serve as the bridging medium, electron transfer superexchange via the π^* -LUMO of the bridge, is the dominant mechanism for metal-metal coupling. However, when π donating conjugated anion ligands serve as the bridge, hole transfer superexchange via the

π -HOMO of the bridge is dominant. The differences can be understood by recognizing that in order for metal-metal coupling to be significant in either system, the π symmetry molecular orbitals of the bridging ligand must be energy matched and capable of interacting simultaneously with the π donor orbitals of Ru(II) and the π acceptor orbitals of Ru(III). For the π acceptor bridged [Ru(III), Ru(II)] complex, the requirement is met by the π^* -LUMO of the bridge. For the corresponding π donor bridged system, it is the π -HOMO of the bridge that meets the requirement.

Mixed-valence complexes are typically classified into three main categories:⁶⁸ (i) Class I: a completely valence trapped system with no coupling between metal ions, (ii) Class II: a valence trapped system with weak coupling between metal ions, and (iii) Class III: the valency of the system is completely delocalized due to strong coupling between metal ions.

The most significant theoretical contribution to the study of intervalence charge transfer in mixed-valence complexes is arguably that provided by the Hush Model.⁶⁹ Importantly, the treatment allows one to evaluate the spectral properties of an intervalence transition and then use this information to assess the extent of metal-metal electronic coupling in the mixed-valence system. By relating the energy of the intervalence transition to the inner-sphere and outer-sphere reorganizational energies of the system (refer to Section 1.4.4), the Hush model has provided the necessary link between the properties of mixed-valence complexes in solution and the Marcus theory of intermolecular electron transfer.⁷⁰ The following section summarizes some of the important concepts developed by Hush, with emphasis being placed on the properties of symmetric mixed-valence systems.

1.4.1 The Hush Model

For a symmetric mixed-valence complex, the simplest case for electron transfer is illustrated by the potential energy configuration diagram shown in Figure 1.4. In this representation, the electron is coupled between donor and acceptor by a single oscillator

that has the same frequency in both the initial (left-hand curve) and final (right-hand curve) states.

Figure 1.4 Potential energy-configuration diagram representing initial and final states for a symmetric mixed-valence complex.

E_{op} is the optical energy required to photoexcite an electron between initial and final states at the same nuclear configuration, or in other words, the intervalence transition (IT) energy. E_{th} represents the activation barrier to thermal electron transfer, whose pathway arises when initial and final states are vibronically coupled. In the absence of any interaction between donor and acceptor metal ions (there is no splitting at the intersection of the potential energy curves), the resonance exchange integral H_{ad} , which is a measure of the degree of electronic coupling between donor and acceptor, is zero ($H_{ad} = 0$). Such behaviour is representative of a Class I mixed-valence system.

When an interaction between donor and acceptor does occur, initial and final states mix causing a distortion in the potential energy curves (splitting at the intersection point), as shown in Figure 1.5. The thermal activation barrier E_{th} decreases as H_{ad} increases with the onset of donor-acceptor coupling.

Figure 1.5 Potential energy-configuration diagram showing the distortion of potential energy curves that results when initial and final states are mixed.

For weakly coupled symmetric Class II mixed-valence complexes, in which the distortion represented by $2H_{ad}$ in Figure 1.5 is small, Hush derived the following relationships for the intervalence band properties:

$$E_{op} = 4E_{th} \quad (1.31)$$

and for the band width at half peak height $\Delta\nu_{1/2}$ (in cm^{-1}),

$$\Delta\nu_{1/2} = (2310E_{op})^{1/2} \quad (1.32)$$

where it is assumed that the IT band is Gaussian shaped.

Hush further showed that, for weakly coupled systems, the intensity $\epsilon_{\max}$ (in $\text{M}^{-1}\text{cm}^{-1}$) of the intervalence transition was related to the extent of coupling H_{ad} (in cm^{-1}) between donor and acceptor:

$$H_{ad} = (2.06 \times 10^{-2}/R) \cdot (E_{op}\epsilon_{\max}\Delta\nu_{1/2})^{1/2} \quad (1.33)$$

where R is the transition dipole moment length (in cm), representing the charge transfer distance. Importantly, the Hush model allows one to estimate the amount of metal-metal coupling given that an intervalence band is experimentally observable and R can be estimated (typically by the metal-metal separation from crystal structure data). However, it should be noted that recent application of electroabsorption spectroscopy to mixed-valence complexes has demonstrated that the actual charge transfer distance is significantly smaller than the metal-metal separation.^{40,41}

For strongly coupled symmetric Class III mixed-valence complexes, a perturbation treatment is no longer valid, as the interaction between donor and acceptor is so great that bonding and antibonding potential energy curves result, as shown in Figure 1.6.

Figure 1.6 Potential energy-configuration diagram for a symmetric Class III mixed-valence complex.

The magnitude of H_{ad} has become so large that the thermal activation barrier $E_{th} = 0$. The system is characterized by a completely delocalized valency, as the odd electron shuttles

freely between metal centers. The extent of metal-metal electronic coupling can be obtained directly from the energy of the intervalence transition:

$$H_{ad} = E_{op}/2 \quad (1.34)$$

1.4.2 The Comproportionation Equilibrium

The comproportionation constant K_C is a measure of mixed-valence complex stability in solution. Importantly, its evaluation provides another means of experimentally assessing the degree of metal-metal coupling in mixed-valence systems.^{67,71} For Class I and Class II complexes, K_C is determined by the equilibrium shown in Scheme 1.4:

Scheme 1.4

and for Class III complexes, by the equilibrium shown in Scheme 1.5,

Scheme 1.5

Experimentally, K_C can be determined from the difference in potential ΔE (in mV) between metal-centered reduction couples, by the Nernst expression shown in Eq. 1.35.

$$K_C = \exp(\Delta E/25.69) \quad (1.35)$$

For Class I and Class II mixed-valence complexes, in which metal-metal coupling is weak or non-existent, K_C is small (typically $< 10^3$). In these cases, the free energy of comproportionation ΔG_C is comprised of four contributions:

$$\Delta G_C = \Delta G_r + \Delta G_e + \Delta G_s + \Delta G_i \quad (1.36)$$

where ΔG_r is the free energy of resonance exchange that represents the stabilization of the mixed-valence complex due to delocalization, ΔG_e is an electrostatic factor that takes into account the repulsion of like charged metal ions, ΔG_s is an entropic factor ($1/2RT \ln 1/4$) that reflects a statistical distribution of the K_C equilibrium shown in Scheme 1.4, and ΔG_i is an inductive or synergistic factor representing the stabilization of one metal oxidation state by the other. For Class I complexes, the only significant contribution to ΔG_C comes from ΔG_s and ΔG_e . For Class II complexes, all four terms contribute to ΔG_C , with ΔG_i being the most significant while ΔG_r is relatively minor.⁷² For symmetric Class II mixed-valence complexes, the free energy of resonance exchange is given by

$$\Delta G_r = (H_{ad})^2/E_{op} \quad (1.37)$$

For Class III complexes, in which metal-metal coupling is strong, K_C is very large (typically $> 10^6$). This reflects the strong bonding interaction between donor and acceptor, that leads to the delocalization of valency. The greatest contribution to ΔG_C comes from ΔG_r , where $\Delta H_r = H_{ad}$.

1.4.3 Criteria for Class II and Class III Mixed-Valence Complexes

Distinguishing between valence trapped Class II and delocalized Class III mixed-valence complexes presents itself as a difficult task. For example, the Creutz-Taube ion ($[\mu\text{-(pyz)}\text{-}\{\text{Ru}(\text{NH}_3)_5\}_2]^{5+}$) has been the subject of extensive physical characterization studies, and it

is only recently that a consensus has been reached in favour of a Class III electronic description.^{40,41,73} The reader is referred to a recent review by Crutchley,⁹ in which an exhaustive set of diruthenium mixed-valence complexes (both symmetric and asymmetric) have been categorized under Class II and Class III headings. The following summarizes the criteria that were used for the symmetric systems.

Class III

For a symmetric mixed-valence complexes to conform to a Class III description, its experimentally determined comproportionation constant K_C should be very large (typically $>10^6$). However, it is important to recognize that for complexes in which the metal-metal separation is small, factors other than those associated with metal-metal coupling can make significant contributions to K_C . The other major criterion for a Class III designation requires that the spectral properties of the experimentally observed intervalence transition do not conform to Hush theory. This includes that the band width at half height $\Delta\nu_{1/2}$ predicted by Hush theory (from Eq. 1.32 in Section 1.4.1) be significantly larger than that observed experimentally; the extinction coefficient $\epsilon_{\max}$ is large (typically $>10^3 \text{ M}^{-1} \text{ cm}^{-1}$); and the IT energy is solvent independent.

Class II

For a symmetric mixed-valence complexes to conform to a Class II description, its experimentally determined comproportionation constant K_C should be small (typically $<10^3$). Secondly, the spectral properties of the experimentally observed intervalence transition must conform to Hush theory including that $\Delta\nu_{1/2}$ is approximately equal to the value predicted by Hush theory (from Eq. 1.32 in Section 1.4.1); $\epsilon_{\max}$ is small; and the IT energy is solvent dependent.

As a general rule, when the experimentally determined value of $\Delta v_{1/2}$ is significantly less than the theoretical value and K_c is large, Class III behaviour is approached and a system can be designated as borderline Class II/Class III.

1.4.4 Solvent Effects in Class II Mixed-Valence Complexes

From Hush theory,⁶⁹ E_{op} for a weakly coupled symmetric mixed-valence system can be approximated by

$$E_{op} = \chi_i + \chi_o + \Delta E' \quad (1.38)$$

where χ_i is the inner-sphere reorganizational energy, χ_o is the outer-sphere reorganizational energy and $\Delta E'$ takes into account any additional energy associated with excitation to either a spin-orbit or a ligand field excited state. If χ_i and $\Delta E'$ are assumed to be solvent independent for a given Class II system, then variations in E_{op} with solvent should be linearly proportional to the solvent term $(1/D_{op} - 1/D_s)$ found in the Marcus-Hush expression for χ_o :

$$\chi_o = e^2(1/r - 1/d)(1/D_{op} - 1/D_s) \quad (1.39)$$

where r is the molecular trapping site radius, d is the distance between metal centers, and D_{op} and D_s are the optical and static dielectric constants of the solvents. The linear correlation between E_{op} and $(1/D_{op} - 1/D_s)$ has been demonstrated by a number of weakly coupled symmetric Class II mixed-valence complexes,⁷⁴ thereby giving support to the Hush model. However, for asymmetric complexes of the type, $[(bpy)_2RuCl(\mu-pyz)Ru(NH_3)_4L]^{4+}$, a solvent donor number (DN) dependent contribution to the Frank-Condon barrier of approximately 0.006 eV/DN overwhelms the $(1/D_{op} - 1/D_s)$ solvent term observed in symmetric systems.⁷⁵ Based on a study by Curtis *et al.*,⁷⁶ of

solvatochromism in the charge transfer transitions of mononuclear Ru(II) and Ru(III) ammine complexes, the origin of this solvent effect has been ascribed to a donor-acceptor (hydrogen bonding type) interaction involving the solvent's non bonding electrons and the protons of the ammine (NH_3) ligands coordinated to Ru(III) (refer to Scheme 1.3 in Section 1.2.5). The strength of this interaction depends on the acidity of the ammine protons, which is greater for an ammine bound to Ru(III) compared to Ru(II). The net effect of this interaction is the transfer of electron density from the partially deprotonated ammine to the Ru(III) ion.

In mixed-valence dinuclear ruthenium complexes, this preferential solvation or valence trapping of the Ru(III) coordination sphere as opposed to that of Ru(II) stabilizes the oxidation state of the former, thereby creating an energy barrier to the delocalization of the odd electron which leads to a decrease in the magnitude of metal-metal coupling. Preferential solvation leading to a reduction in metal-metal coupling has also been demonstrated for some symmetric ruthenium ammine mixed-valence complexes.⁷⁷ In addition, the interaction of these systems with crown ethers was shown to have a similar effect.¹⁵ It should be noted that in the above mentioned diruthenium complexes, the ruthenium ions are bridged by π acceptor ligands, thus the dominant pathway for superexchange metal-metal coupling is expected to involve the LUMO of the bridging ligand.

1.5 Research Objectives

The focus of this research work centers around the selective perturbation of metal-metal superexchange coupling, by both inner-sphere and outer-sphere manipulations, in diruthenium pentaammine systems bridged by 1,4-dicyanamidobenzene dianion ligands. Intimately linked to these studies, is the need for a fundamental understanding of the

electronic nature of the ruthenium-cyanamide bonding interaction found in mononuclear systems. To this effect, five main research objectives can be stated:

1. To synthesize and characterize a series of mononuclear pentaammineruthenium(III) complexes of 1,4-dicyanamidobenzene monoanion and dianion ligands; then examine by spectroscopic and electrochemical methods, the inner-sphere perturbations of the Ru(III)-cyanamide π bond that result from both deprotonation and varying the π donor strength of the coordinated cyanamide ligand.

2. To synthesize and characterize a mononuclear pentaammineruthenium(IV) complex of a 1,4-dicyanamidobenzene dianion ligand; then examine by spectroscopic, electrochemical and magnetic methods, the inner-sphere perturbation of the ruthenium-cyanamide π bond that results from oxidation of Ru(III) to Ru(IV).

3. For a series of dinuclear pentaammineruthenium(III) complexes of 1,4-dicyanamidobenzene dianion ligands, $[\text{Ru(III)}, \text{Ru(III)}]$: examine by spectroscopic, electrochemical and magnetic methods, both an outer-sphere and inner-sphere perturbation of the Ru(III) -cyanamide π bond and hence metal-metal antiferromagnetic superexchange coupling that result from, respectively, a donor-acceptor interaction between solvent nonbonding electrons and the protons of the ammine ligands coordinated to Ru(III) and a variation in the π donor strength of the bridging cyanamide ligand (in solution and in the solid-state).

4. To generate, by spectroelectrochemical methods, the mixed-valence $[\text{Ru(III)}, \text{Ru(II)}]$ complexes of 1,4-dicyanamidobenzene dianion ligands; then examine by spectroscopic and electrochemical methods, both the outer-sphere (varying solvent) and inner-sphere (varying the π donor strength of the bridging cyanamide ligand in a given solvent) perturbations of the Ru(III) -cyanamide π bond and hence metal-metal hole-transfer superexchange coupling.

5. To synthesize and characterize a mixed-valence [Ru(IV), Ru(III)] complex of a 1,4-dicyanamidobenzene dianion ligand; then examine by spectroscopic and magnetic methods, the nature of the metal-metal interaction.

1.6 Design Criteria for Superexchange and its Perturbation in the Dinuclear Systems

Pertaining to the dinuclear systems, the fulfilment of the outlined research objectives (refer to Section 1.5) requires that they possess certain unique properties. The following discussion summarizes these necessary design parameters for the three main 1,4-dicyanamidobenzene dianion ligand bridged diruthenium pentaammine systems, that includes the [Ru(III), Ru(III)], the [Ru(III), Ru(II)] and the [Ru(IV), Ru(III)] complexes.

Nature of the 1,4-Dicyanamidobenzene Dianion Bridging Ligand

The 1,4-dicyanamidobenzene dianion ligand can be classified as a conjugated anion π donor bridging ligand. Therefore, its π symmetry HOMO is expected to serve as the dominant pathway for metal-metal antiferromagnetic superexchange coupling in the [Ru(III), Ru(III)] and [Ru(IV), Ru(III)] systems, and the dominant pathway for metal-metal hole-transfer superexchange coupling in the [Ru(III), Ru(II)] systems. In general, for metal-metal superexchange coupling to be significant in the above mentioned systems, in which the metal-metal separations are $>10 \text{ \AA}$, the HOMO of the 1,4-dicyanamidobenzene dianion bridging ligand must be symmetry and energy matched as closely as possible with the $d\pi$ orbitals of the ruthenium ions involved. In particular, with the $d\pi$ acceptor orbitals of Ru(III). Furthermore, the HOMO must be continuous in nature (spanning the entire bridging ligand), such that it can interact simultaneously with both metal ions. Therefore, to meet the energy requirements, the bridging ligand must possess suitable redox properties rendering it readily oxidizable when coordinated to a pentaammineruthenium(III) metal center. Concerns regarding symmetry and continuity, can be addressed by ensuring that

the bridging ligand is planar or close to it. However, it is important to recognize that a planar bridging ligand that leads to a rigid dimeric framework in the solid-state, and in doing so optimizes the effective overlap between the HOMO and the metal orbitals, may not maintain complex rigidity in solution. Consequently, metal-metal coupling may be reduced.

Another important property of the 1,4-dicyanamidobenzene dianion bridging ligand concerns its π donor strength. The incorporation of electron withdrawing and electron donating substituents into the phenyl ring system of the bridging ligand alters or varies its π donor strength. In effect, it is the energy of the HOMO that is being varied. Importantly, any variance in the HOMO energy is expected to significantly perturb its interaction with the Ru(III) $d\pi$ acceptor orbitals, and hence effect metal-metal coupling.

Nature of the Ruthenium Ion

An important property, intrinsic to the nature of the metal center, concerns the relative energies of its $d\pi$ orbitals that are available for bonding. As mentioned, the optimization of overlap between the HOMO of the bridging ligand and the $d\pi$ orbitals of the ruthenium ions involved, requires that their energies be closely matched. The implication is, of course, just as the bridging ligand must possess suitable redox properties, so too must the ruthenium ion. Disregarding outer-sphere contributions, the redox potential of a metal center, is to a large extent, dictated by the nature of the ligands which make up its inner coordination sphere. For the diruthenium pentaammine systems of this thesis, the inner coordination sphere presence of ammine ligands helps to achieve the desired $d\pi$ orbital energies for the ruthenium ions involved.

The actual oxidation state of the metal ion also dictates the redox potential of the metal center and hence the energies of its $d\pi$ orbitals that are available for bonding. For example, oxidation of Ru(III) to Ru(IV) stabilizes the metal $d\pi$ orbitals. Therefore, for the [Ru(IV),

Ru(III)] system compared to the [Ru(III), Ru(III)] system, the energy match between the Ru(IV) $d\pi$ acceptor orbitals and the HOMO of the bridging ligand is expected to be more ideal than the corresponding interaction involving the $d\pi$ acceptor orbitals of Ru(III). Consequently, metal-metal antiferromagnetic superexchange coupling should be enhanced in the former system.

For both the [Ru(III), Ru(III)] and [Ru(III), Ru(II)] systems, the presence of ammine ligands in the inner coordination sphere of Ru(III) is important for another reason. That is, the ammine ligands facilitate an outer-sphere donor-acceptor interaction involving their protons and the solvent's nonbonding electrons. In effect, the preferential solvation of the Ru(III) coordination sphere induces a variation in the energy of its $d\pi$ acceptor orbitals, depending on solvent's donor number. Importantly, any variance in the energy of the Ru(III) $d\pi$ acceptor orbitals is expected to significantly perturb their interaction with the HOMO of the bridging ligand, and hence effect metal-metal coupling. If the outer-sphere perturbation can sufficiently weaken metal-metal coupling, the Ru(III)-cyanamide bond could become fluxional with the rigid complex geometry characteristic of the solid state being replaced by a randomized one.

Nature of the Complex

With regards to necessary properties that must be imparted on the complexes, symmetry is important. In particular, for the mixed-valence [Ru(III), Ru(II)] and [Ru(IV), Ru(III)] systems, complex symmetry simplifies the thermodynamics of electron transfer and hence the analysis of metal-metal electronic coupling.

Complex stability, to ensure ease of preparation and integrity under physical measurement, represents another crucial property. The dinuclear complexes must be relatively inert to ligand substitution, particularly in highly donating solvents. Furthermore, in both solution

and in the solid-state, the complexes should not be susceptible to thermal, photochemical or oxidative decomposition processes.

CHAPTER 2

Experimental

2.1 Starting Materials

2.1.1 Reagents for Ligand Synthesis

Potassium carbonate (reagent grade, anhydrous, Anachemia), magnesium sulfate (reagent grade, anhydrous, Caledon Labs), ammonium thiocyanate (reagent grade, 97.5+%, Aldrich Chemical Co.), benzoyl chloride (reagent grade, 99%, Aldrich Chemical Co.), lead acetate trihydrate (reagent grade, 99+%, Aldrich Chemical Co.), 2-methoxy-1,4-phenylenediamine sulfate hydrate (reagent grade, 95%, Aldrich Chemical Co.), 2,5-diaminotoluene sulfate (reagent grade, 97%, Aldrich Chemical Co.), sodium hydroxide (reagent grade, 97.0%, Anachemia) and glacial acetic acid (reagent grade, 99.7%, Anachemia) were used without further purification.

2-Methyl-1,4-phenylenediamine

2,5-diaminotoluene sulfate (30.01 g, 0.136 mol) was dissolved in basic solution (69.1 g, 0.5 mol potassium carbonate in 500 mL of water). This solution was extracted with 4x250 mL aliquots of chloroform in a 1000 mL separatory funnel. The four organic layers were combined and roto-evaporated to dryness to give a beige precipitate of 2-methyl-1,4-phenylenediamine which was air dried overnight. Yield: 11.49 g (69%).

2-Methoxy-1,4-phenylenediamine:

This was prepared in a similar manner to 2-methyl-1,4-phenylenediamine except that (30.00 g, 0.127 mol) of 2-methoxy-1,4-phenylenediamine sulfate hydrate was used instead of 2,5-diaminotoluene sulfate. Yield: 12.46 g (71%).

2.1.2 Reagents for Metal Complex Synthesis

Ruthenium(III) chloride hydrate (reagent grade, Aldrich Chemical Co.), hydrazine monohydrate (reagent grade, 98%, Aldrich Chemical Co.), ammonium hexafluorophosphate (reagent grade, 99.99%, Aldrich Chemical Co.), tetrabutylammonium bromide (reagent grade, 99%, Aldrich Chemical Co.), tetraethylammonium chloride hydrate (reagent grade, Aldrich Chemical Co.), tetraphenylboron sodium (reagent grade, 99.5+%, Aldrich Chemical Co.), hydrochloric acid (reagent grade, 36.5-38.0%, Anachemia), sulfuric acid (reagent grade, 95-98%, Anachemia), perchloric acid (reagent grade, 70.0-72.0%, Allied Chemical), nitrosonium tetrafluoroborate (reagent grade, Aldrich Chemical Co.) and ammonium cerium(IV) sulfate (anhydrous, Fisher Scientific Chemical Co.) were used as received. Zinc/mercury amalgam was prepared by first cleaning mossy zinc metal (reagent grade, 99.8%, Anachemia) with 1 M HCl and then treating with a saturated solution of mercury(II) chloride (reagent grade, 99%, Aldrich Chemical Co.).

Chloropentaammineruthenium(III) chloride:

This was prepared by a method similar to that of Curtis *et al.*⁷⁵ 10.00 g (0.048 mol) of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ was slowly added to a solution of 82 mL (1.7 mol) of 98% hydrazine in 100 mL of water and then stirred for 16 hours. The resulting burgundy solution was placed on ice and 250 mL of concentrated HCl was added very slowly to it (Caution: This reaction is extremely exothermic). The solution was refluxed for 2 hours and then placed in the

refrigerator for 1-2 hours to afford precipitation. The yellow-orange crude product was filtered and then recrystallized from 0.1 M HCl. The orange cubic crystals of $[\text{Ru}(\text{NH}_3)_5\text{Cl}][\text{Cl}]_2$ which formed were filtered, washed with 0.1 M HCl and diethyl ether and then air dried overnight. Yield: 8.80 g (62%).

Aquopentaammineruthenium(II) hexafluorophosphate:

This was prepared, under argon, in a similar manner to that of Meyer *et al.*⁷⁸ 1.50 g (5.1 mmol) of $[\text{Ru}(\text{NH}_3)_5\text{Cl}][\text{Cl}]_2$ was dissolved with stirring in 150 mL of 0.1 M H_2SO_4 . The solution was gravity filtered and placed into a 250 mL round bottom flask. 30.0 g of freshly prepared Zn/Hg amalgam was placed in a separate 250 mL round bottom flask and both flasks were degassed on a vacuum line. The flask containing the Zn/Hg amalgam was placed in an ice bath and the $[\text{Ru}(\text{NH}_3)_5\text{Cl}][\text{Cl}]_2$ solution transferred to it. This solution was allowed to react for 30 minutes with intermittent venting to remove any evolved H_2 gas. 12.0 g (0.07 mol) of NH_4PF_6 dissolved in 40 mL of distilled water and gravity filtered, had been previously placed into a 250 mL round bottom flask and degassed. The reduced ruthenium solution was transferred to this flask and immediate precipitation of $[\text{Ru}(\text{NH}_3)_5(\text{OH}_2)][\text{PF}_6]_2$ was afforded. The pale yellow product was filtered, washed with 20 mL of degassed cold water and 30 mL of degassed cold diethyl ether and then vacuum dried overnight. Yield: 2.25 g (89%). Note that when the product is stored under argon in the freezer at -18°C , it can be used for up to 2 months.

2.1.3 Solvents

Acetonitrile (anhydrous, 99+%, Aldrich Chemical Co.; HPLC grade, 99.7%, Caledon Labs), nitromethane (99+%, Aldrich Chemical Co.), dimethyl sulfoxide (anhydrous, 99+%, Aldrich Chemical Co.), diethyl ether (anhydrous, 99.0%, Caledon Labs), 1-methyl-2-pyrrolidinone (HPLC grade, 99+%, Aldrich Chemical Co.), chloroform (reagent

grade, 99.8%, Aldrich Chemical Co.), methanol (absolute, Anachemia) and ethanol (absolute, Consolidated Alcohols Ltd.) were used without further purification. Acetone (spectro grade, 99.5%, Caledon Labs) was used as received or dried over 3Å molecular sieves (note that acetone dried in this manner was used within a period of 1 week).

2.1.4 Deuterated Solvents and NMR References

Nitromethane-d₃ (99 atom % D, 1% v/v TMS, Aldrich Chemical Co.), acetonitrile-d₃ (99.5 atom % D, 1% v/v TMS, Aldrich Chemical Co.), acetone-d₆ (99.5 atom % D, 1% v/v TMS, Aldrich Chemical Co.), dimethyl sulfoxide-d₆ (99.9 atom % D, Norell Inc.), deuterium oxide (99.9 atom % D, Aldrich Chemical Co.) were used as received.

Tetramethylsilane (NMR grade, 99.9+%, Aldrich Chemical Co.) and the sodium salt of 2,2-dimethyl-2-silapentane-5-sulfonate (99%, Aldrich Chemical Co.) were used as received.

2.1.5 Electrolytes

Sodium chloride (reagent grade, 99+%, Anachemia) was used as received. Tetrabutylammonium hexafluorophosphate (reagent, 98%, Aldrich Chemical Co.) was recrystallized twice from ethanol and vacuum dried overnight at 118 °C. Sodium perchlorate (anhydrous, 98%, Anachemia) was recrystallized twice from water and vacuum dried overnight at 118 °C.

2.1.6 Ion Exchange Resins

Carboxymethyl(CM)-Sephadex C25 cation exchange resin (bead size: 40-125 µ, Sigma Chemical Co.) and sulfopropyl(SP)-Sephadex C25 cation exchange resin (bead size: 40-125 µ, Sigma Chemical Co.) were used as received.

2.1.7 Cyclic Voltammetry Internal Reference

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

2.2 Synthesis of the 1,4-Dicyanamidobenzene Neutral Ligands

The synthesis of 1,4-dicyanamido-2-methylbenzene (2-MeDicydH₂) and 1,4-dicyanamido-2-methoxybenzene (2-MeODicydH₂) has been previously reported.^{79,80} The following outlines those preparations.

1,4-Dicyanamido-2-methylbenzene (2-MeDicydH₂):

Benzoyl chloride (29.01 g, 0.206 mol) in 200 mL of acetone was added to a refluxing solution of ammonium thiocyanate (15.19 g, 0.200 mol) in 200 mL of acetone. The mixture was further refluxed until a yellow color appeared. 2-methyl-1,4-phenylenediamine (10.00 g, 0.082 mol) in 200 mL of acetone was then added dropwise (using a pressure equalizing dropping funnel) and the entire mixture was left to reflux for an additional 20 minutes. To effectively force all of the desired product out of solution and solubilize the ammonium chloride that formed during the reaction, the warm solution was then slowly added to 1500 mL of distilled water with vigorous stirring. The resulting flocculent pale yellow precipitate was filtered, washed with 500 mL of water followed by 200 mL of methanol and 500 mL of diethyl ether and then air dried overnight.

The benzoylthiourea derivative (38.60 g, 0.086 mol) was dissolved in basic solution (43.0 g, 0.5 mol NaOH in 500 mL of water) and boiled for 10 minutes. After the solution had cooled to 65 °C, a solution of lead acetate trihydrate (72.00 g, 0.190 mol) in 200 mL of water was added to afford desulfurization. The resulting mixture was stirred until it had turned completely black during which time the temperature was maintained between 60 and

65 °C. After filtering the solution on ice, the cold filtrate was neutralized by the slow addition of 60 mL of glacial acetic acid. A white precipitate was formed, filtered off and washed with copious amounts of water until the smell of acetic acid was minimal (note that if the precipitate appears slightly green, more acid should be added). The crude product was air dried overnight and then recrystallized by first dissolving it in an excess amount of hot acetone. The resulting blue solution was gravity filtered hot, concentrated and an equal volume of distilled water was added to it. The now lighter blue solution was placed in the refrigerator overnight. Off-white crystals of 2-MeDicydH₂ formed, were filtered and washed with cold 50/50 v/v acetone/water and then vacuum-dried overnight. Yield: 11.13 g (79%). Anal. Calcd.(%) for C₉H₈N₄: C, 62.78; H, 4.68; N, 32.54. Found(%): C, 62.55; H, 4.68; N, 32.58.

1,4-Dicyanamido-2-methoxybenzene (2-MeODicydH₂):

This was prepared in a similar manner to 2-MeDicydH₂ except for the following starting amounts: benzoyl chloride (32.50 g, 0.231 mol), ammonium thiocyanate (17.60 g, 0.231 mol) and 2-methoxy-1,4-phenylenediamine (12.50 g, 0.090 mol). Yield: 14.13 g (83%). Anal. Calcd.(%) for C₉H₈N₄O: C, 57.44; H, 4.28; N, 29.77. Found(%): C, 56.91; H, 4.50; N, 28.98.

Other 1,4-Dicyanamidobenzene Ligands:

The preparations of 1,4-dicyanamido-2,5-dimethylbenzene (2,5-Me₂DicydH₂), 1,4-dicyanamidobenzene (DicydH₂) and 1,4-dicyanamido-2,5-dichlorobenzene (2,5-Cl₂DicydH₂) have been previously reported.^{43,44} 1,4-dicyanamido-2,3,4,5-tetrachlorobenzene (2,3,4,5-Cl₄DicydH₂) cannot be isolated analytically pure in its neutral protonated form owing to an autopolymerization reaction (refer to Section 3.1.1).

However, the tetraphenylarsonium salt of 1,4-dicyanamido-2,3,4,5-tetrachlorobenzene dianion ($[\text{AsPh}_4]_2[2,3,4,5\text{-Cl}_4\text{Dicyd}]$) has been prepared (refer to Section 3.2.1).

2.3 Synthesis of the Mononuclear Pentaammineruthenium(III) Complexes of 1,4-Dicyanamidobenzene Monoanion Ligands

Caution: Perchlorate salts are hazardous and tend to ignite when scraped. They should only be handled in small quantities (<100 mg) and heating in the presence of organic solvents should be avoided.

(1,4-Dicyanamido-2,5-dimethylbenzene)pentaammineruthenium(III) Perchlorate, $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{DicydH})][\text{ClO}_4]_2 \cdot 0.70$ acetone:

50 mL of acetone was added to freshly prepared $[(\text{NH}_3)_5\text{Ru}(\text{OH}_2)][\text{PF}_6]_2$ (0.98 g, 1.98 mmol) and 2,5-Me₂DicydH₂ (0.50 g, 2.69 mmol). After the mixture was stirred for 30 minutes (air oxidized), 0.75 mL of 1.0 M HClO₄ was added to the green solution. After a further 10 minutes, the blue-green solution was gravity filtered from unreacted 2,5-Me₂DicydH₂, and to the filtrate was added TBAB. The resulting blue precipitate was filtered and washed with acetone and ether. The product was then purified by cation-exchange chromatography on CM-Sephadex C25-120 resin and eluted with 1.0 M NaCl solution. For 0.80 g of the crude bromide product, the column dimensions were 30 cm height by 3.7 cm diameter. To avoid thermal decomposition of the desired mononuclear complex, the separation was performed at temperatures below 20 °C. Elution of the blue product band was preceded by yellow and turquoise bands. The product was forced out of the eluent solution by the addition of NaBPh₄, filtered, washed with cold water and air dried overnight. The crude turquoise tetraphenyl borate salt was then dissolved in a minimum amount of cold acetone, to which TBAB was added precipitating out the bromide product. Dissolution of the crude bromide salt in a minimum amount of cold water,

followed by the addition of NaClO_4 afforded the final perchlorate product which was filtered, then washed with cold water and diethyl ether. The product was recrystallized by ether diffusion into an acetone solution at 7°C , affording bluish-green crystals of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{DicydH})][\text{ClO}_4]_2 \cdot 0.70 \text{ CH}_3\text{COCH}_3$ that were vacuum dried overnight. Yield: 0.195 g (17%). Anal. Calcd.(%) for $\text{C}_{12.1}\text{H}_{28.2}\text{N}_9\text{O}_{8.7}\text{Cl}_2\text{Ru}$: C, 23.79; H, 4.65; N, 20.63. Found(%): C, 23.51; H, 4.73; N, 20.27.

(1,4-Dicyanamidobenzene)pentaammineruthenium(III)
Perchlorate, $[(\text{NH}_3)_5\text{Ru}(\text{DicydH})][\text{ClO}_4]_2 \cdot 0.90 \text{ H}_2\text{O}$:

This complex was prepared in a similar manner to $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{DicydH})][\text{ClO}_4]_2$ except for the following starting amounts: $[(\text{NH}_3)_5\text{Ru}(\text{OH}_2)][\text{PF}_6]_2$ (0.80 g, 1.62 mmol); DicydH₂ (0.38 g, 2.40 mmol) and 1.25 mL of 0.1 M HClO_4 . The purification of this complex was also performed in a similar manner to $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{DicydH})][\text{ClO}_4]_2$ except that 1 mL of water was used along with the 10 mL of acetone in the recrystallization. Yield: 0.230 g (25%). Anal. Calcd.(%) for $\text{C}_8\text{H}_{21.8}\text{N}_9\text{O}_{8.9}\text{Cl}_2\text{Ru}$: C, 17.20; H, 3.93; N, 22.57. Found(%): C, 17.56; H, 3.87; N, 22.21. Note that all reaction and purification steps were carried out at room temperature.

(1,4-Dicyanamido-2,5-dichlorobenzene)pentaammineruthenium(III)
Perchlorate, $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Cl}_2\text{DicydH})][\text{ClO}_4]_2 \cdot 0.20 \text{ acetone}$:

0.30 g (0.61 mmol) of freshly prepared $[(\text{NH}_3)_5\text{Ru}(\text{OH}_2)][\text{PF}_6]_2$ and (0.21 g, 0.92 mmol) of 2,5- $\text{Cl}_2\text{DicydH}_2$ were placed in two separate 50 mL round bottom flasks and purged with argon on a vacuum line. 15 mL of MPD was placed in a third flask and degassed. The MPD was then transferred to the flask containing 2,5- $\text{Cl}_2\text{DicydH}_2$. The resulting pale purple solution was transferred to the flask containing $[(\text{NH}_3)_5\text{Ru}(\text{OH}_2)][\text{PF}_6]_2$ and the mixture stirred under argon for 5 minutes. The yellow solution turned green. To ensure complete oxidation, the solution was stirred in air for an additional 10 minutes. 500 mL of

diethyl ether was added to the now blue solution and then it was placed in the freezer for 2 hours. The diethyl ether was decanted and the resulting dark blue oil was dissolved in 20 mL of acetone. TBAB and an additional 500 mL of acetone were added to the solution and then it was placed in the freezer for 1 hour to afford precipitation. A blue precipitate formed, was filtered and washed with acetone and ether. The product was then purified by cation-exchange chromatography on SP-Sephadex C25-120 resin and eluted with 1.0 M NaCl solution. For 0.24 g of the crude bromide salt, the column dimensions were 30 cm height by 3.7 cm diameter. Note that loading the column with more than 0.3 g of crude bromide salt resulted in a substantial amount being precipitated onto the resin. Elution of the blue product band was preceded by a yellow band. The product eluent solution was concentrated by roto-evaporation at 50 °C and then placed in the refrigerator overnight to afford precipitation. The resulting blue chloride salt was filtered, washed with cold water followed by acetone and diethyl ether. Dissolution of the crude chloride salt in a minimum amount of water, followed by the addition of NaClO₄ afforded the final perchlorate product which was filtered, then washed with cold water and diethyl ether. The product was recrystallized by ether diffusion into 10 mL of an acetone/water (9:1) solution, affording dark blue crystals of [(NH₃)₅Ru(2,5-Cl₂DicydH)]ClO₄]₂ • 0.20 CH₃COCH₃ that were vacuum-dried overnight. Yield: 0.025 g (7%). Anal. Calcd.(%) for C_{8.6}H_{19.2}N₉O_{8.2}Cl₄Ru: C, 16.59; H, 3.11; N, 20.24. Found(%): C, 16.75; H, 3.09; N, 20.41.

2.4 Synthesis of the Mononuclear Pentaammineruthenium(IV) Complexes of 1,4-Dicyanamidobenzene Dianion Ligands

Note that owing to stability problems (ie. reversion to the reduced Ru(III) complex of the monoanion ligand), only the 2,5-Me₂Dicyd²⁻ dianion ligand complex could be isolated analytically pure.

(1,4-Dicyanamido-2,5-dimethylbenzene)pentaammineruthenium(IV) Hexafluorophosphate, [(NH₃)₅Ru(2,5-Me₂Dicyd)][PF₆]₂:

A 10 mL acetone solution containing the chemical oxidant, NOBF₄ (0.044 g, 0.38 mmol), was added to a 10 mL acetone solution of [(NH₃)₅Ru(2,5-Me₂DicydH)][PF₆]₂ (0.20 g, 0.30 mmol) with stirring. The solution color changed from greenish-blue to dark brown almost instantly. After 5 minutes, 100 mL of diethyl ether was added to force the precipitation of the reaction product, which was filtered and washed with fresh diethyl ether. The crude brown product was then dissolved in a minimum amount of acetone to which TBAB was added precipitating the bromide salt, which was then filtered and washed with acetone and diethyl ether. To completely eliminate the presence of any unoxidized complex, NaCl was added to an aqueous solution of the bromide product selectively precipitating the chloride salt of the desired oxidized complex. Dissolution of the chloride salt in a minimum amount of water, followed by the addition of NH₄PF₆ afforded the final hexafluorophosphate product, which was filtered and then washed with cold water and diethyl ether. The product was recrystallized by ether diffusion into an acetone solution affording brown fibrous crystals of [(NH₃)₅Ru(2,5-Me₂Dicyd)][PF₆]₂ that were vacuum-dried overnight. Yield: 0.035 g (18%). Anal. Calcd. for C₁₀H₂₃N₉F₁₂P₂Ru: C, 18.19; H, 3.51; N, 19.09. Found: C, 18.57; H, 3.45; N, 19.02.

2.5 Synthesis of the Dinuclear Pentaammine ([Ru(III), Ru(III)] Complexes of 1,4-Dicyanamidobenzene Dianion Ligands

The synthesis of the [Ru(III), Ru(III)] complexes of 2-MeDicyd²⁻ and 2-MeODicyd²⁻ has been previously reported^{79,80}. In addition to outlining these results, the following section reports a new synthetic methodology for preparing the [Ru(III), Ru(III)] complexes of 2,5-Me₂Dicyd²⁻ and Dicyd²⁻. It must be noted that these latter two complexes in addition to the

[Ru(III), Ru(III)] complexes of 2,5-Cl₂Dicyd²⁻ and 2,3,4,5-Cl₄Dicyd²⁻ were originally synthesized by an inert atmosphere preparation.^{43,44,81}

[μ -(1,4-Dicyanamido-2-methylbenzene)bis(pentaammineruthenium(III))]
Hexafluorophosphate, [μ -(2-MeDicyd)-{(NH₃)₅Ru}₂][PF₆]₄ • 0.75 acetone:

50 mL of acetone was added to freshly prepared [(NH₃)₅Ru(OH₂)](PF₆)₂ (1.00 g, 2.02 mmol) and 2-MeDicydH₂ (0.174 g, 1.01 mmol). The mixture was stirred for 1 hour (air oxidation) during which time the solution color changed from golden yellow to green. The solution was gravity filtered and to the filtrate was added TBAB. The resulting green precipitate was filtered and washed with acetone and ether. The product was then purified by cation-exchange chromatography on CM-Sephadex C25-120 resin and eluted with 1.0 M NaCl solution. For 0.71 g of the crude bromide product, the column dimensions were 30 cm height by 3.7 cm diameter. Elution of the green product band was preceded by yellow and blue bands. The product was forced out of the eluent solution by the addition of NaBPh₄, filtered, washed with water and air dried overnight. The crude brown tetraphenyl borate salt was then dissolved in a minimum amount of acetone, to which TBAB was added precipitating out the bromide product. Dissolution of the crude bromide salt in a minimum amount of water, followed by the addition of NH₄PF₆ afforded the final hexafluorophosphate product which was filtered, then washed with cold water and diethyl ether. The product was recrystallized by ether diffusion into acetone solution, affording bluish-green crystals of [μ -(2-MeDicyd)-{(NH₃)₅Ru}₂][PF₆]₄ • 0.75 acetone that were vacuum-dried overnight. Yield: 0.240 g (10%). Anal. Calcd.(%) for C_{11.25}H_{40.5}N₁₄O_{0.75}P₄F₂₄Ru₂: C, 11.62; H, 3.51; N, 16.86. Found(%): C, 11.66; H, 3.47; N, 17.01.

**[μ -(1,4-Dicyanamido-2-methoxybenzene)bis(pentaammineruthenium(III))]
Hexafluorophosphate, [μ -(2-MeODicyd)-{(NH₃)₅Ru}₂][PF₆]₄:**

This complex was prepared and purified in a similar manner to [μ -(2-MeDicyd)-{(NH₃)₅Ru}₂][PF₆]₄ except for the following starting amounts: [(NH₃)₅Ru(OH₂)][PF₆]₂ (0.50 g, 1.01 mmol) and 2-MeODicydH₂ (0.095 g, 0.50 mmol). Yield: 0.185 g (16%). Anal. Calcd.(%) for C₉H₃₆N₁₄O₄F₂₄Ru₂: C, 9.50; H, 3.19; N, 17.22. Found(%): C, 9.80; H, 3.20; N, 16.65.

**[μ -(1,4-Dicyanamido-2,5-dimethylbenzene)bis(pentaammineruthenium(III))]
Hexafluorophosphate, [μ -(2,5-Me₂Dicyd)-{(NH₃)₅Ru}₂][PF₆]₄ · 1.25 acetone:**

This complex was prepared and purified in a similar manner to [μ -(2-MeDicyd)-{(NH₃)₅Ru}₂][PF₆]₄ except for the following starting amounts: [(NH₃)₅Ru(OH₂)][PF₆]₂ (0.98 g, 1.98 mmol) and 2,5-Me₂DicydH₂ (0.185 g, 0.99 mmol). Yield: 0.265 g (12%). Anal. Calcd.(%) for C_{13.75}H_{45.5}N₁₄O_{1.25}P₄F₂₄Ru₂: C, 13.66; H, 3.79; N, 16.22. Found(%): C, 13.50; H, 4.18; N, 15.93.

**[μ -(1,4-Dicyanamidobenzene)bis(pentaammineruthenium(III))]
Hexafluorophosphate, [μ -(Dicyd)-{(NH₃)₅Ru}₂][PF₆]₄ · 0.33 acetone:**

This complex was prepared and purified in a similar manner to [μ -(2-MeDicyd)-{(NH₃)₅Ru}₂][PF₆]₄ except for the following starting amounts: [(NH₃)₅Ru(OH₂)][PF₆]₂ (0.80 g, 1.62 mmol) and DicydH₂ (0.13 g, 0.82 mmol). Yield: 0.310 g (17%). Anal. Calcd.(%) for C₉H₃₆N₁₄O_{0.33}P₄F₂₄Ru₂: C, 9.58; H, 3.22; N, 17.38. Found(%): C, 9.12; H, 3.12; N, 16.63.

$[\mu-(1,4\text{-Dicyanamido-2,5-dichlorobenzene})\text{bis}\{\text{pentaammineruthenium(II)}\}]\text{Hexafluorophosphate}, [\mu-(2,5\text{-Cl}_2\text{Dicyd})-\{(\text{NH}_3)_5\text{Ru}\}_2][\text{PF}_6]_4 \cdot 1.5 \text{ acetone}:$

The preparation of the chloride salt of this complex has been previously reported employing $[\text{Ph}_4\text{As}]_2[2,5\text{-Cl}_2\text{Dicyd}]$.^{43,44} The hexafluorophosphate salt was obtained by modifying the original preparation in the following manner: After cation-exchange chromatography, the product was forced out of the eluent solution by the addition of NaBPh_4 , filtered, washed with water and air dried overnight. The crude brown tetraphenyl borate salt was then dissolved in a minimum amount of acetone, to which TBAB was added precipitating out the bromide product. Dissolution of the crude bromide salt in a minimum amount of water, followed by the addition of NH_4PF_6 afforded the final hexafluorophosphate product which was filtered, then washed with cold water and diethyl ether. The product was recrystallized by ether diffusion into acetone solution, affording blue crystals of $[\mu-(2,5\text{-Cl}_2\text{Dicyd})-\{(\text{NH}_3)_5\text{Ru}\}_2][\text{PF}_6]_4 \cdot 1.5 \text{ acetone}$ that were vacuum-dried overnight. Yield: 10%. Anal. Calcd.(%) for $\text{C}_{12.5}\text{H}_{41}\text{N}_{14}\text{O}_{1.5}\text{P}_4\text{F}_{24}\text{Cl}_2\text{Ru}_2$: C, 11.87; H, 3.27; N, 15.51. Found(%): C, 11.95; H, 3.29; N, 15.61.

$[\mu-(1,4\text{-Dicyanamido-2,3,4,5-tetrachlorobenzene})\text{bis}\{\text{pentaammineruthenium(II)}\}]\text{Hexafluorophosphate}, [\mu-(2,3,4,5\text{-Cl}_4\text{Dicyd})-\{(\text{NH}_3)_5\text{Ru}\}_2][\text{PF}_6]_4 \cdot 1.25 \text{ acetone}:$

The preparation of the chloride salt of this complex has been previously reported employing $[\text{Ph}_4\text{As}]_2[2,3,4,5\text{-Cl}_4\text{Dicyd}]$.^{44,81} The hexafluorophosphate salt was obtained by modifying the original preparation in the following manner: After cation-exchange chromatography, the product was forced out of the eluent solution by the addition of NaBPh_4 , filtered, washed with water and air dried overnight. The crude brown tetraphenyl borate salt was then dissolved in a minimum amount of acetone, to which TBAB was added precipitating out the bromide product. Dissolution of the crude bromide salt in a minimum amount of water, followed by the addition of NH_4PF_6 afforded the final hexafluorophosphate product which was filtered, then washed with cold water and diethyl

ether. The product was recrystallized by ether diffusion into acetone solution, affording dark blue crystals of $[\mu-(2,3,4,5\text{-Cl}_4\text{Dicyd})-(\text{NH}_3)_5\text{Ru}]_2[\text{PF}_6]_4 \cdot 1.25 \text{ acetone}$ that were vacuum-dried overnight. Yield: 7%. Anal. Calcd.(%) for $\text{C}_{11.75}\text{H}_{37.5}\text{N}_{14}\text{O}_{1.25}\text{P}_4\text{F}_{24}\text{Cl}_4\text{Ru}_2$: C, 10.70; H, 2.87; N, 14.87. Found(%): C, 10.36; H, 2.80; N, 14.48.

2.6 Synthesis of the Dinuclear Pentaammineruthenium ([Ru(IV), Ru(III)] Complexes of 1,4-Dicyanamidobenzene Dianion Ligands

Note that owing to stability problems (ie. reversion to the reduced [Ru(III), Ru(III)] complex of the dianion ligand), only the 2,5-Me₂Dicyd²⁻ dianion ligand could be isolated analytically pure. In this case, the presence of trace acid (refer below) helped maintain complex integrity.

$[\mu-(1,4\text{-Dicyanamido-2,5-dimethylbenzene})\text{bis}\{\text{pentaammineruthenium(IV,III)}\}]\text{Hexafluorophosphate}, [\mu-(2,5\text{-Me}_2\text{Dicyd})-(\text{NH}_3)_5\text{Ru}]_2[\text{PF}_6]_5 \cdot 2 \text{ H}_2\text{O}$

A 5 mL water solution containing the chemical oxidant, $[\text{NH}_4]_2[\text{Ce}(\text{SO}_4)_3]$ (0.033 g, 0.055 mmol), was added to a 5 mL acetone solution of $[\mu-(2,5\text{-Me}_2\text{Dicyd})-(\text{NH}_3)_5\text{Ru}]_2[\text{PF}_6]_4$ (0.050 g, 0.044 mmol) with stirring. The solution color changed from green to bluish-purple and a precipitate formed almost instantly. The sulfate product was filtered, then washed with acetone and diethyl ether. Note that a green filtrate color was indicative of unoxidized [Ru(III), Ru(III)] complex. Dissolution of the crude sulfate salt in a minimum amount of hexafluorophosphoric acid (2×10^{-4} M), followed by the addition of NH_4PF_6 afforded the final hexafluorophosphate product which was filtered, then washed with cold hexafluorophosphoric acid (2×10^{-4} M) and diethyl ether. The product was recrystallized by ether diffusion into an acetone/hexafluorophosphoric acid (4×10^{-3} M) solution at 5 °C, affording blueish-purple crystals of $[\mu-(2,5\text{-Me}_2\text{Dicyd})-$

$\{(\text{NH}_3)_5\text{Ru}\}_2[\text{PF}_6]_5 \cdot 2 \text{H}_2\text{O}$ that were vacuum-dried overnight. Yield: 0.020 g (35%).
Anal. Calcd.(%) for $\text{C}_{10}\text{H}_{42}\text{N}_{14}\text{O}_2\text{P}_5\text{F}_{30}\text{Ru}_2$: C, 9.12; H, 3.21; N, 14.88. Found(%): C, 9.32; H, 3.03; N, 14.60.

2.7 Physical Measurements

2.7.1 Infrared Spectra

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

2.7.2 NMR Spectra

^1H NMR spectra were run on a Bruker AMX-400 NMR spectrometer or a Varian XL-200 NMR spectrometer at 300 K. Chemical shifts were referenced to TMS (0.00 ppm) in non-aqueous solution and to DSS (0.00 ppm) in deuterium oxide. Ultra-Imperial Grade sample tubes (dimensions: 180 mm x 5 mm OD) were made of precision grade pyrex by the Wilmad Glass Company.

2.7.3 Electronic Absorption Spectra

Electronic absorption spectra were recorded on a Cary 5 UV/vis/NIR spectrometer interfaced with a Raven 386/33 Personal Computer online to a Hewlett-Packard Laserjet IID printer. The spectra were measured at ambient temperature using matching quartz cells (1 cm path length) made by Hellma (Canada) Limited. A solvent baseline correction was performed before each run.

2.7.4 Cyclic Voltammetry

Cyclic voltammograms were recorded by using a BAS CV-27 apparatus online to a BAS X-Y recorder. The electrochemical cell consisted of a double-jacketed glass container with an inner volume of approximately 15 mL. 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 cap through which holes had been drilled to permit insertion of electrodes and argon gas inlet and outlet tubes. Non-aqueous cyclic voltammetry was performed in nitromethane, acetonitrile, acetone and dimethyl sulfoxide (all anhydrous) in the presence of 0.1 M TBAH supporting electrolyte. The three-electrode system consisted of a platinum disk working electrode (BAS, 1.6 mm diameter), a platinum wire counter electrode and a silver wire quasi-reference electrode. Ferrocene ($E^\circ = 0.665$ V vs NHE) was used as an internal reference.⁸² Aqueous cyclic voltammetry was performed in distilled/deionized water in the presence of 0.1 M NaClO₄ supporting electrolyte. In this case, the three-electrode system consisted of a glassy-carbon working electrode (BAS, 5 mm diameter), a platinum wire counter electrode and a saturated calomel ($E^\circ = 0.242$ V vs NHE) reference electrode. In both non-aqueous and aqueous experiments, solutions were deoxygenated by bubbling with argon for 30 minutes and blanked with argon prior to each scan.

2.7.5 Spectroelectrochemistry

Spectroelectrochemical studies were performed at ambient temperature with a pyrex-quartz H-cell of published design,⁸³ having a working electrode cell volume of approximately 10 mL and total cell volume of approximately 20 mL. Non-aqueous spectroelectrochemistry was performed in anhydrous acetonitrile in the presence of 0.1 M TBAH supporting electrolyte. The three-electrode system consisted of a platinum mesh working electrode (area = 6.65 cm²), a platinum wire counter electrode and a silver wire quasi-reference electrode. Aqueous spectroelectrochemistry was performed in deuterium oxide in the presence of 0.1 M NaClO₄ supporting electrolyte. The three-electrode system differed

from the non-aqueous case by employing a BAS mini Ag/AgCl reference electrode ($E^\circ = -0.045$ V vs SCE). In both non-aqueous and aqueous experiments, complex concentrations in the working electrode cell were approximately 1.0×10^{-5} M. The solutions were deoxygenated for 30 minutes (prior to electrolysis) and agitated (during electrolysis) by bubbling argon through a two-way teflon needle. A BAS CV-27 apparatus was used to control the electrolysis potential at the working electrode and monitor the coulometry of the system. Note that a blank correction, to correct for the quantity of charge Q required to oxidize or reduce trace impurities in the base electrolyte, was found to be negligible.

2.7.6 Magnetic Susceptibility Measurements

Solution magnetic susceptibility measurements were performed using the ^1H NMR technique known as the Evans method.^{55,56} Spectra were run on a Bruker AMX-400 NMR spectrometer at 300 K. TMS was used as an internal reference in non-aqueous solution while DSS was used as an internal reference in deuterium oxide. Special stem coaxial insert tubes (dimensions: 203 mm x 4 mm OD) with a capillary reference volume of 60 μL (capillary dimensions: 50 mm x 2.5 mm OD) were made of precision grade pyrex by the Wilmad Glass Company.

2.7.7 Elemental Analysis

Elemental analysis were performed by Canadian Microanalytical Services Ltd. in Delta, British Columbia.

2.8 Theoretical Calculations

2.8.1 Extended Hückel Molecular Orbital (EHMO) Calculations

These calculations were performed on the 2,5-Me₂Dicyd²⁻ dianion ligand using the Quantum Chemistry Program Exchange program No. QCMP 011 (Forticon 8) for personal

computers. Calculations were carried out on a Raven 386 PC equipped with a 80387 coprocessor and using Microsoft Fortran (v5.0). A data input file was constructed using bond length and bond angle information obtained from the relevant X-ray crystal structure.⁸⁴

2.8.2 Non-linear Curve Fitting

Non-linear curve fitting was performed on a Raven 386 PC equipped with a 80387 coprocessor using Peakfit(v3.0) from Jandel Scientific. With Peakfit, the oscillator strengths of ligand to metal charge transfer (LMCT) and metal to metal charge transfer (MMCT) transitions were determined by fitting the band profiles to a set of Gaussian bands. For each band the oscillator strength is given by: $f = 4.61 \times 10^{-9} (\sum \epsilon_{\max_n} \cdot \Delta\nu_{1/2_n})$, where for the n th Gaussian band, $\epsilon_{\max}$ is the maximum extinction coefficient in $M^{-1} \text{ cm}^{-1}$ and $\Delta\nu_{1/2}$ is the bandwidth at one-half $\epsilon_{\max}$ in cm^{-1} . The peak analysis software was also used to deconvolute MMCT transitions from LMCT transitions.

CHAPTER 3

Neutral and Dianionic 1,4-Dicyanamidobenzene Ligands

3.1 1,4-Dicyanamidobenzene Neutral Ligands

The preparation of 2,5-Me₂DicydH₂, DicydH₂ and 2,5-Cl₂DicydH₂ has been previously reported.^{43,44} However, results of their characterization (IR and ¹H NMR spectroscopy) appear in this publication for the first time. In the case of 2-MeDicydH₂ and 2-MeODicydH₂, both their preparation and characterization (IR and ¹H NMR spectroscopy) have been previously reported.^{79,80} The following results section summarizes these results.

3.1.1 Synthesis

The preparation of 1,4-dicyanamidobenzene neutral ligands (refer to Scheme 3.1) was carried out in a similar manner to the established methods employed for phenylcyanamide ligands.⁸⁵⁻⁸⁷ The appropriately substituted phenylenediamine was reacted with benzoyl thiocyanate (formed from the reaction between ammonium thiocyanate and benzoyl chloride) to form the benzoylthiourea derivative (A). Heating a basic solution of (A) cleaves the benzoyl groups to afford the thiourea derivative (B). Desulfurization of (B) and the concomitant formation of the 1,4-dicyanamidobenzene dianion (C) is accomplished via reaction with lead(II) acetate under controlled temperature and reaction time conditions (refer to Scheme 3.2b, autopolymerization of the cyanamide ligand can occur during the desulfurization process if excessive heat is used). Neutralization of the solution with acetic acid affords the precipitation of the protonated or neutral 1,4-dicyanamidobenzene ligand (D).

Scheme 3.1

As already eluded to, cyanamide ligands have a tendency to autopolymerize when deprotonated or heated. Previous studies have shown that phenylcyanamide ligands, although far more stable, can also undergo autopolymerization reactions under such conditions and the tendency to do so increases with increasing chloride substitution of the phenyl ring.⁸⁵ Furthermore, owing to the observation that the rate of dimerization of (2,6-dichlorophenyl)cyanamide in dimethyl sulfoxide can be significantly reduced by the addition of trace amounts of acid, it is strongly believed that the rate-determining step of autopolymerization is deprotonation of the cyanamide amine followed by attack of the amide on the nitrile carbon of a neutral cyanamide ligand. The implication is that the neutral and anionic forms of the cyanamide ligand are in an equilibrium in strongly donating or basic solvents. With regards to the preparation of 1,4-dicyanamidobenzene neutral ligands, great care is taken during the desulfurization step to prevent the temperature from exceeding 65 °C. Such precaution prevents dimer formation in all cases except for 2,3,4,5-Cl₄DicydH₂ which cannot be isolated in its neutral form. The dimerization of 2,3,4,5-Cl₄DicydH₂ is shown in Scheme 3.2.

Scheme 3.2

As a preventative measure with regards to polymerization, none of the five 1,4-dicyanamidobenzene neutral ligands were dried under vacuum at elevated temperatures (ie. >100 °C) to remove potential water molecules of crystallization.

3.1.2 Infrared Spectroscopy

The infrared spectrum of 2-MeDicydH₂ is shown in Figure 3.1 while the results of all five 1,4-dicyanamidobenzene neutral ligands are summarized in Table 3.1. All of ligands demonstrate the characteristic cyanamide nitrile stretch $\nu(\text{N}\equiv\text{C})$ in the range of 2215-2235 cm^{-1} . Other prominent vibrations include aromatic $\nu(\text{C}=\text{C})$ stretches between 1475-1525 cm^{-1} , aromatic secondary amine $\nu(\text{C}-\text{N})$ stretches near 1400 cm^{-1} and $\nu(\text{N}-\text{H})$ stretching and $\delta(\text{N}-\text{H})$ deformation vibrations of secondary amines in the range of 3100-3300 cm^{-1} and 1550-1650 cm^{-1} , respectively. The diagnostic imine $\nu(\text{C}=\text{N})$ stretching frequency associated with the dimer ligand (ie. 2,3,4,5-Cl₄DicydH₂ dimer) occurs near 1680 cm^{-1} and is of strong intensity. Note that the results are based on known spectral assignments for similar functionalities.⁸⁸

Figure 3.1 Infrared spectrum of 2-MeDicydH₂ (KBr disc). [Reproduced with permission from Ref. 79. Copyright (1994).]

Table 3.1 Infrared Spectral Data for the 1,4-Dicyanamidobenzene Neutral Ligands (in cm^{-1}).^a

Ligands	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{C})$	$\nu(\text{C}-\text{N})$	$\nu(\text{N}-\text{H})$	$\delta(\text{N}-\text{H})$
2-MeODicydH ₂ ^b	2224(vs)	1518(vs)	1410(s)	3175(s)	1620(w)
2,5-Me ₂ DicydH ₂	2230(vs)	1529(vs)	1409(s)	3184(s)	1621(w)
2-MeDicydH ₂ ^c	2227(vs)	1519(vs)	1412(s)	3183(s)	1626(w)
DicydH ₂	2234(vs)	1531(vs)	1408(s)	3178(s)	1627(w)
2,5-Cl ₂ DicydH ₂	2232(vs)	1515(vs)	1389(s)	3188(s)	1623(w)

^aKBr disc; band intensities: vs=very strong, s=strong, w=weak. ^bfrom Ref. 80. ^cfrom Ref. 79.

3.1.3 ¹H NMR Spectroscopy

The ¹H NMR spectrum of 2-MeDicydH₂ in acetone-d₆ is shown in Figure 3.2. Table 3.2a summarizes the chemical shift assignments of both 2-MeDicydH₂ and 2-MeODicydH₂. For both neutral ligands, the phenyl proton splitting pattern is given the ABX designation owing to the presence of three magnetically nonequivalent phenyl protons.⁸⁹ In the case of 2-MeDicydH₂ (refer to the labelling in Figure 3.2), the phenyl proton in the 3- position (3-phenyl) appears as a doublet centered at 6.91 ppm (6.907, 6.913 ppm) with a small coupling constant $J = 2.4$ Hz indicative of long range ⁴J coupling to 5-phenyl. 5-phenyl itself appears as a pair of two closely spaced doublets centered at 6.94 ppm (6.937 and 6.944 ppm, $J = 2.6$ Hz) and at 6.96 ppm (6.959 and 6.965 ppm, $J = 2.6$ Hz). Vicinal or ³J coupling to 6-phenyl ($J = 8.4$ Hz) plus additional ⁴J coupling to 3-phenyl accounts for the observed splitting pattern. 6-phenyl appears as a doublet centered at 7.14 ppm (7.130 and 7.151 ppm) with $J = 8.4$ Hz indicative of ³J coupling to 5-phenyl. Note that the very weak ⁵J coupling between 3-phenyl and 6-phenyl which would be represented by an approximate value of $J = 1$ Hz was not observed using the 400 MHz instrument. The remainder of the ¹H NMR spectrum includes the 2-methyl protons which appear as a singlet at 2.27 ppm, and the amine N-H protons which appear as a very broad singlet

centered at 8.25 ppm. The latter two assignments are consistent with results based on similar functionalities.⁹⁰ The broadening of the N-H resonance can be largely accounted for by the large electric quadrupole moment of nitrogen. The phenomenon, known as nuclear quadrupole broadening,⁹¹ occurs when the rate of transitions among the spin states of nitrogen is similar to the time required for proton transitions. The result is partial decoupling of hydrogen from nitrogen, and hence, a broadened resonance. As a final note, it must be pointed out that the amine protons integrated slightly low as a result of exchange with water protons.

Figure 3.2 ¹H NMR spectrum of 2-MeDicydH₂ in acetone-d₆ (at 300 K) with a concentration of 11 mM. The singlet at 2.06 ppm is background from acetone-d₆. The singlet at 2.80 ppm is due to water of recrystallization. [Reproduced with permission from Ref. 79. Copyright (1994).]

Table 3.2a ^1H NMR Chemical Shifts of 2-MeDicydH₂ and 2-MeODicydH₂.^a

Ligands	2-Me/2-MeO	3-Ph	5-Ph	6-Ph	amine
2-MeDicydH ₂ ^b	2.27 (s)	6.91 (d)	6.94 (d), 6.96 (d)	7.14 (d)	8.25 (bs)
2-MeODicydH ₂ ^c	3.90 (s)	6.73 (d)	6.76 (d), 6.78 (d)	7.09 (d)	8.40 (bs)

^aAll chemical shifts gave the correct integration for their assignment; the values in ppm are referenced to TMS at 0.00 ppm; the ligand concentrations were 11 mM in acetone-*d*₆; abbreviations: s=singlet, bs=broad singlet, d=doublet. ^bfrom Ref. 79. ^cfrom Ref. 80.

The ^1H NMR chemical shift assignments for the remaining 1,4-dicyanamidobenzene neutral ligands including 2,5-Me₂DicydH₂, DicydH₂ and 2,5-Cl₂DicydH₂ are summarized in Table 3.2b.

Table 3.2b ^1H NMR Chemical Shifts of 2,5-Me₂DicydH₂, DicydH₂ and 2,5-Cl₂DicydH₂.^a

Ligands	2,5-Me	3,6-Ph	amine
2,5-Me ₂ DicydH ₂	2.15 (s)	6.86 (s)	9.23 (bs)
DicydH ₂	----	6.96 (s) ^b	10.07 (bs)
2,5-Cl ₂ DicydH ₂	----	7.22 (s)	10.11 (bs)

^aAll chemical shifts gave the correct integration for their assignment; the values in ppm are referenced to TMS at 0.00 ppm; the ligand concentrations were 23 mM in DMSO-*d*₆; abbreviations: s=singlet, bs=broad singlet. ^bincludes 2,5-phenyl protons.

The results are straightforward owing to the symmetry of the molecules. In all three cases, the phenyl protons appear as singlets in the 6.85 to 7.25 ppm range while the amine protons appear as broad singlets in the 9.20 to 10.20 ppm range. For both the phenyl and amine chemical shifts, the downfield trend on going from 2,5-Me₂DicydH₂ to 2,5-Cl₂DicydH₂ is accounted for by the consideration that as the electron withdrawing nature of the 2,5-phenyl substituents increases the 3,6-phenyl protons and the amine nitrogens will be further deshielded. For 2,5-Me₂DicydH₂, the additional methyl protons appear as a

singlet at the expected position of 2.15 ppm. Finally, the well documented solvent-dependent effect on amine protons⁹² is evident when these results, obtained in DMSO- d_6 , are compared to those for 2-MeDicydH₂ and 2-MeODicydH₂ in acetone- d_6 .

3.2 1,4-Dicyanamidobenzene Dianion Ligands

The 2-MeDicyd²⁻ and 2-MeODicyd²⁻ dianion ligands have not yet been prepared as ionic salts. However, the preparation and characterization (infrared spectroscopy, X-ray crystallography and cyclic voltammetry) of the bis(tetraphenylarsonium) salts (Ph₄As⁺) of 2,5-Me₂Dicyd²⁻, Dicyd²⁻, 2,5-Cl₂Dicyd²⁻ and 2,3,4,5-Cl₄Dicyd²⁻ from their respective neutral counterparts has been previously reported.^{43,44,81} In addition, low temperature ¹³C NMR measurements of [AsPh₄]₂[2,5-Cl₂Dicyd] in methanol- d_4 were performed to estimate the rotation barrier of the cyanamide moiety towards syn/anti-conformer isomerization. Finally, to obtain insight into the nature and energy of the frontier molecular orbitals of the dianion ligands, EHMO calculations were performed on 2,5-Me₂Dicyd²⁻, Dicyd²⁻, 2,5-Cl₂Dicyd²⁻ and 2,3,4,5-Cl₄Dicyd²⁻. To provide necessary background, a summary of these results appears in Sections 3.2.1 to 3.2.6.

3.2.1 Synthesis

The conversion of the 1,4-dicyanamidobenzene neutral ligands is quite straightforward, involving initial deprotonation in basic solution (ie. NaOH) followed by the addition of excess tetraphenylarsonium chloride to precipitate the desired dianionic salt.

3.2.2 Infrared Spectroscopy

The infrared spectra of the four 1,4-dicyanamidobenzene dianion ligands including 2,5-Me₂Dicyd²⁻, Dicyd²⁻, 2,5-Cl₂Dicyd²⁻ and 2,3,4,5-Cl₄Dicyd²⁻ all show the characteristic anionic cyanamide $\nu(\text{N}=\text{C}=\text{N})$ stretch in the 2090-2104 cm⁻¹ range. As well, the aromatic

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$\nu(\text{C}=\text{C})$ stretches in the $1400\text{--}1500\text{ cm}^{-1}$ range are present. The results are summarized in Table 3.3. It is interesting to note that as the electron withdrawing nature of the substituent on the phenyl ring increases (from Me to Cl), so does the energy of the $\nu(\text{N}=\text{C}=\text{N})$ stretching mode. The result is accounted for by the increased electron density on the amide nitrogen leading to a shortening of the nitrile bond length in $[\text{Ph}_4\text{As}]_2[2,5\text{-Me}_2\text{Dicyd}]$ compared to $[\text{Ph}_4\text{As}]_2[2,3,4,5\text{-Cl}_4\text{Licyd}]$ (refer to Section 3.2.3).

Table 3.3 Infrared Spectral Data for the 1,4-Dicyanamidobenzene Dianion Ligands (in cm^{-1}).^a

Ligands ^b	$\nu(\text{N}=\text{C}=\text{N})$	$\nu(\text{C}=\text{C})$
2,5-Me ₂ Dicyd ²⁻	2093(s)	1498(m)
Dicyd ²⁻	2089(s)	1485(m)
2,5-Cl ₂ Dicyd ²⁻	2100(s)	1483(m)
2,3,4,5-Cl ₄ Dicyd ²⁻	2104(s)	1481(m)

^aKBr disc; band intensities: s=strong, m=medium. ^bfrom Ref. 44 and 43.

3.2.3 X-Ray Crystallography

(Note: the estimated standard deviations for both bond lengths and bond angles are given in parentheses).

Rhombohedral shaped crystals of the Ph_4As^+ salts of 2,5-Me₂Dicyd²⁻, Dicyd²⁻, 2,5-Cl₂Dicyd²⁻ and 2,3,4,5-Cl₄Dicyd²⁻ were grown from saturated DMSO solutions under an inert argon atmosphere. In all cases, the dianion ligands are planar with the terminal nitrile nitrogen not deviating out of the plane formed by the phenyl ring by more than 0.3 Å. The cyanamide NCN groups, which adopt an anti conformation, are close to linearity as the NCN bond angle ranges from $177.9(23)^\circ$ in 2,5-Me₂Dicyd²⁻ to $168.8(5)^\circ$ in 2,3,4,5-

$\text{Cl}_4\text{Dicyd}^{2-}$. As previously mentioned (refer to Section 3.2.2), the nitrile bond length varies from 1.167(4) Å in 2,3,4,5- $\text{Cl}_4\text{Dicyd}^{2-}$ to 1.18(3) Å in 2,5- $\text{Me}_2\text{Dicyd}^{2-}$ implying that the electron withdrawing/donating nature of the phenyl group directly affects the length of the nitrile bond. The result is explained by considering the two resonance structures (shown below in Scheme 3.3) that exist for 1,4-dicyanamidobenzene dianion ligands.

Scheme 3.3

Clearly, as the electron withdrawing nature of the R groups increase, resonance form (B) with its implication of a true nitrile CN triple bond is favored over (A) which more closely represents the same nitrile functionality as a CN double bond. The resonance effect also accounts for the variation in the phenyl ring carbon to cyanamide bond length as it ranges from 1.360(6) Å in 2,3,4,5- $\text{Cl}_4\text{Dicyd}^{2-}$ to 1.426(22) Å in 2,5- $\text{Me}_2\text{Dicyd}^{2-}$.

3.2.4 Cyclic Voltammetry

The cyclic voltammetry of the Ph_4As^+ salts of 2,5- $\text{Me}_2\text{Dicyd}^{2-}$, Dicyd^{2-} , 2,5- $\text{Cl}_2\text{Dicyd}^{2-}$ and 2,3,4,5- $\text{Cl}_4\text{Dicyd}^{2-}$ in acetonitrile is characterized by two one-electron oxidation processes as shown in Scheme 3.4.

Scheme 3.4

The first oxidation couple, denoted by E_{L1}° , was found to be quasi-reversible at best (ie. peak to peak separations >80 mV at 100 mVs^{-1} that increase with scan rate) with half-wave potential values ranging from -0.545 V vs NHE for 2,5-Me₂Dicyd²⁻ to -0.025 V vs NHE for 2,3,4,5-Cl₄Dicyd²⁻. The second oxidation couple, denoted by E_{L2}° , was found to be reversible (ie. peak to peak separations of 60 mV independent of scan rate) with half-wave potential values ranging from 0.095 V vs NHE for 2,5-Me₂Dicyd²⁻ to 0.570 V vs NHE for 2,3,4,5-Cl₄Dicyd²⁻. The results are summarized in Table 3.4.

Table 3.4 Oxidation Potentials for the 1,4-Dicyanamidobenzene Dianion Ligands.^a

Ligands ^b	E_{L1}°	E_{L2}°
2,5-Me ₂ Dicyd ²⁻	-0.545 (130)	0.095 (60)
Dicyd ²⁻	-0.465 (125)	0.210 (65)
2,5-Cl ₂ Dicyd ²⁻	-0.175 (75)	0.465 (60)
2,3,4,5-Cl ₄ Dicyd ²⁻	-0.025 (80)	0.570 (70)

^aCouples are reported in volts vs. NHE (scan rate of 100 mVs^{-1}) with the numbers in parenthesis referring to $E_{pa}-E_{pc}$ in mV at a scan rate of 100 mVs^{-1} ; all data are recorded in acetonitrile solution (ionic strength=0.1 M TBAH) at 25°C. ^bfrom references 43, 44 and 81.

The trends in both E_{L1}° and E_{L2}° are quite predictable with both couples shifting in a positive direction, from which it can be inferred that oxidation of the dianion and subsequently that of the monoanion radical is becoming more difficult as the electron withdrawing ability of the phenyl substituents increases. As a final note, the values of E_{L1}°

and E_{L2}° imply that the 1,4-dicyanamidobenzene dianion ligands can be readily oxidized by 1 or 2 electrons. Clearly, the dianion ligands have the potential to be strong donors of electron density (ie. predominantly π , refer to Section 3.2.6).

3.2.5 ^{13}C NMR Spectroscopy

The π coupling between the anionic cyanamide groups and the phenyl ring that fixes the planar geometry of the 1,4-dicyanamidobenzene dianion ligands in the solid state is weak, such that in solution rotation of the cyanamide group out of the plane of the phenyl ring is expected to occur. The rotation barrier for syn/anti isomerization for a variety of dicyanoquinonediimine derivatives has been shown to occur in the range of 13-17 kcal mol⁻¹.⁹³ Owing to the partial double bond character of the phenyl carbon-cyanamide bond in the 1,4-dicyanamidobenzene dianion ligands, which are two electron reduction products of the above mentioned diimine derivatives, the barrier to rotation is predicted to be even less. The low temperature ^{13}C NMR spectrum of $[\text{Ph}_4\text{As}]_2[2,5\text{-Cl}_2\text{Dicyd}]$ in methanol- d_4 was measured to obtain an estimation of the energy barrier to rotation about the phenyl ring carbon-cyanamide bond.^{43,44} The limited data, based on the gradual broadening and coalescence of the cyanamide resonance down to -60 °C, yielded a result of ≤ 9 kcal mol⁻¹. Based on this finding, the assumption that more than one cyanamide anion group conformation (not just the planar anti conformation as occurs in the solid state) exists in equilibrium in solution for the 1,4-dicyanamidobenzene dianion ligands is valid.

3.2.6 EHMO Calculations

To obtain information with regards to the nature and energy of the frontier molecular orbitals of the 1,4-dicyanamidobenzene dianion ligands, EHMO calculations were performed on 2,5-Me₂Dicyd²⁻, Dicyd²⁻, 2,5-Cl₂Dicyd²⁻ and 2,3,4,5-Cl₄Dicyd²⁻ in C_s symmetry.^{43,44} By placing the dianion ligands in the Cartesian xy plane and assuming them to be planar (ie. z coordinate = 0), the x and y coordinates of each atom were

determined. However, an exception to this was the methyl protons of 2,5-Me₂Dicyd²⁻ whose z coordinates were determined.⁹⁴ Among other results, the Forticon 8 program yielded information with regards to the energy of the molecular orbitals, the coefficients of the atomic orbitals that make up the molecular orbitals and the net atomic charges and atomic orbital occupations. The energies of the three π symmetry molecular orbitals including the anti-bonding π^* or LUMO (lowest unoccupied molecular orbital), the nonbonding π_1 or HOMO (highest occupied molecular orbital) and the nonbonding π_2 or SHOMO (second highest occupied molecular orbital) are summarized in Table 3.5.

Table 3.5 Frontier Molecular Orbital Energies for the 1,4-Dicyanamidobenzene Dianion Ligands (in eV).

Ligands	HOMO	SHOMO	ΔE (HOMO-SHOMO)	LUMO
^a 2,5-Me ₂ Dicyd ²⁻	-11.65	-12.47	0.82	-8.21
Dicyd ²⁻	-11.66	-12.42	0.76	-8.25
2,5-Cl ₂ Dicyd ²⁻	-11.71	-12.48	0.77	-9.70
2,3,4,5-Cl ₄ Dicyd ²⁻	-11.58	-12.26	0.68	-9.97

^aFrom Ref. 94.

The results are similar for all four dianion ligands, each with a high lying LUMO and two closely spaced HOMO orbitals. Furthermore, the HOMO and SHOMO are similar to the two nonbonding molecular orbitals (ie. π_{nb1} and π_{nb2} , respectively) that have been defined for anionic phenylcyanamide ligands (refer to Section 4.1.3).

On closer examination of the coefficients of the atomic orbitals that make up the said molecular orbitals, the LUMO is predominantly phenyl ring centered with little contribution from the NCN groups. On the otherhand, both the HOMO and SHOMO which are orthogonal to each other, are significantly delocalized with the former having a large p_z contribution on the majority of atoms while p_x and p_y contributions dominate in the latter.

The increased stabilization of the SHOMO relative to the HOMO is the result of a σ coupling interaction between the phenyl ring system and the amide nitrogen of the NCN group. Figure 3.3 gives a representation of the LUMO, HOMO and SHOMO which constitute the frontier orbitals of the Dicyd²⁻ ligand (note that the lobe sizes are proportional to the atomic orbital coefficients given by the EHMO calculations). Clearly, the planar conformation of the dianion ligands (refer to X-ray results, Section 3.2.3) results in optimal coupling (π and σ) between the anionic cyanamide NCN group and the phenyl ring as exemplified by the HOMO and SHOMO. Thus, both of the occupied molecular orbitals serve as continuous and energetically favorable π systems that span the entire 1,4-dicyanamidobenzene dianion ligand.

Figure 3.3 Frontier orbitals of Dicyd²⁻ from EHMO calculations. Minor orbital contributions are omitted for clarity. [Reproduced with permission from Ref. 43. Copyright (1992) American Chemical Society.]

The energetic ordering of the molecular orbitals (especially the HOMO and SHOMO) among the four dianion ligands, really goes hand in hand with the electrochemical results (refer to Section 3.2.4). For example, the most readily oxidizable dianion ligand is 2,5-Me₂Dicyd²⁻ and indeed it possesses the highest energy HOMO. The trend continues with Dicyd²⁻ followed by 2,5-Cl₂Dicyd²⁻ but breaks down on going to 2,3,4,5-Cl₄Dicyd²⁻. In general, the results simply verify the fact that as electron-withdrawing substituents are added to the phenyl ring, the ligand molecular orbitals become more stable. The effect is most dramatic on the energy of the HOMO as supported by the fact that the difference in energy between the HOMO and SHOMO (ΔE in Table 3.5) is the smallest for 2,3,4,5-Cl₄Dicyd²⁻ and the largest for 2,5-Me₂Dicyd²⁻, keeping in mind that the energy of the SHOMO stays relatively constant for all four dianion ligands. Clearly, the trend in π donor ability of the four dianion ligands would be expected to parallel these results.

To gain further insight into the π donor properties of 1,4-dicyanamidobenzene dianion ligands, the net effective charge of the anionic cyanamide NCN group was determined by summing up the individual atomic contributions of the amide N and C and nitrile N. The results are summarized in Table 3.6.

Table 3.6 Effective Charges on the Cyanamide Groups of the 1,4-Dicyanamidobenzene Dianion Ligands.

Ligands	Eff. NCN
^a 2,5-Me ₂ Dicyd ²⁻	-1.19
Dicyd ²⁻	-1.17
2,5-Cl ₂ Dicyd ²⁻	-1.16
2,3,4,5-Cl ₄ Dicyd ²⁻	-1.11

^aFrom reference 94.

The trend in the NCN effective charge is to decrease as the electron withdrawing nature of the phenyl ring increases. The result is quite predictable given the prior knowledge of the nature of the HOMO in that coupling of the phenyl ring π system into that of the NCN groups π system does indeed occur. Again the results of Table 3.6 support the forgone conclusion that with a larger proportion of effective π electron density associated with its NCN group, 2,5-Me₂Dicyd²⁻ is the strongest π donor.

CHAPTER 4

Mononuclear Pentaammineruthenium(III) and (IV) Complexes

4.1 Pentammineruthenium(III) Complexes of 1,4-Dicyanamidobenzene Monoanion and Dianion Ligands

The mononuclear pentaammineruthenium(III) complexes of the 1,4-dicyanamidobenzene monoanion ligands ($[(\text{NH}_3)_5\text{Ru}(\text{LH})]^{2+}$: where $\text{LH} = 2,5\text{-Me}_2\text{DicydH}^-$, DicydH^- and $2,5\text{-Cl}_2\text{DicydH}^-$) have been synthesized and characterized by IR and electronic absorption spectroscopies as well as cyclic voltammetry. However, their singly deprotonated counterparts ($[(\text{NH}_3)_5\text{Ru}(\text{L})]^+$) cannot be isolated in an analytically pure form due to their tendency to revert back to the monoanion bound form in the presence of trace water or any other potential source of H^+ . Indeed the interconversion between monoanion and dianion bound forms is reversible in aqueous solution as confirmed by UV-vis-NIR spectroscopy (refer to Section 4.1.3). As a result, characterization results (ie. electronic absorption spectroscopy and cyclic voltammetry) of the dianion bound complexes will be based on solution behavior under basic conditions. Comparisons will be drawn with solution behaviour of the monoanion bound complexes under acidic conditions. In this regard, an assessment of the changes in the electronic properties of both systems, brought on by the inner-sphere perturbation of deprotonation, will be made. Note that in the future, analogous studies in non-aqueous solution will be conducted.

4.1.1 Synthesis

The generalized synthesis of the three $[(\text{NH}_3)_5\text{Ru}(\text{LH})]^{2+}$ complexes is outlined in Scheme 4.1. To initiate the synthetic pathway, the appropriate 1,4-dicyanamidobenzene neutral ligand was reacted with $[(\text{NH}_3)_5\text{Ru}(\text{OH}_2)][\text{PF}_6]_2$ in acetone in an approximate 1.5:1 molar

ratio. The reaction was conducted in the open to accommodate air oxidation of Ru(II) to Ru(III), a process that is accompanied by the deprotonation of the neutral cyanamide ligand. Trace HClO_4 was added to ensure that the dominant product of reaction would indeed be the monoanion bound complex. Isolation of a crude bromide salt (**A**) was followed by its purification via cation-exchange (ie. carboxymethyl Sephadex resin) chromatography. Final purification of (**A**) via a series of metathetic conversions (ie. $\text{Ph}_4\text{B}^- \rightarrow \text{Br}^- \rightarrow \text{ClO}_4^-$) is followed by recrystallization, typically as a ClO_4^- salt (**B**) by diffusing diethyl ether into an acetone or acetone/water solution of the complex.

where $\text{LH}_2 = 2,5\text{-Me}_2\text{DicydH}_2$; DicydH_2 ;
 $2,5\text{-Cl}_2\text{DicydH}_2$

Scheme 4.1

In all three complex preparations, molecules of solvation including acetone and water are present in the analytically pure product. Removal of them was not always possible owing to the observation that the complexes could only be vacuum dried at room temperature as elevated temperatures resulted in their thermal decomposition.

Typical yields for $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{DicydH})][\text{ClO}_4]_2$ and $[(\text{NH}_3)_5\text{Ru}(\text{DicydH})][\text{ClO}_4]_2$ were approximately 20%, whereas, a lower yield of approximately 10% was the case for

$[(\text{NH}_3)_5\text{Ru}(2,5\text{-Cl}_2\text{DicydH})][\text{ClO}_4]_2$. Three main reasons accounted for the low yields: 1) more than one product was formed during the course of the reaction; 2) $[(\text{NH}_3)_5\text{Ru}(\text{OH}_2)][\text{PF}_6]_2$ did not completely react; 3) crude material was lost due to its precipitation as a Cl^- salt onto the cation-exchange resin, especially in the case of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Cl}_2\text{DicydH})]^{2+}$, where higher concentrations of electrolyte (ie. NaCl) solution were required to effect elution.

Notable exceptions to the generalized reaction scheme included performing the cation-exchange purification and recrystallization of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{DicydH})][\text{ClO}_4]_2$ at lowered temperatures to prevent thermal decomposition. In the preparation of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Cl}_2\text{DicydH})][\text{ClO}_4]_2$, MPD was used as the reaction solvent due to the low solubility of the $2,5\text{-Cl}_2\text{DicydH}_2$ neutral ligand in acetone. As well, reactant solutions were initially degassed as a means of preventing the oxidation of the $2,5\text{-Cl}_2\text{Dicyd}^{2-}$ dianion ligand to its monoanion radical form, a process that is more facile in strongly donating aprotic solvents (refer to Section 3.1.1, recall that neutral cyanamide ligands are in equilibrium with their anionic counterparts in strongly donating or basic solvents). Furthermore, cation-exchange purification of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Cl}_2\text{DicydH})]^{2+}$ was performed using the more acidic sulfopropyl sephadex resin. Finally, the desired perchlorate salt of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Cl}_2\text{DicydH})]^{2+}$ was obtained via only one metathetic conversion from a chloride salt after cation-exchange purification.

With regards to the cation-exchange column chromatography purification of the $[(\text{NH}_3)_5\text{Ru}(\text{LH})]^{2+}$ complexes, the following describes the results in more detail. To state the obvious, cation species of lower charge are eluted first and it requires higher concentrations of NaCl solution to elute higher charged cation species. In general, the order of column bands for the three complexes under study were as follows: 1) a yellow band that is believed to be unreacted $[(\text{NH}_3)_5\text{Ru}(\text{OH}_2)]^{2+}$; 2) the desired blue product band having a charge of +2; 3) a green band characterized by UV-vis-NIR spectroscopy to be a

dinuclear pentaammineruthenium ($[\text{Ru(III)}, \text{Ru(III)}]$) complex of a 1,4-dicyanamidobenzene dianion ligand, having a charge of +4 (refer to Section 5.1.5). An additional purple band, proceeding the desired mononuclear complex blue band but preceding the dinuclear complex green band, was observed during the purification of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{DicydH})]^{2+}$. A UV-vis-NIR measurement confirmed the purple species to be a $(\text{NH}_3)_5\text{Ru(IV)}$ complex of $2,5\text{-Me}_2\text{Dicyd}^{2-}$ (refer to Section 4.2.3). As a final note, there is no chromatographic evidence for the presence of the dianion bound complexes during the cation-exchange purification of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{DicydH})]^{2+}$ or $[(\text{NH}_3)_5\text{Ru}(\text{DicydH})]^{2+}$ when the neutral conditions of carboxymethyl Sephadex resin/NaCl solution ($\text{pH} = 6.5$) are employed. However, this is not the case during the cation-exchange purification of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Cl}_2\text{DicydH})]^{2+}$ under the same conditions, where the gradual transformation to $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Cl}_2\text{Dicyd})]^+$ (blue band turns green) is observed on the column. Indeed as already eluded to, the cation-exchange purification of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Cl}_2\text{DicydH})]^{2+}$ ($\text{pK}_a = 5.75$ which is the lowest of the three complexes, refer to Section 4.1.4) must be performed under the more acidic conditions of sulfopropyl sephadex resin/NaCl solution ($\text{pH} = 5.0$) to prevent deprotonation.

In terms of solubility properties, the $[(\text{NH}_3)_5\text{Ru}(\text{LH})]^{2+}$ complexes were soluble in water as perchlorate salts but only slightly soluble in common aprotic solvents such as acetone, acetonitrile and DMSO. However, addition of trace amounts of water improved solubility dramatically. All three complexes were stable for an indefinite period of time if stored in the freezer at $-18\text{ }^\circ\text{C}$.

4.1.2 Infrared Spectroscopy

The infrared spectrum of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{DicydH})][\text{ClO}_4]_2$ is shown in Figure 4.1 while the results of all three $[(\text{NH}_3)_5\text{Ru}(\text{LH})]^{2+}$ complexes are summarized in Table 4.1. In all of the cases, the characteristic cyanamide $\nu(\text{N}=\text{C}=\text{N})$ stretch is evident in the 2100-

2130 cm^{-1} range. The fact that coordination shifts the cyanamide stretch to higher energies by 10-30 cm^{-1} compared to the free ligand values (refer to Table 3.3) can be accounted for by invoking an inductive effect between Ru(III) and the cyanamide nitrile group. Other diagnostic vibrations associated with cyanamide ligand include the nitrile $\nu(\text{N}\equiv\text{C})$ stretch near 2220 cm^{-1} indicative of an uncoordinated neutral cyanamide group and the aromatic $\nu(\text{C}=\text{C})$ stretch in the 1500-1510 cm^{-1} range. The presence of ammine (NH_3) groups in the inner coordination sphere of Ru(III) is also verified in the infrared spectra of the complexes. Based on reported values for mononuclear hexaammineruthenium(III) complexes,⁹⁵ the ammine vibrational modes present include the $\nu(\text{N-H})$ stretch in the 3250-3350 cm^{-1} range and the $\delta(\text{N-H})$ degenerate deformation or bend in the 1600-1635 cm^{-1} range. Finally, the presence of the perchlorate counter anion which is common to all three complexes, is verified by a $\nu(\text{Cl-O})$ stretch in the 1100-1120 cm^{-1} range, consistent with previously reported results for ionic perchlorate complexes.⁹⁶

Figure 4.1 Infrared spectrum of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{DicydH})][\text{ClO}_4]_2$ (KBr disc).

Table 4.1 Infrared Spectral Data for the Mononuclear Pentaammine-ruthenium(III) Complexes of 1,4-Dicyanamidobenzene Monoanion Ligands (in cm^{-1}).^a

Complexes ^b	$\nu(\text{N}=\text{C}=\text{N})$	$\nu(\text{N}=\text{C})$	$\nu(\text{C}=\text{C})$	$\nu(\text{N}-\text{H})$	$\delta(\text{N}-\text{H})$	$\nu(\text{Cl}-\text{O})$
2,5-Me ₂ DicydH ⁻	2104(s)	2220(m)	1508(m)	3324,3266(vs)	1610(m)	1101(vs)
DicydH ⁻	2105(s)	2216(m)	1504(m)	3332,3266(vs)	1627(m)	1104(vs)
2,5-Cl ₂ DicydH ⁻	2129(s)	2220(m)	1501(m)	3280(vs)	1632(m)	1116(vs)

^aKBr disc; band intensities: vs=very strong, s=strong, m=medium, w=weak. ^bonly ligands shown for clarity.

4.1.3 Electronic Absorption Spectroscopy

The UV-vis-NIR (ie. 310-1300 nm) absorption spectrum of $[(\text{NH}_3)_5\text{Ru}(\text{DicydH})][\text{ClO}_4]_2$ in aqueous solution (at pH = 4.41) and its singly deprotonated counterpart, namely $[(\text{NH}_3)_5\text{Ru}(\text{Dicyd})]^+$ (at pH = 10.86), is shown in Figure 4.2 while the results of all three $[(\text{NH}_3)_5\text{Ru}(\text{LH})]^{2+}$ complexes and their dianion counterparts are summarized in Table 4.2. The characteristic spectral assignments are based on previous spectroscopic studies of mononuclear pentaammineruthenium(III) complexes of anionic phenylcyanamide ligands in which the microsymmetry was assigned to be C_{2v} .^{46,86} The following discussion summarizes those results and shows how they can be extended towards the system at hand.

Figure 4.2 UV-vis-NIR absorption spectra of $[(\text{NH}_3)_5\text{Ru}(\text{DicydH})]^{2+}$ at pH 4.41 (dashed line), and $[(\text{NH}_3)_5\text{Ru}(\text{Dicyd})]^+$ at pH 10.86 (solid line), both with a concentration of 6.464×10^{-5} (ionic strength = 0.625 M NaClO_4).

As previously mentioned, the anionic cyanamide group is a resonance stabilized π system ($\text{Ph-N}^-\text{C}=\text{N} \leftrightarrow \text{Ph-N}=\text{C}=\text{N}^-$), which when coordinated to Ru(III) should shift the resonance equilibrium towards the $\text{Ph-N}=\text{C}=\text{N}^-$ resonance form. There are two pairs of π symmetry nonbonding electrons that can delocalize into the this three-atom π system resulting in two orthogonal molecular orbitals, $\pi_{\text{nb}1}$ and $\pi_{\text{nb}2}$, shown below in which atomic orbital size approximates the magnitude of the electron density.

Figure 4.3 Nonbonding π orbitals of the anionic phenylcyanamide ligand (pcyd^-) from EHMO calculations. The phenyl ring is in the xy plane. Minor orbital contributions are omitted for clarity. [Reproduced with permission from Ref. 97. Copyright (1994)]

Note that $\pi_{\text{nb}1}$ and $\pi_{\text{nb}2}$ are nondegenerate in energy ($\pi_{\text{nb}2}$ is more stable) because only $\pi_{\text{nb}2}$ can delocalize into the phenyl ring in a σ fashion. The result has been confirmed by EHMO calculations on the phenylcyanamide anion which indeed showed that $\pi_{\text{nb}2}$ is the SHOMO ($\pi_{\text{nb}2}$ is 0.49 eV more stable than the $\pi_{\text{nb}1}$).⁹⁷ The π interaction between these two ligand centered molecular orbitals and the $d\pi^*$ orbitals of Ru(III), which is a strong π acid, gives rise to two ligand to metal charge-transfer (LMCT) transitions in the visible region of the complex's electronic absorption spectrum.

With regard to the $[(\text{NH}_3)_5\text{Ru}(\text{LH})]^{2+}$ and $[(\text{NH}_3)_5\text{Ru}(\text{L})]^+$ complexes, the lower energy LMCT band has been assigned to an allowed $b_1^* \leftarrow b_1$ ($d\pi^* \leftarrow \pi_1$) transition while the higher energy LMCT band has been assigned to a symmetry forbidden $b_1^* \leftarrow b_2$ ($d\pi^* \leftarrow \pi_2$) transition. With reference to Table 4.2, for the monoanion bound complex, the $b_1^* \leftarrow b_1$ LMCT transition varies from 771 nm for $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{DicydH})]^{2+}$ to 680 nm for $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Cl}_2\text{DicydH})]^{2+}$. For the dianion bound complex, the same transition varies from 926 nm for $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})]^+$ to 834 nm for $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Cl}_2\text{Dicyd})]^+$. The $b_1^* \leftarrow b_2$ LMCT transition occurs in the 371-376 nm range for all three monoanion bound complexes, while for the dianion bound complexes, the range is from 367 nm for $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})]^+$ to 332 nm for $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Cl}_2\text{Dicyd})]^+$. Owing to the fact that the $b_1^* \leftarrow b_1$ LMCT band unlike the $b_1^* \leftarrow b_2$ LMCT band, is completely separated from any other absorption, its oscillator strength f can be determined experimentally,⁹⁸ assuming Gaussian band shape, by: $f = (4.61 \times 10^{-9})\epsilon_{\text{max}}\Delta\nu_{1/2}$, where ϵ_{max} is the extinction coefficient at maximum band wavelength and $\Delta\nu_{1/2}$ is the bandwidth at half ϵ_{max} . For the monoanion bound complexes, the oscillator strengths range from 0.189 for $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{DicydH})]^{2+}$ to 0.137 for $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Cl}_2\text{DicydH})]^{2+}$, while for the dianion bound complexes, the range is from 0.215 for $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})]^+$ to 0.155 for $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Cl}_2\text{Dicyd})]^+$. With regard to the UV region of the electronic absorption spectra of the complexes at hand, no formal spectral assignments have been made. However, based on previous studies of pentaammineruthenium(III) complexes of anionic phenylcyanamide ligands, the bands present are believed to be the result of ligand centered $\pi^* \leftarrow \pi$ transitions.⁴⁶

Unlike the majority of pentaammineruthenium(III) complexes of anionic phenylcyanamide ligands, the spectra of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})]^+$ and $[(\text{NH}_3)_5\text{Ru}(\text{Dicyd})]^+$ show splitting of both the low and high energy LMCT bands. Since these LMCT transitions are singly degenerate, such splitting could be regarded as evidence for a conformer equilibrium

in solution. The equilibrium could be made up of the bent and linear Ru(III) coordination conformers found in the X-ray structure of the dinuclear complex, $[\mu\text{-(Dicyd)}\text{-(NH}_3)_5\text{Ru}]_2[\text{OTs}]_4$ (refer to Section 5.1.3). However the equilibrium is more likely the result of syn and anti in-plane and out-of-plane dianion ligand conformations, as the uncoordinated cyanamide group is free to rotate (refer to Section 3.2.5). Of course, vibrational splitting is also a possibility.

Table 4.2 Electronic Absorption Spectral Data for the Mononuclear Pentaammineruthenium(III) Complexes of 1,4-Dicyanamidobenzene Monoanion and Dianion Ligands.^a

Complexes ^b	LMCT	
	$b_1^* \leftarrow b_2$	$b_1^* \leftarrow b_1$
^c 2,5-Me ₂ DicydH ⁻	371 (3.46)	771 (3.81) [0.189]
^d 2,5-Me ₂ Dicyd ²⁻	367 (3.65), 410 (sh)	926 (3.94) [0.215]
^e DicydH ⁻	376 (3.44)	723 (3.76) [0.144]
^f Dicyd ²⁻	355 (3.60), 399 (sh)	952 (3.84) [0.169]
^g 2,5-Cl ₂ DicydH ⁻	371 (3.47)	680 (3.75) [0.137]
^h 2,5-Cl ₂ Dicyd ²⁻	332 (3.81), 401 (3.50)	834 (3.79) [0.155]

^aAll data are recorded in aqueous solution (ionic strength=0.625M NaClO₄) and are in nm (log ϵ in parentheses and oscillator strength, calculated from $f = 4.61 \times 10^{-9} \epsilon_{\text{max}} \Delta\nu_{1/2}$, in brackets); sh=shoulder.

^bonly ligands shown for clarity. ^cconcentration= 6.563×10^{-5} M; pH=5.13. ^dpH=9.48. ^econcentration= 6.464×10^{-5} M; pH=4.41. ^fpH=10.86. ^gconcentration= 6.391×10^{-5} M; pH=3.06. ^hpH=9.41.

A comparison of the lower energy $b_1^* \leftarrow b_1$ LMCT bands for both the monoanion and dianion bound complexes of Table 4.2 reveals a trend of increasing LMCT optical energy E_{op} and decreasing oscillator strength as the electron-withdrawing nature of the phenyl ring increases. The trend is explained by considering that while both ligand and metal π orbitals are stabilized (refer to redox results in Section 4.1.5) as electron-withdrawing substituents are added to the phenyl ring, the ligand orbital is stabilized to a

greater extent. Clearly in terms of π basicity, 2,5-Cl₂DicydH⁻ and 2,5-Cl₂Dicyd²⁻ are the weakest donors while 2,5-Me₂DicydH⁻ and 2,5-Me₂Dicyd²⁻ are the strongest donors. To explain further, the placement of electron donor or withdrawing substituents on the phenyl ring "tunes" the σ and π basicity of an anionic cyanamide ligand. However, the degree of π basicity and hence π bonding with Ru(III) is very sensitive to the electron density coefficient of the terminal cyanamide nitrogen of the ligand's π_1 MO. Electron-withdrawing substituents on the phenyl ring would shift electron density away from the terminal nitrogen, reducing its contribution to the π_1 . The end result would be a reduction in the effective overlap with the b_1 ($d\pi^*$) orbital of Ru(III). Indeed, for both monoanion and dianion bound complexes, the trend in the $b_1^* \leftarrow b_1$ LMCT oscillator strength is to decrease with the increasing electron-withdrawing nature of the phenyl ring. From theory,⁹⁸ the oscillator strength f is proportional to the overlap integral between donor and acceptor orbitals S and the transition dipole length R which can be approximated to be the separation between donor and acceptor wave functions in Å. Note that for the ruthenium-cyanamide $b_1^* \leftarrow b_1$ LMCT chromophore, S can be expressed as a π overlap integral:^{46,47} $S_\pi = C(N)S_1$ where $C(N)$ is the electron density coefficient of the terminal cyanamide nitrogen that contributes to the π_{nb} MO of the cyanamide group and S_1 is the optimum π overlap that can occur between anion nitrogen $2p$ and Ru(III) $4d$ orbitals at a given separation. Previous studies of a series of pentaammineruthenium(III) complexes of anionic phenylcyanamide ligands have shown that the $b_1^* \leftarrow b_1$ LMCT oscillator strength decreases as the π donor ability of the cyanamide ligand decreases even though the transition dipole length increases.⁴⁶ In this situation, it was concluded that the degree of π orbital overlap and not the transition dipole length, is the dominant factor in accounting for the trend in the LMCT oscillator strength.

To account for the decreased optical energy and increased oscillator strength of the $b_1^* \leftarrow b_1$ LMCT transition upon deprotonation of the $[(\text{NH}_3)_5\text{Ru}(\text{LH})]^{2+}$ complexes to form their

dianion bound counterparts, an increase in the latter's HOMO energy (destabilization) must be invoked. This is illustrated qualitatively in the molecular orbital energy level diagram of Figure 4.4, where (a) represents the π interaction between π_1 of a 1,4-dicyanamidobenzene monoanion ligand and the b_1 ($d\pi^*$) orbital of Ru(III) while in (b) a similar interaction involving the higher energy π_1 level of a 1,4-dicyanamidobenzene dianion ligand is shown.

Figure 4.4 Qualitative MO energy level diagram showing the relative energies of the $b_1^* \leftarrow b_1$ ($d\pi^* \leftarrow \pi_1$) LMCT transition for the (a) $[(\text{NH}_3)_5\text{Ru}(\text{LH})]^{2+}$ and (b) $[(\text{NH}_3)_5\text{Ru}(\text{L})]^+$ complexes.

The increase in LMCT oscillator strength upon deprotonation can be accounted for by an increasing π orbital overlap between donor and acceptor as measured by the π overlap integral (note that the manner in which the transition dipole length effects the $b_1^* \leftarrow b_1$ LMCT oscillator strength upon deprotonation is not known). To elaborate, the increased energy of the dianion π_1 orbital with respect to that of the monoanion increases the π electron density (ie. a more diffuse π orbital nature) around the terminal cyanamide nitrogen (note that this behavior is analogous to when the electron-donating nature of the phenyl ring

system is increased). The implication is a greater effective π overlap between π_1 of the dianion and the b_1 ($d\pi^*$) orbital of Ru(III). Indeed, Figure 4.4 shows that the energy match between donor and acceptor becomes more favourable upon deprotonation. In essence, the covalent character of the Ru(III)-cyanamide charge transfer state is increased as reflected by the greater energy separation between the b_1 MO and the ligand's π_1 HOMO for the $[(\text{NH}_3)_5\text{Ru}(\text{L})]^+$ complexes.

4.1.4 pKa Determination

The pKa of all three $[(\text{NH}_3)_5\text{Ru}(\text{LH})]^{2+}$ complexes has been determined in aqueous solution by monitoring the absorbance changes (of λ_{max}) associated with the disappearance of the $b_1^* \leftarrow b_1$ LMCT transition over a pH range of 3.0 to 10.0. The concomitant appearance of the $b_1^* \leftarrow b_1$ LMCT transition characteristic of the dianion bound complex was accompanied by the formation of a single tight isosbestic point in all cases, indicating the reversibility of the deprotonation process. S-shaped pH curves (pH versus absorbance) were plotted from which the pKa values were interpolated (refer to Table 4.3).

Table 4.3 pKa Data for the Mononuclear Pentaammineruthenium(III) Complexes of 1,4-Dicyanamidobenzene Monoanion Ligands.^a

Complexes	pKa
$[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{DicydH}^-/2,5\text{-Me}_2\text{Dicyd}^{2-})]^{2+/+}$	7.00
$[(\text{NH}_3)_5\text{Ru}(\text{DicydH}^-/\text{Dicyd}^{2-})]^{2+/+}$	6.85
$[(\text{NH}_3)_5\text{Ru}(2,5\text{-Cl}_2\text{DicydH}^-/2,5\text{-Cl}_2\text{Dicyd}^{2-})]^{2+/+}$	5.60

^aVolumetric solutions (ionic strength = 0.625 M NaClO_4) containing the appropriate concentrations of HClO_4 and NaOH were used to obtain the desired pH.

The results indicate that $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Cl}_2\text{DicydH})]^{2+}$ is the most readily deprotonated to form its dianion bound counterpart while $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{DicydH})]^{2+}$ is the most difficult to deprotonate. Clearly the amine proton of the former complex is the most acidic,

a property that can be accounted for by inductive arguments. As previously detailed, the phenyl ring system is both π and σ coupled into the cyanamide NCN group. The presence of electron-withdrawing groups on the phenyl ring would inductively draw electron density away from the NCN group, and in particular the amine nitrogen, thus increasing the acidity of the amine proton. The opposite is true for $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{DicydH})]^{2+}$ whose amine proton is the least acidic.

4.1.5 Cyclic Voltammetry

The cyclic voltammogram of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{DicydH})][\text{ClO}_4]_2$ in aqueous solution (at pH = 5.09) and its singly deprotonated counterpart, namely $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})]^+$ (at pH = 9.48), are shown in Figures 4.5 and 4.6, respectively, while the results of all three $[(\text{NH}_3)_5\text{Ru}(\text{LH})]^{2+}$ complexes and their dianion counterparts are summarized in Table 4.4. The cyclic voltammetry of the monoanion bound complexes under acidic conditions are characterized by one-electron Ru(III/II) reduction couples that are quasi-reversible at best, denoted by $E^\circ_{\text{M}(\text{H}^+)}$, as shown by Eq. a) of Scheme 4.2.

Scheme 4.2

The half-wave potential values vary from 0.009 V vs. NHE for $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{DicydH})]^{2+}$ to 0.152 V vs. NHE for $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Cl}_2\text{DicydH})]^{2+}$ with peak to peak ($E_{\text{pa}}-E_{\text{pc}}$) separations >100 mV at 100 mVs^{-1} that increase with scan rate. The oxidation processes of the $[(\text{NH}_3)_5\text{Ru}(\text{LH})]^{2+}$ complexes under acidic conditions were not studied in detail as the predicted ligand centered oxidations are either not present or irreversible under normal scan rate conditions of 100 mVs^{-1} .

The cyclic voltammetry of the dianion bound complexes are characterized by quasi-reversible one-electron Ru(III/II) reduction couples, denoted by $E^\circ_{\text{M}(\text{OH}^-)}$, as shown by Eq. b) of Scheme 4.2. The half-wave potential values vary from -0.091 V vs. NHE for $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})]^+$ to -0.026 V vs. NHE for $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Cl}_2\text{Dicyd})]^+$ with peak to peak separations >60 mV at 100 mVs^{-1} that increase with scan rate. The redox chemistry of the $[(\text{NH}_3)_5\text{Ru}(\text{L})]^+$ complexes is also characterized by two one-electron oxidation processes as shown by Eq. c) of Scheme 4.2, the first of which is the metal-centered Ru(III/IV) oxidation couple, denoted by $E^\circ_{\text{oxid}_1}$. The product of the second oxidation process, denoted by $E^\circ_{\text{oxid}_2}$, is not known for certain but is believed to be either a pentaammineruthenium(IV) complex of the monoanion radical ligand or a pentaammineruthenium(III) complex of the neutral fully oxidized ligand (refer to Section 3.2.4, dianion ligand-centered oxidations). For $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})]^+$, both $E^\circ_{\text{oxid}_1}$ and $E^\circ_{\text{oxid}_2}$ are quasi-reversible couples having half-wave potential values of 0.323 V and 0.723 V vs. NHE, respectively, and both with peak to peak separations >60 mV at 100 mVs^{-1} that increase with scan rate. For $[(\text{NH}_3)_5\text{Ru}(\text{Dicyd})]^+$ and $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Cl}_2\text{Dicyd})]^+$, both ligand centered oxidation couples are quasi-reversible at best (refer to Table 4.4 for the half-wave potential values), having peak to peak separations >85 mV at 100 mVs^{-1} that increase with scan rate.

Figure 4.5 Cyclic voltammogram of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{DicydH})][\text{ClO}_4]_2$ in water (0.1 M NaCl) at a pH = 5.09; negative direction at a scan rate of 100 mVs^{-1} .

Table 4.4 Redox Potentials for the Mononuclear Pentaammine-ruthenium(III) Complexes of 1,4-Dicyanamidobenzene Monoanion and Dianion Ligands.^a

Complexes ^b	$E^\circ_{\text{M}(\text{H}^+)}$	$E^\circ_{\text{M}(\text{OH}^-)}$	$E^\circ_{\text{oxid}_1}$	$E^\circ_{\text{oxid}_2}$
^c 2,5-Me ₂ DicydH ⁻	0.009 (123)	---	---	---
^d 2,5-Me ₂ Dicyd ²⁻	---	-0.091 (65)	0.323 (72)	0.723 (62)
^e DicydH ⁻	0.030 (125)	---	---	---
^f Dicyd ²⁻	---	-0.079 (82)	0.415 (85)	0.827 (90)
^g 2,5-Cl ₂ DicydH ⁻	0.152 (100)	---	---	---
^h 2,5-Cl ₂ Dicyd ²⁻	---	-0.026 (60)	0.540 (120)	0.937 (90)

^aCouples are reported in volts vs. NHE (scan rate of 100 mVs^{-1}) with the numbers in parenthesis referring to $E_{\text{pa}}-E_{\text{pc}}$ in mV at a scan rate of 100 mVs^{-1} ; all data are recorded in aqueous solution (ionic strength=0.1 M NaCl) at 25° C containing the appropriate concentrations of HClO₄ and NaOH to obtain the desired pH.

^bonly ligands shown for clarity. ^cpH=5.09. ^dpH=9.48. ^epH=4.45. ^fpH=10.75. ^gpH=3.03. ^hpH=9.48.

Figure 4.6 Cyclic voltammogram of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})]^+$ in water (0.1 M NaCl) at a pH = 9.48. (a) negative direction at a scan rate of 100 mVs^{-1} . (b) positive direction at a scan rate of 100 mVs^{-1} .

With reference to Table 4.4, for the dianion bound complexes, the trend in the Ru(III/IV) oxidation potentials shows that $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})]^+$ is the most readily oxidized and that $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Cl}_2\text{Dicyd})]^+$ is the most difficult to oxidize. The result is readily attributable to the substituent effect of electron donating methyl groups as opposed to electron withdrawing chloro groups.

The act of deprotonating the $[(\text{NH}_3)_5\text{Ru}(\text{LH})]^{2+}$ complexes shifts the Ru(III/II) reduction potential in a negative direction. Since Ru(III) is a π acid, its oxidation state should be stabilized by strong π donor ligands thereby suggesting that the 1,4-dicyanamidobenzene dianion ligands are stronger π donors than their monoanion counterparts. This conclusion is paralleled by that drawn from a comparison of spectral results (E_{op} and the oscillator strength of the $b_1^* \leftarrow b_1$ LMCT transition) between the $[(\text{NH}_3)_5\text{Ru}(\text{LH})]^{2+}$ and $[(\text{NH}_3)_5\text{Ru}(\text{L})]^+$ complexes (refer to Section 4.1.3). Finally, the trend in the Ru(III/II) reduction potentials for both the monoanion and dianion bound complexes is analogous to that observed in a previous study of a series of pentaammineruthenium(III) complexes of anionic phenylcyanamide ligands, where the π donor strength of cyanamide ligand was varied.⁴⁶ Again the trend can be readily rationalized by recognizing that the Ru(III) oxidation state will be increasingly stabilized by stronger π donor ligands. Indeed the complexes containing the strongest π donor ligands, namely $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{DicydH})]^{2+}$ and $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})]^+$, demonstrate the most negative Ru(III/II) reduction potentials while the opposite is true for $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Cl}_2\text{DicydH})]^{2+}$ and $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Cl}_2\text{Dicyd})]^+$.

4.2 Pentaammineruthenium(IV) Complexes of 1,4-Dicyanamidobenzene Dianion Ligands

The mononuclear pentaammineruthenium(IV) complex of the $2,5\text{-Me}_2\text{Dicyd}^{2-}$ dianion ligand ($[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})]^{2+}$) has been synthesized via the chemical oxidation of

$[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{DicydH})]^{2+}$. The Ru(IV) complex has been characterized by IR, ^1H NMR and electronic absorption spectroscopies as well as cyclic voltammetry and solution magnetic susceptibility measurements. In addition, spectroelectrochemical studies in acetonitrile have shown that the reduction of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})]^{2+}$ forms a mixture of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})]^+$ and $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{DicydH})]^{2+}$ in a reversible one-electron ($n = 0.94 \text{ eq mole}^{-1}$) process. The ^1H NMR results in particular, provide strong support for what has been designated as the diamagnetic pentaammineruthenium(IV) complex of the $2,5\text{-Me}_2\text{Dicyd}^{2-}$ dianion ligand, thereby, helping resolve the debate as to the true nature of the chemical oxidation product of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{DicydH})]^{2+}$. Note that the pentaammineruthenium(IV) complexes of Dicyd^{2-} and $2,5\text{-Cl}_2\text{Dicyd}^{2-}$ can be generated in solution, but isolation of analytically pure solids has not been possible owing to their tendency to revert back to the reduced pentaammineruthenium(III) complex of the respective 1,4-dicyanamidobenzene monoanion ligand. Future studies will focus on the generation of these complexes by spectroelectrochemical methods.

4.2.1 Synthesis

The synthesis of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})]^{2+}$ is outlined in Scheme 4.3. The reaction is quite straight forward involving the direct chemical oxidation of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{DicydH})]^{2+}$ in acetone, with a slight excess of NOBF_4 (note that the analogous chemical oxidation of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{DicydH})]^{2+}$ could also be afforded in aqueous solution using $[(\text{NH}_4)_2\text{Ce}][\text{SO}_4]_3$). The oxidized product is precipitated out of solution as a crude tetrafluoroborate salt (A) by the addition of diethyl ether. Purification of (A) via a series of metathetic conversions (ie. $\text{BF}_4^- \rightarrow \text{Br}^- \rightarrow \text{Cl}^- \rightarrow \text{PF}_6^-$) is followed by recrystallization, typically as a PF_6^- salt (B) by diffusing diethyl ether into an acetone solution of the complex.

Scheme 4.3

As previously mentioned, the pentaammineruthenium(IV) complexes of Dicyd²⁻ and 2,5-Cl₂Dicyd²⁻ could be generated in acetone solution as verified by UV-vis-NIR spectroscopy, but their isolation as analytically pure solids was precluded by their tendency to be reduced and protonated in the presence of trace amounts of water. However, $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})][\text{PF}_6]_2$ could be isolated as an analytically pure solid in typical yields of approximately 20%. The relatively low yields can be largely attributed to incomplete oxidation of the pentaammineruthenium(III) precursor complex. Note that the successful removal of unoxidized $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{DicydH})]^{2+}$ is achieved via a $\text{Br}^- \rightarrow \text{Cl}^-$ conversion, taking advantage of the greater solubility of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{DicydH})][\text{Cl}]_2$ in aqueous solution compared to $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})][\text{Cl}]_2$.

As a final note, the hexafluorophosphate salt of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})]^{2+}$ was very soluble in common aprotic solvents such as acetone, acetonitrile and DMSO. The complex was stable for an indefinite period of time if stored in the freezer at -18 °C.

4.2.2 Infrared Spectroscopy

The infrared spectrum of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})][\text{PF}_6]_2$ is shown in Figure 4.7 (note that the sample was a KBr disc). The $\nu(\text{N}=\text{C}=\text{N})$ stretch of the Ru(IV)-coordinated anionic cyanamide group occurs as a strongly intense band at 2102 cm^{-1} . In addition, the presence of ammine (NH_3) groups in the inner coordination sphere of Ru(IV) is also evident with the occurrence of a strong $\nu(\text{N-H})$ stretching band in the $3290\text{-}3380\text{ cm}^{-1}$ range and a $\delta(\text{N-H})$ degenerate deformation band, also of strong intensity, at 1609 cm^{-1} . Finally, the presence of the hexafluorophosphate counter anion is verified by a very strong $\nu(\text{P-F})$ stretching band at 841 cm^{-1} .⁹⁹

Figure 4.7 Infrared spectrum of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})][\text{PF}_6]_2$ (KBr disc).

4.2.3 Electronic Absorption Spectroscopy

The UV-vis-NIR (ie. 310-1300 nm) absorption spectrum of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})][\text{PF}_6]_2$ in aqueous solution (at neutral pH) is shown in Figure 4.8. Also shown at the same concentration, is the UV-vis-NIR spectrum of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})]^+$ in aqueous solution at a pH = 9.48 (from Section 4.1.3, fully deprotonated product of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{DicydH})][\text{ClO}_4]_2$). The presence of the characteristic low and high energy LMCT transitions associated with the dianion bound pentaammineruthenium(III) complex are also evident in the spectrum of the dianion bound pentaammineruthenium(IV) complex, however, the band energies and extinction coefficients are markedly different. The data of Table 4.5 summarizes this point.

Figure 4.8 UV-vis-NIR absorption spectra of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})]^{2+}$ at neutral pH (solid line), and $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})]^+$ at pH=9.48 (dashed line), both with a concentration of 6.563×10^{-5} (ionic strength = 0.625 M NaClO_4).

Table 4.5 Electronic Absorption Spectral Data for the Mononuclear Pentaammineruthenium(III) and (IV) Complexes of the 1,4-Dicyanamido-2,5-dimethylbenzene Dianion Ligand.^a

Complexes	$b_1^* \leftarrow b_2$ LMCT	$b_1^* \leftarrow b_1$ LMCT
$b[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})]^{2+}$	513 (3.95)	889 (4.47) [0.590]
$c[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})]^+$	367 (3.65)	926 (3.94) [0.215]

^aAll data are recorded in aqueous solution (ionic strength=0.625M NaClO₄) and are in nm (log ϵ in parentheses and oscillator strength, calculated from $f = 4.61 \times 10^{-9} \epsilon_{\text{max}} \Delta\nu_{1/2}$, in brackets); concentration=6.563 $\times 10^{-5}$ M. ^bneutral pH. ^cpH=9.48, data taken from Table 4.2.

As well, note that in the UV region of the electronic absorption spectrum of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})][\text{PF}_6]_2$, two bands at 204 (not shown in Figure 4.8) and 321 nm with extinction coefficients of 21720 and 10410 $\text{M}^{-1}\text{cm}^{-1}$ respectively, have been formally assigned to ligand centered $\pi^* \leftarrow \pi$ transitions.

Clearly upon oxidation of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})]^+$ to form $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})]^{2+}$, the extinction coefficient of the $b_1^* \leftarrow b_2$ LMCT transition increases by approximately twofold while E_{op} decreases by 0.96 eV. Similarly for the $b_1^* \leftarrow b_1$ LMCT transition, the extinction coefficient increases by more than a factor of three but E_{op} increases by 0.06 eV. The changes in the extinction coefficient and energy of both LMCT transitions upon oxidation, can be rationalized by considering the qualitative molecular orbital energy level diagram for the pentaammineruthenium(III) and (IV) complexes of 2,5-Me₂Dicyd²⁻ shown in Figure 4.9 (note that the microsymmetry of both the Ru(III) and Ru(IV) centers is C_{2v}).

The increase in extinction coefficient for both the $b_1^* \leftarrow b_2$ and $b_1^* \leftarrow b_1$ LMCT transitions of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})]^{2+}$ compared to $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})]^+$ is readily explained by recognizing that the b_1^* level is unoccupied in the former complex, thus the probability of transition to it is doubled. The experimental oscillator strength of the $b_1^* \leftarrow b_1$ LMCT transition is actually 2.3 times larger for the Ru(IV) complex compared to

that of the Ru(III) complex. In order to understand the changes in the relative energies of the two LMCT transitions, a lowering in energy of the metal $d\pi^*$ orbitals upon oxidation to Ru(IV) must be invoked. As a result, the π bonding interaction between the b_1 ($d\pi^*$) orbital of Ru(IV) and the HOMO (π_1) of 2,5-Me₂Dicyd²⁻ is increased relative to the π interaction between the b_2 ($d\pi^*$) orbital and the SHOMO (π_2). The implication of such a strong π interaction is a greater effective π overlap between π_1 of the cyanamide dianion and the b_1 ($d\pi^*$) orbital of Ru(IV). Indeed, Figure 4.9 shows that the energy match between donor and acceptor becomes more favourable upon oxidation. In essence, the covalent character of the Ru(IV)-cyanamide charge transfer state is increased as reflected by the greater energy separation between the b_1 MO and the ligand's π_1 HOMO for [(NH₃)₅Ru(2,5-Me₂Dicyd)]²⁺.

Figure 4.9 Qualitative MO energy level diagram showing the relative energies of the $b_1^* \leftarrow b_1$ and $b_1^* \leftarrow b_2$ LMCT transitions for 2,5-Me₂Dicyd²⁻ bound to (a) (NH₃)₅Ru(III) and (b) (NH₃)₅Ru(IV).

4.2.4 Cyclic Voltammetry

The cyclic voltammetry of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})][\text{PF}_6]_2$ in acetonitrile as shown in Figure 4.10 is characterized by two metal centered one-electron reduction processes as outlined by Eq. a) of Scheme 4.4.

Scheme 4.4

The Ru(IV/III) reduction couple, denoted by $E^\circ_{\text{M}_1}$, was found to be quasi-reversible (ie. a peak to peak separation of 73 mV at 100 mVs^{-1} that increases with scan rate) having a half-wave potential value of 0.226 V vs. NHE. The second reduction, namely, the Ru(III/II) couple as denoted by $E^\circ_{\text{M}_2}$, was found to be at best quasi-reversible (ie. a peak to peak separation of 95 mV at 100 mVs^{-1} that increases with scan rate) having a half-wave potential value of -0.113 V vs. NHE. This compares to a value of -0.091 V vs NHE for the analogous Ru(III/II) couple of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})]^+$ in aqueous solution at pH = 9.48 (refer to Section 4.1.5). The difference is attributed to a solvent shift. The loss of reversibility with regards to the Ru(III/II) reduction process in acetonitrile compared to aqueous solution (pH = 9.48) can be rationalized by the consideration that the formation of $[(\text{NH}_3)_5\text{Ru}(\text{NCCH}_3)]^{2+}$ (ie. loss of $2,5\text{-Me}_2\text{Dicyd}^{2-}$ upon reduction) is potentially a more favorable process compared to the formation of $[(\text{NH}_3)_5\text{Ru}(\text{OH})]^+$.

Figure 4.10 Cyclic voltammogram of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})][\text{PF}_6]_2$ in acetonitrile (0.1 M TBAH). (a) negative direction at a scan rate of 100 mVs^{-1} . (b) positive direction at a scan rate of 100 mVs^{-1} .

The one-electron oxidation of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})][\text{PF}_6]_2$, as denoted by E°_{oxid} , generates one of two possible products as shown by Eq. b) of Scheme 4.4. The couple was found to be quasi-reversible (ie. a peak to peak separation of 77 mV at 100 mVs^{-1} that increases with scan rate) having a half-wave potential value of 0.997 V vs. NHE. Note that this potential is some 0.274 V positive of the half-wave potential for the analogous $E^\circ_{\text{oxid}_2}$ couple of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})]^+$ in aqueous solution at pH = 9.48 (refer to Section 4.1.5).

In addition to obtaining the cyclic voltammetry of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})]^{2+}$ in aqueous solution and hence eliminating discrepancies in half-wave potential values due to solvent shifts and pH conditions, future studies will involve the use of spectroelectrochemical methods to identify the nature of the oxidation product of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})]^{2+}$.

4.2.5 Spectroelectrochemistry

In order to verify that the reduction of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})]^{2+}$ is a reversible one-electron process that yields $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})]^+$, spectroelectrochemical and coulometric experiments were performed (refer to Section 2.7.5 for the details of the experiment including cell design and experimental procedure). The results were as follows. Within approximately 55 seconds of applying the electrolysis reduction potential $E_{\text{red.}} = -0.350 \text{ V vs Ag/Ag}^+$ to a 0.1 M TBAH/acetonitrile solution of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})]^{2+}$, the UV-vis-NIR spectral profile of a mixture of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})]^+$ and $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{DicydH})]^{2+}$ was generated. Note that the presence of the protonated complex is ascribed to acid impurities in solution and that future spectroelectrochemical studies will be carried out under basic conditions. The reduction was deemed to be complete when the application of $E_{\text{red.}}$ for an additional minute did not alter the initially generated profile of the Ru(III) complex. Application of the electrolysis

oxidation potential $E_{\text{OxId.}} = 0.050 \text{ V}$ vs Ag/Ag^+ to the reduced solution for approximately 12 minutes resulted in the complete (100%) reformation of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})]^{2+}$ as evidenced by the generation of its original UV-vis-NIR spectral profile. Clearly, the spectroelectrochemical results verify that the Ru(IV/III) reduction process is indeed reversible. Furthermore, coulometric measurements demonstrated that the Ru(IV/III) reduction process was as well a one-electron event. Through the use of Faraday's Law: $n = Q/FN$, where Q is the quantity of electricity or charge in coulombs (C) to effect complete electrolysis, F is the Faraday constant having a value of 96485 C eq^{-1} and N is the number of moles of material in solution that has been electrolyzed, the number of electron equivalents per mole of material electrolyzed (eq mole^{-1}), denoted as n , was calculated to be $0.94 \text{ eq mole}^{-1}$ (note that $Q = 10.33 \text{ mC}$ and $N = 1.140 \times 10^{-7} \text{ moles}$).

4.2.6 ^1H NMR Spectroscopy

The ^1H NMR spectrum of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})][\text{PF}_6]_2$ in acetonitrile- d_3 at 300 K is shown in Figure 4.11.

Figure 4.11 ^1H NMR spectrum of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})][\text{PF}_6]_2$ in acetonitrile- d_3 (at 300 K) with a concentration of 11 mM. The singlet at 1.93 ppm is background from acetonitrile- d_3 . The singlet at 2.06 ppm is due to acetone solvent of recrystallization.

At first glance, the most striking feature of the spectrum is the large downfield shift experienced by the trans-NH₃ protons (present as a broad singlet at 8.27 ppm vs. TMS, and integrating for three protons) relative to the chemical shift position of the cis NH₃ protons (present as a broad singlet at 3.04 ppm and integrating for twelve protons) when compared to the typical behaviour of diamagnetic pentaammineruthenium(II) complexes of π accepting ligands.

For example, in the ¹H NMR spectrum of [(NH₃)₅Ru(2,6-Cl₂pcydH)][PF₆]₂, where 2,6-Cl₂pcydH is the weakly π accepting (2,6-dichlorophenyl)cyanamide neutral ligand, the chemical shift associated with the trans-NH₃ protons occurs at 2.97 ppm while that associated with the cis-NH₃ protons occurs at 2.53 ppm.⁸⁵ The splitting of the trans- and cis-ammines, $\Delta(\text{trans-cisNH}_3)$, is 0.44 ppm in this case compared to 5.23 ppm for [(NH₃)₅Ru(2,5-Me₂Dicyd)][PF₆]₂. Similarly, for the pentaammineruthenium(II) complexes of the stronger π accepting ligands of dimethyl acetylenedicarboxylate (DMAD)¹⁰⁰ and fumaric acid,¹⁰¹ $\Delta(\text{trans-cisNH}_3)$ values of 1.55 and 2.10 ppm, respectively, are observed. In these systems, the authors suggested that the deshielding of the trans-NH₃ protons was the result of a moderate π backbonding interaction between the π accepting ligands and Ru(II). In fact, the largest trans effect in these types of systems has been observed in the ¹H NMR spectrum of the pentaammineruthenium(II) complex of *p*-benzoquinone diimine where $\Delta(\text{trans-cisNH}_3)$ has a value of 2.99 ppm.¹⁰² In this case, the authors proposed that the magnitude of $\Delta(\text{trans-cisNH}_3)$ was a gauge of the π backbonding interaction, thereby implying that *p*-benzoquinone diimine is a stronger π acceptor compared to fumaric acid which in turn is stronger than DMAD.

In the case of [(NH₃)₅Ru(2,5-Me₂Dicyd)][PF₆]₂, although a π backbonding interaction between Ru(IV) and 2,5-Me₂Dicyd²⁻ might be considered, it does not appear to be appropriate given the magnitude of $\Delta(\text{trans-cisNH}_3)$ and the fact that 2,5-Me₂Dicyd²⁻ is expected to be a poorer π acceptor relative to its neutral counterpart (if the π accepting

strength of 2,5-Me₂DicydH₂ is equated to that of a neutral phenylcyanamide such as 2,6-Cl₂pcydH). As a result, a different bonding interaction that somehow links the trans-NH₃, the ruthenium metal center and the cyanamide ligand, must be invoked to account for what this author believes to be an unprecedented directional effect imposed on an ammine ligand coordinated to a diamagnetic metal center.

[(NH₃)₅Ru(2,5-Me₂Dicyd)][PF₆]₂ is best described as being diamagnetic and consisting of a low spin pentaammineruthenium(IV) metal center coordinated to the 2,5-Me₂Dicyd²⁻ dianion ligand in a π interaction. The interaction is depicted in the qualitative MO scheme of Figure 4.9b, in which the large energy separation between b₁* and b₂* levels accounts for the diamagnetic ground state (the energy required to uncouple spins in the b₂* level is large). Let us now consider the interaction between the Ru(IV)-cyanamide π bond and the trans-NH₃ as shown in Figure 4.12. In the xz plane, electron density associated with a trans-NH₃ sp² hybridized σ orbital, which is involved in σ bonding with a proton 1s orbital, can interact in a π fashion with the unoccupied b₁*_{xz} (of metal $d\pi$ character) molecular orbital of [(NH₃)₅Ru(2,5-Me₂Dicyd)]²⁺ via a hyperconjugation mechanism. The interaction sets up a three-center π bonding network in the xz plane, in which the Ru(IV)-cyanamide π bond can selectively polarize trans-NH₃ electron density towards itself, thereby creating the directional effect. In contrast, the cis-NH₃ protons do not display a large anisotropy, as they reside in the xy plane, and hence do not experience a significant inductive pull from the Ru(IV)-cyanamide π bond. Recall, with reference to Figure 4.9b, that the π interaction between Ru(IV) and the 2,5-Me₂Dicyd²⁻ dianion ligand results from the mixing of a metal $d\pi^*$ _{xz} orbital with a nitrogen $p\pi_x$ orbital, the latter of which is part of the π_1 HOMO of the ligand. Note that such a mixing of metal $d\pi$ orbitals with ligand $p\pi$ orbitals has also been invoked to describe the origin of transverse conductivity in the Cu(Me₂DCNQI)₂ molecular metal,⁶ where Me₂DCNQI is the radical anion form of 2,5-dimethyl-*N,N'*-dicyanoquinone diimine. In addition, it must be

mentioned that a σ interaction between the trans-NH₃, Ru(IV) and the dianion ligand almost certainly makes a contribution to the overall directional effect, but this author believes that a π interaction is dominant since the valence electron removed from [(NH₃)₅Ru(2,5-Me₂DicydH)]²⁺ upon oxidation to form [(NH₃)₅Ru(2,5-Me₂Dicyd)]²⁺ is of π symmetry.

Figure 4.12 A three-center π bonding interaction between a trans-NH₃, Ru(IV) and a 1,4-dicyanamidobenzene dianion ligand.

The experimental justification for such a three-center π interaction, where one of the trans-NH₃ protons is selectively linked into the π bonding framework of the Ru(IV)-cyanamide bond, came from the observation of the ¹H NMR spectrum of [(NH₃)₅Ru(2,5-Me₂Dicyd)][PF₆]₂ in acetone-d₆ at 210 K. At this lowered temperature the broad trans-NH₃ resonance split into two separate resonances (16.29 and 16.36 ppm vs. TMS at 0.00 ppm) with the high field peak integrating for one proton and the low field peak integrating for two protons. Clearly, the implication is that one of the trans-NH₃ protons is locked into a chemical environment that is different than that of the other two protons.

Referring back to ¹H NMR spectrum of [(NH₃)₅Ru(2,5-Me₂Dicyd)][PF₆]₂ in acetonitrile-d₃, the trans-effect also has ramifications with regards to the chemical shift positions of the

cis-NH₃ protons as well as the protons of the 2,5-Me₂Dicyd²⁻ ligand. For example, the cis-NH₃ protons lying in the yz plane as shown in Figure 4.12 are not in the direct π pathway that accounts for the trans effect, however, their electron density does experience some polarization towards the Ru(IV)-cyanamide bond resulting in a small degree of deshielding (ie. 0.51 ppm relative to the cis-NH₃ protons of [(NH₃)₅Ru(2,6-Cl₂pcydH)][PF₆]₂). The phenyl and methyl protons (refer to the labelling in Figure 4.11), their resonances already split due to the asymmetry of the complex, are also effected as the phenyl ring is coupled to the cyanamide NCN moiety in both a π and σ fashion. To elaborate, the 6-phenyl and 2-methyl protons (in the 6- and 2- phenyl ring positions, respectively) which occur as singlets at 6.54 and 0.28 ppm and integrate for one and three protons, respectively, are shielded owing to their closer proximity to the ruthenium-cyanamide bond. On the otherhand, the 3-phenyl and 5-methyl protons which occur as singlets at 8.44 and 2.74 ppm and integrate for one and three protons, respectively, are deshielded. Note that shielding/deshielding of the phenyl and methyl protons of the coordinated ligand is with respect to their chemical shift positions in the ¹H NMR spectrum of the free neutral ligand (2,5-Me₂DicydH₂) in acetonitrile-d₃, where for example the 3,6-phenyl protons occur as a singlet resonance at 6.98 ppm and the 2,5-methyl protons occur as a singlet resonance at 2.27 ppm.

The room temperature ¹H NMR spectrum of [(NH₃)₅Ru(2,5-Me₂Dicyd)][PF₆]₂ in acetonitrile-d₃ provides strong support for the complexes designation of being in a diamagnetic ground state. The support is based on the fact that upon coordination to the ruthenium metal center, neither the phenyl nor methyl protons shift significantly from their free neutral ligand values as would be the case upon coordination to a paramagnetic metal center. Similarly, although effected to a greater extent, the chemical shift positions of the ammine ligand protons (the trans-NH₃ in particular) are still within the 0-10 ppm range associated with a diamagnetic molecule and therefore on this basis do not reflect

coordination to a paramagnetic metal center. An example of the paramagnetic effect can be seen by making reference to the ^1H NMR spectrum of $[(\text{NH}_3)_5\text{Ru}(2\text{-Clpcyd})][\text{PF}_6]_2$ in acetonitrile- d_3 (refer to Section 5.1.8a), where 2-Clpcyd is the (2-chlorophenyl)cyanamide anionic ligand. In this complex, the presence of an unpaired Ru(III) electron density induces very large isotropic shifts $\Delta\nu$ in the chemical shift positions of the various proton nuclei. Recall that the isotropic shift is comprised of contact and pseudocontact contributions (refer to Section 1.3). In the case of the cis- and trans- NH_3 protons, which are in close proximity to Ru(III), the through-bond contact term dominates resulting in very large downfield isotropic shifts in their resonances to 67.31 and >280 ppm, respectively. For the phenyl ring protons, the through-space pseudocontact term dominates. Note that a pseudocontact shift, although normally smaller in magnitude than a contact shift, is dependent on the geometry of the relevant nuclei with respect to the paramagnetic metal center. As a result, both upfield and downfield isotropic shifts are possible. For $[(\text{NH}_3)_5\text{Ru}(2\text{-Clpcyd})][\text{PF}_6]_2$, the protons in the 3- and 5-phenyl positions are downfield shifted appearing as two closely spaced singlets at 29.37 and 29.48 ppm, respectively, whereas the protons in the 4- and 6-phenyl positions are upfield shifted appearing as singlets at -40.18 and -46.06 ppm, respectively.

Finally, if $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})][\text{PF}_6]_2$ is indeed diamagnetic in acetonitrile- d_3 at 300 K, it represents one of the few examples of a Ru(IV) coordination compound that demonstrates this type of behaviour.¹⁰³ A solution magnetic susceptibility measurement should provide further support for such a diamagnetic designation (refer to Section 4.2.8).

4.2.7 Nature of the Oxidation Product

This experimenter believes that the debate over whether the product formed when $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{DicydH})]^{2+}$ is chemically oxidized is the pentaammineruthenium(IV) complex of the $2,5\text{-Me}_2\text{Dicyd}^{2-}$ dianion ligand or the pentaammineruthenium(III) complex

of the 2,5-Me₂Dicyd⁻ monoanion radical ligand, has been resolved by the ¹H NMR spectral results presented in the previous section. The winner is the pentaammineruthenium(IV) complex of the 2,5-Me₂Dicyd²⁻ dianion ligand!

Let us now consider fundamental differences in ruthenium-cyanamide bonding between these two complexes that account for this resolution. Even though the pentaammineruthenium(III) complex of the 2,5-Me₂Dicyd⁻ monoanion radical ligand has one fewer electrons than its dianion bound counterpart, it is expected to possess unpaired electron density (of metal character) and therefore display paramagnetic behaviour. With reference to the qualitative MO diagram of [(NH₃)₅Ru(2,5-Me₂Dicyd)]⁺ shown in Figure 4.9a, the MO scheme for the monoanion radical bound complex would be very similar. The difference being that both the b₁ and b₂ MO's together with their anti-bonding counterparts would be lowered in energy due to the fact that the π₁ and π₂ levels of the monoanion radical ligand are of lower energy. However, the energy separation between the b₁* and b₂* MO's would be essentially the same, resulting in an energetically favourable situation for unpaired electron density to reside in the b₁* level (the energy required to uncouple spins in the b₂* level is small). With reference to Figure 4.12, a π interaction between the trans-NH₃ and the partially occupied b₁* level of the pentaammineruthenium(III) complex of the monoanion radical ligand would result in the protons of the trans-NH₃ experiencing a very large paramagnetic contact shift induced by unpaired electron density (refer to Section 5.1.8a for a more complete discussion of contact shift and the spin delocalization mechanism in pentaammineruthenium(III)-cyanamide systems). On the otherhand, the situation is very different for the pentaammineruthenium(IV) complex of the Me₂Dicyd²⁻ dianion ligand. As already eluded to, the large energy separation between the b₁* and b₂* MO's implies that the ground state is diamagnetic (the energy required to uncouple spins in the b₂* level is large). As a result, in its interaction with the empty b₁* level, the trans-NH₃ does not experience a

paramagnetic contact shift. The ^1H NMR spectroscopy presented in Section 4.2.6 confirms this result.

4.2.8 Solution Magnetic Susceptibility Measurements

Via the Evans method, a paramagnetically induced isotropic shift $-\Delta f = 1.733$ Hz of the TMS ^1H NMR resonance was observed. Using this value of $-\Delta f$, the molar susceptibility χ_m of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})][\text{PF}_6]_2$ in acetonitrile- d_3 at 300 K was determined to be $9.41 \times 10^{-5} \text{ cm}^3 \text{ mole}^{-1}$ (refer to Eq. 1.17 in Section 1.3.2). Assuming a spin-only model, the effective magnetic moment per ruthenium ($\mu_{\text{eff}}/\text{Ru}$) and the number of unpaired electrons per ruthenium (n/Ru) were calculated from the corrected molar magnetic susceptibility χ'_m (to solve for χ'_m , refer to Eqs. 1.11 and 1.12 in Section 1.3.1 and to the Appendix for the summed up diamagnetic contributions of individual atoms and bonds in $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})][\text{PF}_6]_2$) to be $0.99 \mu_B$ and 0.41 unpaired electrons, respectively (refer to Eqs. 1.10 and 1.15 in Section 1.3.1).

The result shows that a significant quantity of paramagnetic species exists in solution, however, its origin must be questioned as the lack of paramagnetic contact shifting in the ^1H NMR spectrum shown in Figure 4.11 indicates that the majority of complex in solution is indeed the diamagnetic pentaammineruthenium(IV) complex of the $2,5\text{-Me}_2\text{Dicyd}^{2-}$ dianion ligand. Therefore, the measured paramagnetism must be due to an impurity. Note that in the Evans method, the small upfield isotropic shift experienced by the internal reference TMS is due solely to the through-space or pseudocontact (and not contact) term. Therefore, an impurity such as the pentaammineruthenium(III) complex of the $2,5\text{-Me}_2\text{Dicyd}^-$ monoanion radical ligand could account for the measured level of paramagnetism. Support for this argument is based on the observation that upon a second recrystallization of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})][\text{PF}_6]_2$, the molar susceptibility in acetonitrile- d_3 decreased by a factor of 2.66 (ie. from $2.50 \times 10^{-4} \text{ cm}^3 \text{ mole}^{-1}$ to 9.41×10^{-5}

$\text{cm}^3\text{mole}^{-1}$). In addition, the ^1H NMR spectrum was cleaner. Note that the decrease in magnetic susceptibility represents an 8% decrease in the number of unpaired electrons and therefore in the amount of paramagnetic impurity.

Another possible paramagnetic impurity is the pentaammineruthenium(III) complex of the 2,5-Me₂DicydH⁻ monoanion ligand ($[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{DicydH})]^{2+}$) as it represents a potential decomposition product of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})]^{2+}$ if left in the presence of trace water for extended periods of time (refer to Section 4.2.1). A preliminary observation whereby the molar susceptibility of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})][\text{PF}_6]_2$ in acetonitrile- d_3 increased from 9.41×10^{-5} to $9.77 \times 10^{-5} \text{ cm}^3 \text{ mole}^{-1}$ over a period of 1.5 hours may lend some credence to a decomposition process, however, additional studies employing both ^1H NMR and electronic absorption spectroscopies as means of monitoring decomposition over extended periods of time must be performed.

CHAPTER 5

Dinuclear Pentaammineruthenium Complexes:

[Ru(III), Ru(III)] and [Ru(IV), Ru(III)]

5.1 [Ru(III), Ru(III)] Complexes of 1,4-Dicyanamidobenzene Dianion Ligands

The [Ru(III), Ru(III)] complexes of the 1,4-dicyanamidobenzene dianion ligands ($[\mu-(L)-\{(NH_3)_5Ru\}_2]^{4+}$: where $L = 2,5-Me_2Dicyd^{2-}$, $Dicyd^{2-}$, $2,5-Cl_2Dicyd^{2-}$ and $2,3,4,5-Cl_4Dicyd^{2-}$) have been previously prepared and characterized by IR and aqueous electronic absorption spectroscopies, X-ray crystallography, solid-state temperature dependent magnetic susceptibility measurements and aqueous cyclic voltammetry.^{43,44,81} Recently two additional dinuclear complexes, namely, those where $L = 2-MeDicyd^-$ and $2-MeODicyd^-$, have been prepared and similarly characterized.^{79,80} In addition to summarizing these results, the following results section goes further as it demonstrates and attempts to explain the solvent dependency of the electronic and magnetic properties of the six dinuclear complexes. In this regard, the probes used include 1H NMR and electronic absorption spectroscopies, cyclic voltammetry and solution magnetic susceptibility measurements. Furthermore the solvent dependency of the electronic properties of the mixed-valence [Ru(III), Ru(II)] systems, generated by spectroelectrochemical studies, will also be analyzed.

5.1.1 Synthesis

The generalized synthesis of the [Ru(III), Ru(III)] complexes of $2-MeODicyd^{2-}$, $2,5-Me_2Dicyd^{2-}$, $2-MeDicyd^{2-}$ and $Dicyd^{2-}$ is outlined in Scheme 5.1. Compared to the originally reported preparation of the dinuclear complexes of Me_2Dicyd^{2-} and

Dicyd²⁻,^{43,44} where an inert-atmosphere environment was employed in the initial stages of the reaction, Scheme 5.1 represents a superior synthetic pathway. For example, reaction yields are either on par or in some cases greater than those based on the originally reported preparation. Furthermore, the deployment of Scheme 5.1 is much simpler and more time efficient as the use of often cumbersome vacuum line techniques is avoided. To initiate Scheme 5.1, the appropriate 1,4-dicyanamidobenzene neutral ligand was reacted with $[(\text{NH}_3)_5\text{Ru}(\text{OH}_2)][\text{PF}_6]_2$ in acetone in an approximate 1:2 molar ratio. The reaction was conducted in the open to accommodate air oxidation of Ru(II) to Ru(III), a process that is accompanied by the deprotonation of the neutral cyanamide ligand. Isolation of a crude bromide salt (A) was followed by its purification via cation-exchange (ie. carboxymethyl Sephadex resin) chromatography. Final purification of (A) via a series of metathetic conversions (ie. $\text{Ph}_4\text{B}^- \rightarrow \text{Br}^- \rightarrow \text{PF}_6^-$) is followed by recrystallization, typically as a PF_6^- salt (B) by diffusing diethyl ether into an acetone solution of the complex.

where $\text{LH}_2 = 2\text{-MeODicydH}_2; 2,5\text{-Me}_2\text{DicydH}_2;$
 $2\text{-MeDicydH}_2; \text{DicydH}_2$

Scheme 5.1

In the initial stages of reaction, the $[\text{Ru}(\text{III}), \text{Ru}(\text{III})]$ complexes of $2,5\text{-Cl}_2\text{Dicyd}^{2-}$ and $2,3,4,5\text{-Cl}_4\text{Dicyd}^{2-}$ were prepared by the originally reported method that involved the inert

atmosphere reaction of $[(\text{NH}_3)_5\text{Ru}(\text{OH}_2)]\text{PF}_6)_2$ with the Ph_4As^+ salt of the respective dianion ligand in acetone in a 2.2:1 molar ratio.^{43,44,81} However, after subsequent exposure to air to afford the oxidation of Ru(II) to Ru(III), the remainder of Scheme 5.1 was adhered to beginning with the isolation of the crude Br^- salt and ending with the isolation of a purified hexafluorophosphate product. Note that the reasoning behind such variation in the initial stages of the reaction scheme for these two particular complexes is primarily due to two factors. Firstly, the very low solubility of the neutral ligands (2,5- $\text{Cl}_2\text{DicydH}_2$ and 2,3,4,5- $\text{Cl}_4\text{DicydH}_2$) in acetone had to be overcome. Secondly, the tendency of the dianion ligand when dissolved in acetone solution to oxidize to its monoanion radical form in the presence of oxygen had to be averted by carrying out the reaction in an argon atmosphere.

Similar to what was observed for the mononuclear pentaammineruthenium(III) complexes of 1,4-dicyanamidobenzene monoanion ligands, the recrystallization (ie. slow diffusion of ether into an acetone solution of the product) of each of the six dinuclear complexes resulted in the association of solvent acetone molecules with the pure products as verified by elemental analysis results. Note that the association of polar solvent molecules (ie. water, acetone, ether, etc.) with transition metal ammine complexes is quite a common occurrence. Again, drying of the dinuclear complexes for any extended periods at elevated temperatures could not be performed owing to their tendency to decompose.

Typical yields for the [Ru(III), Ru(III)] complexes of 2-MeODicyd²⁻, 2,5-Me₂Dicyd²⁻, 2-MeDicyd²⁻ and Dicyd²⁻ were in the 10-20% range while in the case of the 2,5- $\text{Cl}_2\text{Dicyd}^{2-}$ and 2,3,4,5- $\text{Cl}_4\text{Dicyd}^{2-}$ complexes, yields were typically below 10%. The primary reasons for the low yields were: 1) more than one product was formed during the course of the reaction; 2) $[(\text{NH}_3)_5\text{Ru}(\text{OH}_2)]\text{PF}_6)_2$ did not completely react; 3) crude material was lost due to its precipitation (as a Cl^- salt) onto the cation-exchange resin, especially in the

case of $[\mu-(2,5\text{-Cl}_2\text{Dicyd})-\{(\text{NH}_3)_5\text{Ru}\}_2]^{4+}$ and $[\mu-(2,3,4,5\text{-Cl}_4\text{Dicyd})-\{(\text{NH}_3)_5\text{Ru}\}_2]^{4+}$ where higher concentrations of electrolyte solution (NaCl) were required to effect elution.

With regards to the cation-exchange column chromatography purification of the dinuclear complexes, the following describes the results in more detail. Beginning with the lowest positively charged species, the general order of column bands for the six complexes under study were as follows: 1) a yellow band believed to be unreacted $[(\text{NH}_3)_5\text{Ru}(\text{OH}_2)]^{2+}$; 2) a blue band characterized by UV-vis-NIR spectroscopy (refer to Section 4.1.3) to be a mononuclear pentaammineruthenium(III) complex of a 1,4-dicyanamidobenzene monoanion ligand, having a charge of $+2$; 3) the desired green product band having a charge of $+4$.

In terms of solubility properties, the dinuclear complexes (hexafluorophosphate salts) were soluble in common aprotic solvents such as acetone, acetonitrile and DMSO. All six of the dinuclear complexes were stable for an indefinite period of time if stored in the freezer at $-18\text{ }^\circ\text{C}$.

5.1.2 Infrared Spectroscopy

The infrared spectrum of $[\mu-(2\text{-MeDicyd})-\{(\text{NH}_3)_5\text{Ru}\}_2][\text{PF}_6]_4$ is shown in Figure 5.1 while the results of all six dinuclear complexes are summarized in Table 5.1. Note that the infrared results pertaining to the perchlorate salts of $[\mu-(2,5\text{-Me}_2\text{Dicyd})-\{(\text{NH}_3)_5\text{Ru}\}_2]^{4+}$ and $[\mu-(\text{Dicyd})-\{(\text{NH}_3)_5\text{Ru}\}_2]^{4+}$, and the chloride salts of $[\mu-(2,5\text{-Cl}_2\text{Dicyd})-\{(\text{NH}_3)_5\text{Ru}\}_2]^{4+}$ and $[\mu-(2,3,4,5\text{-Cl}_4\text{Dicyd})-\{(\text{NH}_3)_5\text{Ru}\}_2]^{4+}$ have been previously reported.^{43,44} In all cases, the characteristic cyanamide $\nu(\text{N}=\text{C}=\text{N})$ stretch is evident in the $2085\text{-}2110\text{ cm}^{-1}$ range. Other diagnostic vibrations associated with the cyanamide ligand include the aromatic $\nu(\text{C}=\text{C})$ stretch in the $1440\text{-}1480\text{ cm}^{-1}$ range. Note that the frequencies of the cyanamide $\nu(\text{N}=\text{C}=\text{N})$ and aromatic $\nu(\text{C}=\text{C})$ stretches are quite similar to those observed in the IR spectra of the Ph_4As^+ salts of the 1,4-dicyanamidobenzene

dianion ligands (refer to Section 3.2.2). The presence of ammine (NH_3) groups in the inner coordination sphere of Ru(III) is also verified in the infrared spectra of the complexes. The ammine vibrational modes present include the $\nu(\text{N-H})$ stretch in the $3150\text{--}3350\text{ cm}^{-1}$ range and the $\delta(\text{N-H})$ degenerate deformation near 1625 cm^{-1} . Finally, the presence of both the hexafluorophosphate and perchlorate counter anions is verified by the occurrence of a $\nu(\text{P-F})$ stretch near 835 cm^{-1} and by that of a $\nu(\text{Cl-O})$ stretch near 1090 cm^{-1} , respectively.

Figure 5.1 Infrared spectrum of $[\mu\text{-(2-MeDicyd)}\text{-}\{(\text{NH}_3)_5\text{Ru}\}_2][\text{PF}_6]_4$ (KBr disc). [Reproduced with permission from Ref. 79. Copyright (1994).]

Table 5.1 Infrared Spectral Data for the [Ru(III), Ru(III)] Complexes of 1,4-Dicyanamidobenzene Dianion Ligands (in cm^{-1}).^a

Complexes ^b	$\nu(\text{N}=\text{C}=\text{N})$	$\nu(\text{C}=\text{C})$	$\nu(\text{N}-\text{H})$	$\delta(\text{N}-\text{H})$	$\nu(\text{P}-\text{F})/\nu(\text{Cl}-\text{O})$
^c 2-MeODicyd ²⁻	2106 (s)	1479 (w)	3290, 3236, 3165 (s)	1625 (m)	835 (vs)
^d 2,5-Me ₂ Dicyd ²⁻	2088 (s)	1477, 1440 (m)	3339, 3271, 3210 (s)	1623 (m)	1088 (vs)
^e 2-MeDicyd ²⁻	2096 (s)	1478 (w)	3273, 3237 3158 (s)	1626 (m)	836 (vs)
^f Dicyd ²⁻	2087 (s)	1469 (w)	3333, 3267, 3200 (s)	1625 (m)	1091 (vs)
^g 2,5-Cl ₂ Dicyd ²⁻	2098 (s)	1465 (m)	3227, 3151 (s)	1624 (m)	-----
^h 2,3,4,5-Cl ₄ Dicyd ²⁻	2102 (s)	1471 (m)	3222, 3163 (s)	1623 (m)	-----

^aKBr disc; band intensities: vs=very strong, s=strong, m=medium, w=weak. ^bonly ligands shown for clarity. ^cPF₆⁻ complex salt, from Ref. 80. ^{d,f}ClO₄⁻ complex salts, from Ref. 44 and 43. ^ePF₆⁻ complex salt, from Ref. 79. ^{g,h}Cl⁻ complex salts, from Ref. 44 and 43.

5.1.3 X-Ray Crystallography

(Note: that the estimated standard deviations for both bond lengths and bond angles are given in parentheses).

Previously reported crystallographic studies of $[\mu\text{-(Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{OTs}]_4 \cdot \text{acetone}$, where OTs⁻ is the tosylate anion, demonstrated that two coordination isomers exist.^{43,44} The result is shown in Figure 5.2.

Figure 5.2 Crystal structures of the two conformers A and B of $[\mu\text{-(Dicyd)}\text{-}\{(\text{NH}_3)_5\text{Ru}\}_2][\text{OTs}]_4 \cdot \text{acetone}$. The tosylate anion and acetone molecule are omitted for clarity. [Reproduced with permission from Ref. 43. Copyright (1992) American Chemical Society.]

In the 'linear' form A, the $\text{Ru}(1)\text{-N}(6)\text{-C}(1)$ bond angle is $175.1(10)^\circ$, however in "bent" form B, the corresponding bond angle is only $149.8(12)^\circ$. This latter result was quite surprising since a previous crystal structure of the mononuclear complex, $[(\text{NH}_3)_5\text{Ru}(2,3\text{-Cl}_2\text{pcyd})][\text{SO}_4] \cdot \text{ethanol}$, where 2,3- Cl_2pcyd is the (2,3-dichlorophenyl)cyanamide anion, showed a corresponding bond angle of $171.4(10)^\circ$.⁴⁶ Furthermore, the linear form should be more stable than that of the bent as it maximizes the π interaction between the π acid $\text{Ru}(\text{III})$ and the π donor cyanamide group. Note that the existence of two conformers in the solid state is verified by the presence of two $\nu(\text{N}=\text{C}=\text{N})$ stretching bands at 2099 and 2082 cm^{-1} in the IR spectrum of $[\mu\text{-(Dicyd)}\text{-}\{(\text{NH}_3)_5\text{Ru}\}_2][\text{OTs}]_4$. Similar coordination forms have been observed in the crystal structure of $[\text{Cu}(\text{bipy})(2,3\text{-Cl}_2\text{pcyd})_2]$, and again multiple

$\nu(\text{N}=\text{C}=\text{N})$ stretching bands were observed in the solid state IR spectrum.¹⁰⁴ It is important to note that the IR spectrum of the perchlorate salt of $[\mu\text{-(Dicyd)}\text{-(NH}_3)_5\text{Ru}_2]^{4+}$ as well as the IR spectra of $[\mu\text{-(2,5-Me}_2\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{ClO}_4]_4$, $[\mu\text{-(2,5-Cl}_2\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{Cl}]_4$ and $[\mu\text{-(2,3,4,5-Cl}_4\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{Cl}]_4$ all display a single $\nu(\text{N}=\text{C}=\text{N})$ stretching band (refer to Table 5.1). This is strong evidence for there being only one conformer present in the solid state of these complexes. The implication is that the existence of two conformers may be due to the nature of the counter ion in terms of its role in crystal packing. As a result, it appears that obtaining the presently elusive crystal structure of $[\mu\text{-(Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{ClO}_4]_4$ is the only means in which the question will be answered.

In comparing the crystal structures of $[\mu\text{-(Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{OTs}]_4$ and the free Dicyd^{2-} ligand (ie. Ph_4As^+ salt, refer to Section 3.2.3), the overall NCN bond length and CN bond lengths do not change significantly upon coordination. However, the bond that connects the cyanamide group to the phenyl ring does demonstrate some marked changes. In conformer A, $\text{N}(7)\text{-C}(2)$ is $1.376(17)$ Å which is very close to the free ligand value of $1.388(8)$ Å. The corresponding bond in conformer B, $\text{N}(14)\text{-C}(6)$, is much longer at $1.468(23)$ Å indicating very little if any double bond character. Note that typical N-C single bonds are 1.43 Å in length.¹⁰⁵ In addition, the phenyl ring carbon-carbon bond lengths in conformer A are very close to those of free Dicyd^{2-} ranging from $1.386(20)$ to $1.406(20)$ Å, while those of conformer B show significant distortion ranging from $1.28(3)$ to $1.49(3)$ Å.

The ruthenium ions in both of the dimeric conformers are in essentially octahedral environments as none of the N-Ru-N angles amongst the ammine groups (NH_3) deviate by more than 4° away from 90° . Furthermore, the ruthenium-cyanamide bond length in both conformers compares quite closely to that in the mononuclear complex of $[(\text{NH}_3)_5\text{Ru}(2,3\text{-Cl}_2\text{pcyd})][\text{SO}_4]$.⁴⁶ To be more specific, the $\text{Ru}(1)\text{-N}(6)$ bond length in conformer A is

1.938(11) Å and in conformer **B**, Ru(2)-N(13) is 1.969(13) Å compared with a value of 1.980(12) Å in the mononuclear complex. With regards to a trans effect on the ammine ligand trans to the cyanamide group, it does not appear to be significant as all of the ruthenium-ammine nitrogen bonds in both conformers are similar, ranging from 2.078(10) to 2.161(12) Å. The corresponding range for [(NH₃)₅Ru(2,3-Cl₂pcyd)][SO₄] is 2.100(13) to 2.14(12) Å.

The crystal structure of [μ-(Dicyd)-{(NH₃)₅Ru}₂][OTs]₄ verifies that the geometry of the Dicyd²⁻ bridging ligand in both conformers is indeed nearly planar with the cyanamide groups being in an anti configuration. However, when coordination to Ru(III) is considered, only conformer **A** appears to have the optimal geometry for coupling between metal centers via the π system of the bridging ligand. Indeed for conformer **A**, the best plane formed by N(6), Ru(1), N(2), N(5) and N(3) is tilted only 12° with respect to the plane of the phenyl ring carbons compared to the same dihedral angle of 30° in conformer **B**. Such a loss of planarity in conformer **B** is most likely the result of the nonlinearity of the Ru(2)-N(13)-C(5) bond angle.

Finally, the intra- and intermolecular Ru-Ru distances in both dimeric conformers must be mentioned. For conformer **A**, the Ru(1)-Ru(1)_a through bond distance is 15.7 Å and the through space distance is 13.11(10) Å. For conformer **B**, the Ru(2)-Ru(2)_b through bond distance is 15.9 Å and the through space distance is 13.27(11) Å. The shortest intermolecular distance was between Ru(1) and Ru(2) at 7.61(5) Å.

5.1.4 Solid-State Magnetic Susceptibility Measurements

Previously reported solid-state temperature dependent (ie. 5 to 300 K) magnetic susceptibility measurements of [μ-(2-MeDicyd)-{(NH₃)₅Ru}₂][PF₆]₄ and [μ-(2-MeODicyd)-{(NH₃)₅Ru}₂][PF₆]₄ were performed at Memorial University, St. John's, Newfoundland, by Professor L. Thompson using an Oxford Instruments Superconducting

Faraday system equipped with a Sartorius 4432 microbalance.^{79,80} Similar measurements, also previously reported, of $[\mu\text{-(2,5-Me}_2\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{ClO}_4]_4$, the ClO_4^- and OTs^- salts of $[\mu\text{-(Dicyd)}\text{-(NH}_3)_5\text{Ru}_2]^{4+}$, $[\mu\text{-(2,5-Cl}_2\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{Cl}]_4$ and $[\mu\text{-(2,3,4,5-Cl}_4\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{Cl}]_4$ were performed at McMaster University, Hamilton, Ontario, by Professor J. E. Greedan.^{43,44} Note that the high temperature range (ie. >300 K) could not be accessed due to instrumental limits and thermal decomposition of the complexes.

The temperature dependence of the molar magnetic susceptibility of $[\mu\text{-(Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{OTs}]_4$ (shown in Figure 5.3) displays a broad χ_{max} characteristic of intramolecular antiferromagnetic exchange between metal ions. The complexes, $[\mu\text{-(2,5-Cl}_2\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{Cl}]_4$ and $[\mu\text{-(2,3,4,5-Cl}_4\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{Cl}]_4$, display similar behaviour. However, $[\mu\text{-(2-MeODicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{PF}_6]_4$, $[\mu\text{-(2-MeDicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{PF}_6]_4$, $[\mu\text{-(2,5-Me}_2\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{ClO}_4]_4$ and $[\mu\text{-(Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{ClO}_4]_4$ are diamagnetic at room temperature, apparently undergoing far stronger antiferromagnetic exchange with χ_{max} occurring at temperatures >300 K. For these latter complexes, intermolecular exchange can be ruled out since this type of behaviour normally results in a phase transition to a long-range ordered state and is characterized by a sharp maximum at the transition or Neel temperature. Intermolecular exchange has been observed in mononuclear Ru(III) complexes with similar ligands, however, the effect occurs at much lower temperatures than those of this study.⁴⁹ Note that all of the complexes displayed a rapid increase in susceptibility at temperatures <40 K. In the case of the $[\text{Ru(III)}, \text{Ru(III)}]$ complexes of this study, this paramagnetic tail is due to a monomeric pentaammineruthenium(III) impurity or an impurity associated with the oxidation of the dianion ligand.

Figure 5.3 Experimental (•) and modeled (—), by using the modified Bleaney-Bowers expression, temperature dependencies of the molar magnetic susceptibility for $[\mu\text{-(Dicyd)}\text{-}\{(\text{NH}_3)_5\text{Ru}\}_2][\text{OTs}]_4$. [Reproduced with permission from Ref. 43. Copyright (1992) American Chemical Society.]

The antiferromagnetic exchange coupling constant $-J$ ($\mathcal{H} = -JS_a \cdot S_b$) for the $[\text{Ru(III)}, \text{Ru(III)}]$ complexes, was obtained by modeling the temperature dependent magnetic susceptibility data (as shown by the line drawn through the data points in Figure 5.3) with the modified spin-only Bleaney-Bowers expression (refer to Eq. 1.5 in Section 1.2.4). The best fits gave the $-J$ values that are summarized in Table 5.2.

Table 5.2 Antiferromagnetic Exchange Data for the [Ru(III), Ru(III)] Complexes of 1,4-Dicyanamidobenzene Dianion Ligands.^a

Complexes	$-J^b$	ΔE^c	H_{ab}^d
^e $[\mu-(2,5\text{-Me}_2\text{Dicyd})-\{(\text{NH}_3)_5\text{Ru}\}_2][\text{ClO}_4]_4$	≥ 400	0.46	≥ 1200
^f $[\mu-(2\text{-MeODicyd})-\{(\text{NH}_3)_5\text{Ru}\}_2][\text{PF}_6]_4$	≥ 400	0.49	≥ 1200
^g $[\mu-(2\text{-MeDicyd})-\{(\text{NH}_3)_5\text{Ru}\}_2][\text{PF}_6]_4$	≥ 400	0.54	≥ 1200
^h $[\mu-(\text{Dicyd})-\{(\text{NH}_3)_5\text{Ru}\}_2][\text{ClO}_4]_4$	≤ 400	0.67	< 1200
ⁱ $[\mu-(\text{Dicyd})-\{(\text{NH}_3)_5\text{Ru}\}_2][\text{OTs}]_4$	100	---	590
^j $[\mu-(2,5\text{-Cl}_2\text{Dicyd})-\{(\text{NH}_3)_5\text{Ru}\}_2][\text{Cl}]_4$	95.9	0.81	590
^k $[\mu-(2,3,4,5\text{-Cl}_4\text{Dicyd})-\{(\text{NH}_3)_5\text{Ru}\}_2][\text{Cl}]_4$	61.9	0.99	460

^aThe values of $-J$ and H_{ab} for the [Ru(III), Ru(III)] complexes of 2,5-Me₂Dicyd²⁻, 2-MeODicyd²⁻, 2-MeDicyd²⁻ and Dicyd²⁻ (ClO₄⁻ complex salt only) are estimated. ^bexchange coupling constant (in cm⁻¹) estimated from $\chi_m = C/(T - \theta) + (2Ng^2\beta^2/3kT) [1 + (1/3)\exp(-2J/kT)]^{-1} + \chi_p$, where the convention for $-J$ is ($\mathcal{H} = -JS_a \cdot S_b$). ^cenergy gap (in eV) estimated from $\Delta E = E_{op} - \lambda$ where E_{op} is the $b_1^* \leftarrow b_1$ LMCT energy in aqueous solution and λ is a correction term (refer to text). ^delectronic exchange integral (in cm⁻¹) estimated from $2J = 2H_{ab}^2/E_{op}$ where E_{op} is the MMCT energy (refer to text). ^{e,h-k}from Ref. 44 and 43. ^ffrom Ref. 80. ^gfrom Ref. 79.

Antiferromagnetic coupling of this magnitude at an estimated through space separation between metal ions of 13.2 Å is unprecedented for any metal ion dimer system,^{1,106} and has been shown to be due to a continuous and energetically favourable superexchange pathway involving the magnetic $d\pi$ orbitals of the Ru(III) ions and the π symmetry frontier molecular orbitals of the bridging 1,4-dicyanamidobenzene dianion ligands.

To elaborate, with reference to the results of EHMO calculations performed on the bis(tetraphenylarsonium) salts of the 1,4-dicyanamidobenzene dianion ligands (refer to Section 3.2.6), both the HOMO and SHOMO are of π symmetry and span the entire molecule. Note that for the dianion ligands as a whole (excluding 2-MeODicyd²⁻ and 2-MeDicyd²⁻ for which EHMO calculations have not been performed), the electron density coefficients of HOMO and SHOMO are essentially the same with differences being readily

ascribable to the nature of the substituents on the phenyl ring. Recall that the X-ray structural determination of $[\mu\text{-(Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{OTs}]_4$ (refer to Section 5.1.3) showed that the planarity of the Dicyd^{2-} ligand was retained upon coordination. However, two conformations of the dinuclear complex were observed. In the case of conformer A, where both Ru(III)-cyanamide bonds are essentially linear, the dianion ligand's HOMO possesses an optimum orientation that enables it to simultaneously interact with the exchange coupled $d\pi_{xz}$ orbitals of the Ru(III) ions. For conformer B, where both Ru(III)-cyanamide bonds are bent, it is the SHOMO of the dianion ligand that has the correct orientation to simultaneously interact with the exchange coupled $d\pi_{xy}$ orbitals of the Ru(III) ions. Therefore, independent of which conformation the dinuclear complex adopts, a continuous and energetically favourable π exchange pathway between Ru(III) ions exists.

The trend of increasing antiferromagnetic coupling on going from the [Ru(III), Ru(III)] complex of 2,3,4,5- $\text{Cl}_4\text{Dicyd}^{2-}$ to that of 2,5- $\text{Me}_2\text{Dicyd}^{2-}$ is the result of an inner-sphere perturbation of the Ru(III)-cyanamide π bond. The rationalization is that the energy gap ΔE between the magnetic $d\pi$ orbitals of Ru(III) and the π symmetry HOMO of the dianion ligand decreases as the π donor strength of the bridging ligand increases. ΔE can be estimated (refer to the results in Table 5.2) from the energy E_{op} of the $b_1^* \leftarrow b_1$ LMCT transition taking into account a correction term λ (refer to Eq. 1.4 in Section 1.2.3), that compensates for the change in inner and outer coordination sphere configurations resulting from a transition into an excited vibrational level of the excited electronic state. Note that λ has been assigned the value of 0.75 eV. This represents the average of 0.61 eV, which is the intercept of the linear correlation between E_{op} and the difference between ligand and metal redox potentials for a series of pentaammineruthenium(III) complexes of anionic phenylcyanamide ligands found in Ref. 46, and 0.88 eV, the average MMCT band energy of the mixed-valence [Ru(III), Ru(II)] complexes ($[\mu\text{-(L)}\text{-(NH}_3)_5\text{Ru}_2]^{3+}$) of the six 1,4-dicyanamidobenzene dianion ligands (refer to Table 5.5 of Section 5.1.5b). It should also

be pointed out that the $b_1^* \leftarrow b_1$ LMCT oscillator strength (refer to Table 5.3a-f of Section 5.1.5a), which is related to the overlap between the π symmetry HOMO of the dianion ligands and the $d\pi$ orbitals of Ru(III), also increases as the energy gap decreases. This result is not unexpected as the $b_1^* \leftarrow b_1$ LMCT transition figures prominently in the superexchange mechanism.

The effect of the planarity of the 1,4-dicyanamidobenzene dianion ligand on the magnitude of superexchange has been illustrated by the study of $[\mu-(2,3,4,5\text{-Me}_4\text{Dicyd})\text{-(NH}_3)_5\text{Ru}_2][\text{ClO}_4]_4$.⁴⁵ Temperature dependent magnetic susceptibility data gave, after modeling with the modified Bleaney-Bowers expression, $-J = 110 \text{ cm}^{-1}$ ($\mathcal{H} = -JS_a \cdot S_b$). An EHMO calculation showed that the π symmetry HOMO of $2,3,4,5\text{-Me}_4\text{Dicyd}^{2-}$ had most of its electron density localized on the phenyl ring, verifying that steric repulsion forces the cyanamide groups into an anti configuration out of the phenyl ring plane. The result would be a poorer overlap with the magnetic $d\pi$ orbitals of Ru(III) and reduced superexchange compared to the other planar dianion ligand derivatives. Note that for $[\mu-(2,3,4,5\text{-Me}_4\text{Dicyd})\text{-(NH}_3)_5\text{Ru}_2][\text{ClO}_4]_4$, the energy gap ΔE has been estimated to be 0.76 eV, which is close to that of $[\mu-(2,5\text{-Cl}_2\text{Dicyd})\text{-(NH}_3)_5\text{Ru}_2][\text{Cl}]_4$, suggesting that the energy gap between the HOMO of the dianion ligand and the magnetic $d\pi$ orbitals of Ru(III) may be the dominant factor in determining the magnitude of $-J$.

The counteranion dependence of $-J$ for $[\mu\text{-(Dicyd)}\text{-(NH}_3)_5\text{Ru}_2]^{4+}$ must be addressed. Note that variations in the exchange coupling constant produced by a counter anion effect are normally the result of intermolecular exchange interactions.^{49,107} However, in the case of $[\mu\text{-(Dicyd)}\text{-(NH}_3)_5\text{Ru}_2]^{4+}$, an absolute difference in J of approximately 300 cm^{-1} is much too large to be accounted for by the weak intermolecular interactions known to exist between octahedral Ru(III) ions.¹⁰⁸ A more probable explanation is that hydrogen bonding interactions in the crystal lattice between counteranions and solvent molecules with ammine ligands coordinated to Ru(III) can facilitate the decoupling of Ru(III) from the

cyanamide ligand.⁴⁷ With reference to Section 5.1.7, solvent dependent antiferromagnetic exchange has been demonstrated by the observation that for solutions of the [Ru(III), Ru(II)] complexes, paramagnetism increases with solvent donor number (ie. on going from nitromethane to dimethyl sulfoxide). Note that the solution ¹H NMR spectra (refer to Section 5.1.8) demonstrate that the integrity of the dinuclear complexes is maintained over the entire solvent range.

The electronic exchange integral H_{ab} for the [Ru(III), Ru(III)] complexes of this study can be estimated (refer to the results in Table 5.2) from the magnetic data by using Bertrand's expression (refer to Eq. 1.3 in Section 1.2.2). For large metal-metal separations, as is the case for the dinuclear complexes at hand, H_{ab} can be readily estimated from the metal to metal charge transfer (MMCT) energy E'_{op} and the exchange coupling constant $-J$. Unfortunately, the MMCT band for the [Ru(III), Ru(III)] complexes has not been observed experimentally, as it is believed that the intense low energy LMCT bands obscure these transitions (refer to Section 5.1.5). However, a good estimate of E'_{op} is 2.6 eV, which is simply the difference in the PES d -orbital binding energies of [Ru(NH₃)₆][Cl]₃ and [Ru(en)₃][ZnCl₄].¹⁰⁶ Importantly, the increasing trend in H_{ab} parallels that of $-J$ as ΔE decreases, reflective of the inner-sphere perturbation (increasing the π donor strength of the bridging ligand) of the Ru(III)-cyanamide bond.

As a final note, as a means of deconvoluting the intense low energy LMCT bands from the predicted MMCT bands of the [Ru(III), Ru(III)] complexes, future work will examine the application of electroabsorption spectroscopy to MMCT transitions.⁴⁰⁻⁴²

5.1.5 Electronic Absorption Spectroscopy

The solvent dependent electronic absorption spectral data for both the [Ru(III), Ru(III)] and the mixed-valence [Ru(III), Ru(II)] complexes of the 1,4-dicyanamidobenzene dianion ligands are presented in separate subsections.

5.1.5a [Ru(III), Ru(III)] Complexes

The UV-vis-NIR (ie. 200 to 1400 nm) absorption spectra of $[\mu\text{-(2,5-Me}_2\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{ClO}_4]_4$, $[\mu\text{-(Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{ClO}_4]_4$, $[\mu\text{-(2,5-Cl}_2\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{Cl}]_4$ and $[\mu\text{-(2,3,4,5-Cl}_4\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{Cl}]_4$ in aqueous solution have been previously reported.^{43,44,81} Also previously reported, are the UV-vis-NIR (ie. 200 to 2200 nm) spectra of $[\mu\text{-(2-MeDicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{PF}_6]_4$ and $[\mu\text{-(2-MeODicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{PF}_6]_4$ in acetonitrile.^{79,80} The following subsection expands on these results by demonstrating the outer-sphere (varying solvent) dependency of the electronic absorption spectral features, in particular the $b_1^* \leftarrow b_1$ LMCT transition, for the six [Ru(III), Ru(III)] complexes in a range of solvents that includes nitromethane, acetonitrile, acetone, DMSO and water. In addition, the inner-sphere (varying the π donor strength of the bridging ligand) dependency of the $b_1^* \leftarrow b_1$ LMCT transition, in a given solvent, will be examined. Owing to the fact that the LMCT transition figures very prominently in the superexchange mechanism, this data will permit the examination of both the outer- and inner-sphere dependency of metal-metal coupling in the $[\mu\text{-(L)}\text{-(NH}_3)_5\text{Ru}_2]^{4+}$ complexes.

The electronic absorption band assignments of the [Ru(III), Ru(III)] complexes are identical to what has been previously discussed for mononuclear pentaammineruthenium(III) complexes of 1,4-dicyanamidobenzene monoanion and dianion ligands (refer to Section 4.1.3) and anionic phenylcyanamide ligands.^{46,86} With regards

to individual band properties, both differences and similarities exist between the $[\mu\text{-(L)}\text{-(NH}_3)_5\text{Ru}]_2]^{4+}$ and $[(\text{NH}_3)_5\text{Ru(L)}]^+$ complexes, where $\text{L} = 2,5\text{-Me}_2\text{Dicyd}^{2-}$, Dicyd^{2-} and $2,5\text{-Cl}_2\text{Dicyd}^{2-}$. The most obvious difference pertains to the observation that the experimental intensity (and oscillator strength) of the lowest energy $b_1^* \leftarrow b_1$ LMCT transition is approximately two times larger for the dinuclear complexes. For example, in aqueous solution, ϵ_{max} for the $b_1^* \leftarrow b_1$ LMCT transition of $[\mu\text{-(2,5-Me}_2\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}]_2]^{4+}$ has a value of $15488 \text{ cm}^{-1} \text{ M}^{-1}$ ($f = 0.388$), whereas, for the analogous transition of $[(\text{NH}_3)_5\text{Ru(2,5-Me}_2\text{Dicyd)}]^+$, ϵ_{max} has a value of $8710 \text{ cm}^{-1} \text{ M}^{-1}$ ($f = 0.215$). The approximate doubling in intensity and oscillator strength is, of course, consistent with the fact that there are two Ru(III)-cyanamide chromophores present in the dinuclear complexes. The most notable similarity in band properties (not observed when $\text{L} = 2,5\text{-Cl}_2\text{Dicyd}^{2-}$) is concerned with both the $b_1^* \leftarrow b_1$ LMCT transition and the higher energy $b_1^* \leftarrow b_2$ LMCT transition, and the observation that they split into what appears to be two overlapping bands. Note that for the six dinuclear complexes, the splitting of the LMCT bands was not restricted to aqueous solution, as it was also observed in nitromethane, acetonitrile, acetone and DMSO (indicated as shoulders in Table 5.3a-f). Recall what has been previously discussed in the case of the $[(\text{NH}_3)_5\text{Ru(L)}]^+$ complexes, in that since these LMCT transitions are singly degenerate, such splitting could be regarded as evidence for a conformer equilibrium in solution. One such equilibrium could be made up of the bent and linear Ru(III) coordination conformers found in the X-ray structure of $[\mu\text{-(Dicyd)}\text{-(NH}_3)_5\text{Ru}]_2][\text{OTs}]_4$ (refer to Section 5.1.3). Another possibility exists if the cyanamide groups of the dianion ligand are free to rotate, thereby, setting up an equilibrium between syn and anti in-plane and out-of-plane ligand conformations (refer to Section 3.2.5). Of course, vibrational splitting is also a possibility.

The solvent dependency of the electronic absorption features of the six $[\mu\text{-(L)}\text{-(NH}_3)_5\text{Ru}]_2][\text{PF}_6]_4$ complexes is summarized in Table 5.3a-f. Note that due to solvent

cut-offs of 390 nm for nitromethane and 340 nm for acetone, the ligand centered $\pi^* \leftarrow \pi$ transitions were not observed in these solvents. As well, the solvent cut-off of 275 nm prevented the observation of the highest energy $\pi^* \leftarrow \pi$ transition in DMSO. The lowest energy $b_1^* \leftarrow b_1$ LMCT transition, which figures prominently in the superexchange mechanism, is the dominant feature of the electronic absorption spectra of the [Ru(III), Ru(III)] complexes. The transition is highly solvent dependent, as illustrated by the vis-NIR (ie. 500 to 1500 nm) spectrum of $[\mu\text{-(2,5-Me}_2\text{Dicyd)}\text{-}\{(\text{NH}_3)_5\text{Ru}\}_2][\text{PF}_6]_4$ shown in Figure 5.4.

Figure 5.4 Lowest energy LMCT band of $[\mu\text{-(2,5-Me}_2\text{Dicyd)}\text{-}\{(\text{NH}_3)_5\text{Ru}\}_2][\text{PF}_6]_4$, with a concentration of 9.925×10^{-6} M in (A) nitromethane, (B) acetonitrile, (C) acetone, and (D) DMSO.

Table 5.3a Solvent-Dependent Electronic Absorption Spectral Data for [μ -(2-MeODicyd)- $\{(\text{NH}_3)_5\text{Ru}\}_2\}[\text{PF}_6]_4$.^a

Solvents ^b	$\pi^* \leftarrow \pi$	LMCT	
		$b_1^* \leftarrow b_2$	$b_1^* \leftarrow b_1$
nitromethane (2.7)	c	394 (3.84), 498 (sh)	1111 (4.80) [0.726], 932 (sh)
acetonitrile (14.1)	214 (4.54), 273 (4.13), 294 (sh)	388 (3.79), 485 (sh)	1125 (4.79) [0.730], 923 (sh)
acetone (17.0)	c	385 (3.70), 462 (sh)	1115 (4.62) [0.591], 913 (sh)
DMSO (29.8)	279 (4.29), 314 (sh)	380 (3.73)	977 (4.22) [0.376], 815 (sh)
water (18.0)	213 (4.52), 268 (4.23), 301 (sh)	359 (3.70)	999 (4.20) [0.398], 801 (sh)

^aAll data are in nm (log ϵ in parentheses and the total oscillator strength from two Ru(III)-cyanamide chromophores, calculated from $f = 4.61 \times 10^{-9} \epsilon_{\text{max}} \Delta\nu_{1/2}$, in brackets); concentration = 1.291×10^{-5} M; sh=shoulder; data in acetonitrile is from Ref. 80. ^bsolvent donor numbers in parentheses. ^cnot observed because of solvent cut-off.

Table 5.3b Solvent-Dependent Electronic Absorption Spectral Data for [μ -(2,5-Me₂Dicyd)- $\{(\text{NH}_3)_5\text{Ru}\}_2\}[\text{PF}_6]_4$.^a

Solvents ^b	$\pi^* \leftarrow \pi$	LMCT	
		$b_1^* \leftarrow b_2$	$b_1^* \leftarrow b_1$
nitromethane (2.7)	c	395 (3.78), 509 (sh)	1101 (4.83) [0.718], 871 (sh)
acetonitrile (14.1)	212 (4.48), 275 (4.15)	385 (3.70), 478 (sh)	1121 (4.81) [0.684], 850 (sh)
acetone (17.0)	c	384 (3.60)	1118 (4.63) [0.550], 843 (sh)
DMSO (29.8)	280 (4.32)	377 (3.78)	1011 (4.20) [0.372], 810 (sh)
water (18.0)	211 (4.50), 263 (4.24), 303 (sh)	358 (3.65)	1022 (4.19) [0.388], 793 (sh)

^aAll data are in nm (log ϵ in parentheses and the total oscillator strength from two Ru(III)-cyanamide chromophores, calculated from $f = 4.61 \times 10^{-9} \epsilon_{\text{max}} \Delta\nu_{1/2}$, in brackets); concentration = 9.925×10^{-6} M; sh=shoulder. ^bsolvent donor numbers in parentheses. ^cnot observed because of solvent cut-off.

Table 5.3c Solvent-Dependent Electronic Absorption Spectral Data for $[\mu\text{-(2-MeDicyd)}\text{-(NH}_3)_5\text{Ru}]_2[\text{PF}_6]_4$.^a

Solvents ^b	$\pi^* \leftarrow \pi$	LMCT	
		$b_1^* \leftarrow b_2$	$b_1^* \leftarrow b_1$
nitromethane (2.7)	c	398 (3.79), 493 (sh)	1106 (4.79) [0.661], 937 (sh)
acetonitrile (14.1)	207 (4.49), 273 (4.18)	392 (3.66), 481 (sh)	1109 (4.74) [0.642], 911 (sh)
acetone (17.0)	c	383 (3.66)	1105 (4.60) [0.553], 878 (sh)
DMSO (29.8)	277 (4.30)	380 (3.74)	970 (4.18) [0.346], 805 (sh)
water (18.0)	207 (4.48), 265 (4.25)	362 (3.63)	965 (4.15) [0.364], 784 (sh)

^aAll data are in nm (log ϵ in parentheses and the total oscillator strength from two Ru(III)-cyanamide chromophores, calculated from $f = 4.61 \times 10^{-9} \epsilon_{\text{max}} \Delta\nu_{1/2}$, in brackets); concentration = 1.290×10^{-5} M; sh=shoulder; data in acetonitrile is from Ref. 79. ^bsolvent donor numbers in parentheses. ^cnot observed because of solvent cut-off.

Table 5.3d Solvent-Dependent Electronic Absorption Spectral Data for $[\mu\text{-(Dicyd)}\text{-(NH}_3)_5\text{Ru}]_2[\text{PF}_6]_4$.^a

Solvents ^b	$\pi^* \leftarrow \pi$	LMCT	
		$b_1^* \leftarrow b_2$	$b_1^* \leftarrow b_1$
nitromethane (2.7)	c	403 (3.66), 502 (sh)	1107 (4.80) [0.675], 913 (sh)
acetonitrile (14.1)	202 (4.48), 273 (4.22)	397 (3.66)	1094 (4.66) [0.606], 904 (sh)
acetone (17.0)	c	382 (3.63)	1087 (4.47) [0.477], 876 (sh)
DMSO (29.8)	282 (4.34)	367 (3.75)	904 (4.15) [0.351]
water (18.0)	202 (4.51), 267 (4.37)	359 (3.66)	871 (4.13) [0.351]

^aAll data are in nm (log ϵ in parentheses and the total oscillator strength from two Ru(III)-cyanamide chromophores, calculated from $f = 4.61 \times 10^{-9} \epsilon_{\text{max}} \Delta\nu_{1/2}$, in brackets); concentration = 1.401×10^{-5} M; sh=shoulder. ^bsolvent donor numbers in parentheses. ^cnot observed because of solvent cut-off.

Table 5.3e Solvent-Dependent Electronic Absorption Spectral Data for $[\mu-(2,5\text{-Cl}_2\text{Dicyd})-(\text{NH}_3)_5\text{Ru}]_2[\text{PF}_6]_4$.^a

Solvents ^b	$\pi^* \leftarrow \pi$	LMCT	
		$b_1^* \leftarrow b_2$	$b_1^* \leftarrow b_1$
nitromethane (2.7)	c	397 (3.69)	1089 (4.51) [0.537], 871 (sh)
acetonitrile (14.1)	218 (4.52), 281 (4.34), 314 (sh)	383 (3.75)	1006 (4.34) [0.468], 852 (sh)
acetone (17.0)	c	369 (3.78)	963 (4.22) [0.400], 827 (sh)
DMSO (29.8)	286 (4.40), 331 (sh)	394 (3.77)	791 (4.06) [0.275]
water (18.0)	215 (4.53), 272 (4.44), 327 (sh)	365 (3.83)	794 (4.10) [0.337]

^aAll data are in nm (log ϵ in parentheses and the total oscillator strength from two Ru(III)-cyanamide chromophores, calculated from $f = 4.61 \times 10^{-9} \epsilon_{\text{max}} \Delta\nu_{1/2}$, in brackets); concentration = 1.329×10^{-5} M; sh=shoulder. ^bsolvent donor numbers in parentheses. c=not observed because of solvent cut-off.

Table 5.3f Solvent-Dependent Electronic Absorption Spectral Data for $[\mu-(2,3,4,5\text{-Cl}_4\text{Dicyd})-(\text{NH}_3)_5\text{Ru}]_2[\text{PF}_6]_4$.^a

Solvents ^b	$\pi^* \leftarrow \pi$	LMCT	
		$b_1^* \leftarrow b_2$	$b_1^* \leftarrow b_1$
nitromethane (2.7)	c	400 (3.81)	953 (4.21) [0.409], 842 (sh)
acetonitrile (14.1)	223 (4.60), 287 (4.31), 336 (sh)	402 (3.85)	833 (4.15) [0.366]
acetone (17.0)	c	397 (3.81)	782 (4.07) [0.299]
DMSO (29.8)	279 (4.69), 339 (sh)	397 (3.81)	716 (3.95) [0.223]
water (18.0)	223 (4.51), 278 (4.20), 326 (sh)	395 (3.63)	711 (3.85) [0.209]

^aAll data are in nm (log ϵ in parentheses and the total oscillator strength from two Ru(III)-cyanamide chromophores, calculated from $f = 4.61 \times 10^{-9} \epsilon_{\text{max}} \Delta\nu_{1/2}$, in brackets); concentration = 1.395×10^{-5} M; sh=shoulder. ^bsolvent donor numbers in parentheses. c=not observed because of solvent cut-off.

With reference to the results of Table 5.3a-f, a clear trend in both the $b_1^* \leftarrow b_1$ LMCT optical energy E_{op} and total oscillator strength (which is the sum of the contributions from both Ru(III)-cyanamide chromophores) emerges. The trend, which is representative of an outer-sphere perturbation of the Ru(III)-cyanamide π bond, sees E_{op} increase and the oscillator strength decrease, for a given dinuclear complex, as the solvent's donor number increases. For example, in the case of $[\mu-(2,5\text{-Me}_2\text{Dicyd})-\{(\text{NH}_3)_5\text{Ru}\}_2][\text{PF}_6]_4$, E_{op} is the smallest in nitromethane and the largest in DMSO. The opposite is true for the LMCT oscillator strength. Notably, nitromethane and DMSO possess the smallest and largest donor numbers,¹⁰⁹ respectively, of the four aprotic solvents under study. Importantly, a similar trend has been previously reported for mononuclear pentaamminruthenium(III) complexes of anionic phenylcyanamide ligands where it was inferred that increases in E_{op} and decreases in the oscillator strength for the $b_1^* \leftarrow b_1$ LMCT transition with increasing solvent donor number were the direct consequence of an increasing energy separation and hence decreasing overlap between cyanamide anion π donor and Ru(III) $d\pi$ acceptor orbitals.⁴⁷ Extended to the dinuclear complexes, the analogy is an increasing energy separation and decreasing overlap between the π symmetry HOMO of the bridging ligand and the $d\pi$ orbitals of the Ru(III) ions. The non-bonding electron pairs of large donor number solvents strongly interact with the protons of the ammine ligands coordinated to Ru(III) in an outer-sphere interaction (refer to Scheme 1.3 in Section 1.2.5) causing electron density to flow to Ru(III), which destabilizes its $d\pi$ acceptor orbitals and thereby weakens the Ru(III)-cyanamide π bond. Water, on the otherhand, behaves differently as it is also an electron acceptor and can weaken the Ru(III)-cyanamide bond by protonation of the cyanamide group. In essence, the outer-sphere perturbation is causing the Ru(III) ions to become decoupled from the cyanamide groups of the bridging dianion ligand and hence, the superexchange pathway. In this regard, E_{op} and the oscillator strength for the $b_1^* \leftarrow b_1$ LMCT transition serve as a means of probing or gauging the magnitude of metal-metal coupling in the [Ru(III), Ru(III)] complexes as a function of solvent. Indeed, the

truth of this statement will be manifested with the observation that these dinuclear complexes display solvent dependent antiferromagnetic exchange (refer to Section 5.1.7).

Another trend that emerges from the results of Table 5.3a-f, which is representative of an inner-sphere perturbation of the Ru(III)-cyanamide π bond, sees E_{op} for the $b_1^* \leftarrow b_1$ LMCT transition increase and the oscillator strength decrease, for a given solvent, as the π donor strength of the coordinated 1,4-dicyanamidobenzene dianion ligand decreases. For example, in the case of nitromethane, E_{op} is the smallest for $[\mu-(2\text{-MeODicyd})-(\text{NH}_3)_5\text{Ru}]_2[\text{PF}_6]_4$ and the largest for $[\mu-(2,3,4,5\text{-Cl}_4\text{Dicyd})-(\text{NH}_3)_5\text{Ru}]_2[\text{PF}_6]_4$. The opposite is true for the LMCT oscillator strength. The implication is that 2-MeODicyd^{2-} is the strongest π donor and $2,3,4,5\text{-Cl}_4\text{Dicyd}^{2-}$ is the weakest. Similar behaviour in E_{op} and the oscillator strength of the $b_1^* \leftarrow b_1$ LMCT transition pertaining to mononuclear pentaammineruthenium(III) complexes of 1,4-dicyanamidobenzene monoanion and dianion ligands (refer to Section 4.1.3) and anionic phenylcyanamide ligands^{46,47b} has been observed. In these two studies, an increasing energy separation and hence decreasing overlap between cyanamide anion π donor and Ru(III) $d\pi$ acceptor orbitals, as the π basicity of the cyanamide ligand decreased, was used to rationalize the observed trends in both E_{op} and the oscillator strength of the LMCT transition. Extended to the dinuclear complexes, the analogy is an increasing energy separation and decreasing overlap between the π symmetry HOMO of the bridging ligand and the $d\pi$ orbitals of the Ru(III) ions. In this case, an inner sphere perturbation is causing a decoupling of the Ru(III) ions from the superexchange pathway.

5.1.5b [Ru(III), Ru(II)] Complexes

The UV-visible-NIR absorption spectra of $[\mu\text{-(Dicyd)}\text{-(NH}_3)_5\text{Ru}]_2^{4+}$, [Ru(III), Ru(III)], and its one-electron reduction product, [Ru(III), Ru(II)], obtained by spectroelectrochemical methods in aqueous (ie. 200 to 1800 nm) and acetonitrile (ie. 200 to 2200 nm) solution, is shown in Figure 5.5. Note that the two-electron reduction product, [Ru(II), Ru(II)], does not absorb in the specified regions. In aqueous solution, the reduction of the [Ru(III), Ru(III)] complex (Figure 5.5Ia) to form the mixed-valence [Ru(III), Ru(II)] species results in a steady decrease in the intensity of the $b_1^* \leftarrow b_1$ LMCT absorption band (from $\epsilon = 13490 \text{ M}^{-1}\text{cm}^{-1}$ to $\epsilon = 7200 \text{ M}^{-1}\text{cm}^{-1}$), and a concomitant growth of a NIR π^* absorption tail. The spectrum of the [Ru(III), Ru(II)] complex (Figure 5.5Ib) was obtained just prior to the loss of isosbestic behaviour, brought on by the formation of the [Ru(II), Ru(II)] species. Importantly, at this point of reduction, a coulometric measurement verified that one electron ($n = 1.07 \text{ eq mole}^{-1}$) had been transferred. The NIR tail has been assigned to an intervalence (IT) transition, which is partially obscured by the relatively intense LMCT band. Note that in aqueous solution, re-oxidation of the [Ru(III), Ru(II)] species did not result in the complete regeneration of [Ru(III), Ru(III)] complex. This is likely due to the lability of pentaamminruthenium(II) to ligand substitution. In acetonitrile, the one-electron reduction ($n = 1.02 \text{ eq mole}^{-1}$) of the [Ru(III), Ru(III)] complex (Figure 5.5IIa) to form the mixed-valence [Ru(III), Ru(II)] species (Figure 5.5IIb) results in the appearance of a new distinct band in the NIR, that has been assigned to an intervalence transition. Unlike the behaviour observed in aqueous solution, the re-oxidation of the [Ru(III), Ru(II)] species to form the [Ru(III), Ru(III)] complex was completely reversible.

Figure 5.5 Vis-NIR absorption spectra of $[\mu\text{-(Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{PF}_6]_4$ and its electrochemically produced mixed-valence complex in I D_2O (0.1 M NaClO_4) solution with a concentration of 3.165×10^{-5} M, and II acetonitrile (0.1 M TBAH) solution with a concentration of 1.888×10^{-5} M. **a** and **b** represent the $[\text{Ru(III)}, \text{Ru(III)}]$ and $[\text{Ru(III)}, \text{Ru(II)}]$ complexes, respectively. The weak absorptions near 1700 and 1900 nm in II are instrumental artifacts that arise from large background absorption by the solvent.

Owing to the fact that the LMCT and IT transitions displayed by the $[\text{Ru(III)}, \text{Ru(II)}]$ complex in both aqueous and acetonitrile solution are overlapping, a Hush model treatment of IT band properties could not be performed. Instead, the IT and LMCT transitions were deconvoluted from each other by using non-linear curve fitting analysis. Figure 5.6 shows that four Gaussian bands (chosen arbitrarily and not reflecting any expected transitions) were used to fit the $b_1^* \leftarrow b_1$ LMCT band profile of the $[\text{Ru(III)}, \text{Ru(III)}]$ complex in aqueous solution. This fit (keeping the relative properties of the Gaussian contributions constant) with the addition of a low energy Gaussian band to represent the IT transition,

was then used to model the band profile of the [Ru(III), Ru(II)] as shown in Figure 5.7. Note that for the [Ru(III), Ru(II)] complex in aqueous solution, the fit had a square of the correlation coefficient $R^2 = 0.998$ while in acetonitrile, a similar analysis had $R^2 = 0.996$ for the [Ru(III), Ru(II)] complex. Values of E_{op} , ϵ_{max} and $\Delta\nu_{1/2}$ for the fitted low energy Gaussian IT band are summarized in Table 5.4.

Table 5.4 Solvent-Dependent Electronic Absorption Spectral Data for the Intervalence Transition of $[\mu\text{-(Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{PF}_6]_3$.^a

Solvents	E_{op}	ϵ_{max}	$\Delta\nu_{1/2}$	f	calcd. $\Delta\nu_{1/2}$ ^b	H_{ad} ^c	H_{ad} ^d
acetonitrile	6912	19373	2635	0.235	3996	927	3456
D ₂ O	8185	2710	4087	0.051	4348	470	4063

^aAll data are in cm^{-1} except for ϵ_{max} which is in $\text{M}^{-1}\text{cm}^{-1}$ and oscillator strength which is calculated from $f = 4.61 \times 10^{-9} \epsilon_{max} \Delta\nu_{1/2}$; complex concentration = 1.958×10^{-5} M in acetonitrile and 3.023×10^{-5} M in D₂O. ^bcalculated Hush limit of $\Delta\nu_{1/2} = (2310E_{op})^{1/2}$ for a Class II system. ^cresonance exchange integral calculated from Hush theory is given by: $H_{ad} = (2.06 \times 10^{-2}/R) \cdot (E_{op}\epsilon_{max}\Delta\nu_{1/2})^{1/2}$ for a Class II system, where R is the transition dipole length (refer to text). ^d $H_{ad} = E_{op}/2$ for a Class III system.

Figure 5.6 Multiple Gaussian band fit of the LMCT transition profile of $[\mu\text{-(Dicyd)}\text{-(NH}_3)_5\text{Ru}_2]^{4+}$ in aqueous solution (from Figure 5.51a). The glitch at 12500 cm^{-1} is an instrumental artifact.

Figure 5.7 Multiple Gaussian band fit of the LMCT and IT transition profiles of $[\mu\text{-(Dicyd)}\text{-}\{(\text{NH}_3)_5\text{Ru}\}_2]^{3+}$ in aqueous solution (from Figure 5.5Ib). The glitch at 12500 cm^{-1} is an instrumental artifact.

It is important to note that in the preceding curve fitting analysis, two main assumptions were made. Firstly, the IT transition was described by a single Gaussian band, a condition that is not always observed experimentally.¹¹⁰ Secondly, the energy and band shape of the $b_1^* \leftarrow b_1$ LMCT transition does not change when one of the Ru(III)-cyanamide chromophores is reduced. A good test of the last assumption is given by the observation that for the [Ru(III), Cu(II)] complex of $[(\text{NH}_3)_5\text{Ru}(\mu\text{-Dicyd})\text{Cu}(\text{L})]^{2+}$, where $\text{L} = 1,3\text{-Bis}(\Delta\text{-pyridylimino})\text{isoindolinato}$,¹¹¹ the Ru(III)-cyanamide LMCT transition in acetonitrile has essentially the same profile as that seen for $[\mu\text{-(Dicyd)}\text{-}\{(\text{NH}_3)_5\text{Ru}\}_2]^{3+}$ in acetonitrile.

In Table 5.4, the Hush Theory calculated (refer to Eq. 1.32 in Section 1.4.1) $\Delta\nu_{1/2} = 4348\text{ cm}^{-1}$ for the [Ru(III), Ru(II)] complex in aqueous solution is in close agreement with the

curve fitted value of 4087 cm^{-1} , which is consistent with a weakly coupled Class II mixed-valence system. In contrast, the calculated $\Delta\nu_{1/2} = 3996\text{ cm}^{-1}$ for the $[\text{Ru(III)}, \text{Ru(II)}]$ complex in acetonitrile is significantly larger than the curve fitted value of 2635 cm^{-1} and therefore does not obey Hush Theory. The behaviour in acetonitrile is probably best described as being characteristic of a strongly coupled Class II mixed-valence system, intermediate between Class II and Class III. Table 5.4 also shows the magnitude of the resonance exchange integral H_{ad} , based on Class II and Class III behaviour (refer to Eqs. 1.33 and 1.34, respectively, in Section 1.4.1) for the $[\text{Ru(III)}, \text{Ru(II)}]$ complex in both acetonitrile and aqueous solution. Note that for the Class II calculation of H_{ad} , the transition dipole length R can be approximated to be $13.2\text{ \AA}$ (which is the through space distance between Ru(III) ions determined from the crystal structure analysis of $[\mu\text{-(Dicyd)}\text{-(NH}_3)_5\text{Ru}]_2[\text{OTs}]_4$, refer to Section 5.1.3). Given the class designations based on $\Delta\nu_{1/2}$, the magnitude of H_{ad} for the $[\text{Ru(III)}, \text{Ru(II)}]$ complex in acetonitrile is 2-7x larger than that in aqueous solution. Therefore, electronic coupling in the mixed-valence $[\text{Ru(III)}, \text{Ru(II)}]$ complex in acetonitrile is significantly greater than that in aqueous solution. The statement is supported by comproportionation constants of 6.84×10^4 and 55 in acetonitrile and aqueous solution, respectively (refer to Table 5.6d in Section 5.1.6). It is also important to point out that the IT oscillator strength of the $[\text{Ru(III)}, \text{Ru(II)}]$ complex, of which the $b_1^* \leftarrow b_1$ LMCT oscillator strength is a significant component, is almost 5x larger in acetonitrile compared to aqueous solution. The origin of this solvent dependent metal-metal coupling warrants further examination.

The stabilization energy (based on the weak coupling model) of superexchange metal-metal coupling in $[\mu\text{-(Dicyd)}\text{-(NH}_3)_5\text{Ru}]_2^{3+}$ results when the ground state mixes with the excited LMCT state as shown in Scheme 5.2.

Scheme 5.2

The stabilization, and hence superexchange, will be enhanced when the symmetry and energy parameters of the metal (Ru(III) and Ru(II)) $d\pi$ orbitals and the continuous π symmetry HOMO of the bridging Dicyd²⁻ ligand are closely matched. Recall the outer-sphere dependency of the $b_1^* \leftarrow b_1$ LMCT oscillator strength for the [Ru(III), Ru(III)] complex. With reference to Table 5.3d, $f = 0.351$ and 0.606 in aqueous and acetonitrile solution, respectively, from which it was inferred that the solvent's effect in decoupling the Ru(III) ions from the cyanamide groups of the bridging Dicyd²⁻ ligand is less in the case of acetonitrile, thus the Ru(III)-cyanamide π overlap is greater. In the mixed-valence [Ru(III), Ru(II)] complex, the preferential solvation or valence trapping of the Ru(III) coordination sphere (refer to Scheme 1.3 in Section 1.2.5) as opposed to that of Ru(II) stabilizes the oxidation state of the former (the acidity of an ammine proton is greater for an ammine bound to Ru(III)), thereby creating an energy barrier to the delocalization of the odd electron which leads to a decrease in the magnitude of metal-metal coupling. In effect, the $d\pi$ acceptor orbitals of Ru(III) are being decoupled from the superexchange pathway. The stronger the donor-acceptor interaction is between the the non-bonding electron pairs of the solvent and the protons of the ammine ligands coordinated to Ru(III) (note that in aqueous solution, protonation of the bridging ligand is an additional complication), the greater the energy barrier to delocalization and hence the weaker the metal-metal coupling. Outer-sphere donor-acceptor interactions have been invoked to rationalize solvent^{75,77,112} and crown ether¹⁵ induced valence trapping in other mixed-valence ruthenium ammine complexes. However, in these systems, the ruthenium ions are bridged

by π acceptor ligands where the dominant superexchange pathway for metal-metal coupling is expected to involve the LUMO of the bridging ligand.

Table 5.5 summarizes the electronic absorption spectral data for the intervalence transition of all six mixed-valence [Ru(III), Ru(II)] complexes in acetonitrile solution. The trend in the calculated Hush limit of $\Delta\nu_{1/2}$ compared to the value obtained from curve fitting analysis suggests that on going from the [Ru(III), Ru(II)] complex of 2-MeODicyd²⁻ to that of 2,3,4,5-Cl₄Dicyd²⁻, a borderline ClassII/Class III system designation is being transformed into one of a weakly coupled Class II. Table 5.5 also shows the magnitude of the resonance exchange integral H_{ad} , based on Class II and Class III behaviour for all six [Ru(III), Ru(II)] complexes in acetonitrile. Given the class designations based on $\Delta\nu_{1/2}$, the magnitude of H_{ad} for $[\mu\text{-(2-MeODicyd)}\text{-(NH}_3)_5\text{Ru}]_2^{3+}$ is 1.5-5x larger than that for $[\mu\text{-(2,3,4,5-Cl}_4\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}]_2^{3+}$. Therefore, electronic coupling decreases on going from the mixed-valence [Ru(III), Ru(II)] complex of 2-MeODicyd²⁻ to that of 2,3,4,5-Cl₄Dicyd²⁻. The statement is supported by a similar trend in comproportionation constants evaluated in acetonitrile, ranging from 1.74×10^5 for $[\mu\text{-(2-MeODicyd)}\text{-(NH}_3)_5\text{Ru}]_2^{3+}$ to 330 for $[\mu\text{-(2,3,4,5-Cl}_4\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}]_2^{3+}$ (refer to Tables 5.6a-f in Section 5.1.6). Furthermore, the trend in the resonance exchange integral H_{ad} is paralleled by the trend in the IT oscillator strength (f is almost 2x larger for $[\mu\text{-(2-MeODicyd)}\text{-(NH}_3)_5\text{Ru}]_2^{3+}$ compared to $[\mu\text{-(2,3,4,5-Cl}_4\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}]_2^{3+}$) from which it can be inferred that weaker metal-metal coupling is the result of poorer overlap between the $d\pi$ acceptor orbitals of Ru(III) and the π symmetry HOMO of the bridging dianion ligand. As was displayed by the [Ru(III), Ru(III)] complexes in a given solvent (refer to Table 5.3a-f), the inner-sphere perturbation of decreasing the π donor strength of the 1,4-dicyanamidobenzene dianion ligand results in a decoupling of the Ru(III) $d\pi$ orbitals from the superexchange pathway.

Table 5.5 Electronic Absorption Spectral Data for the Intervalence Transition of the [Ru(III), Ru(II)] Complexes of 1,4-Dicyanamidobenzene Dianion Ligands in Acetonitrile.^a

Complexes ^b	E_{op}	ϵ_{max}	$\Delta\nu_{1/2}$	f	calcd. $\Delta\nu_{1/2}$ ^c	H_{ad} ^d	H_{ad} ^e
f 2-MeODicyd ²⁻	7225	24743	2447	0.279	4085	1032	3613
g 2,5-Me ₂ Dicyd ²⁻	7115	20262	2341	0.218	4054	907	3558
h 2-MeDicyd ²⁻	6947	22226	2384	0.244	4006	947	3474
i Dicyd ²⁻	6912	19373	2635	0.235	3996	927	3456
j 2,5-Cl ₂ Dicyd ²⁻	6751	16293	3227	0.242	3949	930	3376
k 2,3,4,5-Cl ₄ Dicyd ²⁻	7392	8149	4025	0.151	4132	768	3696

^aAll data are in cm⁻¹ except for ϵ_{max} which is in M⁻¹cm⁻¹ and oscillator strength which is calculated from $f = 4.61 \times 10^{-9} \epsilon_{max} \Delta\nu_{1/2}$. ^bPF₆⁻ salts, only ligands shown for clarity. ^ccalculated Hush limit of $\Delta\nu_{1/2} = (2310E_{op})^{1/2}$ for a Class II system. ^dresonance exchange integral calculated from Hush theory is given by: $H_{ad} = (2.06 \times 10^{-2}/R) \cdot (E_{op}\epsilon_{max}\Delta\nu_{1/2})^{1/2}$ for a Class II system, where R is the transition dipole length (refer to text). ^e $H_{ad} = E_{op}/2$ for a Class III system. ^fconcentration=9.262 x 10⁻⁶ M, from Ref. 80. ^gconcentration=1.049 x 10⁻⁵ M. ^hconcentration=8.054 x 10⁻⁶ M, from Ref. 79. ⁱconcentration=1.958 x 10⁻⁵ M. ^jconcentration=9.459 x 10⁻⁶ M. ^kconcentration=9.765 x 10⁻⁶ M.

In order to perform a comprehensive evaluation of solvent perturbed superexchange in the mixed-valence dinuclear complexes of this study, future work will focus on obtaining (by spectroelectrochemical methods) the NIR absorption spectra of all six [Ru(III), Ru(II)] complexes in the expanded solvent range that includes nitromethane, acetonitrile, acetone, DMSO and water. However, preliminary studies have shown that problems associated with reversibility and complex stability will have to be overcome.

5.1.6 Cyclic Voltammetry

The cyclic voltammetry of [μ -(2,5-Me₂Dicyd)-{(NH₃)₅Ru}₂][ClO₄]₄, [μ -(Dicyd)-{(NH₃)₅Ru}₂][ClO₄]₄, [μ -(2,5-Cl₂Dicyd)-{(NH₃)₅Ru}₂][Cl]₄ and [μ -(2,3,4,5-

$\text{Cl}_4\text{Dicyd})\text{-(NH}_3)_5\text{Ru}_2][\text{Cl}]_4$ in aqueous solution has been previously reported.^{43,44,81} Also previously reported, is the cyclic voltammetry of $[\mu\text{-(2-MeDicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{PF}_6]_4$ and $[\mu\text{-(2-MeODicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{PF}_6]_4$ in acetonitrile.^{79,80} The following subsection expands on these results by demonstrating the outer-sphere (varying solvent) dependency of the redox couples for the six $[\text{Ru(III)}, \text{Ru(III)}]$ complexes in a range of solvents that includes nitromethane, acetonitrile, acetone, DMSO and water. In addition, the inner-sphere (varying the π donor strength of the bridging ligand) dependency of the redox couples, in a given solvent, will be examined. Importantly, these data will permit the examination of both the outer- and inner-sphere dependency of metal-metal coupling in the mixed-valence $[\text{Ru(III)}, \text{Ru(II)}]$ complexes.

The cyclic voltammograms of $[\mu\text{-(Dicyd)}\text{-(NH}_3)_5\text{Ru}_2]^{4+}$ in all five solvents are shown in Figures 5.8 to 5.12, inclusive, while the solvent dependent redox couples for all six $[\text{Ru(III)}, \text{Ru(III)}]$ complexes are summarized in Table 5.6a-f. The redox assignments are based on previous studies of mononuclear pentaammineruthenium(III) complexes of 1,4-dicyanamidobenzene monoanion and dianion ligands (refer to Section 4.1.5) and anionic phenylcyanamide ligands.^{46,86} In general, the cyclic voltammetry of the dinuclear complexes are characterized by two consecutive one-electron Ru(III/II) reduction couples, denoted by $E^\circ_{\text{M}_1}$ and $E^\circ_{\text{M}_2}$, as shown by Eq. a) of Scheme 5.3. However, in aqueous solution, $E^\circ_{\text{M}_1}$ and $E^\circ_{\text{M}_2}$ are closely overlapping such that a single two-electron couple, denoted by E^*_M , is actually observed. The redox chemistry is also characterized by two one-electron oxidation processes as shown by Eq. b) of Scheme 5.3, the first of which is a Ru(IV/III) process, denoted by $E^\circ_{\text{oxid}_1}$, to generate the mixed-valence dianion bridged $[\text{Ru(IV)}, \text{Ru(III)}]$ complex. The product of the second oxidation process, denoted by $E^\circ_{\text{oxid}_2}$, is not known for certain but is believed to be either a $[\text{Ru(IV)}, \text{Ru(III)}]$ complex bridged by the monoanion radical ligand or a $[\text{Ru(III)}, \text{Ru(III)}]$ complex bridged by the neutral fully oxidized ligand (refer to Section 3.2.4, dianion ligand-centered oxidations).

Note that previous studies have assigned $E^{\circ}_{\text{oxid}_1}$ and $E^{\circ}_{\text{oxid}_2}$ as two ligand centered oxidations that have been shifted anodically upon coordination to Ru(III).^{43,44,81} However, recent spectroelectrochemical studies (refer to Section 5.2.4) have suggested $E^{\circ}_{\text{oxid}_1}$ to be a metal-centered Ru(III/IV) oxidation couple. Additional spectroelectrochemical work is required to identify the exact nature of the second oxidation product.

Scheme 5.3

The reversibility of the redox couples for the six [Ru(III), Ru(III)] complexes varies depending on the solvent conditions and on the nature of the bridging ligand. The following discussion summarizes these differences. In nitromethane, both $E^{\circ}_{\text{M}_1}$ and $E^{\circ}_{\text{M}_2}$ are quasi-reversible with peak to peak ($E_{\text{pa}} - E_{\text{pc}}$) separations in the 60-75 and 65-80 mV range, respectively, at 100 mVs⁻¹ that increase with scan rate. The exception occurs for [μ -(2,5-Me₂Dicyd)-{(NH₃)₅Ru}₂][Ph₄B]₄, where both $E^{\circ}_{\text{M}_1}$ and $E^{\circ}_{\text{M}_2}$ are at best quasi-reversible, displaying peak to peak separations of 100 and 85 mV, respectively, at 1 Vs⁻¹. At scan rates below 1 Vs⁻¹, $E^{\circ}_{\text{M}_2}$ becomes irreversible with the loss of its oxidation wave and appearance of a high anodic current at 0.227 V vs. NHE. The high current of the anodic wave suggests that the fully reduced [Ru(II), Ru(II)] complex has been deposited on the electrode. For the oxidation couples in nitromethane, $E^{\circ}_{\text{oxid}_1}$ is quasi-reversible with

peak to peak separations in the 60-90 mV range independent of scan rate. Owing to interference from the oxidation processes associated with the the Ph_4B^- complex counteranion, the positively shifted $E^\circ_{\text{oxid}_1}$ couples of $[\mu\text{-(2,5-Cl}_2\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{Ph}_4\text{B}]_4$ and $[\mu\text{-(2,3,4,5-Cl}_4\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{Ph}_4\text{B}]_4$ were not observed. For the same reason, $E^\circ_{\text{oxid}_2}$ was not observed for these two latter complexes and also not for $[\mu\text{-(2-MeODicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{Ph}_4\text{B}]_4$ and $[\mu\text{-(2-MeDicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{Ph}_4\text{B}]_4$. However, for both $[\mu\text{-(2,5-Me}_2\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{PF}_6]_4$ and $[\mu\text{-(Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{PF}_6]_4$, $E^\circ_{\text{oxid}_2}$ is quasi-reversible with peak to peak separations of 75 and 68 mV, respectively, at 100 mVs^{-1} that increase with scan rate. It should be noted that except for $[\mu\text{-(2,5-Me}_2\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{PF}_6]_4$ and $[\mu\text{-(Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{PF}_6]_4$, PF_6^- complex salts were not sufficiently soluble in nitromethane to conduct cyclic voltammetry measurements. Instead the very versatile Ph_4B^- complex salts were used. In acetonitrile, both $E^\circ_{\text{M}_1}$ and $E^\circ_{\text{M}_2}$ are at best quasi-reversible with peak to peak separations in the 75-125 and 85-120 mV range, respectively, at $1\text{-}2 \text{ Vs}^{-1}$. Similar to behaviour in nitromethane, at scan rates below 1 Vs^{-1} for the $[\text{Ru(III)}, \text{Ru(III)}]$ complexes of 2-MeODicyd^{2-} , 2-MeDicyd^{2-} and Dicyd^{2-} and at scan rates below 2 Vs^{-1} for the $[\text{Ru(III)}, \text{Ru(III)}]$ complexes of $2,5\text{-Cl}_2\text{Dicyd}^{2-}$ and $2,3,4,5\text{-Cl}_4\text{Dicyd}^{2-}$, $E^\circ_{\text{M}_2}$ becomes irreversible with the loss of its oxidation wave and appearance of a high anodic current. The exception occurs for $[\mu\text{-(2,5-Me}_2\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{PF}_6]_4$, where both $E^\circ_{\text{M}_1}$ and $E^\circ_{\text{M}_2}$ are quasi-reversible with peak to peak separations of 83 and 77 mV, respectively, at 200 mVs^{-1} that increase with scan rate. For the oxidation couples in acetonitrile, $E^\circ_{\text{oxid}_1}$ is quasi-reversible with peak to peak separations in the 60-90 mV range independent of scan rate. $E^\circ_{\text{oxid}_2}$ is also quasi-reversible (less reversible than $E^\circ_{\text{oxid}_1}$) with peak to peak separations in the 80-90 mV range at 100 mVs^{-1} that increase with scan rate. In acetone, both $E^\circ_{\text{M}_1}$ and $E^\circ_{\text{M}_2}$ are at best quasi-reversible with peak to peak separations in the 90-140 and 85-135 mV range, respectively, at $1\text{-}3 \text{ Vs}^{-1}$. Similar to behaviour in nitromethane and acetonitrile, at scan rates below 1 Vs^{-1} for the $[\text{Ru(III)}, \text{Ru(III)}]$ complexes of 2-MeDicyd^{2-}

and Dicyd²⁻ and at scan rates below 2 Vs⁻¹ for the [Ru(III), Ru(III)] complex of 2,5-Me₂Dicyd²⁻ and at scan rates below 3 Vs⁻¹ for the [Ru(III), Ru(III)] complexes of 2,5-Cl₂Dicyd²⁻ and 2,3,4,5-Cl₄Dicyd²⁻, $E^\circ_{M_2}$ becomes irreversible with the loss of its oxidation wave and appearance of a high anodic current. The exception occurs for $[\mu-(2\text{-MeODicyd})-(\text{NH}_3)_5\text{Ru}]_2[\text{PF}_6]_4$, where both $E^\circ_{M_1}$ and $E^\circ_{M_2}$ are quasi-reversible with peak to peak separations of 60 and 75 mV, respectively, at 100 mVs⁻¹ that increase with scan rate. For the oxidation couples in acetone, $E^\circ_{\text{oxid}_1}$ is quasi-reversible with peak to peak separations in the 75-80 mV range at 100 mVs⁻¹ that increase with scan rate. The exceptions are $[\mu-(2\text{-MeODicyd})-(\text{NH}_3)_5\text{Ru}]_2[\text{PF}_6]_4$ and $[\mu-(2\text{-MeDicyd})-(\text{NH}_3)_5\text{Ru}]_2[\text{PF}_6]_4$, where $E^\circ_{\text{oxid}_1}$ is at best quasi-reversible with peak to peak separations of 90 mV (at 1 Vs⁻¹) and 110 mV (at 500 mVs⁻¹), respectively, that are scan rate dependent. $E^\circ_{\text{oxid}_2}$ is at best quasi-reversible (less reversible than $E^\circ_{\text{oxid}_1}$) with peak to peak separations in the 95-140 mV range at 100 mVs⁻¹ that increase with scan rate. Note that $E^\circ_{\text{oxid}_2}$ for $[\mu-(2,3,4,5\text{-Cl}_4\text{Dicyd})-(\text{NH}_3)_5\text{Ru}]_2[\text{PF}_6]_4$ is irreversible as only the anodic wave with $E_{\text{pa}} = 1.505$ V vs. NHE is observed at 100 mVs⁻¹. For the exceptions of $[\mu-(2\text{-MeODicyd})-(\text{NH}_3)_5\text{Ru}]_2[\text{PF}_6]_4$ and $[\mu-(2\text{-MeDicyd})-(\text{NH}_3)_5\text{Ru}]_2[\text{PF}_6]_4$, $E^\circ_{\text{oxid}_2}$ is at best quasi-reversible with peak to peak separations of 130 mV (at 1 Vs⁻¹) and 105 mV (at 500 mVs⁻¹), respectively, that are scan rate dependent. In DMSO, both $E^\circ_{M_1}$ and $E^\circ_{M_2}$ are quasi-reversible with peak to peak separations in the 60-75 and 60-70 mV range, respectively, at 100 mVs⁻¹, that increase with scan rate. For the oxidation couples in DMSO, $E^\circ_{\text{oxid}_1}$ is quasi-reversible with peak to peak separations in the 65-80 mV range at 100 mVs⁻¹, that increase with scan rate. $E^\circ_{\text{oxid}_2}$ is at best pseudo-reversible (less reversible than $E^\circ_{\text{oxid}_1}$) with peak to peak separations in the 90-105 mV range at 100 mVs⁻¹ that increase with scan rate. For $[\mu-(\text{Dicyd})-(\text{NH}_3)_5\text{Ru}]_2[\text{PF}_6]_4$, $E^\circ_{\text{oxid}_2}$ is irreversible as its anodic to cathodic current intensity ratio (i_a/i_c) is greater than unity. Note that the positively shifted $E^\circ_{\text{oxid}_2}$ couples of $[\mu-(2,5\text{-Cl}_2\text{Dicyd})-(\text{NH}_3)_5\text{Ru}]_2[\text{PF}_6]_4$ and $[\mu-(2,3,4,5\text{-Cl}_4\text{Dicyd})-(\text{NH}_3)_5\text{Ru}]_2[\text{PF}_6]_4$ are not observed within the solvent's positive

limit. In aqueous solution, as previously mentioned, E^*_M is the only metal-centered reduction couple observed. Evidence that supports the claim that E^*_M is actually comprised of closely overlapping $E^\circ_{M_1}$ and $E^\circ_{M_2}$ couples includes the following. Firstly, the current intensity of E^*_M ($i_a + i_c$) is approximately twice as large as that for $E^\circ_{\text{oxid}_1}$ and $E^\circ_{\text{oxid}_2}$ couples that are believed to be one-electron events. Secondly, the peak to peak separation for E^*_M ranges from 90-150 mV (depending on the complex) at 100 mVs⁻¹ and is scan rate independent. Finally, there is a slight shoulder evident in the cyclic voltammograms of $[\mu-(2,5\text{-Me}_2\text{Dicyd})-(\text{NH}_3)_5\text{Ru}_2][\text{ClO}_4]_4$,^{43,44} $[\mu-(2\text{-MeODicyd})-(\text{NH}_3)_5\text{Ru}_2][\text{Cl}]_4$ and $[\mu-(2\text{-MeDicyd})-(\text{NH}_3)_5\text{Ru}_2][\text{Cl}]_4$. To determine the potential values of the individual metal couples, $E^\circ_{M_1}$ and $E^\circ_{M_2}$, from the cyclic voltammetry data, specific methods can be employed. They include the method of Myers and Shain^{113,114} where ΔE° (the calculated separation between the individual metal redox couples, $E^\circ_{M_1}$ and $E^\circ_{M_2}$) is determined from experimentally found values of $E_p - E_{p/2}$ (the difference between the peak potential and the half peak potential). Richardson and Taube¹¹⁵ have extended this work and applied it to diruthenium pentaammines. In order to apply this analysis, each separate redox process must be reversible over a wide scan range, and the switching potential must be at least 250 mV beyond E^*_M so that peak distortion can be minimized. In our study of [Ru(III), Ru(III)] complexes, the second criterion has been met and the first appears to be valid. For the oxidation couples in aqueous solution, $E^\circ_{\text{oxid}_1}$ is quasi-reversible with peak to peak separations in the 60-100 mV range at 100 mVs⁻¹, that increase with scan rate. $E^\circ_{\text{oxid}_2}$ is at best pseudo-reversible (less reversible than $E^\circ_{\text{oxid}_1}$) with peak to peak separations in the 90-105 mV range at 100 mVs⁻¹ that increase with scan rate. Note that $E^\circ_{\text{oxid}_2}$ for $[\mu-(2,3,4,5\text{-Cl}_4\text{Dicyd})-(\text{NH}_3)_5\text{Ru}_2][\text{Cl}]_4$ is irreversible as only the anodic wave with $E_{\text{pa}} = 1.032$ V vs. NHE is observed at 100 mVs⁻¹.

Figure 5.8 Cyclic voltammogram of $[\mu\text{-(Dicyd)}-\{(\text{NH}_3)_5\text{Ru}\}_2][\text{PF}_6]_4$ in nitromethane (0.1 M TBAH). (a) negative direction at a scan rate of 100 mVs^{-1} . (b) positive direction at a scan rate of 100 mVs^{-1} .

Figure 5.9 Cyclic voltammogram of $[\mu\text{-(Dicyd)}-\{(\text{NH}_3)_5\text{Ru}\}_2][\text{PF}_6]_4$ in acetonitrile (0.1 M TBAH). (a) negative direction at a scan rate of 1 Vs^{-1} . (b) positive direction at a scan rate of 100 mVs^{-1} .

Figure 5.10 Cyclic voltammogram of $[\mu\text{-(Dicyd)}\text{-}\{(\text{NH}_3)_5\text{Ru}\}_2][\text{PF}_6]_4$ in acetone (0.1 M TBAH). (a) negative direction at a scan rate of 1 Vs^{-1} . (b) positive direction at a scan rate of 100 mVs^{-1} .

Figure 5.11 Cyclic voltammogram of $[\mu\text{-(Dicyd)}-\{(\text{NH}_3)_5\text{Ru}\}_2][\text{PF}_6]_4$ in DMSO (0.1 M TBAH). (a) negative direction at a scan rate of 100 mVs^{-1} . (b) positive direction at a scan rate of 100 mVs^{-1} .

Figure 5.12 Cyclic voltammogram of $[\mu\text{-(Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{Cl}]_4$ in water (0.1 M NaClO_4). (a) negative direction at a scan rate of 100 mVs^{-1} . (b) positive direction at a scan rate of 100 mVs^{-1} .

Table 5.6a Solvent-Dependent Redox Couples and Comproportionation Constants for $[\mu-(2\text{-MeODicyd})-(\text{NH}_3)_5\text{Ru}]_2[\text{PF}_6]_4$.^a

Solvents ^b	$E^\circ_{\text{M}_1}$	$E^\circ_{\text{M}_2}$	ΔE°	K_{C}^{d}	$E^\circ_{\text{oxid}_1}$	$E^\circ_{\text{oxid}_2}$
nitromethane (2.7)	0.243 (68)	-0.083 (80)	326	3.24×10^5	0.922 (80)	e
acetonitrile (14.1)	0.097 (110)	-0.213 (90)	310	1.74×10^5	0.757 (90)	1.252 (115)
acetone (17.0)	-0.005 (60)	-0.283 (75)	288	7.39×10^4	0.660 (90)	1.155 (130)
DMSO (29.8)	-0.223 (65)	-0.413 (65)	190	1629	0.573 (65)	1.070 (90)
water (18.0)	-0.009 ^f	-0.118 ^f	109	70	0.560 (100)	0.947 (110)

^aAll couples are reported vs. NHE in V with $E_{\text{pa}} - E_{\text{pc}}$ in parentheses in mV; data in nitromethane (0.1 M TBAH) is based on a Ph_4B^- complex salt at a scan rate=100 mV s^{-1} ; data in acetonitrile (0.1 M TBAH) was obtained at an anodic scan rate=100 mV s^{-1} and a cathodic scan rate=1 V s^{-1} , from Ref. 80; data in acetone (0.1 M TBAH) was obtained at an anodic scan rate=1 V s^{-1} and a cathodic scan rate=100 mV s^{-1} ; data in DMSO (0.1 M TBAH) was obtained at a scan rate=100 mV s^{-1} ; data in water (0.1 M NaClO_4) is based on a Cl^- complex salt at a scan rate=100 mV s^{-1} ; all data recorded at 25°C. ^bsolvent donor number in parentheses. ^ccalculated potential difference between $E^\circ_{\text{M}_1}$ and $E^\circ_{\text{M}_2}$ in mV. ^dcomproportionation constant calculated from $K_{\text{C}} = \exp(\Delta E/25.69)$. ^eobserved by oxidation processes associated with Ph_4B^- determined by a graphical method (refer to text), actually observe a single 2 e^- reduction couple $E^\circ_{\text{M}} = -0.063$ V vs. NHE with $E_{\text{pa}} - E_{\text{pc}} = 150$ mV.

Table 5.6b Solvent-Dependent Redox Couples and Comproportionation Constants for $[\mu-(2,5\text{-Me}_2\text{Dicyd})-(\text{NH}_3)_5\text{Ru}]_2[\text{PF}_6]_4$.^a

Solvents ^b	$E^\circ_{M_1}$	$E^\circ_{M_2}$	ΔE^c	K_C^d	$E^\circ_{\text{oxid}_1}$	$E^\circ_{\text{oxid}_2}$
nitromethane (2.7)	0.217 (100)	-0.151 (85)	368	1.66×10^6	0.870 (65)	1.260 (75)
acetonitrile (14.1)	0.089 (83)	-0.251 (77)	340	5.59×10^5	0.767 (72)	1.205 (79)
acetone (17.0)	-0.024 (110)	-0.349 (120)	325	3.12×10^5	0.678 (77)	1.139 (105)
DMSO (29.8)	-0.163 (70)	-0.361 (65)	198	2224	0.582 (70)	1.050 (105)
water (18.0)	-0.032 ^e	-0.117 ^e	85	27	0.539 (80)	0.912 (125)

^aAll couples are reported vs. NHE in V with $E_{pa} - E_{pc}$ in parentheses in mV; data in nitromethane (0.1 M TBAH); metal-centered couples are based on a Ph_4B^- complex salt at a scan rate = 1 V s^{-1} while ligand-centered couples are based on a PF_6^- complex salt at a scan rate = 100 mV s^{-1} ; data in acetonitrile (0.1 M TBAH) was obtained at a scan rate = 200 mV s^{-1} ; data in acetone (0.1 M TBAH) was obtained at an anodic scan rate = 100 mV s^{-1} and a cathodic scan rate = 2 V s^{-1} ; data in DMSO (0.1 M TBAH) was obtained at a scan rate = 100 mV s^{-1} ; data in water (0.1 M NaCl) is based on a ClO_4^- complex salt at a scan rate = 100 mV s^{-1} , from Ref. 44 and 43; all data recorded at 25°C . ^bSolvent donor number in parentheses. ^ccalculated potential difference between $E^\circ_{M_1}$ and $E^\circ_{M_2}$ in mV. ^dcomproportionation constant calculated from $K_C = \exp(\Delta E/25.69)$. ^edetermined by a graphical method (refer to text), actually observe a single $2 e^-$ reduction couple $E^\circ_M = -0.073 \text{ V}$ vs. NHE with $E_{pa} - E_{pc} = 135 \text{ mV}$.

Table 5.6c Solvent-Dependent Redox Couples and Comproportionation Constants for $[\mu-(2\text{-MeDicyd})-(\text{NH}_3)_5\text{Ru}]_2[\text{PF}_6]_4$.^a

Solvents ^b	$E^\circ_{\text{M}_1}$	$E^\circ_{\text{M}_2}$	ΔE^c	K_C^d	$E^\circ_{\text{oxid}_1}$	$E^\circ_{\text{oxid}_2}$
nitromethane (2.7)	0.243 (73)	-0.096 (75)	339	5.38×10^5	0.937 (90)	e
acetonitrile (14.1)	0.046 (75)	-0.242 (90)	288	7.39×10^4	0.798 (85)	1.269 (80)
acetone 17.0)	-0.019 (92)	-0.300 (87)	281	5.63×10^4	0.677 (110)	1.190 (105)
DMSO (29.8)	-0.263 (60)	-0.433 (69)	170	748	0.600 (70)	1.055 (100)
water (18.0)	-0.013 ^f	-0.109 ^f	96	42	0.590 (75)	0.935 (105)

^aAll couples are reported vs. NHE in V with $E_{\text{pa}} - E_{\text{pc}}$ in parentheses in mV; data in nitromethane (0.1 M TBAH) is based on a Ph_4B^- complex salt at a scan rate=100 mVs^{-1} ; data in acetonitrile (0.1 M TBAH) was obtained at an anodic scan rate=100 mVs^{-1} and a cathodic scan rate = 1 Vs^{-1} , from Ref. 79; data in acetone (0.1 M TBAH) was obtained at an anodic scan rate=500 mVs^{-1} and a cathodic scan rate=1 Vs^{-1} ; data in DMSO (0.1 M TBAH) was obtained at a scan rate=100 mVs^{-1} ; data in water (0.1 M NaClO_4^-) is based on a Cl^- complex salt at a scan rate=100 mVs^{-1} ; all data recorded at 25°C. ^bSolvent donor number in parentheses. ^ccalculated potential difference between $E^\circ_{\text{M}_1}$ and $E^\circ_{\text{M}_2}$ in mV. ^dcomproportionation constant calculated from $K_C = \exp(\Delta E/25.69)$. ^eobserved by oxidation processes associated with Ph_4B^- . ^fdetermined by a graphical method (refer to text), actually observe a single 2 e^- reduction couple $E^*_{\text{M}} = -0.061$ V vs. NHE with $E_{\text{pa}} - E_{\text{pc}} = 135$ mV.

Table 5.6d Solvent-Dependent Redox Couples and Comproportionation Constants for $[\mu\text{-Dicyd}-(\text{NH}_3)_5\text{Ru}_2][\text{PF}_6]_4$.^a

Solvents ^b	$E^\circ\text{M}_1$	$E^\circ\text{M}_2$	ΔE^c	K_C^d	$E^\circ_{\text{oxid}_1}$	$E^\circ_{\text{oxid}_2}$
nitromethane (2.7)	0.253 (63)	-0.060 (80)	313	1.96×10^5	0.974 (60)	1.406 (68)
acetonitrile (14.1)	0.131 (89)	-0.155 (87)	286	6.84×10^4	0.830 (65)	1.292 (80)
acetone (17.0)	0.013 (110)	-0.232 (100)	245	1.39×10^4	0.769 (78)	1.258 (95)
DMSO (29.8)	-0.144 (73)	-0.311 (68)	167	666	0.622 (67)	1.068 (85) ^e
water (18.0)	-0.004 ^f	-0.107 ^f	103	55	0.647 (75)	0.987 (95)

^aAll couples are reported vs. NHE in V with $E_{\text{pa}} - E_{\text{pc}}$ in parentheses in mV; data in nitromethane (0.1 M TBAH) was obtained at a scan rate= 100 mVs⁻¹; data in acetonitrile and acetone (both with 0.1 M TBAH) was obtained at an anodic scan rate= 100 mVs⁻¹ and a cathodic scan rate= 1 Vs⁻¹; data in DMSO (0.1 M TBAH) was obtained at a scan rate= 100 mVs⁻¹; data in water (0.1 M NaClO₄) is based on a Cl⁻ complex salt at a scan rate= 100 mVs⁻¹; all data recorded at 25° C. ^bSolvent donor number in parentheses. ^ccalculated potential difference between $E^\circ\text{M}_1$ and $E^\circ\text{M}_2$ in mV. ^dcomproportionation constant calculated from $K_C = \exp(\Delta E/25.69)$. ^eirreversible as $i_a/i_c > 1$. ^fdetermined by a graphical method (refer to text), actually observe a single 2 e⁻ reduction couple $E^\circ\text{M} = -0.055$ V vs. NHE with $E_{\text{pa}} - E_{\text{pc}} = 95$ mV.

Table 5.6e Solvent-Dependent Redox Couples and Comproportionation Constants for $[\mu-(2,5\text{-Cl}_2\text{Dicyd})-(\text{NH}_3)_5\text{Ru}]_2[\text{PF}_6]_4$.^a

Solvents ^b	$E^\circ_{\text{M}_1}$	$E^\circ_{\text{M}_2}$	ΔE^c	K_C^d	$E^\circ_{\text{oxid}_1}$	$E^\circ_{\text{oxid}_2}$
nitromethane (2.7)	0.323 (65)	0.092 (65)	231	8037	e	e
acetonitrile (14.1)	0.192 (125)	-0.020 (120)	212	3836	1.000 (60)	1.455 (90)
acetone (17.0)	0.052 (137)	-0.144 (133)	196	2058	0.916 (80)	1.376 (140)
DMSO (29.8)	-0.180 (70)	-0.310 (70)	130	158	0.828 (75)	f
water (18.0)	0.036 ^g	-0.042 ^g	78	21	0.814 (60)	1.13 (110)

^aAll couples are reported vs. NHE in V with $E_{\text{pa}} - E_{\text{pc}}$ in parentheses in mV; data in nitromethane (0.1 M TBAH) based on a Ph_4B^- complex salt at a scan rate=100 mVs⁻¹; data in acetonitrile (0.1 M TBAH) was obtained at an anodic scan rate=100 mVs⁻¹ and a cathodic scan rate=2 Vs⁻¹; data in acetone (0.1 M TBAH) was obtained at an anodic scan rate=100 mVs⁻¹ and a cathodic scan rate=3 Vs⁻¹; data in DMSO (0.1 M TBAH) was obtained at a scan rate=100 mVs⁻¹; data in water (0.1 M NaCl) is based on a Cl^- complex salt at a scan rate=100 mVs⁻¹, from Ref. 44 and 43; all data recorded at 25° C. ^bSolvent donor number in parentheses. ^ccalculated potential difference between $E^\circ_{\text{M}_1}$ and $E^\circ_{\text{M}_2}$ in mV. ^dcomproportionation constant calculated from $K_C = \exp(\Delta E/25.69)$. ^eobserved by oxidation processes associated with the Ph_4B^- counter anion. ^fnot observed. ^gdetermined by a graphical method (refer to text), actually observe a single 2 e⁻ reduction couple $E^\circ_{\text{M}} = -0.003$ V vs. NHE with $E_{\text{pa}} - E_{\text{pc}} = 90$ mV.

Table 5.6f Solvent-Dependent Redox Couples and Comproportionation Constants for $[\mu-(2,3,4,5\text{-Cl}_4\text{Dicyd})-(\text{NH}_3)_5\text{Ru}]_2[\text{PF}_6]_4$.^a

Solvents ^b	$E^\circ_{M_1}$	$E^\circ_{M_2}$	ΔE^c	K_C^d	$E^\circ_{\text{oxid}_1}$	$E^\circ_{\text{oxid}_2}$
nitromethane (2.7)	0.340 (60)	0.182 (75)	158	469	e	e
acetonitrile (14.1)	0.200 (110)	0.051 (88)	149	330	1.112 (70)	1.563 (85)
acetone (17.0)	0.043 (120)	-0.097 (100)	140	233	1.028 (75)	1.505 ^f
DMSO (29.8)	-0.154 (60)	-0.269 (60)	115	88	0.966 (80)	g
water (18.0)	-0.002 ^h	-0.067 ^h	65	13	0.892 (85)	1.032 ^f

^aAll couples are reported vs. NHE in V with $E_{pa} - E_{pc}$ in parentheses in mV; data in nitromethane (0.1 M TBAH) based on a Ph_4B^- complex salt at a scan rate=100 mVs⁻¹; data in acetonitrile (0.1 M TBAH) was obtained at an anodic scan rate=100 mVs⁻¹ and a cathodic scan rate=2 Vs⁻¹; data in acetone (0.1 M TBAH) was obtained at an anodic scan rate=100 mVs⁻¹ and a cathodic scan rate=3 Vs⁻¹; data in DMSO (0.1 M TBAH) was obtained at a scan rate=100 mVs⁻¹; data in water (0.1 M NaCl) is based on a Cl^- complex salt at a scan rate=100 mVs⁻¹, from Ref. 43,44 and 81; all data recorded at 25° C. ^bSolvent donor number in parentheses. ^ccalculated potential difference between $E^\circ_{M_1}$ and $E^\circ_{M_2}$ in mV. ^dcomproportionation constant calculated from $K_C = \exp(\Delta E/25.69)$. ^eobserved by oxidation processes associated with the Ph_4B^- counter anion. ^fonly the anodic peak is observed. ^gnot observed. ^hdetermined by a graphical method (refer to text), actually observe a single 2 e⁻ reduction couple $E^\circ_{M_1} = -0.033$ V vs. NHE with $E_{pa} - E_{pc} = 90$ mV.

Owing to both outer-sphere (varying solvent) and inner-sphere (varying the π donor strength of the bridging ligand) perturbations of the Ru(III)-cyanamide bond, two generalized trends in the redox couples of the [Ru(III), Ru(III)] complexes are observed. With regards to the solvent dependency, the data of Table 5.6a-f shows that, for a given [Ru(III), Ru(III)] complex, all the redox couples including $E^\circ_{M_1}$, $E^\circ_{M_2}$, $E^\circ_{\text{oxid}_1}$ and $E^\circ_{\text{oxid}_2}$ shift negatively as the solvent's donor number increases. Recall the outer-sphere donor-acceptor interaction between the non-bonding electron pairs of the solvent and the protons of the ammine ligands coordinated to Ru(III). As this interaction increases, the $d\pi$ orbitals of Ru(III) become increasingly destabilized making the process of adding electron density (reduction) to them more difficult. This is reflected by the negative shifts in $E^\circ_{M_1}$ and $E^\circ_{M_2}$, both of which involve Ru(III/II) reduction processes. Note that the potential of $E^\circ_{M_2}$ in aqueous solution does not follow the trend in solvent donor number, as witnessed by a significant negative shift from its value in acetone, a solvent whose donor number is similar to that of water. The shift is likely due to protonation of the cyanamide group bound to Ru(III), which would make reduction of the metal center more facile.⁸⁵ As far as oxidation is concerned, it becomes increasingly facile to remove electron density from destabilized Ru(III) $d\pi$ orbitals, and hence the reason for the negative shift in $E^\circ_{\text{oxid}_1}$ as the solvent's donor number increases.

With regards to the dependency on the π donor strength of the bridging ligand, the data of Table 5.6a-f show that, for a given solvent, all the redox couples including $E^\circ_{M_1}$, $E^\circ_{M_2}$, $E^\circ_{\text{oxid}_1}$ and $E^\circ_{\text{oxid}_2}$ shift positively as the π basicity of the coordinated 1,4-dicyananidobenzene dianion ligand decreases. These trends are not new as previous studies of mononuclear pentaammineruthenium(III) complexes of 1,4-dicyanamidobenzene monoanion and dianion ligands (refer to Section 4.1.5) and anionic phenylcyanamide ligands have revealed similar behaviour.⁴⁶ Quite simply, the trend in both $E^\circ_{M_1}$ and $E^\circ_{M_2}$ can be rationalized by recognizing that the oxidation state of Ru(III) should be stabilized by

π donor ligands. The stronger the π basicity of the ligand is, the greater the stabilization of Ru(III) should be. The trend in $E^\circ_{\text{oxid}_1}$ is readily attributable to the substituent effect of electron donating methoxy and methyl groups as opposed to chloro groups.

Both an outer-sphere and an inner-sphere dependency of metal-metal coupling in the mixed valent [Ru(III), Ru(II)] complexes is evident from the data of Table 5.6a-f. With regards to the solvent dependency, the separation between Ru(III/II) reduction couples ($\Delta E = E^\circ_{M_1} - E^\circ_{M_2}$) and hence the comproportionation constant K_c , for a given dinuclear complex, decrease as the solvent's donor number increases. The comproportionation constant (refer to Eq. 1.35 in Section 1.4.2) is a measure of mixed-valence complex stability in solution and for the dinuclear complexes of this study, is defined as shown in Scheme 5.4.

Scheme 5.4

For the [Ru(III), Ru(II)] complexes of 2-MeODicyd²⁻, 2,5-Me₂Dicyd²⁻, 2-MeODicyd²⁻ and Dicyd²⁻, the unprecedented K_c solvent dependence is consistent with a transformation from strongly coupled borderline ClassII/Class III properties in nitromethane to weakly coupled Class II behaviour in DMSO and aqueous solution. The suggestion that the boundary between localized and delocalized properties is being attained in nitromethane has its merits in the observation that $\Delta E = 368$ mV for $[\mu\text{-(2,5-Me}_2\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}_2]^{4+}$ in nitromethane. Such separation in Ru(III/II) reduction potentials is close to that seen for other borderline ClassII/Class III complexes. For example, the Creutz-Taube ion $[\mu\text{-(pyz)}\text{-(NH}_3)_5\text{Ru}_2]^{5+}$ in nitromethane has $\Delta E = 430$ mV, which is largely independent of solvent.^{73g} In the case of the [Ru(III), Ru(II)] complexes of 2,5-Cl₂Dicyd²⁻ and 2,3,4,5-

$\text{Cl}_4\text{Dicyd}^{2-}$, the K_c solvent dependence is more consistent with a transformation from weakly coupled Class II properties in nitromethane to very weakly coupled Class II behaviour in DMSO and aqueous solution. As previously discussed in detail, decreasing metal-metal coupling in the mixed-valence $[\text{Ru(III)}, \text{Ru(II)}]$ complexes as the solvent's donor number increases is consistent with an increased solvent donor-amine acceptor interaction that decouples the Ru(III) $d\pi$ acceptor orbitals from the superexchange pathway. Note that ΔE and hence K_c values in aqueous solution do not follow the trend in donor number. This may be due to protonation of the cyanamide group bound to Ru(II) ,⁸⁵ which would significantly perturb the bridging ligand HOMO and reduce metal-metal coupling.

With regards to the dependency of metal-metal coupling in the mixed-valence $[\text{Ru(III)}, \text{Ru(II)}]$ complexes on the π donor strength of the bridging ligand, ΔE and hence K_c , for a given solvent, decrease as the π basicity of the coordinated bridging ligand decreases. This remarkable K_c inner-sphere dependence of the mixed-valence $[\text{Ru(III)}, \text{Ru(II)}]$ complexes is consistent with a transformation from strongly coupled borderline ClassII/Class III properties for $[\mu-(2,5\text{-Me}_2\text{Dicyd})\text{-}\{(\text{NH}_3)_5\text{Ru}\}_2]^{3+}$ to weakly coupled Class II behaviour for $[\mu-(2,3,4,5\text{-Cl}_4\text{Dicyd})\text{-}\{(\text{NH}_3)_5\text{Ru}\}_2]^{3+}$. As previously discussed, decreasing metal-metal coupling in the mixed-valence $[\text{Ru(III)}, \text{Ru(II)}]$ complexes as the π donor strength of the coordinated bridging ligand decreases is consistent with a decreased overlap between Ru(III) $d\pi$ acceptor orbitals and the π symmetry HOMO of the bridging ligand thereby decoupling the former from the superexchange pathway.

Finally, recall that for strongly coupled mixed-valence systems (such as the $[\text{Ru(III)}, \text{Ru(II)}]$ complexes in acetonitrile) where K_c is very large, the greatest contribution to the free energy of comproportionation ΔG_c (refer to Eq. 1.36 in Section 1.4.2) is derived from the free energy of resonance exchange ΔG_r . Given that $\Delta H_r \approx H_{ad}$ for a system that is borderline Class II/ClassIII, the trends in K_c should parallel the trends in H_{ad} . By cross-

referencing the data of Table 5.5 with that of Table 5.6a-f, one can see that the relationship is indeed adhered to for the [Ru(III), Ru(II)] complexes in acetonitrile.

5.1.7 Solution Magnetic Susceptibility Measurements

The following subsection demonstrates the outer-sphere (varying solvent) dependency of the magnetic susceptibility, and hence the effective moment per Ru(III) ion, for the six [Ru(III), Ru(III)] complexes in a range of deuterated solvents that includes nitromethane, acetonitrile, acetone, DMSO and water. In addition, the inner-sphere (varying the π donor strength of the bridging ligand) dependency of the magnetic susceptibility and the effective moment, in a given solvent, will be examined. Importantly, the data will permit the examination of both the outer-sphere and inner-sphere dependency of antiferromagnetic metal-metal coupling in the [Ru(III), Ru(III)] complexes.

Via the Evans method, the induced isotropic shifts $-\Delta f$ of the TMS ^1H NMR resonance were measured for all six [Ru(III), Ru(III)] complexes over the complete solvent range. For each value of $-\Delta f$, the molar susceptibility χ_m at 300 K was calculated (refer to Eq. 1.17 in Section 1.3.2). Assuming a spin-only model, the effective moment per Ru(III) ($\mu_{\text{eff}}/\text{Ru(III)}$) and the number of unpaired electrons per Ru(III) ($n/\text{Ru(III)}$) could then be calculated (refer to Eqs. 1.10 and 1.15 in Section 1.3.1) from the corrected molar magnetic susceptibility χ'_m (to solve for χ'_m , refer to Eqs. 1.11 and 1.12 in Section 1.3.1 and to the Appendix for the summed up diamagnetic contributions of individual atoms and bonds in the [Ru(III), Ru(III)] complexes). A summary of the $-\Delta f$, $\mu_{\text{eff}}/\text{Ru(III)}$ and $n/\text{Ru(III)}$ values that were obtained is given in Table 5.7a-f. Note that in all cases, the lowest level of paramagnetism displayed by the [Ru(III), Ru(III)] complexes was in nitromethane. This observation coupled with the fact that the PF_6^- complex salts were only slightly soluble in nitromethane, prevented the value of $-\Delta f$ from being detected beyond the digital resolution (0.30 to 0.50 Hz depending on the sweep width) of the NMR spectrometer. The complex,

$[\mu-(2,5\text{-Me}_2\text{Dicyd})-\{(\text{NH}_3)_5\text{Ru}\}_2][\text{PF}_6]_4$, has been designated as being diamagnetic in nitromethane at room temperature based on the observation that its ^1H NMR spectrum in nitromethane- d_3 (refer to Figure 5.13 in Section 5.1.8) is the most reflective of such behaviour as compared to the other $[\text{Ru}(\text{III}), \text{Ru}(\text{III})]$ complexes. Indeed, the $[\text{Ru}(\text{III}), \text{Ru}(\text{III})]$ complexes of 2-MeODicyd^{2-} , 2-MeDicyd^{2-} , Dicyd^{2-} , $2,5\text{-Cl}_2\text{Dicyd}^{2-}$ and $2,3,4,5\text{-Cl}_4\text{Dicyd}^{2-}$ all displayed varying degrees of paramagnetism in nitromethane as reflected by their ^1H NMR spectra (refer to Figures 5.14 to 5.18, respectively in Section 5.1.8). In these cases, the values of $-\Delta f$ were interpolated from a contact shift plot ($\Delta\nu_c$ of the trans- NH_3 vs $-\Delta f$, refer to Figure 5.19 in Section 5.1.8a).

Similar to the trends observed in the electronic absorption spectral data (E_{op} and oscillator strength of the $b_1^* \leftarrow b_1$ LMCT transition, refer to Table 5.3a-f in Section 5.1.5) for the $[\text{Ru}(\text{III}), \text{Ru}(\text{III})]$ complexes, the trends in the magnetic data of Table 5.7a-f are the result of the previously indicated outer-sphere and inner-sphere perturbations of the $\text{Ru}(\text{III})$ -cyanamide bond that have ramifications with respect to the magnitude of metal-metal coupling in the $[\text{Ru}(\text{III}), \text{Ru}(\text{III})]$ systems. With regards to the solvent dependency of the magnetic data ($\mu_{\text{eff}}/\text{Ru}(\text{III})$ and $n/\text{Ru}(\text{III})$) for a given dinuclear complex, paramagnetism is minimized and in some cases diamagnetism is achieved (ie. $[\mu-(2,5\text{-Me}_2\text{Dicyd})-\{(\text{NH}_3)_5\text{Ru}\}_2][\text{PF}_6]_4$ in nitromethane, whereas, DMSO and aqueous solutions of the $[\text{Ru}(\text{III}), \text{Ru}(\text{III})]$ complexes are paramagnetic. The ^1H NMR spectroscopy of the $[\text{Ru}(\text{III}), \text{Ru}(\text{III})]$ complexes shows that complex integrity is maintained in all of the solvents of the study. As previously eluded to, the ^1H NMR spectroscopy also shows solvent dependent chemical shifts which reflect the paramagnetism of the system (refer to Section 5.1.8). The onset of paramagnetism in DMSO and aqueous solution is the result of a reduction in metal-metal antiferromagnetic coupling and the thermal population of the excited triplet state. As previously detailed, the outer-sphere solvent donor-acceptor ammine interaction results in a decoupling of the $\text{Ru}(\text{III})$ ions from the cyanamide groups

of the bridging ligand, and hence the superexchange pathway. In aqueous solution, the additional complication of protonating the bridging ligand even further weakens the Ru(III)-cyanamide bond leading to greater paramagnetism. The trend of increasing paramagnetism and decreasing $b_1^* \leftarrow b_1$ LMCT oscillator strength, as the solvent's donor number increases, confirms that overlap in the Ru(III)-cyanamide π bond parallels metal-metal coupling. Even though the [Ru(III), Ru(III)] systems are attaining paramagnetism in DMSO and aqueous solution, in only one case is the limiting value of $\mu_{\text{eff}}/\text{Ru(III)}$ reached, that would be indicative of a truly paramagnetic low spin Ru(III) complex. Table 5.8 summarizes the magnetic susceptibility results that were obtained in the solvents of this study for the mononuclear complex, $[(\text{NH}_3)_5\text{Ru}(2\text{-Clpcyd})][\text{PF}_6]_2$, where 2-Clpcyd is the (2-chlorophenyl)cyanamide anionic ligand. The data are independent of solvent yielding an average $\mu_{\text{eff}}/\text{Ru(III)} = 2.055 \mu_B$, a value that is suitably in the range (1.9 to 2.1 μ_B) of other experimentally determined magnetic moments for low spin Ru(III) complexes.⁵⁴ For the purposes of this study, it represents a maximum limit in paramagnetism for a low spin Ru(III)-cyanamide coordination complex, in which unpaired spin density is not shared between the metal and its coordination sphere. Based on this requirement, the only [Ru(III), Ru(III)] complex of this study to approach this limiting value is $[\mu\text{-(2,3,4,5-Cl}_4\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{Cl}]_4$ in D₂O with $\mu_{\text{eff}}/\text{Ru(III)} = 1.863 \mu_B$. Given this level of paramagnetism, it is safe to say that metal-metal antiferromagnetic coupling in $[\mu\text{-(2,3,4,5-Cl}_4\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{Cl}]_4$ when dissolved in aqueous solution is very weak.

The main system property that leads to an optimization of metal-metal antiferromagnetic superexchange coupling in the [Ru(III), Ru(III)] complexes, is a close matching of symmetry and energy parameters between the magnetic $d\pi$ orbitals of Ru(III) and the continuous π symmetry HOMO of the bridging ligand. Also important is the requirement that the HOMO or superexchange pathway be continuous and span the entire bridging ligand. The implication of an optimized superexchange interaction is that the π orbital

overlap between Ru(III) and the cyanamide bridging ligand is significantly effective, leading to a highly ordered or rigid complex geometry in the solid-state. As it has been attested to, by magnetic as well as spectroscopic and electrochemical data, the outer-sphere perturbation of solvent disrupts the superexchange interaction in the [Ru(III), Ru(III)] complexes. In effect, the perturbation induces fluxionality in the complex thereby leading to a randomized geometry. For example, the decoupling of Ru(III) from the cyanamide groups (NCN) of the bridging ligand, via the solvent donor-acceptor ammine interaction, induces a fluxionality in the Ru(III)-cyanamide nitrile nitrogen bond. The effect will be the greatest in highly donating solvents such as DMSO. In addition, the accepting properties of water can lead to protonation of the cyanamide groups, decoupling them from the phenyl ring, thus inducing fluxionality in the amide nitrogen-phenyl ring carbon bond. In the case of $[\mu-(2,3,4,5\text{-Cl}_4\text{Dicyd})\text{-}(\text{NH}_3)_5\text{Ru}]_2[\text{Cl}]_4$ in D_2O , the latter mechanism is believed to be a dominant factor in reducing complex rigidity and hence attenuating metal-metal antiferromagnetic coupling.

Table 5.7a Solvent-Dependent Magnetic Data for $[\mu-(2\text{-MeODicyd})\text{-}(\text{NH}_3)_5\text{Ru}]_2[\text{PF}_6]_4$.^a

Deuterated solvents	$-\Delta_f^b$	$^c\mu_{\text{eff}}/\text{Ru}^{3+}$	d_n/Ru^{3+}
nitromethane	0.63 ^e	0.595	0.16
acetonitrile	2.70	0.650	0.19
acetone	6.03	0.728	0.24
DMSO	36.09	1.229	0.58
water	51.00	1.381	0.71

^aThe complex concentration was 11 mM except in nitromethane- d_3 where it was 1.8 mM; data in D_2O is based on a Cl^- complex salt. ^bisotropic shift (in Hz) of TMS from the Evans method; NMR digital resolution was between 0.30 and 0.50 Hz depending on sweep width. ^cspin-only effective magnetic moment (in μ_B) calculated from $\mu_{\text{eff}} = 2.83(\chi_m T)^{1/2}$. ^dnumber of unpaired electrons calculated from $\mu_{\text{eff}} = [n(n+2)]^{1/2}$. ^einterpolated from Figure 5.19.

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Table 5.7b Solvent-Dependent Magnetic Data for $[\mu-(2,5\text{-Me}_2\text{Dicyd})\text{-(NH}_3)_5\text{Ru}]_2[\text{PF}_6]_4$.^a

Deuterated solvents	$-\Delta f^b$	$^c\mu_{\text{eff}}/\text{Ru}^{3+}$	$^d n/\text{Ru}^{3+}$
nitromethane	0	diam.	0
acetonitrile	5.14	0.725	0.24
acetone	6.32	0.751	0.25
DMSO	29.97	1.155	0.53
water	42.06	1.269	0.62

^aThe complex concentration was 11 mM except in nitromethane- d_3 where it was 1.8 mM; data in D_2O is based on a Cl^- complex salt. ^bisotropic shift (in Hz) of TMS from the Evans method; NMR digital resolution was between 0.30 and 0.50 Hz depending on sweep width. ^cspin-only effective magnetic moment (in μ_B) calculated from $\mu_{\text{eff}} = 2.83(\chi_m T)^{1/2}$. ^dnumber of unpaired electrons calculated from $\mu_{\text{eff}} = [n(n+2)]^{1/2}$.

Table 5.7c Solvent-Dependent Magnetic Data for $[\mu-(2\text{-MeDicyd})\text{-(NH}_3)_5\text{Ru}]_2[\text{PF}_6]_4$.^a

Deuterated solvents	$-\Delta f^b$	$^c\mu_{\text{eff}}/\text{Ru}^{3+}$	$^d n/\text{Ru}^{3+}$
nitromethane	1.17 ^e	0.620	0.18
acetonitrile	5.93	0.734	0.24
acetone	6.85	0.755	0.25
DMSO	37.00	1.246	0.60
water	50.87	1.378	0.70

^aThe complex concentration was 11 mM except in nitromethane- d_3 where it was 1.8 mM; data in D_2O is based on a Cl^- complex salt. ^bisotropic shift (in Hz) of TMS from the Evans method; NMR digital resolution was between 0.30 and 0.50 Hz depending on sweep width. ^cspin-only effective magnetic moment (in μ_B) calculated from $\mu_{\text{eff}} = 2.83(\chi_m T)^{1/2}$. ^dnumber of unpaired electrons calculated from $\mu_{\text{eff}} = [n(n+2)]^{1/2}$. ^einterpolated from Figure 5.19.

Table 5.7d Solvent-Dependent Magnetic Data for $[\mu\text{-(Dicyd)}\text{-(NH}_3)_5\text{Ru}]_2[\text{PF}_6]_4$.^a

Deuterated solvents	$-\Delta f^b$	$^c\mu_{\text{eff}}/\text{Ru}^{3+}$	d_n/Ru^{3+}
nitromethane	2.50 ^e	0.642	0.19
acetonitrile	9.20	0.794	0.28
acetone	13.71	0.882	0.33
DMSO	37.80	1.250	0.60
water	49.07	1.351	0.68

^aThe complex concentration was 11 mM except in nitromethane-d₃ where it was 1.8 mM; data in D₂O is based on a Cl⁻ complex salt. ^bisotropic shift (in Hz) of TMS from the Evans method; NMR digital resolution was between 0.30 and 0.50 Hz depending on sweep width. ^cspin-only effective magnetic moment (in μ_B) calculated from $\mu_{\text{eff}} = 2.83(\chi_m T)^{1/2}$. ^dnumber of unpaired electrons calculated from $\mu_{\text{eff}} = [n(n+2)]^{1/2}$. ^einterpolated from Figure 5.19.

Table 5.7e Solvent-Dependent Magnetic Data for $[\mu\text{-(2,5-Cl}_2\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}]_2[\text{PF}_6]_4$.^a

Deuterated solvents	$-\Delta f^b$	$^c\mu_{\text{eff}}/\text{Ru}^{3+}$	d_n/Ru^{3+}
nitromethane	15.18 ^e	0.931	0.37
acetonitrile	26.09	1.105	0.49
acetone	31.86	1.188	0.55
DMSO	46.94	1.379	0.70
water	70.88	1.597	0.88

^aThe complex concentration was 11 mM except in nitromethane-d₃ where it was 0.45 mM; data in D₂O is based on a Cl⁻ complex salt. ^bisotropic shift (in Hz) of TMS from the Evans method; NMR digital resolution was between 0.30 and 0.50 Hz depending on sweep width. ^cspin-only effective magnetic moment (in μ_B) calculated from $\mu_{\text{eff}} = 2.83(\chi_m T)^{1/2}$. ^dnumber of unpaired electrons calculated from $\mu_{\text{eff}} = [n(n+2)]^{1/2}$. ^einterpolated from Figure 5.19.

Table 5.7f Solvent-Dependent Magnetic Data for $[\mu\text{-(2,3,4,5-Cl}_4\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}]_2[\text{PF}_6]_4$.^a

Deuterated solvents	$-\Delta f^b$	$^c\mu_{\text{eff}}/\text{Ru}^{3+}$	$^d n/\text{Ru}^{3+}$
nitromethane	35.16 ^e	1.239	0.59
acetonitrile	39.76	1.296	0.637
acetone	40.36	1.303	0.643
DMSO	50.33	1.423	0.74
water	98.62	1.863	1.11

^aThe complex concentration was 11 mM except in nitromethane-d₃ where it was 0.9 mM; data in D₂O is based on a Cl⁻ complex salt. ^bisotropic shift (in Hz) of TMS from the Evans method; NMR digital resolution was between 0.30 and 0.50 Hz depending on sweep width. ^cspin-only effective magnetic moment (in μ_B) calculated from $\mu_{\text{eff}} = 2.83(\chi'_m T)^{1/2}$. ^dnumber of unpaired electrons calculated from $\mu_{\text{eff}} = [n(n+2)]^{1/2}$. ^einterpolated from Figure 5.19.

Table 5.8 Solvent-Dependent Magnetic Data for the Mononuclear Complex, $[(\text{NH}_3)_5\text{Ru(2-Clpycd)}][\text{PF}_6]_2$.^a

Deuterated solvents	$^b\mu_{\text{eff}}/\text{Ru}^{3+}$	$^c n/\text{Ru}^{3+}$
nitromethane	1.986	1.22
acetonitrile	2.052	1.28
acetone	2.024	1.26
DMSO	2.081	1.31
water	2.131	1.35

^aThe complex concentration was 11 mM except in nitromethane-d₃ where it was 3.1 mM and in acetone-d₆ where it was 69.4 mM; data in D₂O is based on a Cl⁻ complex salt. ^bspin-only effective magnetic moment (in μ_B) calculated from $\mu_{\text{eff}} = 2.83(\chi'_m T)^{1/2}$. ^cnumber of unpaired electrons calculated from $\mu_{\text{eff}} = [n(n+2)]^{1/2}$.

The magnetic data for the [Ru(III), Ru(III)] complexes are also dependent on the π donor strength of the bridging ligand. With reference to Table 5.7a-f, both $\mu_{\text{eff}}/\text{Ru(III)}$ and $n/\text{Ru(III)}$, for a given solvent, increase as the π donor strength of the bridging ligand decreases. In the [Ru(III), Ru(III)] complexes of 2,5-Me₂Dicyd²⁻ and 2-MeODicyd²⁻, paramagnetism reaches a minimum in all the solvents of the study, whereas in [μ -(2,3,4,5-Cl₄Dicyd)-{(NH₃)₅Ru}₂]⁴⁺, paramagnetism is maximized in all the solvents. The increase in paramagnetism is again the result of a reduction in metal-metal antiferromagnetic coupling and the thermal population of the excited triplet state. However in this case, the Ru(III) ions become decoupled from the cyanamide groups of the bridging ligand, and hence the superexchange pathway, because of decreased orbital overlap between the π symmetry HOMO of the bridging ligand and the $d\pi$ acceptor orbitals of Ru(III). Recall the similar behaviour of the $b_1^* \leftarrow b_1$ LMCT oscillator strength, confirming once again that overlap in the Ru(III)-cyanamide π bond parallels metal-metal coupling. It is interesting to point out that the inner-sphere dependency (in a given solvent) of metal-metal antiferromagnetic coupling for the [Ru(III), Ru(III)] complexes is predictable based on the observation of a similar inner-sphere dependency of $-J$, determined from solid-state measurements (refer to Table 5.2 in Section 5.1.4).

5.1.8 ¹H NMR Spectroscopy

The ¹H NMR spectra of the [Ru(III), Ru(III)] complexes in the deuterated versions of nitromethane, acetonitrile, acetone, DMSO and water have been obtained. Note that in the case of [μ -(2-MeDicyd)-{(NH₃)₅Ru}₂][PF₆]₄ and [μ -(2-MeODicyd)-{(NH₃)₅Ru}₂][PF₆]₄, their ¹H NMR spectra in acetonitrile-d₃ have been previously reported.^{79,80} Figures 5.13 to 5.18 inclusive show the ¹H NMR spectra of all six [Ru(III), Ru(III)] complexes in nitromethane-d₃ (in all cases, the singlets at 2.10 and 4.34 ppm are background from nitromethane-d₃, whereas the singlet at 2.06 ppm is due to acetone solvent of recrystallization). The complete summary of the ¹H NMR chemical

shifts for each [Ru(III), Ru(III)] complex in each of the solvents of this study is given in Table 5.9a-f.

Figure 5.13 ^1H NMR spectrum of $[\mu\text{-(2-MeODicyd)}\text{-}\{(\text{NH}_3)_5\text{Ru}\}_2][\text{PF}_6]_4$ in nitromethane- d_3 (at 300 K) with a concentration of 1.8 mM.

Figure 5.14 ^1H NMR spectrum of $[\mu\text{-(2,5-Me}_2\text{Dicyd)}\text{-}\{(\text{NH}_3)_5\text{Ru}\}_2][\text{PF}_6]_4$ in nitromethane- d_3 (at 300 K) with a concentration of 1.8 mM.

Figure 5.15 ^1H NMR spectrum of $[\mu\text{-(2-MeDicyd)}\text{-}\{(\text{NH}_3)_5\text{Ru}\}_2][\text{PF}_6]_4$ in nitromethane- d_3 (at 300 K) with a concentration of 1.8 mM.

Figure 5.16 ^1H NMR spectrum of $[\mu\text{-(Dicyd)}\text{-}\{(\text{NH}_3)_5\text{Ru}\}_2][\text{PF}_6]_4$ in nitromethane- d_3 (at 300 K) with a concentration of 1.8 mM.

Figure 5.17 ^1H NMR spectrum of $[\mu\text{-(2,5-Cl}_2\text{Dicyd)}\text{-(NH}_3\text{)}_5\text{Ru}]_2[\text{PF}_6]_4$ in nitromethane- d_3 (at 300 K) with a concentration of 0.9 mM.

Figure 5.18 ^1H NMR spectrum of $[\mu\text{-(2,3,4,5-Cl}_4\text{Dicyd)}\text{-(NH}_3\text{)}_5\text{Ru}]_2[\text{PF}_6]_4$ in nitromethane- d_3 (at 300 K) with a concentration of 0.9 mM.

Table 5.9a Solvent-Dependent ^1H NMR Chemical Shifts of $[\mu-(2\text{-MeODicyd})-(\text{NH}_3)_5\text{Ru}]_2[\text{PF}_6]_4$.^a

Deuterated solvents	trans-NH ₃ ^b	cis-NH ₃ ^b	2-OMe ^c	3-Ph ^c	6-Ph ^b	5-Ph ^b
nitromethane	8.34	2.96	3.84	6.85	7.27	7.41
acetonitrile	23.70	5.77	4.23	5.69	4.82	5.09
acetone	40.54	10.53	4.68	4.39	1.83	2.49
DMSO	179.21	45.39	6.81	-3.04	-11.92	-10.39
water	d	d	7.76	-2.23	-11.91	-9.96

^aAll chemical shifts gave the correct integration for their assignment; the values in ppm are referenced to TMS (0.00 ppm) for nonaqueous solutions and to DSS (0.00 ppm) for D₂O; the complex concentration was 11 mM except in nitromethane where it was 1.8 mM; data in acetonitrile-d₃ is from Ref. 80.

^bdoublet. ^csinglet. ^dnot observed, probably because of rapid deuterium exchange.

Table 5.9b Solvent-Dependent ^1H NMR Chemical Shifts of $[\mu-(2,5\text{-Me}_2\text{Dicyd})-(\text{NH}_3)_5\text{Ru}]_2[\text{PF}_6]_4$.^a

Deuterated solvents	trans-NH ₃	cis-NH ₃	2,5-Me	3,6-Ph
nitromethane	6.92	2.96	2.12	7.10
acetonitrile	18.75	5.58	3.75	5.27
acetone	36.87	10.49	5.91	2.91
DMSO	167.17	43.81	17.11	-8.44
water	b	b	17.04	-6.58

^aAll chemical shifts are singlets and gave the correct integration for their assignment; the values in ppm are referenced to TMS (0.00 ppm) for nonaqueous solutions and to DSS (0.00 ppm) for D₂O; the complex concentration was 11 mM except in nitromethane where it was 1.8 mM. ^bnot observed, probably because of rapid deuterium exchange.

Table 5.9c Solvent-Dependent ^1H NMR Chemical Shifts of $[\mu\text{-(2-MeDicyd)}\text{-(NH}_3)_5\text{Ru}]_2[\text{PF}_6]_4$.^a

Deuterated solvents	trans-NH ₃ ^b	cis-NH ₃ ^b	2-Me ^c	3-Ph ^c	6-Ph ^b	5-Ph ^b
nitromethane	11.15	3.53	2.83	6.63	7.05	7.25
acetonitrile	34.04	8.14	5.85	3.57	3.64	3.99
acetone	56.67	13.83	8.39	1.00	0.69	0.96
DMSO	189.07	48.26	17.44	-7.96	-10.51	-9.69
water	d	d	17.74	-6.36	-9.50	-8.76

^aAll chemical shifts gave the correct integration for their assignment; the values in ppm are referenced to TMS (0.00 ppm) for nonaqueous solutions and to DSS (0.00 ppm) for D₂O; the complex concentration was 11 mM except in nitromethane where it was 1.8 mM; data in acetonitrile-d₃ is from Ref. 79.

^bdoublet. ^csinglet. ^dnot observed, probably because of rapid deuterium exchange.

Table 5.9d Solvent-Dependent ^1H NMR Chemical Shifts of $[(\mu\text{-Dicyd)}\text{-(NH}_3)_5\text{Ru}]_2[\text{PF}_6]_4$.^a

Deuterated solvents	trans-NH ₃	cis-NH ₃	Phenyl
nitromethane	18.24	4.90	6.12
acetonitrile	50.53	11.74	1.72
acetone	76.49	18.12	-1.18
DMSO	201.72	52.18	-8.99
water	b	b	-8.44

^aAll chemical shifts are singlets and gave the correct integration for their assignment; the values in ppm are referenced to TMS (0.00 ppm) for nonaqueous solutions and to DSS (0.00 ppm) for D₂O; the complex concentration was 11 mM except in nitromethane where it was 1.8 mM. ^bnot observed, probably because of rapid deuterium exchange.

Table 5.9e Solvent-Dependent ^1H NMR Chemical Shifts of $[\mu\text{-(2,5-Cl}_2\text{Dicyd)-}(\text{NH}_3)_5\text{Ru}]_2[\text{PF}_6]_4$.^a

Deuterated solvents	trans-NH ₃	cis-NH ₃	3,6-Phenyl
nitromethane	85.31	20.92	-2.28
acetonitrile	140.33	34.52	-7.12
acetone	174.05	43.64	-8.74
DMSO	245.11	67.13	-8.30
water	b	b	-7.89

^aAll chemical shifts are singlets and gave the correct integration for their assignment; the values in ppm are referenced to TMS (0.00 ppm) for nonaqueous solutions and to DSS (0.00 ppm) for D₂O; the complex concentration was 11 mM except in nitromethane where it was 0.45 mM. **b**not observed, probably because of rapid deuterium exchange.

Table 5.9f Solvent-Dependent ^1H NMR Chemical Shifts of $[\mu\text{-(2,3,4,5-Cl}_4\text{Dicyd)-}(\text{NH}_3)_5\text{Ru}]_2[\text{PF}_6]_4$.^a

Deuterated solvents	trans-NH ₃	cis-NH ₃
nitromethane	182.20	37.41
acetonitrile	226.19	48.54
acetone	246.66	55.03
DMSO	275.80	72.87
water	b	b

^aAll chemical shifts are singlets and gave the correct integration for their assignment; the values in ppm are referenced to TMS (0.00 ppm) for nonaqueous solutions and to DSS (0.00 ppm) for D₂O; the complex concentration was 11 mM except in nitromethane where it was 0.9 mM. **b**not observed, probably because of rapid deuterium exchange.

With reference to Table 5.9a-f, the ^1H NMR chemical shifts of the $[\text{Ru(III)}, \text{Ru(III)}]$ complexes, like the magnetic data of Table 5.7a-f in the preceding section, reflect the onset of paramagnetism as caused by outer-sphere (varying the solvent) and inner-sphere (varying the π donor strength of the bridging ligand) perturbations of the Ru(III) -cyanamide bond. The ammine ligand (both *cis* and *trans*) protons are subject to contact shifts while the phenyl, methyl and methoxy protons are subject to pseudocontact shifts.

5.1.8a Contact Shifted Ammine Protons

Both the *trans*- and *cis*- NH_3 protons of the $[\text{Ru(III)}, \text{Ru(III)}]$ complexes demonstrate a solvent-dependent contact interaction, in which the magnitude of the contact shift $\Delta\nu_c$ becomes increasingly more positive (larger downfield shift) as the paramagnetism of the system increases. Based on the proposed spin-only model (refer to Eq. 1.27 in Section 1.3.5), the magnitude of the contact shift $\Delta\nu_c$ experienced by the ammine protons, for a given $[\text{Ru(III)}, \text{Ru(III)}]$ complex in a given solvent, is directly proportional to the level of paramagnetism displayed by the system (as measured by $-\Delta f$ from the Evans method). Note that $\Delta\nu_c$, as it pertains to the $[\text{Ru(III)}, \text{Ru(III)}]$ complexes of this study, corresponds to the difference in the chemical shift position of the ammine protons in a paramagnetic environment compared to a diamagnetic environment, where the latter is defined by the chemical shift positions of the ammine protons in $[\mu-(2,5\text{-Me}_2\text{Dicyd})\text{-(NH}_3)_5\text{Ru}]_2[\text{PF}_6]_4$ when dissolved in nitromethane- d_3 .

It follows that a plot of $\Delta\nu_c$ versus $-\Delta f$ as a function of solvent, for both the *trans*- and *cis*- NH_3 protons, should be linear with a negative y-intercept. Importantly, upon evaluation of the slope and y-intercept (refer to Eqs. 1.29 and 1.30 in Section 1.3.5), one can obtain an estimate of the contact hyperfine coupling constant A_c and the average diamagnetic susceptibility of the $[\text{Ru(III)}, \text{Ru(III)}]$ complexes, respectively. Figures 5.19 and 5.20, which represent the experimentally obtained solvent dependent contact shift plots of the

trans- and cis-NH₃ protons, respectively, are indeed linear relationships. Based on a simple linear curve fitting analysis, the slope and y-intercept from the trans-NH₃ contact shift plot, were found to be 2124 and -760 Hz, respectively, while the corresponding values from the cis-NH₃ contact shift plot were found to be 533 and -700 Hz, respectively. In both cases, the square of the correlation coefficient R^2 was 0.987.

The maximum value of $\Delta\nu_c$ observed in both contact shift plots occurs for $[\mu\text{-(2,3,4,5-Cl}_4\text{Dicyd)}\text{-(NH}_3\text{)}_5\text{Ru}_2][\text{PF}_6]_4$ in DMSO- d_6 . With reference to Table 5.9f, the chemical shifts of the trans- and cis-NH₃ protons for this complex are at 275.80 and 72.87 ppm, respectively. When compared to chemical shifts of >280 and 67.31 ppm for the trans- and cis-NH₃ protons, respectively, of $[(\text{NH}_3)_5\text{Ru(2-Clpcyd)}][\text{PF}_6]_2$ in acetonitrile- d_3 , it can be concluded that the maximum level of paramagnetism attributable to a low spin Ru(III) complex has either been reached or almost reached in the case of $[\mu\text{-(2,3,4,5-Cl}_4\text{Dicyd)}\text{-(NH}_3\text{)}_5\text{Ru}_2][\text{PF}_6]_4$ dissolved in DMSO. Note that neither of the contact shift plots include data from D₂O measurements as rapid deuterium exchange prevents the observation of the trans- and cis-NH₃ resonances in aqueous solution.

Figure 5.19 Solvent-dependent contact shift plot of $\Delta\nu_c$ versus $-\Delta f$ for the trans-NH₃ protons of the $[\mu\text{-(L)-}\{(\text{NH}_3)_5\text{Ru}\}_2]^{4+}$ complexes at a concentration of 11 mM.

Figure 5.20 Solvent-dependent contact shift plot of $\Delta\nu_c$ versus $-\Delta f$ for the cis-NH₃ protons of the $[\mu\text{-(L)-}\{(\text{NH}_3)_5\text{Ru}\}_2]^{4+}$ complexes at a concentration of 11 mM.

Since the contact behaviour for both the trans- and cis-NH₃ protons is characterized by increasingly larger positive $\Delta\nu_c$ values as the paramagnetism of the system increases, the direct delocalization contribution to the contact interaction can be said to be dominant over the spin polarization contribution. Therefore, it becomes more appropriate to refer to the contact hyperfine coupling constant as A_d rather than A_c . For the [Ru(III), Ru(III)] complexes, the estimated magnitude of A_d will be indicative of the extent of the direct delocalization contribution, in terms of the amount of unpaired spin density that is transferred from Ru(III) onto the ammine ligands. Ultimately, in order for a contact shift to result, this net spin density must find its way to the ammine proton 1s orbital. In this context, A_d expresses the probability of this occurring (refer to Eq. 1.21 in Section 1.3.3a). From the slopes of the contact shift plots for the trans- and cis-NH₃ protons, the estimated values of the contact hyperfine coupling constant (expressed as A_d/h in MHz where h is the Plank constant) were found to be 4.66 and 1.16 MHz, respectively. Based on these experimentally determined values of A_d/h , the amount of spin density ρ delocalized into an

amine proton 1s orbital per unit of Ru(III) spin, was estimated from the McConnell equation (refer to Eq. 1.24 in Section 1.3.4) to be 0.0033 for the trans-NH₃ protons and 0.0008 for the cis-NH₃ protons. Reflective of the significant anisotropy of the contact shifts between the trans- and cis-ammines (the slope of contact shift plot for the trans-NH₃ protons is 4x larger than that for the cis-NH₃ protons), the results are interpreted in terms of a highly directional direct delocalization mechanism in which Ru(III) unpaired spin density is preferentially delocalized onto the trans-NH₃ (refer below). The reader should note that the contact hyperfine coupling constant is, by convention, positive when the direct delocalization mechanism dominates the contact interaction. In addition, since the free electron *g*-factor ($g_e = 2.0023$) was used as an estimate of the rotationally averaged *g*-value (g_{avg}) for the [Ru(III), Ru(III)] complexes in solution, the contact hyperfine coupling constant is expressed as A_d/h (in MHz).

The preferential delocalization of Ru(III) π symmetry unpaired spin density onto the trans-NH₃ can be conceptualized by considering the following mechanism. For the [Ru(III), Ru(III)] complexes, the three-center π bonding interaction depicted in Figure 4.12 in Section 4.2.6 involves a 1,4-dicyanamidobenzene dianion ligand, Ru(III) instead of Ru(IV), and a trans-NH₃. The $b_1^*_{xz}$ molecular orbital (of metal $d\pi$ character) formed between Ru(III) and the cyanamide ligand, formally contains one unpaired electron. This spin density can be delocalized via a π hyperconjugation mechanism into a trans-NH₃ sp^2 hybridized σ orbital, which in turn is involved in σ bonding with a proton 1s orbital. The result is a significant contact interaction experienced by the trans-NH₃ protons. For the cis-NH₃ protons, the contact interaction is much smaller, as they are not intimately linked into the cyanamide/Ru(III)/trans-NH₃ π network (cis-NH₃ groups lie in the *xy* plane, refer to Figure 4.12), and hence are only subjected to a fractional amount of delocalized unpaired spin density.

For the dinuclear complexes, $([\mu-(L)-\{(py)(NH_3)_4Ru\}_2][PF_6]_4)^{116}$ where $L = 2,5-Me_2Dicyd^{2-}$, $Dicyd^{2-}$, $2,5-Cl_2Dicyd^{2-}$ and $2,3,4,5-Cl_4Dicyd^{2-}$, the *cis*-NH₃ protons display solvent-dependent contact shifting that is similar to that observed for the ammine protons of the [Ru(III), Ru(III)] complexes of this study. The diruthenium tetraammine system is therefore treatable under the spin-only model proposed for the diruthenium pentaammine system. It follows for the *cis*-NH₃ protons of the former, that the contact interaction be dominated by the direct delocalization contribution. From the slope of the contact shift plot for the *cis*-NH₃ protons, an estimated value for the contact hyperfine coupling constant A_d/h was found to be 1.36 MHz. In terms of the amount of spin density delocalized into the *cis*-ammine proton 1s orbital per unit of Ru(III) spin, ρ was estimated to be 0.0010. This corresponds to approximately 1.2x the amount of spin density delocalized onto the *cis*-NH₃ protons in the tetraammine complexes compared to the pentaammine complexes. It follows that the Ru(III)-(cis-NH₃) interaction is somewhat stronger in the former. In simple terms, the small difference in ρ can be rationalized by considering that in the absence of a *trans*-NH₃ ligand, unpaired spin density is forcibly delocalized onto the *cis*-NH₃ protons.

5.1.8b Pseudocontact Shifted Phenyl Protons

The 3,6-phenyl protons of the [Ru(III), Ru(III)] complexes demonstrate a solvent-dependent pseudocontact interaction, in which the magnitude of the pseudocontact shift $\Delta\nu_{pc}$ becomes increasingly more negative (larger upfield shift) as the paramagnetism of the system increases. Although the spin-only model has not been worked out for the pseudocontact interaction, the absolute magnitude of the pseudocontact shift $|\Delta\nu_{pc}|$ experienced by the 3,6-phenyl protons, for a given [Ru(III), Ru(III)] complex in a given solvent, is expected to be directly proportional to the level of paramagnetism displayed by the system (as measured by $-\Delta f$ from the Evans method). Note that $\Delta\nu_{pc}$, as it pertains to the [Ru(II), Ru(III)] complexes of this study, corresponds to the difference in the chemical

shift position of the 3,6-phenyl protons in a paramagnetic environment compared to a diamagnetic environment, where the latter is defined by the chemical shift positions of the 3,6-phenyl protons in $[\mu-(2,5\text{-Me}_2\text{Dicyd})\text{-(NH}_3)_5\text{Ru}_2][\text{PF}_6]_4$ when dissolved in nitromethane- d_3 .

Similar to the contact shift plots for the ammine protons, a plot of $-\Delta\nu_{\text{pc}}$ versus $-\Delta f$ for the 3,6-phenyl protons should be linear. However, with reference to the experimentally obtained plot shown in Figure 5.21, this is not the case. In fact, only a partial linear relationship ($R^2 = 0.983$) is observed up to the point indicated by the arrow ($[\mu-(2,5\text{-Cl}_2\text{Dicyd})\text{-(NH}_3)_5\text{Ru}_2][\text{PF}_6]_4$ in acetone- d_6). Beyond this point, $-\Delta\nu_{\text{pc}}$ appears to level off as $-\Delta f$ increases, thereby suggesting that a breakdown of the model has occurred. The reader should note that the pseudocontact shift plot was created from a limited data set, based on the $-\Delta\nu_{\text{pc}}$ values for 3,6-phenyl protons in the $[\text{Ru(III)}, \text{Ru(III)}]$ complexes of $2,5\text{-Me}_2\text{Dicyd}^{2-}$, Dicyd^{2-} and $2,5\text{-Cl}_2\text{Dicyd}^{2-}$. In addition, because of poor complex solubility, the $-\Delta f$ values for the above mentioned complexes in nitromethane- d_3 could not be obtained using the Evans method, so therefore, had to be interpolated from the trans- NH_3 contact shift plot (Figure 5.19).

Since the magnitude of the pseudocontact shift is determined to a large extent by the geometry of the nuclei in question with respect to the paramagnetic metal center (the geometric factor, refer to Eq. 1.22 in Section 1.3.3b), the observation that $-\Delta\nu_{\text{pc}}$ appears to reach a limiting value is indicative of a fluxional complex geometry in DMSO and aqueous solution. For the $[\text{Ru(III)}, \text{Ru(III)}]$ complexes of Dicyd^{2-} and $2,5\text{-Cl}_2\text{Dicyd}^{2-}$ dissolved in DMSO and aqueous solution, for which the $-\Delta\nu_{\text{pc}}$ values appear to be constant, paramagnetism is being maximized as the limit of $\mu_{\text{eff}}/\text{Ru(III)}$ for a low spin Ru(III)

Figure 5.21 Solvent-dependent pseudocontact shift plot of $-\Delta\nu_{pc}$ versus $-\Delta f$ for the 3,6-phenyl protons of the $[\mu-(L)-\{(NH_3)_5Ru\}_2]^{4+}$ complexes at a concentration of 11 mM.

complex is being approached. As previously eluded to (refer to Section 5.1.7), the loss of complex rigidity in DMSO and aqueous solution leads to an attenuation or reduction in metal-metal antiferromagnetic coupling. The point in the pseudocontact plot indicated by the arrow ($[\mu-(2,5-Cl_2Dicyd)-\{(NH_3)_5Ru\}_2][PF_6]_4$ in acetone- d_6) may very well represent a boundary between strongly and weakly coupled systems.

The pseudocontact interaction, based on a point dipole model description, is the result of a through-space non-exchange type coupling between electron magnetic moments localized on the metal and nuclear magnetic moments localized on the ligand. For each of the $[Ru(III), Ru(III)]$ complexes dissolved in the various solvents, a complete evaluation of the pseudocontact shift (including magnitude and direction) experienced by the 3,6-phenyl protons, requires knowledge of the spin density distribution over the entire molecule such that the magnetic g anisotropy can be determined. Furthermore, a static model based on crystal structure data, is needed so that the geometry and distance dependence of the 3,6-

phenyl protons with respect to the paramagnetic Ru(III) metal center can be approximated. At present, these considerations have yet to be addressed, thus paving the way for future studies.

5.1.9 Experimental Evaluation of $-J$ in Solution

In order to evaluate the magnitude of the antiferromagnetic exchange coupling constant in solution, the temperature dependence of the contact shift $\Delta\nu_c$ associated with the trans-NH₃ protons in $[\mu-(2,5\text{-Me}_2\text{Dicyd})-\{(\text{NH}_3)_5\text{Ru}\}_2][\text{PF}_6]_4$ was examined. A preliminary study was conducted in acetonitrile-*d*₃ under a limited temperature range (ie. 340 to 250 K). The results demonstrated a downfield shift in the trans-NH₃ resonance (positive $\Delta\nu_c$) as the temperature decreased. For the [Ru(III), Ru(III)] systems of this study, a positive $\Delta\nu_c$ is consistent with an increase in paramagnetism. The result is opposite to what is typically observed,^{50,51} as based on spin-state equilibria, the thermal population of the triplet excited state and hence paramagnetism are expected to decrease as the temperature of the system is decreased and vice-versa. For the [Ru(III), Ru(III)] complexes, such behaviour in solution is consistent with the idea that the solvent donor-acceptor ammine interaction, which leads to a reduction in metal-metal antiferromagnetic coupling, increases and becomes dominant as the temperature is lowered.

5.2 [Ru(IV), Ru(III)] Complexes of 1,4-Dicyanamidobenzene Dianion Ligands

The [Ru(IV), Ru(III)] complex of the 2,5-Me₂Dicyd²⁻ dianion ligand ([μ-(2,5-Me₂Dicyd)-(NH₃)₅Ru]₂]⁵⁺) has been synthesized via the chemical oxidation of [μ-(2,5-Me₂Dicyd)-(NH₃)₅Ru]₂]⁴⁺. The mixed-valence [Ru(IV), Ru(III)] complex has been characterized by IR, ¹H NMR and electronic absorption spectroscopies as well as solution magnetic susceptibility measurements. In addition, spectroelectrochemical studies in acetonitrile have verified that the oxidation of the [Ru(III), Ru(III)] complex to form the [Ru(IV), Ru(III)] species is indeed a reversible one-electron (*n* = 1.02 eqmole⁻¹) process. Importantly, ¹H NMR and solution magnetic susceptibility measurements in acetonitrile-*d*₃ indicated that [μ-(2,5-Me₂Dicyd)-(NH₃)₅Ru]₂][PF₆]₅ displays an intermediate level of paramagnetism, suggesting that the odd electron is delocalized on the NMR time scale. Note that the [Ru(IV), Ru(III)] complexes of Dicyd²⁻ and 2,5-Cl₂Dicyd²⁻ can be generated in solution, but isolation of analytically pure solids has not been possible owing to their tendency to revert back to the respective [Ru(III), Ru(III)] complex. Future studies will focus on the generation of these complexes by spectroelectrochemical methods.

5.2.1 Synthesis

The synthesis of [μ-(2,5-Me₂Dicyd)-(NH₃)₅Ru]₂]⁵⁺ is outlined in Scheme 5.5. The reaction is quite straight forward involving the direct chemical oxidation of [μ-(2,5-Me₂Dicyd)-(NH₃)₅Ru]₂]⁴⁺ in acetone with a slight excess of [NH₄]₂[Ce(SO₄)₃] (dissolved in aqueous solution). Precipitation of a crude sulfate salt (A) immediately follows. Purification of (A) via a metathetic conversion (ie. SO₄²⁻ → PF₆⁻) is followed by recrystallization, typically as a PF₆⁻ salt (B) by diffusing diethyl ether into an acetone solution of the complex. Note that the metathesis and recrystallization steps are performed in the presence of trace hexafluorophosphoric acid.

Scheme 5.5

As previously mentioned, the [Ru(IV), Ru(III)] complexes of Dicyd²⁻ and 2,5-Cl₂Dicyd²⁻ could be generated in acetone solution as verified by UV-vis-NIR spectroscopy, but their isolation as analytically pure solids was precluded by their tendency to be reduced back to their respective [Ru(III), Ru(III)] forms. However, [μ-(2,5-Me₂Dicyd)-{(NH₃)₅Ru}₂][PF₆]₅ could be isolated as an analytically pure solid in typical yields of approximately 35%. The relatively low yields can be largely attributed to incomplete oxidation of the [Ru(III), Ru(III)] precursor complex. Note that the successful removal of unoxidized [μ-(2,5-Me₂Dicyd)-{(NH₃)₅Ru}₂]⁴⁺ is achieved by taking advantage of the greater solubility of [μ-(2,5-Me₂Dicyd)-{(NH₃)₅Ru}₂][SO₄]₂ in aqueous solution compared to [μ-(2,5-Me₂Dicyd)-{(NH₃)₅Ru}₂]₂[SO₄]₅.

As a final note, the hexafluorophosphate salt of [μ-(2,5-Me₂Dicyd)-{(NH₃)₅Ru}₂]⁵⁺ was very soluble in common aprotic solvents such as acetone, acetonitrile and DMSO. However, to maintain complex integrity in solution for extended periods of time, trace amounts of hexafluorophosphoric acid had to be added. In the solid-state, the complex was stable for an indefinite period of time if stored in the freezer at -18 °C.

5.2.2 Infrared Spectroscopy

The infrared spectrum of $[\mu\text{-(2,5-Me}_2\text{Dicyd)}\text{-(NH}_3\text{)}_5\text{Ru}_2][\text{PF}_6]_5$ is shown in Figure 5.22. The $\nu(\text{N}=\text{C}=\text{N})$ stretch of the coordinated anionic cyanamide group occurs as a weak-medium intense band at 2119 cm^{-1} . Note that two separate cyanamide stretching frequencies, indicative of cyanamide coordination to Ru(IV) and Ru(III), were not observed. In addition, for $[\mu\text{-(2,5-Me}_2\text{Dicyd)}\text{-(NH}_3\text{)}_5\text{Ru}_2][\text{ClO}_4]_4$, the $\nu(\text{N}=\text{C}=\text{N})$ stretch is 31 cm^{-1} lower at 2088 cm^{-1} (refer to Table 5.1 in Section 5.1.2). This may be evidence for a delocalized mixed-valence [Ru(IV), Ru(III)] complex on the IR time scale. The presence of ammine (NH_3) groups in the inner coordination sphere of ruthenium is also evident with the occurrence of strong $\nu(\text{N-H})$ stretching bands in the $3150\text{--}3280\text{ cm}^{-1}$ range and a $\delta(\text{N-H})$ degenerate deformation band of medium intensity at 1624 cm^{-1} . Finally, the presence of the hexafluorophosphate counter anion is verified by a very strong $\nu(\text{P-F})$ stretching band at 833 cm^{-1} .⁹⁹

Figure 5.22 Infrared spectrum of $[\mu\text{-(2,5-Me}_2\text{Dicyd)}\text{-(NH}_3\text{)}_5\text{Ru}_2][\text{PF}_6]_5$ (KBr disc).

5.2.3 Electronic Absorption Spectroscopy

The UV-vis-NIR (ie. 200-1500 nm) absorption spectrum of $[\mu\text{-(2,5-Me}_2\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}]_2[\text{PF}_6]_5$ in acetonitrile is shown in Figure 5.23 with the observed spectral transitions being summarized in Table 5.10. The data are consistent with the presence of LMCT transitions associated with both Ru(IV) and Ru(III)-cyanamide chromophores, thereby suggesting that the mixed-valence [Ru(IV), Ru(III)] complex is localized on the electronic absorption time scale. For example, the $b_1^* \leftarrow b_1$ and $b_1^* \leftarrow b_2$ LMCT transitions at 1118 and 326 nm, respectively, are associated with coordination of the anionic cyanamide group to Ru(III) (refer to Table 5.3b in Section 5.1.5a). However, indicative of the presence of only one Ru(III)-cyanamide chromophore in $[\mu\text{-(2,5-Me}_2\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}]_2^{5+}$, the intensity of the lower energy $b_1^* \leftarrow b_1$ LMCT transition is approximately 1/3 of that found in $[\mu\text{-(2,5-Me}_2\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}]_2^{4+}$. For the $b_1^* \leftarrow b_2$ LMCT transition, which is shifted to higher energy in the [Ru(IV), Ru(III)] complex compared to that for the [Ru(III), Ru(III)] complex, intensity comparisons cannot be made as a ligand centered $\pi^* \leftarrow \pi$ transition overlaps the $b_1^* \leftarrow b_2$ LMCT transition in the former complex.

The $b_1^* \leftarrow b_1$ and $b_1^* \leftarrow b_2$ LMCT transitions at 857 and 538 nm, respectively, are associated with coordination of the anionic cyanamide group to Ru(IV) (note that for the mononuclear pentaammineruthenium(IV) complex, $[(\text{NH}_3)_5\text{Ru(2,5-Me}_2\text{Dicyd)}]^{2+}$, the $b_1^* \leftarrow b_1$ and $b_1^* \leftarrow b_2$ LMCT transitions occur at 904 and 486 nm, respectively, in acetonitrile¹¹⁷). The reader is referred to Figure 4.9 in Section 4.2.3 for the qualitative MO energy level description of the LMCT transitions for the mononuclear pentaammineruthenium(III) and (IV) complexes of 2,5-Me₂Dicyd²⁻. The absorption band centered at 761 nm in the [Ru(IV), Ru(III)] complex has also been assigned to a $b_1^* \leftarrow b_1$ LMCT transition associated with the Ru(IV)-cyanamide chromophore (it was initially speculated that this band was the result of an IT transition, refer below). The splitting of

the $b_1^* \leftarrow b_1$ LMCT transition has been previously observed for mononuclear pentaammineruthenium(III) and [Ru(III), Ru(III)] complexes of 1,4-dicyanamidobenzene dianion ligands (refer to Sections 4.1.3 and 5.1.5a, respectively). Since the $b_1^* \leftarrow b_1$ LMCT transition is singly degenerate, such splitting was regarded as evidence for a conformer equilibrium in solution. Vibrational splitting is also a possibility.

Figure 5.23 UV-vis-NIR absorption spectrum of $[\mu-(2,5\text{-Me}_2\text{Dicyd})\text{-}\{(\text{NH}_3)_5\text{Ru}\}_2][\text{PF}_6]_5$ in acetonitrile with a concentration of 1.336×10^{-5} M.

The ligand centered $\pi^* \leftarrow \pi$ transitions at 207 and 304 nm in $[\mu-(2,5\text{-Me}_2\text{Dicyd})\text{-}\{(\text{NH}_3)_5\text{Ru}\}_2]^{5+}$ are at positions intermediate to those found in $[\mu-(2,5\text{-Me}_2\text{Dicyd})\text{-}\{(\text{NH}_3)_5\text{Ru}\}_2]^{4+}$ (at 212 and 274 nm, refer to Table 5.3b in Section 5.1.5a) and $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})]^{2+}$ (at 202 and 315 nm, refer to Ref. 117). Such behaviour is again reflective of the bridging $2,5\text{-Me}_2\text{Dicyd}^{2-}$ ligand experiencing the presence of both Ru(III) and Ru(IV) coordination.

Table 5.10 Electronic Absorption Spectral Data for [(2,5-Me₂Dicyd)-{(NH₃)₅Ru}₂][PF₆]₅ in Acetonitrile^a

$\pi^* \leftarrow \pi$	LMCT	
	$b_1^* \leftarrow b_2$	$b_1^* \leftarrow b_1$
207 (4.38), 304 (sh)	326 (3.87), 360 (sh) 538 (sh)	1118 (4.28), 761 (4.46), 857 (4.45)

^aAll data are in nm (log ϵ in parentheses); concentration = 1.336×10^{-5} M; sh=shoulder.

An intervalence band for $[\mu-(2,5\text{-Me}_2\text{Dicyd})\text{-}\{(\text{NH}_3)_5\text{Ru}\}_2]^{5+}$ has not been observed experimentally (refer to Figure 5.23), as it is believed that the intense low energy LMCT bands obscure this transition. Any speculation that the band at 761 nm was due to an IT transition was removed when the addition of trace amounts of a chemical oxidant (such as NOBF₄) to an acetonitrile solution of the [Ru(IV), Ru(III)] complex resulted in the maintenance of the $b_1^* \leftarrow b_1$ (including the band at 761 nm) and $b_1^* \leftarrow b_2$ LMCT transitions associated with the Ru(IV)-cyanamide chromophore and the concomitant disappearance of the $b_1^* \leftarrow b_1$ LMCT transition associated with the Ru(III)-cyanamide chromophore. Future work will examine the application of electroabsorption spectroscopy⁴⁰⁻⁴² as a means of deconvoluting the intense low energy LMCT bands from the predicted MMCT band of the [Ru(IV), Ru(III)] complex.

5.2.4 Spectroelectrochemistry

In order to verify that the oxidation of $[\mu-(2,5\text{-Me}_2\text{Dicyd})\text{-}\{(\text{NH}_3)_5\text{Ru}\}_2]^{4+}$ is a reversible one-electron process yielding $[\mu-(2,5\text{-Me}_2\text{Dicyd})\text{-}\{(\text{NH}_3)_5\text{Ru}\}_2]^{5+}$, spectroelectrochemical and coulometric experiments were performed (refer to Section 2.7.5 for the details of the experiment including cell design and experimental procedure). The results were as follows. Within approximately 4 minutes of applying the electrolysis oxidation potential $E_{\text{oxid.}} = 0.600$ V vs Ag/Ag⁺ to a 0.1 M TBAH/acetonitrile solution of the [Ru(III), Ru(III)] complex, the UV-vis-NIR spectral profile of the mixed-valence [Ru(IV), Ru(III)] complex

was generated. The oxidation was deemed to be complete when the application of E_{Oxid} for an additional minute did not alter the initially generated profile of the [Ru(IV), Ru(III)] complex. Application of the electrolysis reduction potential $E_{\text{red.}} = 0.100 \text{ V vs Ag/Ag}^+$ to the oxidized solution for approximately 5 minutes resulted in the almost complete (95%) reformation of $[\mu\text{-(2,5-Me}_2\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}_2]^{4+}$, as evidenced by the generation of its original UV-vis-NIR spectral profile. It is strongly believed that upon repetition of these spectroelectrochemical studies, good technique will prevail, and complete reversibility will be obtained. However, the current spectroelectrochemical results indicate that the $\text{Ru}^{\text{III,III}}/\text{Ru}^{\text{IV,III}}$ oxidation process is almost reversible. Furthermore, coulometric measurements demonstrated that the $\text{Ru}^{\text{III,III}}/\text{Ru}^{\text{IV,III}}$ oxidation process was as well a one-electron event. Through the use of Faraday's Law (refer to Section 4.2.5), the number of electron equivalents per mole of material electrolyzed n was calculated to be $1.02 \text{ eq mole}^{-1}$ (note that the total charge $Q = 11.58 \text{ mC}$ and the number of moles of electrolyzed complex $N = 1.173 \times 10^{-7} \text{ moles}$).

5.2.5 Solution Magnetic Susceptibility Measurements

Via the Evans method, a paramagnetically induced isotropic shift $-\Delta f = 26.89 \text{ Hz}$ of the TMS ^1H NMR resonance was observed. Using this value of $-\Delta f$, the molar susceptibility χ_m of $[\mu\text{-(2,5-Me}_2\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{PF}_6]_5$ in acetonitrile- d_3 at 300 K was determined to be $1.46 \times 10^{-3} \text{ cm}^3\text{mole}^{-1}$ (refer to Eq. 1.17 in Section 1.3.2). Assuming a spin-only model, the effective moment per ruthenium ($\mu_{\text{eff}}/\text{Ru}$) and the number of unpaired electrons per ruthenium (n/Ru) were calculated from the molar magnetic susceptibility χ'_m (to solve for χ'_m , refer to Eqs. 1.11 and 1.12 in Section 1.3.1 and to the Appendix for the summed up diamagnetic contributions of individual atoms and bonds in $[\mu\text{-(2,5-Me}_2\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{PF}_6]_5$) to be $1.12 \mu_B$ and 0.50 unpaired electrons, respectively (refer to Eqs. 1.10 and 1.15 in Section 1.3.1).

The measured values of μ_{eff} and n for the mixed-valence [Ru(IV), Ru(III)] complex are indicative of an intermediate level of paramagnetism when compared to those values obtained for the mononuclear Ru(IV) complex of $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})][\text{PF}_6]_2$ and the mononuclear Ru(III) complex of $[(\text{NH}_3)_5\text{Ru}(2\text{-Clpcyd})][\text{PF}_6]_2$ in acetonitrile- d_3 (refer to Sections 4.2.8 and 5.1.7, respectively). Recall that $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})][\text{PF}_6]_2$ was designated as being diamagnetic, whereas $[(\text{NH}_3)_5\text{Ru}(2\text{-Clpcyd})][\text{PF}_6]_2$ represented a maximum limit in paramagnetism for a low spin Ru(III)-cyanamide coordination complex where unpaired spin density is not shared between the metal and its coordination sphere. The implication for the mixed-valence [Ru(IV), Ru(III)] system is that the unpaired spin originating on Ru(III), is shared between the metal ions and their coordination spheres and is thus delocalized over the entire molecule on the NMR time scale. As a result, each ruthenium ion contributes 1/2 of an electron spin. Presumably, the π symmetry HOMO of the $2,5\text{-Me}_2\text{Dicyd}^{2-}$ bridging ligand is serving as an efficient medium for the delocalization of electron density.

Importantly, the ^1H NMR spectroscopy of $[\mu\text{-(}2,5\text{-Me}_2\text{Dicyd)}\text{-(}(\text{NH}_3)_5\text{Ru)}_2][\text{PF}_6]_5$ in acetonitrile- d_3 (refer to Section 5.2.6) supports the claim of the odd electron being delocalized on the NMR time scale. In addition, the chemical shifts of the relevant nuclei reflect what has been designated as an intermediate level of paramagnetism for the mixed-valence [Ru(IV), Ru(III)] complex.

5.2.6 ^1H NMR Spectroscopy

The ^1H NMR spectrum of $[\mu\text{-(}2,5\text{-Me}_2\text{Dicyd)}\text{-(}(\text{NH}_3)_5\text{Ru)}_2][\text{PF}_6]_5$ in acetonitrile- d_3 at 300 K is shown in Figure 5.24. At first glance, the most striking feature of the spectrum is the lack of asymmetry in the resonances associated with the relevant nuclei (in particular, the protons of the ammine groups), as might be expected for a mixed-valence complex. As

cluded to in the previous section, this is strong evidence for delocalization of the odd electron over the entire [Ru(IV), Ru(III)] molecule on the NMR time scale.

Figure 5.24 ^1H NMR spectrum of $[\mu\text{-(2,5-Me}_2\text{Dicyd)}\text{-}\{(\text{NH}_3)_5\text{Ru}\}_2][\text{PF}_6]_5$ in acetonitrile- d_3 (at 300 K) with a concentration of 11 mM. The singlet at 2.80 ppm is due to water of recrystallization.

The designation of an intermediate level of paramagnetism (between that found for $[(\text{NH}_3)_5\text{Ru(2,5-Me}_2\text{Dicyd)}][\text{PF}_6]_2$ and $[(\text{NH}_3)_5\text{Ru(2-Clpcyd)}][\text{PF}_6]_2$) for the [Ru(IV), Ru(III)] complex in acetonitrile, based on the measured values of μ_{eff} and n , is supported by the the chemical shift positions of the relevant nuclei as shown in the ^1H NMR spectrum of Figure 5.24. For example, the proton resonances associated with the trans- and cis- NH_3 groups in the [Ru(IV), Ru(III)] complex are contact shifted to 149.40 and 60.35 ppm (vs. TMS at 0.00 ppm), respectively. Compare this chemical shift position for the trans- NH_3 protons to that found in $[(\text{NH}_3)_5\text{Ru(2,5-Me}_2\text{Dicyd)}][\text{PF}_6]_2$ (at 8.27 ppm, refer to Section 4.2.6) and in $[(\text{NH}_3)_5\text{Ru(2-Clpcyd)}][\text{PF}_6]_2$ (>280 ppm, refer to Section 5.1.8a). The 3,6-phenyl and 2,5-methyl protons in the [Ru(IV), Ru(III)] complex are pseudocontact

shifted to 13.81 and -12.78 ppm, respectively. Again compare this chemical shift position for the 3,6-phenyl protons to that found in $[(\text{NH}_3)_5\text{Ru}(2,5\text{-Me}_2\text{Dicyd})][\text{PF}_6]_2$ (near 7.5 ppm) and in $[(\text{NH}_3)_5\text{Ru}(2\text{-Clpcyd})][\text{PF}_6]_2$ (near 29.4 ppm for the 3,5-phenyl protons). It is important to note that the above quoted chemical shifts for the $[\text{Ru}(\text{IV}), \text{Ru}(\text{III})]$ complex are singlets and gave the correct integration for their assignment.

In summary, both the lack of complex asymmetry and the designation of an intermediate level of paramagnetism for the mixed-valence $[\text{Ru}(\text{IV}), \text{Ru}(\text{III})]$ complex are strongly supportive of the odd electron being delocalized on the NMR time scale. For this to occur, the continuous and energetically favourable π symmetry HOMO of the 2,5- $\text{Me}_2\text{Dicyd}^{2-}$ bridging ligand must be simultaneously interacting with the $d\pi$ orbitals of both $\text{Ru}(\text{IV})$ and $\text{Ru}(\text{III})$. If the description prior to any metal-metal interaction is one in which three spins are uncoupled, one residing on $\text{Ru}(\text{III})$ and two on $\text{Ru}(\text{IV})$, antiferromagnetic exchange coupling via the superexchange pathway provided by the π -HOMO would result in one net unpaired spin. The question arises as to how this odd electron may be delocalized.

With reference to the results of extensive spectroscopic and electrochemical studies performed on mononuclear pentaammineruthenium(III) and (IV) complexes of 1,4-dicyanamidobenzene dianion ligands (refer to Sections 4.1 and 4.2), both $\text{Ru}(\text{III})$ and $\text{Ru}(\text{IV})$ to a larger extent, are capable of forming strong π interactions with the anionic cyanamide group. Given that symmetry and energy requirements have been met by the mixed-valence $[\text{Ru}(\text{IV}), \text{Ru}(\text{III})]$ system, let us conceptualize the mechanism of delocalizing π symmetry unpaired spin density, originating on $\text{Ru}(\text{III})$, over the entire molecule. Recall the three-center π bonding interaction between a 1,4-dicyanamidobenzene dianion ligand, $\text{Ru}(\text{IV})$ and a trans- NH_3 (refer to Figure 4.12 in Section 4.2.6), in which the ability of the $\text{Ru}(\text{IV})$ -cyanamide π bond to polarize trans- NH_3 electron density towards itself via a π hyperconjugation mechanism, accounted for the anisotropy of the trans- NH_3 ligand compared to the cis- NH_3 ligands. When extended to the mixed-valence $[\text{Ru}(\text{IV}),$

Ru(III)] complex, the strong Ru(IV)-cyanamide π bond can polarize Ru(III) $d\pi$ electron density towards itself via the π -HOMO of the 2,5-Me₂Dicyd²⁻ bridging ligand. As a result of this directional movement of electron density, the amount of unpaired spin density residing on Ru(III) is decreased. This is reflected by the smaller contact shift (less spin delocalization) experienced by the protons of the trans-NH₃ ligand bound to Ru(III) in the [Ru(IV), Ru(III)] complex, compared to the situation in [(NH₃)₅Ru(2-Clpcyd)][PF₆]₂ (refer to Section 5.1.8a for an explanation of the mechanism of contact shift experienced by a trans-NH₃ bound to a Ru(III)-cyanamide moiety). In essence, on the NMR time scale, each ruthenium ion contributes 1/2 of an electron spin.

CHAPTER 6

Conclusions and Future Studies

6.1 Conclusions

This thesis has achieved the research objectives that were outlined in Section 1.5. It has dealt with the synthesis and characterization of mononuclear pentaammineruthenium(III) and (IV) complexes of 1,4-dicyanamidobenzene anionic ligands. These studies were particularly valuable in terms of providing a fundamental understanding of the electronic nature of the ruthenium-cyanamide bonding interaction, and also in establishing the general synthetic pathway for the preparation of pentaammineruthenium cyanamide systems. Notable results include first, the observation that the deprotonation of a coordinated 1,4-dicyanamidobenzene monoanion ligand strengthens the Ru(III)-cyanamide π interaction. Secondly, the extent of Ru(III)-cyanamide π orbital overlap demonstrated an inner-sphere dependency on the π donor strength of the 1,4-dicyanamidobenzene ligand, whether monoanionic or dianionic. Finally, oxidation of Ru(III) to Ru(IV) when coordinated to a 1,4-dicyanamidobenzene dianion ligand, strengthens the ruthenium-cyanamide π interaction.

For the [Ru(III), Ru(III)] complexes, electronic absorption spectroscopy and electrochemical data demonstrated that the strength of the Ru(III)-cyanamide π interaction was dependent, and thus, could be controlled by varying the solvent donor number (outer-sphere perturbation) and as well by varying the π donor strength (inner-sphere perturbation) of the bridging ligand. Solution magnetic susceptibility and ^1H NMR data indicated that the paramagnetism of the system could be similarly controlled. It was concluded that the weakening of the Ru(III)-cyanamide π bond accompanied by the onset of paramagnetism, was the result of a reduction in metal-metal antiferromagnetic

superexchange coupling. Not unexpectedly, in a given solvent, the inner-sphere dependency of metal-metal antiferromagnetic coupling parallels a similar inner-sphere dependency of $-J$, determined from solid-state measurements. Although $-J$ has not yet been evaluated experimentally in solution for the [Ru(III), Ru(III)] complexes, a preliminary ^1H NMR investigation of the solvent-dependent pseudocontact shifted 3,6-phenyl protons suggests that in DMSO and aqueous solution, metal-metal antiferromagnetic coupling is weakened as the fixed complex geometry characteristic of the solid-state is replaced by a fluxional one. The implication is that the resonance stabilization energy between metal centers has been reduced to the point where metal-metal coupling is no longer sufficiently strong enough to maintain dimeric rigidity. Finally, for the [Ru(III), Ru(III)] complexes in solution, the contact hyperfine coupling constant A_d/h was estimated to be 4.66 and 1.16 MHz for the trans- and cis-NH₃ protons, respectively. The results were interpreted in terms of a highly directional (in the xz plane) direct delocalization mechanism in which Ru(III) unpaired spin density is preferentially delocalized onto the trans-NH₃ via a π hyperconjugation mechanism. The cis-NH₃ groups, which lie in the orthogonal xy plane, only experience a fractional amount of delocalized unpaired spin density.

For the mixed-valence [Ru(III), Ru(II)] complexes, a Hush analysis of IT band properties demonstrated that the extent of metal-metal electronic coupling as measured by H_{ad} was dependent, and thus, could be controlled by both the outer-sphere (note that only aqueous and acetonitrile solutions have been studied) and inner-sphere perturbations of the Ru(III)-cyanamide π interaction. The results were consistent with a transformation from weakly coupled Class II properties to borderline Class II/Class III properties as the solvent donor number decreased and the π donor strength of the bridging ligand increased. Importantly, a comprehensive set of comproportionation data supported these conclusions. For the [Ru(III), Ru(II)] complexes of 2-MeODicyd²⁻, 2,5-Me₂Dicyd²⁻, 2-MeDicyd²⁻, and Dicyd²⁻ in acetonitrile, a borderline Class II/Class III description is based primarily on the fact that

$\Delta v_{1/2}$ predicted by Hush theory is significantly larger than that observed experimentally and the magnitude of K_c is large (between 10^4 and 10^5). Furthermore, H_{ad} (estimated from the difference in potential ΔE between metal-centered reduction couples) is closer in magnitude to that obtained for a purely Class III system as opposed to a purely Class II system. Finally, the inner-sphere dependency of H_{ad} for the [Ru(III), Ru(II)] complexes in acetonitrile, parallels a similar inner-sphere dependency of H_{ab} for the [Ru(III), Ru(III)] complexes, estimated from solid-state measurements of $-J$. The result is strong evidence for the superexchange pathways being essentially the same in both systems.

For the [Ru(IV), Ru(III)] complex of 2,5-Me₂Dicyd²⁻, the increased stabilization of the Ru(IV) $d\pi$ orbitals compared to those of Ru(III), implies that their energies will be more closely matched to that of the π -HOMO of the bridging ligand, thus metal-metal antiferromagnetic superexchange coupling should be enhanced compared to the [Ru(III), Ru(III)] complex. ¹H NMR and solution magnetic susceptibility data demonstrate that the odd electron is delocalized on the NMR time scale with each ruthenium ion contributing 1/2 of an electron spin. An intervalence transition has not been observed experimentally, however, conclusive spectroelectrochemical studies have yet to be completed. Nevertheless, the system may be potentially important in the design of conductive mixed valency oligomers.

6.2 Future Studies

Many viable studies have yet to be conducted on the systems that have been discussed in this research thesis. They include the following:

For the [Ru(III), Ru(III)] systems, the experimental evaluation of $-J$ in solution is an important study. Also important, is the application of electroabsorption spectroscopy as a means of deconvoluting intense low energy LMCT bands from the predicted MMCT bands. Finally, preliminary studies have indicated that acceptors such as water can

protonate the cyanamide (NCN) group of the bridging ligand, significantly perturbing its HOMO, leading to a reduction in metal-metal antiferromagnetic superexchange coupling. An examination of this effect using a series of protic solvents with varying acceptor strengths would be valuable. For the [Ru(III), Ru(II)] systems, generating the intervalence transitions of all six wavefunctions in the complete solvent range, and hence evaluating the outer-sphere dependency of H_{ad} remains the single most important study to be completed. Pertaining to the [Ru(IV), Ru(III)] system, the synthesis of a potentially conducting mixed-valency oligomer is the long-term goal. However, as a first step, the preparation of the following trans complex would be useful: $L-M_1-L-M_2-L$, where $L = 2,5\text{-Me}_2\text{Dicyd}^{2-}$ and $M_1 = [\text{Ru}(\text{NH}_3)_4]^{4+}$ or $[\text{Ru}(\text{en})_2]^{4+}$ and $M_2 = [\text{Ru}(\text{NH}_3)_4]^{3+}$ or $[\text{Ru}(\text{en})_2]^{3+}$ (en = ethylenediamine).

Finally, the synthesis of novel dinuclear complexes based on the systems of this research thesis will not only increase our understanding of metal-metal superexchange coupling, but may also be applicable to the design of electronic and magnetic molecular materials. Recently, as a means of selectively perturbing metal-metal coupling in the [Ru(III), Ru(III)] and [Ru(III), Ru(II)] systems of this research thesis, the donor ammine ligands in the inner coordination sphere of ruthenium were replaced with π accepting diimine ligands. The result was an enhanced metal-metal interaction as described below:

For the dinuclear complexes, $([\mu\text{-(L)}\text{-(py)}(\text{NH}_3)_4\text{Ru}]_2)[\text{PF}_6]_4$:¹¹⁶ where $L = 2,5\text{-Me}_2\text{Dicyd}^{2-}$, Dicyd^{2-} , $2,5\text{-Cl}_2\text{Dicyd}^{2-}$ and $2,3,4,5\text{-Cl}_4\text{Dicyd}^{2-}$), a lower limit for the antiferromagnetic exchange coupling constant was evaluated from temperature dependent molar susceptibility measurements to be $-J \geq 400 \text{ cm}^{-1}$ ($\mathcal{H} = -J\hat{S}_a \cdot \hat{S}_b$), indicative of strong metal-metal antiferromagnetic superexchange coupling in the solid-state. In addition, metal-metal antiferromagnetic coupling was shown to be dependent on the outer-sphere perturbation of varying the solvent donor number, with paramagnetism setting in in DMSO. Metal-metal electronic coupling in the mixed-valence analogues, $[\mu\text{-(L)}\text{-(py)}(\text{NH}_3)_4\text{Ru}]_2$

$\{(\text{py})(\text{NH}_3)_4\text{Ru}\}_2\}^{3+}$, displayed a similar outer-sphere dependency, with a delocalized Class III description being ascribed to $[\mu-(2,5\text{-Me}_2\text{Dicyd})-\{(\text{py})(\text{NH}_3)_4\text{Ru}\}_2]^{3+}$ in acetonitrile ($K_c = 5.78 \times 10^6$). The dinuclear mixed-valence complex, $[\mu-(\text{Dicyd})-\{(\text{terpy})(\text{bpy})\text{Ru}\}_2]^{3+}$,¹¹⁸ demonstrates even stronger metal-metal electronic coupling in acetonitrile with $K_c = 2.75 \times 10^7$. For both diimine-containing mixed-valence [Ru(III), Ru(II)] systems compared to the ammine-containing mixed-valence [Ru(III), Ru(II)] complexes of this research thesis, a delocalized description for metal-metal coupling in the former is due to an enhanced π interaction between the Ru(III) $d\pi$ acceptor orbitals and the cyanamide groups of the bridging ligand. The enhanced π interaction is ascribed to the fact that the replacement of ammine ligands with diimine ligands increases the stability of the ruthenium $d\pi$ orbitals in both the 2+ and 3+ oxidation states because of the diimine's π acceptor properties and poorer σ donor properties compared to the ammine ligand. To complete the study of how metal-metal coupling is perturbed by sequentially replacing ammine ligands in the inner coordination sphere of ruthenium with π accepting diimine ligands, the following mixed-valence systems have yet to be prepared: $[\mu-(\text{L})-\{(\text{bpy})(\text{NH}_3)_3\text{Ru}\}_2]^{3+}$, $[\mu-(\text{L})-\{(\text{terpy})(\text{NH}_3)_2\text{Ru}\}_2]^{3+}$ and $[\mu-(\text{L})-\{(\text{bpy})_2(\text{NH}_3)\text{Ru}\}_2]^{3+}$ where L is a 1,4-dicyanamidobenzene dianion ligand.

Another example of selectively perturbing metal-metal coupling in the [Ru(III), Ru(III)] and [Ru(III), Ru(II)] systems of this research thesis, is to alter the nature of the 1,4-dicyanamidobenzene dianion bridging ligand. One idea is to increase the bridging ligand's degree of conjugation by employing 1,4-dicyanamido- derivatives of naphthalene, phenanthrene and pyrene (note that the corresponding anionic cyanamide derivatives have been previously prepared⁹⁷). Although the increased metal-metal separation would tend to reduce metal-metal superexchange coupling, conjugation is expected to raise the energy of the bridge's π -HOMO thereby leading to a more optimal energy match with the Ru(III) $d\pi$ acceptor orbitals and hence enhanced metal-metal superexchange coupling.

In closing, the design of novel electronic and magnetic molecular materials based on dinuclear metal systems is a rapidly developing field. It is hoped that this research work conducted on the diruthenium pentaammine systems of 1,4-dicyanamidobenzene dianion ligands proves to be an important contribution.

Appendix

Molar Diamagnetic Susceptibilities

Note: The molar diamagnetic susceptibility χ_{diam} of the various pentaammineruthenium complexes of 1,4-dicyanamidobenzene monoanion and dianion derivatives is obtained by summing up the diamagnetic contributions, known as Pasca's constants,¹¹⁹ of the individual atoms and bonds that constitute the given complex.

Complexes	$-\chi_{\text{diam}} (\times 10^{-6} \text{ cm}^3 \text{ mole}^{-1})$
$[\mu\text{-(2-MeODicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{PF}_6]_4$	555.45
$[\mu\text{-(2-MeODicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{Cl}]_4$	404.37
$[\mu\text{-(2,5-Me}_2\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{PF}_6]_4$	562.70
$[\mu\text{-(2,5-Me}_2\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{Cl}]_4$	399.90
$[\mu\text{-(2-MeDicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{PF}_6]_4$	550.84
$[\mu\text{-(2-MeDicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{Cl}]_4$	399.76
$[\mu\text{-(Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{PF}_6]_4$	538.98
$[\mu\text{-(Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{Cl}]_4$	376.18
$[\mu\text{-(2,5-Cl}_2\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{PF}_6]_4$	567.12
$[\mu\text{-(2,5-Cl}_2\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{Cl}]_4$	404.32

$[\mu\text{-(2,3,4,5-Cl}_4\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{PF}_6]_4$	595.26
$[\mu\text{-(2,3,4,5-Cl}_4\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{Cl}]_4$	432.46
$[\mu\text{-(2,5-Me}_2\text{Dicyd)}\text{-(NH}_3)_5\text{Ru}_2][\text{PF}_6]_5$	626.80
$[(\text{NH}_3)_5\text{Ru(2,5-Me}_2\text{Dicyd)}][\text{PF}_6]_2$	314.50
$[(\text{NH}_3)_5\text{Ru(2-Clpcyd)}][\text{PF}_6]_2$	311.07
$[(\text{NH}_3)_5\text{Ru(2-Clpcyd)}][\text{Cl}]_2$	229.67

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