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AN INVESTIGATION OF SUPEREXCHANGE IN
DINUCLEAR RUTHENIUM COMPLEXES

by
CHRISTOPHER E. B. EVANS, B.Sc.

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

Department of Chemistry

Carleton University
Ottawa, Ontario
October, 1997

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to the Faculty of Graduate Studies and Research
acceptance of the thesis,

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submitted by
CHRISTOPHER E. B. EVANS, B.Sc.

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

Chair, Department of Chemistry

Thesis Supervisor

External Examiner

Carleton University
December, 1997

Abstract

Four dinuclear ruthenium complexes $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-L})][\text{ClO}_4]_4$, $\text{L} = \text{Me}_2\text{dicyd}^{2-}$, dicyd^{2-} , $\text{Cl}\text{dicyd}^{2-}$, and $\text{Cl}_2\text{dicyd}^{2-}$ ($\text{dicyd}^{2-} = 1,4\text{-dicyanamidobenzene dianion}$), have been synthesized and characterized via magnetic resonance, electrochemical, and electronic absorption spectroscopic techniques. This data, along with that for analogue complexes of the form $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-L})][\text{PF}_6]_4$ and $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-L})][\text{PF}_6]_4$, $\text{L} = \text{Me}_2\text{dicyd}^{2-}$, dicyd^{2-} , $\text{Cl}_2\text{dicyd}^{2-}$, and $\text{Cl}_4\text{dicyd}^{2-}$, permitted an unprecedented opportunity to test the predictive capabilities of the Hush and CNS models of metal-metal coupling. Response of the magnitude of metal-metal coupling in the mixed-valent state to inner-sphere (both ligand and metal centred) and outer-sphere (solvent) electronic perturbations allowed the degree of coupling to be controlled over a broad range, and indicated that superexchange occurs in these systems via the hole-transfer mechanism. Treatment of the data by the theoretical models of interest suggested that while the Hush model is restricted to the treatment of very weakly coupled Class II systems, the CNS model's predictions of effective metal-metal coupling correlate linearly with electrochemical measures of this quantity for even very strongly coupled Class II systems. Breakdown of the CNS model (*i.e.* loss of linear correlation) appears to coincide with the onset of Class III (valence delocalized) behaviour, and this is rationalized in terms of the inherent assumptions of the CNS model. A number of further studies are proposed to clarify this relationship.

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List of Abbreviations

A3B	complex of the form $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-L})][\text{ClO}_4]_4$
A4P	complex of the form $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-L})][\text{PF}_6]_4$
A5	complex of the form $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-L})][\text{PF}_6]_4$
AC	acetone
AN	acetonitrile
bipy	2,2'-bipyridine
Calcd	Calculated
Cldicyd ²⁻	2-chloro-1,4-dicyanamidobenzene dianion
Cl ₂ dicyd ²⁻	2,5-dichloro-1,4-dicyanamidobenzene dianion
Cl ₄ dicyd ²⁻	2,3,5,6-tetrachloro-1,4-dicyanamidobenzene dianion
COSY	CORrelated SpectroscopY (Homonuclear Shift Correlation)
dicyd	a member of the dicyd ²⁻ family of ligands
dicyd ²⁻	1,4-dicyanamidobenzene dianion
DMSO	dimethylsulfoxide
HOMO	Highest Occupied Molecular Orbital
IR	Infrared
IT	Intervalence Transition
LMCT	Ligand-to-Metal Charge Transfer
LUMO	Lowest Unoccupied Molecular Orbital
Me ₂ dicyd ²⁻	2,5-dimethyl-1,4-dicyanamidobenzene dianion

MLCT	Metal-to-Ligand Charge Transfer
MMCT	Metal-to-Metal Charge Transfer
NM	nitromethane
NMR	Nuclear Magnetic Resonance
NOESY	Nuclear Overhauser Enhancement Spectroscopy
OTTLE	Optically Transparent Thin Layer Electrochemistry
pentaammine	complex of the form $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-L})][\text{PF}_6]_4$
py	pyridine
tetraammine	complex of the form $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-L})][\text{PF}_6]_4$
triammine	complex of the form $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-L})][\text{ClO}_4]_4$
UV-Vis-NIR	Ultraviolet-Visible-near Infrared

Chapter 1

Introduction

The study of metal-metal interactions in bi- and polymetallic systems has been driven both by the role of long-range electron transfer in many biological processes¹ and more recently by the possible uses of such systems as novel materials. Polypyridyl ruthenium (and osmium) complexes, for example, have received much attention for their possible roles in photochemical molecular devices (PMDs)² such as multielectron-transfer catalysts for water splitting,³ solar energy converters,⁴ or “‘molecular light switches’ for DNA”.⁵ A recent review discussed the role of mixed-valence dinuclear complexes in the design of molecular wires and switches.⁶

In a political climate increasingly preoccupied with the “practicality” and “applicability” of its science, materials research is coming increasingly to the fore as the field of the future. Ironically, to engage properly in the purposeful design of materials possessing particular properties, the materials scientist must be guided by the knowledge obtained by fundamental (basic) research. Without the tools and insights afforded by basic research, empirical materials science will be destined to creep along aimlessly, with significant discoveries more the result of blind chance than directed inquiry.

Ideally, the materials researcher will be able to anticipate the behaviour of a given new material from spectroscopic characterization of its subunits or building blocks. If a new material, then, required tuning to produce a specific behaviour, research could be

performed on a more tractable system to test the efficacy of proposed synthetic stratagems, saving time and resources and perhaps avoiding a reliance on theoretical modelling of uncertain applicability.

1.1 General Introduction

Metal-metal interactions in a given system may arise from trivial (coulombic) interactions or from (direct or effective) coupling of the metals' wavefunctions. When two metal centres interact sufficiently, the possibility exists for electron transfer to occur between them. The conceptual and theoretical framework for understanding thermal outer-sphere electron transfer was first provided by Marcus in a series of publications in 1957 and 1958.⁷ Interest in the behaviour of such compounds as Prussian blue, the iron complex of the form $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$, spurred interest in mixed-valence systems. In 1967 reviews by Robin and Day⁸ and Allen and Hush⁹ gave impetus to the study of mixed-valence complexes - complexes containing metal centres of inequivalent oxidation state; formalism was added later that same year by Hush's publication of his theoretical model^{10,11} linking the spectroscopic properties of mixed-valence complexes to the intermolecular electron transfer theory of Marcus.

Robin and Day, in their review,⁸ proposed a classification system for mixed-valence complexes which is now generally accepted. In this system, completely valence trapped complexes (no coupling between the metal centres) are termed Class I. Complexes in which the valence electrons are fully delocalized (very strong coupling

between the metal centres) are termed Class III. The intermediate Class II is constituted by all complexes whose behaviour falls between these extremes.

In complexes which are even moderately strongly coupled (*i.e.* not Class I), Hush's treatment predicts the existence of a charge transfer band for optically induced electron-transfer, and that the properties of the charge transfer band will reflect the degree of coupling between the metal centres. Such an event is termed metal-to-metal charge transfer (MMCT) or more commonly, because the two metals have different oxidation states (valencies), an intervalence transition (IT).

In 1969 Creutz and Taube¹² reported their studies on the novel dinuclear ruthenium complex $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-pz})]^{5+}$, pz = pyrazine, the much studied Creutz-Taube ion,¹³ launching experimental efforts in the new field. Since then, a great body of work on the study of mixed-valence complexes has come into being. Ruthenium, with its ability to form stable coordination complexes in both the Ru(II) and Ru(III) oxidation states and its well developed synthetic coordination chemistry,¹⁴ has become the metal of choice for studying electron transfer and exchange. Dinuclear complexes of ruthenium comprise the largest single group of mixed-valence complexes¹⁵ and have been widely studied. Reviews in 1983 by Creutz¹³ and in 1994 by Crutchley¹⁵ have discussed advances in the field in detail.

1.2 Metal-Metal Coupling

Superexchange is the term given to electron exchange or charge transfer between two metal centres which is mediated by the orbitals of a bridging ligand. A simple schematic energy level diagram for superexchange in a dinuclear mixed-valence ruthenium complex containing one Ru(III) and one Ru(II) centre is given in figure 1.2.1.

Figure 1.2.1 - Schematic representation of the hole-transfer superexchange mechanism representing the concerted event as two sequential electron transfer events between the bridging ligand's π -HOMO and the ruthenium acceptor and donor d_{xz} orbitals.

The mechanism of the concerted superexchange event can be represented as two stepwise electron-transfer events, the first between the bridging ligand's π -HOMO and the Ru(III) (π -acceptor) orbitals and the second between the Ru(II) (π -donor) orbitals and the bridge π -HOMO. Because the concerted event effectively represents an electron-hole moving across the system from the acceptor to the donor end, the mechanism portrayed in figure

1.2.1 is termed “hole-transfer superexchange”. The analogous “electron-transfer superexchange” occurs when the bridging ligand’s LUMO provides the pathway, and the mechanistic sequence of steps is reversed relative to the hole-transfer mechanism, consisting of an initial electron transfer from the donor metal to the empty bridge orbital, and a subsequent electron transfer from the bridge to the acceptor metal. In this case the concerted event is that of an electron moving from the donor end of the system to the acceptor end.

Since the bridging ligand is so intimately involved in superexchange, it is unsurprising that there are certain requirements thereupon for effective mediation. These are that the ligand possess an orbital spanning the entire molecule, which is symmetrically and energetically matched to the metal centres’ orbitals such that it can interact simultaneously with both metal centres.¹⁵ It is thus not surprising that to obtain substantial coupling an extended π system is necessary (*e.g.* all Class III systems reviewed in (15)), whereas coupling via a σ -framework is typically far weaker.¹⁶

In very strongly coupled systems, furthermore, the covalent nature of the bonding is increased,¹⁵ and the question of formal oxidation states often becomes blurred. Kaim’s studies on $[\{\text{Ru}(\text{bipy})_2\}_2(\mu\text{-adc-R})]^{n+}$, where adc-R is the azodicarbonyl ligand and $n = 2 - 4$, indicate an ambivalence for the $n = 3$ complex between the mixed-valent $\text{Ru(II)}-(\text{adc-R})^{2-}\text{-Ru(III)}$ form and the radical $\text{Ru(II)}-(\text{adc-R})^{\bullet}\text{-Ru(II)}$ form.¹⁷ Such ligand behaviour is termed “non-innocence”, and is of particular importance whenever coupling becomes strong. In the tetranuclear complexes $[\{\text{Ru}(\text{NH}_3)_5\}_4(\mu_4\text{-TCNX})]^{n+}$, TCNX = tetracyanoethene (TCNE), tetracyano-*p*-quinodimethane (TCNQ), 2,3,5,6-

tetracyanobenzene (TCNB), and 1,2,4,5-tetracyanopyrazine (TCNP), for example, which have been characterized as Class III from the existence of four equivalent metal sites when $n = 6-8, 10$,¹⁸ the $n = 8$ complex has recently been shown to exhibit unexpected paramagnetism.¹⁹ For the TCNE complex, this paramagnetism reached saturation at a value consistent with one unpaired spin although the TCNB and TCNQ exhibited greater paramagnetism, and didn't reach saturation within the range of the experiment.¹⁹ Since the $n = 8$ complex formally contains only Ru(II) centres and the neutral ligand, the effect of non-innocence is apparent.

The role of the nature of the metal centre on the degree of coupling was shown by Curtis who observed decreasing coupling in a series of analogs to the Creutz-Taube ion as σ -donating amines were systematically replaced by increasingly π -accepting ligands.^{20,21} Further, this research noted much weaker coupling in asymmetric complexes relative to their symmetric analogs.²⁰ This latter result has been shown to occur for outer-sphere as well as inner-sphere asymmetry by the work of Hupp in which the Creutz-Taube ion was end-capped with crown-ethers.²² When only one end was so capped, coupling was significantly attenuated, but when both ends were capped, and the symmetry of the system thus restored, Class III behaviour was regained and the spectral properties largely returned to those of the free species.²³

Outer-sphere perturbations based on solvent have also received much interest. The delocalized valency of Class III complexes provides stabilization to the system akin to aromaticity in organic compounds. The systems thus resist perturbations which would remove this condition and as such E_{op} for Class III complexes is solvent independent, and

the transitions are characterized as electronic excitations rather than charge transfer events. For Class II systems, however, the transitions are charge transfers and according to Marcus-Hush theory the solvent dependence of E_{op} to outer-sphere reorganization should correlate linearly with $(1/D_{op} - 1/D_s)$, where D_{op} and D_s are the solvent's optical and static dielectric constants, respectively.^{10,13,15} It has been noted, however, that complexes with ammine spectator ligands often²⁴ exhibit markedly different solvent dependences, which has been ascribed by Meyer to specific donor-acceptor interactions between the solvent and the ammine protons (see section 4.2).²⁵ A number of empirical parameters for solvent polarity exist. A review by Reichardt²⁶ in 1965 identified no less than six such parameters, including the Z -values of Kosower²⁷ and the E_T -values of Reichardt et. al..²⁶ In searching for an appropriate model for the solvent dependence of his complexes Meyer noted of the aforementioned parameters that "they are not simply related to any single intrinsic solvent property that is interpretable on the molecular level such as dielectric constant, refractive index, or dipole moment. Most importantly, there is no theoretical basis at the microscopic level for understanding the origin of such scales."²⁵ The Donor Numbers (D.N.) of Gutmann, however, based on the reaction enthalpies of various donors with $SbCl_5$ under fixed conditions,²⁸ were adopted by Meyer as the empirical solvent parameters of choice as they presumably measured a specific molecular property (the "donicity") of the solvent. In fact, numerous studies have confirmed the appropriateness of donor number for modelling solvation effects.²⁹⁻³⁴ More recently, efforts have been aimed at deconvoluting specific (non-continuum) and non-specific (continuum) effects,³⁵ and it is known that specific solvation effects tend to be about an order of magnitude

larger than non-specific effects.^{30,31,36} Further, specific solvation is not restricted to ammine complexes. Studies on cyano complexes revealed similar effects, although these correlated to Gutmann Acceptor Numbers (A.N.) rather than donor numbers.³⁶ Similarly, the generality of the importance of specific interactions is highlighted by the effect of “inert” electrolytes, particularly on asymmetric complexes.³⁷

1.3 Experimental Determination of Metal-Metal Coupling

The degree of metal-metal coupling in a complex affects the nature and properties of the bands in its electronic absorption spectrum. The following sections (1.4 and 1.5) deal with the theoretical models for extracting the magnitude of the coupling elements from these spectra. In order to test such theoretical treatments, however, it is important to have a direct experimental measure of the magnitude of coupling for comparative purposes. Such a measure is available through the technique of cyclic voltammetry (CV) which allows for direct determination of the stability of the mixed-valent state via the comproportionation constant, K_c , which is defined for the equilibrium shown in eq 1.3.1.

Eq 1.3.1 can be viewed as the sum of the two metal-centred redox events defined by eq 1.3.2.

Thus, the CV experiment yields directly a free energy of comproportionation by first calculating the separation between the metal-centred couples, $\Delta E = E^\circ_{M2} - E^\circ_{M1}$, and relating this quantity to K_c via the Nernst equation (1.3.5). The free energy of comproportionation can be obtained directly from K_c according to $\Delta G_c = -RT \ln(K_c)$.

Given
$$E = E^\circ - \frac{RT}{nF} \ln Q \quad (1.3.3)$$

and recognizing that the driving force for comproportionation, $E^\circ = \Delta E$, leads to

$$\Delta E = \frac{RT}{nF} \ln K_c \quad (1.3.4)$$

or, for ΔE in volts, to the more useful form

$$K_c = 10^{16.91(\Delta E)} \quad (1.3.5)$$

in which the prefactor has been numerically evaluated at 298 K for a one electron event.

Although ΔG_c is available directly from the CV experiment, it is not itself a direct measure of metal-metal coupling. This is because ΔG_c contains contributions from a number of factors. A full consideration of this is given in section 4.3.

1.4 The Hush Model

Despite the advent of a number of sophisticated theoretical models,³⁸ notably PKS Theory,³⁹ for describing the properties of intervalence transitions, Hush's model has been, since its inception, the mainstay of analysis of mixed-valence complexes. Unlike its more calculation intensive counterparts, the conceptual simplicity and ease of application of the Hush model have made it the tool of choice for synthetic chemists. (Note: Although the

author refers to the model simply as “The Hush Model”, others prefer to term it the Mulliken-Hush Formalism, as Hush essentially applied earlier work by Mulliken to the specific problem of mixed-valence complexes.⁴⁰⁾

The Hush model evaluates metal-metal coupling directly from experimental measurement of IT bands. A potential energy diagram such as that shown in figure 1.4.1 may be constructed for a two-state system, where the potential energy surfaces represent the diabatic initial (Ψ_d) and final (Ψ_a) wavefunctions.

Figure 1.4.1 - Potential energy diagram of the diabatic initial (Ψ_d) and final (Ψ_a) wavefunctions for a symmetric mixed-valence complex.

In this nomenclature, Ψ_d represents the situation M-L-M', where M is a Ru(III) centre and M' a Ru(II) centre. Ψ_a then represents the situation M'-L-M'', the diabatic final state after electron transfer between the donor (Ru^{II}) and acceptor (Ru^{III}) metal centres. If the diabatic states are now allowed to mix to form the normalized adiabatic states Ψ_1 and Ψ_2

$$\Psi_1 = c_d \Psi_d + c_a \Psi_a \quad (1.4.1a)$$

$$\Psi_2 = c_d \Psi_a - c_a \Psi_d \quad (1.4.1b)$$

where $c_d^2 + c_a^2 = 1$, the resultant potential energy diagram is that given by figure 1.4.2.

Figure 1.4.2 - Potential energy diagram of the adiabatic initial (Ψ_1) and final (Ψ_2) wavefunctions for a symmetric Class II mixed-valence complex.

The nomenclature of eq 1.4.1 is that of (40), which derives expressions for the adiabatic energies E_1 and E_2 (for the states Ψ_1 and Ψ_2) and for c_d and c_a which are exact for any orthonormal two-state model in which overlap may be ignored ($S_{ad} = 0$),⁴⁰ and result in eq 1.4.2

$$|c_a c_d| = \frac{|H_{ad}|}{(E_2 - E_1)} = \frac{1}{2} \left[1 - \left(\frac{\Delta_{ad}}{E_2 - E_1} \right)^2 \right]^{1/2} \quad (1.4.2)$$

where H_{ad} is the matrix element coupling the diabatic states and Δ_{ad} is the energy difference between the diabatic states. Previous treatment of such systems has assumed eq 1.4.2 (or its equivalent) to be true only (*e.g.* the perturbation treatment of donor-acceptor interactions of Murrell)⁴¹ in the weak coupling limit where $|c_d| \approx 1$, $|c_a| \approx |H_{ad}|/\Delta_{ad} \ll 1$, and $(E_2 - E_1) \approx \Delta_{ad}$. The adiabatic wavefunctions of eq 1.4.1 are then given by eq 1.4.3

$$\Psi_1 = \Psi_d + \alpha_{ad} \Psi_a \quad (1.4.3a)$$

$$\Psi_2 = \Psi_a + \alpha_{da} \Psi_d \quad (1.4.3b)$$

although since $\alpha_{da} + \alpha_{ad} + S_{ad} = 0$, when overlap between Ψ_1 and Ψ_2 is ignored (*i.e.* $S_{ad} = 0$), $|\alpha_{da}| = |\alpha_{ad}| = \alpha$ and the adiabatic wavefunctions are expressed by eq 1.4.4,

$$\Psi_1 = \Psi_d + \alpha \Psi_a \quad (1.4.4a)$$

$$\Psi_2 = \Psi_a - \alpha \Psi_d \quad (1.4.4b)$$

their more common form, whereby $\alpha = |H_{ad}|/v_{\max}$.

Starting with non-stationary state wavefunctions (*i.e.* without the Born-Oppenheimer approximation) allows for the finite probability of radiationless (*i.e.* thermal) electron transfer through coupling of the electronic wavefunctions to lattice vibrations. In the high temperature limit (*i.e.* where tunneling effects may be ignored), Hush showed that both the single frequency model and the dielectric continuum model result in eq 1.4.5 for symmetric systems.¹⁰

$$E_{op} = 4E_{th} \quad (1.4.5)$$

Hush further states that in the high temperature limit, the bandshapes will tend to be gaussian, and showed that eq 1.4.6 may be used to relate the experimental bandwidth,

$$\Delta\nu_{1/2} = (2310v_{\max})^{1/2} \quad (1.4.6)$$

$\Delta\nu_{1/2}$ to the absorption maximum, $E_{op} = v_{\max}$, when $\Delta\nu_{1/2}$ is defined as the bandwidth when

$$\frac{I_v v_{\max}}{I_{\max} v} = \frac{1}{2} \quad (1.4.7)$$

instead of the more common $I_v/I_{\max} = 1/2$, to take into account the unusual broadness of the experimentally observed bands.¹⁰

Hush's ubiquitous equation for evaluating the donor-acceptor coupling element, H_{ad} , is derived from a perturbative treatment of the oscillator strength, f , of the IT band which is obtained experimentally as

$$f = 4.32 \times 10^{-9} \int \epsilon \, d\nu \quad (1.4.8)$$

and which can be approximated by

$$f = 4.61 \times 10^{-9} \epsilon_{\max} \Delta\nu_{1/2} \quad (1.4.9)$$

where $\epsilon_{\max}$ is the experimental molar absorptivity of the IT band and $\Delta\nu_{1/2}$ the experimental bandwidth at half height.²⁰ Theoretically, f is given by

$$f = 1.085 \times 10^{-5} \nu D^2 \quad (1.4.10)$$

for a one electron transition, where ν is $\nu_{\max}$ when the bandshape is gaussian and D , the dipole strength of the transition, is related to the transition dipole moment, M , by $D = M/e$. Substituting eq 1.4.4 into $M = \langle \Psi_1 | e\mathbf{r} | \Psi_2 \rangle$ yields $M \approx \alpha eR$, where R is the transition dipole moment length. Recalling that $\alpha = |H_{ad}|/\nu_{\max}$, eqs 1.4.9 and 1.4.10 may be directly equated to yield

$$H_{ad} = \frac{2.06 \times 10^{-2}}{r} \left(\epsilon_{\max} \cdot \Delta\nu_{1/2} \cdot \nu_{\max} \right)^{1/2} \quad (1.4.11)$$

where the transition dipole moment length, R (the distance through which charge moves during the transition), has been taken to be the donor-acceptor separation, r .

Experimental determination of H_{ad} is then directly possible from eq 1.4.11 using r in Å and all other quantities in cm^{-1} (with $\epsilon_{\max}$ in $\text{M}^{-1} \cdot \text{cm}^{-1}$, of course).

When H_{ad} becomes sufficiently large, the coupling between the two centres is such that the thermal barrier to electron transfer disappears. This is the Class III regime of

Robin and Day, and the potential energy diagram of figure 1.4.2 becomes that of figure 1.4.3. For a Class III system the relationship between H_{ad} and E_{op} may be described simply via eq 1.4.12.

$$E_{op} = 2H_{ad} \quad (1.4.12)$$

Figure 1.4.3 - Potential energy diagram of the adiabatic initial (Ψ_1) and final (Ψ_2) wave-functions for a symmetric Class III mixed-valence complex.

1.5 The CNS Model

Although Hush's model is strictly limited in scope to the treatment of weakly coupled systems, it remained the mainstay of the lay-chemists' repertoire from its inception until 1994 when Creutz, Newton, and Sutin (CNS) reported a novel approach to the problem of evaluating metal-metal coupling elements in mixed-valence complexes.⁴⁰ Conceptually, their approach differs dramatically from Hush's. Where his model considers the intensity of the IT band directly, CNS approach the matter from the perspective of the superexchange mechanism itself, considering net metal-metal interaction to be a reflection

of the coupling between either metal and its end of the bridging ligand.⁴⁰ This treatment retains the advantageous ease of application of the Hush model but has been shown to be more generally applicable.⁴²

Consider a prototypical dinuclear complex of the form M-L-M' which is described by diabatic wavefunctions describing the electron localized respectively on the donor (metal centre M, Ψ_d) and acceptor (metal centre M', Ψ_a) ends of the complex.

Figure 1.5.1 - Schematic representation of the potential energy profiles for the donor (MLM'), acceptor (M'LM'), and intermeditate charge transfer (ML~M'') states. The charge transfer events are labelled as initial (i), final (f), and intervalence (IT). Eq 1.5.8 may be understood through their consideration. Adapted from (44).

If, for each superexchange pathway, the diabatic wavefunctions mix via a single charge-transfer excited state (see figure 1.5.1), and both electron- and hole-transfer pathway contributions are considered, second-order Rayleigh-Schrödinger perturbation theory (RSPT) results in an initial state wavefunction (Ψ_1) of the form given by eq 1.5.1.⁴³

$$\Psi_1 = \Psi_d + \frac{H_{ad}}{\Delta E_{ad}} \Psi_a + \left[\frac{H_{de}H_{ea}}{\Delta E_{de}\Delta E_{ad}} + \frac{H_{dh}H_{ha}}{\Delta E_{dh}\Delta E_{ad}} + \frac{H_{dd}H_{ad}}{(\Delta E_{ad})^2} \right] \Psi_a \quad (1.5.1)$$

The subscripts e and h denote, respectively, the charge transfer states involved in the electron- and hole-transfer pathways. Since the metal centres are far removed from one another, direct interaction of their orbitals (and thus H_{ad}) can be assumed to be zero. Because the diabatic donor wavefunction is localized on M, and the acceptor wavefunction on M', and because the charge transfer states for both pathways involve the ligand, L, the subscripts d, e, and a of eq 1.5.1 may be replaced with M, L, and M', respectively, to reflect the experimentally observable origins of the various parameters. Since the electron-transfer superexchange pathway is expressed by MLCT bands, and the hole-transfer superexchange pathway by LMCT bands (see section 1.2), the coupling elements H_{de} , H_{ea} , H_{dh} , and H_{ha} may thus be equivalently named H_{ML} , $H_{M'L}$, H_{LM} , and $H_{LM'}$. The energy gaps ΔE_{de} , ΔE_{dh} , and ΔE_{ad} are similarly named ΔE_{ML} , ΔE_{LM} , and E_{IT} where the first and second terms are both E_{CT}^i for their respective pathways (see figure 1.5.1). Eq 1.5.1 may then be rewritten in the new nomenclature as eq 1.5.2.

$$\Psi_i = \Psi_d + \left[\frac{H_{ML}H_{M'L}}{\Delta E_{ML}\Delta E_{IT}} + \frac{H_{LM}H_{LM'}}{\Delta E_{LM}\Delta E_{IT}} \right] \Psi_a \quad (1.5.2)$$

Considering only one (the electron-transfer) pathway, Newton (the 'N' of CNS) determined an expression for $H_{MLM'}$ (where $H_{MLM'}$ describes the effective coupling between M and M' just as H_{ad} describes their direct coupling) from consideration of the optical transition moment of the intervalence transition,⁴⁴

$$|\mu_{op}| = er \frac{|H_{MLM'}|}{E_{IT}} \quad (1.5.3)$$

(cf. M in section 1.4). Solving $\mu_{op} = \langle \Psi_1 | \mu | \Psi_2 \rangle$ with RSPT wavefunctions of the type given in eq 1.5.2 yields

$$|\mu_{op}| = e r H_{ML} H_{M'L} \left[\frac{\Delta E_{ML} + \Delta E_{M'L}}{2(E_{IT})(\Delta E_{ML})(\Delta E_{M'L})} \right] \quad (1.5.4)$$

where $\Delta E_{ML} = E_{CT}^f$ from figure 1.5.1. Eq 1.5.3 may be equated with eq 1.5.4 to yield eq 1.5.5

$$H_{MLM'} = H_{ML} H_{M'L} \left[\frac{1}{2} \left(\frac{1}{\Delta E_{ML}} + \frac{1}{\Delta E_{M'L}} \right) \right] \quad (1.5.5)$$

which expands to eq 1.5.6 when contributions from both possible superexchange pathways are considered.

$$H_{MLM'} = \frac{H_{ML} H_{M'L}}{2\Delta E_{ML}^{eff}} + \frac{H_{LM} H_{LM'}}{\Delta E_{LM}^{eff}} \quad (1.5.6)$$

The first term of eq 1.5.6 deals with contributions from the electron-transfer superexchange pathway, while the second term deals with contributions from the hole-transfer superexchange pathway. The superscript “eff” on the ΔE terms indicates that it represents an effective (*i.e.* reduced) energy gap (see eq 1.5.5). The “asymmetry” of eq 1.5.6 with respect to the factor of two in the denominator arises because the MLCT states, but not the LMCT states, are degenerate.*

Often one pathway will dominate a given system's behaviour in which case only the term of eq 1.5.6 dealing with that pathway need be considered. In the case, for example, of complexes in which superexchange occurs predominantly via the hole-transfer

* The form of eq 1.5.6 differs from the corresponding equation in (40). That eq 1.5.6 is the correct form to use when both Ru(II) MLCT and Ru(III) LMCT states contribute to superexchange was pointed out to our group by Dr. Norman Sutin in private communication with Dr. R. J. Crutchley. (cf. (42)).

pathway only the second term of eq 1.5.6 is considered. For such a complex the adiabatic coupling element H_{LM} represents a “true” LMCT coupling element between the ligand and a Ru(III) centre while $H_{LM'}$ represents an LMCT involving the donor metal M bearing (instantaneously) the acceptor metal’s oxidation state. (*i.e.* a Ru(III) centre with all its bond lengths and its solvation sphere appropriate to Ru(II)). Since this latter quantity is experimentally unavailable, evaluation of $H_{LM'}$ contains the intrinsic error of the necessary assumption that $H_{LM} = H_{LM'}$. With this assumption, however, the practical form of eq 1.5.6 simplifies to eq 1.5.7

$$H_{\Delta\Lambda'} = \frac{H_{LM}^2}{\Delta E_{LM}^{eff}} \quad (1.5.7)$$

The effective energy gap is simply the reduced energy difference between E_{CT}^i and E_{CT}^f and may be evaluated experimentally according to eq 1.5.8

$$\Delta E_{LM}^{eff} = \left[0.5 \left(\frac{1}{E_{LMCT}} + \frac{1}{E_{LMCT} - E_{IT}} \right) \right]^{-1} \quad (1.5.8)$$

where $E_{LMCT} = E_{CT}^i$ and the denominator of the second term is E_{CT}^f (see figure 1.5.1).

Integral to making eq 1.5.7 (or similarly eq 1.5.6) into a useful equation for the synthetic chemist was the revisitation of the derivation of eq 1.4.11 by CNS (see section 1.4) which showed it was exact within any two-state model in which overlap could be neglected, and could thus be used to calculate any of the metal-ligand coupling elements of this model. Eq 1.5.7 may thus (potentially) be evaluated entirely from experimental electronic absorption data if the donor-acceptor separation, r , is known. It is interesting to note that eq 1.5.8 is the only part of the CNS treatment which requires experimental

determination of the IT band. If a reasonable estimate of E_{IT} can be made, $H_{MM'}$ may be determined exclusively using data from the charge transfer spectrum of the fully oxidized (or fully reduced) complex. CNS themselves, in fact, estimated certain $H_{MM'}$ using data from mononuclear complexes.⁴⁰

It should be noted that use of eq. 1.4.11 to solve for the various metal-ligand coupling elements introduces another source of error not explicitly dealt with in this section, but significant nonetheless. This is the assumption that $R = r$, that the transition dipole moment is equal to the donor-acceptor separation (see section 1.4). In fact, it is well known that as systems become more strongly coupled, the wavefunctions of M and M' become increasingly delocalized onto the bridging ligand. This causes R to be less than r , with the discrepancy increasing as a function of coupling. Corrections for this discrepancy require the experimental evaluation of R (commonly called μ in literature) using electroabsorption (Stark) spectroscopy.⁴⁵ Such corrections are incorporated into the evaluation of coupling elements in such models as Newton's "Generalized Mulliken-Hush" approach, which defines the diabatic states in a general fashion by assuming a transition dipole moment of zero between diabatic states localized on different centres.⁴⁶ Hupp has recently utilized Stark spectroscopy to highlight the "remarkable" distance dependence of R on orbital orientation.⁴⁷

1.6 Hole-Transfer Superexchange

The study of superexchange in mixed-valence dinuclear ruthenium complexes has been dominated by systems in which this behaviour occurs via the electron transfer pathway. Such systems typically incorporate bridges exhibiting π -acid behaviour, and having low-energy LUMOs, with the prototypical example being pyrazine and with a great number being polypyridyl in nature.¹⁵ Thus, the various theoretical models describing superexchange have traditionally been investigated from only one experimental standpoint.

The ligand dicyd²⁻, 1,4-dicyanamidobenzene dianion (see figure 1.6.1), and its many substituted analogs with their high energy π -HOMOs,^{48,49} allow for the study of hole transfer superexchange when incorporated into a number of ruthenium-based complexes.^{42,49-55}

Figure 1.6.1 - The bridging ligand 1,4-dicyanamidobenzene dianion (dicyd²⁻).

In this regard, the dicyd²⁻ family of ligands is extremely rare, joining such other multiatom ligands as the malonitrile anion,⁵⁶ the triazole anion,⁵⁷ the bibenzimidazolate dianion,⁵⁸ the tetrapyridylbiphenyl dianion,⁵⁹ the azodicarbonyl dianion,^{17,60} bipyridylbenzodiimidazole and bipyridylthiazolobenzothiazole,⁶¹ pyrazyltriaazole,⁶² and all their respective derivatives in the select group of ligands which mediate metal-metal coupling via the hole-transfer

superexchange mechanism. Of the systems listed, furthermore, only the dicyanamidobenzene dianions and the azodicarbonyl dianions act purely as π -donors and thus exclusively via the hole-transfer mechanism.⁵⁰ Thus, the study of complexes incorporating the dicyd²⁻ family of ligands affords a rare opportunity for testing the various theoretical models of metal-metal coupling on their treatment of hole-transfer, as opposed to electron-transfer, superexchange.

1.7 Electronic Factors Affecting Superexchange

The relative energy levels for the ruthenium and ligand orbitals presented in figure 1.2.1 are appropriate to a mixed-valence ruthenium complex incorporating a ligand with a high energy π -HOMO such as the members of the dicyd²⁻ family. Interactions between the metal πd orbitals and the ligand π -HOMO will provide, in light of the ligand's continuous π -HOMO,^{15,48,49} a suitable " π -way" for superexchange. At each end of the ligand, the cyanamide chromophores' interactions with the metal centres will be governed by the degree of energetic matching of their orbitals. As this energetic matching is optimized, metal-ligand coupling should increase and, consequently, metal-metal coupling.

Control of the orbital energies may be effected directly or indirectly. Direct perturbations include the addition of electron donating or withdrawing substituents to the ligand's phenyl ring which will raise or lower, respectively, the energy of the π -HOMO. The energy of the metal centres' πd orbitals may likewise be perturbed through the nature of the spectator ligands. Strong σ -donating spectator ligands may be replaced with

weaker σ -donors or π -acid spectator ligands to stabilize the d-orbitals. Indirect control may be effected by outer-sphere solvent perturbations. Such interactions will likewise serve to alter the orbital energies and thus tune the metal-ligand (and thus metal-metal) interactions. (This subject is treated in greater detail in section 4.2).

1.8 Research Goals

This thesis comprises a largely completed study of metal-ligand interactions in dinuclear ruthenium complexes through a series of specific outer- and inner-sphere perturbations to the systems with an eye to understanding the electronic factors affecting superexchange therein. The electronic perturbations mentioned in section 1.7 will be effected systematically and the systems' responses monitored via electrochemical, electronic absorption spectroscopic techniques.

Three families of complexes will be compared, each incorporating four dicyd²⁻ family ligands in dinuclear complexes based on pentaammineruthenium(III) (A5), tetraamminepyridineruthenium(III) (A4P), and triammine(bipyridine)ruthenium(III) (A3B) inner coordination spheres. Outer-sphere perturbations will be studied in five solvents spanning a broad range of solvent donor numbers: nitromethane (NM), acetonitrile (AN), acetone (AC), dimethylsulfoxide (DMSO), and water (H₂O).

Work on the pentaammine systems has previously showed that they are too strongly coupled for treatment by the Hush model;^{42,48} this situation should persist for the more strongly coupled systems. The CNS model, however, showed itself to be more

broadly applicable, with a good correlation between its predictions and the electrochemical data.⁴² As the systems become more strongly coupled, however, increasing covalency in the ruthenium-cyanamide bonding is expected to attenuate the oscillator strengths, f , of the LMCT bands. (As the systems become increasingly strongly coupled, overlap will eventually be optimized. Further matching of the ligand and metal orbitals will have the effect of reducing the transition dipole moment length, R , which will decrease oscillator strength.)^{63,64} The degree of covalency, however, should not affect the trend in actual metal-metal coupling since covalency increases concurrently with optimization of the energy match between the metal and ligand orbitals. This should result in the relationship between f and the electrochemically determined magnitude of coupling given in figure 1.8.1.

Figure 1.8.1 - Conceptual relationship expected between LMCT band oscillator strength, f_{LMCT} , and the electrochemically determined magnitude of metal-metal coupling.

Further, because the CNS model is restricted to systems in which overlap can be neglected, an experimentally determined f vs. metal-metal coupling plot should predict the point at which the model's overlap criterion is no longer met. (Covalency, of course, implies orbital overlap.)

In the absence of covalency, the CNS model predicts that metal-metal coupling will increase linearly with increasing LMCT oscillator strength. (Here it must be recalled that the H_{LM} term is proportional to f^2 while $H_{MM'}$ is proportional to H_{LM}^2 !) Thus, as the inflection point of the f vs. metal-metal coupling plot is approached, the CNS model should break down. If either the inflection point or the inverted region of the plot coincide with the onset of Class III behaviour, this might provide a general way of determining the existence of such behaviour via the CNS model.

The goal of this thesis is to test our understanding of the electronic factors affecting superexchange through systematic application of a series of inner- and outer-sphere perturbations to test, ultimately, the limits of the CNS model and the relationship between breakdown of the CNS model and the extent of delocalization of the valence electrons.

Chapter 2

Experimental

2.1 Starting Materials

2.1.1 Reagents for ligand synthesis

Ammonium thiocyanate (ACS reagent grade, 97.5+%, Aldrich), benzoyl chloride (99%, Aldrich), 2-chloro-1,4-phenylenediamine sulfate (95%, Aldrich), glacial acetic acid (ACS reagent grade, $\leq 99.7\%$, Anachemia), lead(II) acetate trihydrate (ACS reagent grade, 99+%, Aldrich), potassium carbonate (anhydrous, Anachemia), and sodium hydroxide (ACS reagent grade, 99.0%, Anachemia) were used as received without further purification.

2.1.2 Reagents for complex synthesis

Ammonium hexafluorophosphate (99.5%, Alfa Aesar), cerium(IV) ammonium nitrate (99+%, Alfa Aesar), hydrazine monohydrate (98%, Aldrich), hydrochloric acid (ACS reagent grade, 36.5 - 38.0%, Anachemia), mercuric chloride (ACS reagent grade, 99.5+%, Anachemia), ruthenium(III) chloride hydrate (99.9%, Alfa Aesar), sodium bisulfite (certified ACS, Fisher), sodium tetraphenylborate (ACS reagent grade, 99.5+%,

Alpha Aesar; Strem), tetrabutylammonium bromide (99%, Aldrich), and zinc (mossy, ACS reagent grade, $\geq 99.8\%$, Anachemia) were used as received.

2.1.3 Compressed gases

Argon (industrial grade, 99.998%, BOC), sulfur dioxide (99.98%, Matheson).

2.1.4 Ion exchange resins and drying agents

CM Sephadex C25 (Carboxymethyl Sephadex) cation exchanger (bead size: 40-125 μm , Sigma) and phosphorus pentoxide (ACS reagent grade, 98+%, Anachemia) were used as received. Aluminum oxide (neutral, chromatography grade, Woelm) was activated by heating to 300 $^{\circ}\text{C}$ for several hours in a muffle furnace.

2.1.5 Electrochemistry and NMR internal references

Tetramethylsilane (TMS) (NMR grade, 99.9+%, Aldrich) was used as received.

Dicyclopentadienyliron (ferrocene) (reagent grade, J. T. Baker) was purified by sublimation.

2.1.6 Electrolytes

Sodium chloride (ACS reagent grade, 99+%, Anachemia) was used as received.

Potassium chloride (ACS reagent grade, Anachemia) was recrystallized twice from water and vacuum dried overnight at 120 °C. Tetrabutylammonium hexafluorophosphate (TBAH) (ACS reagent grade, 98%, Aldrich) was recrystallized twice from 1:0.5 ethanol:water and vacuum dried overnight at 120 °C.

2.2 Solvents

2.2.1 Solvents for synthesis

Acetonitrile (Accusolv, 99.9+%, Anachemia), chloroform (pesticide grade, Fisher), diethyl ether (anhydrous, 99.0%, Caledon Labs), and ethanol (absolute, Commercial Alcohols) were used as received without further purification. Acetone (lab grade, Anachemia) was distilled under glass before use.

2.2.2 Solvents for spectroscopy and electrochemistry

All organic solvents used for spectroscopy or electrochemistry were distilled in glass under reduced pressure and stored under argon. With the exception of acetone (Accusolv, 99.9+%, Anachemia), all solvents were dried with an appropriate reagent. Acetonitrile

(Accusolv, 99.9+%, Anachemia) was distilled in the presence of phosphorus pentoxide. Dimethyl sulfoxide (Accusolv, 99.9+%, Anachemia) and nitromethane (HPLC grade, 96+%, Sigma) were dried overnight with, and distilled in the presence of, activated alumina. Distilled water was deionized using a Millipore MILLI-Q 4-bowl Plus (analytical) deionizer.

2.2.3 Solvents for NMR spectrometry

Acetonitrile- d_3 (99.6 atom % D, Aldrich), dimethyl sulfoxide- d_6 (99.9 atom % D, CDN Isotopes), and nitromethane- d_3 (99 atom % D, Aldrich) were used as received.

2.3 Metal Complex Precursor Syntheses

2.3.1 Chloropentaammineruthenium(III) chloride - $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$

The synthesis of $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ can be quite lively owing to the great exothermicity of two of the steps. Further, the quality of hydrazine monohydrate is seemingly quite important to the “good behaviour” of the reaction. Occasionally, batches of hydrazine had to be discarded as they resulted in extremely poor yields of products. The synthesis presented here is a modification of that described by Naklicki⁴⁸ and based upon the method ascribed to Clarke,⁶⁵ and is designed to minimize interference due to the

quality of the hydrazine, and to minimize the likelihood of the reaction becoming self-catalytic in the first step.

$\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (10g, 43 mmol, F.W. 234.46^a g·mol⁻¹) is finely divided and slowly added to a solution of 98% hydrazine monohydrate (82 mL, 1.56 mol - 36X excess @ 1:1, F.W. 50.07 g·mol⁻¹) in water (100 mL) with stirring over a period of approximately 30 minutes. (Note: if this step is hurried, or if any chunks of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ are added, the reaction will tend to become self-catalytic and boil over.) The resultant burgundy solution is allowed to stir for 16 hours. With the solution in an ice bath, HCl (conc.) (250 mL, 2.15 mol, F.W. 36.46 g·mol⁻¹) is then carefully added over approximately 30 minutes. (Again, this reaction is highly exothermic, and must be carefully monitored! Note: If the solution became translucent or clear after the 16 hours of stirring, it has probably completely formed $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$, and the HCl addition will be even more dangerous!) Once the addition of acid is complete, the solution is removed from the ice bath, fitted with a condensor column, and refluxed for two hours. Often the HCl addition is accompanied by the formation of copious quantities of ammonium salts. If this is the case, the solution should be filtered while hot immediately after the reflux. Whether requiring filtration or not, the solution should then be allowed to cool to room temperature. The resultant orange crystals are collected by vacuum filtration yielding crude $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ (10.14 g, 35 mmol, 81% yield, F.W. 292.58 g·mol⁻¹). Recrystallization is effected in boiling 0.1 M HCl at a ratio of ~35 mL/g of crude product, yielding, after slowly cooling to room

^a Aesar lists the %Ru of this compound as 43.21%, making $x=1.47$, thus the approximate formulation $\text{RuCl}_3 \cdot 1.5\text{H}_2\text{O}$ and the F.W. listed.

temperature, deep orange crystals of $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ (8.03 g, 27 mmol, 63% yield, F.W. 292.58 $\text{g}\cdot\text{mol}^{-1}$) which are washed sparingly with 0.1 M HCl, acetone, and diethyl ether before being vacuum dried overnight.

2.3.2 *trans*-chlorotetraamminesulfonylruthenium(II) chloride -

The following provides a detailed outline of the method of Vogt⁶⁶ for the synthesis of the title complex.

$[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ (5 g, 17 mmol, F.W. 292.58 $\text{g}\cdot\text{mol}^{-1}$) is dissolved in a solution of NaHSO_3 (7.1 g, 68 mmol - 4X excess, F.W. 104.06 $\text{g}\cdot\text{mol}^{-1}$) in water (200 mL) at a stable temperature of 80 °C. When the orange crystals have completely dissolved, a slow stream of SO_2 (g) is commenced. After an induction period of several minutes, the orange solution becomes cloudy and a yellow precipitate appears. The gas flow is continued for 90 minutes, and the reaction vessel subsequently cooled (16 hours/overnight typically). The fine yellowish powder *trans*- $[\text{Ru}(\text{NH}_3)_4(\text{HSO}_3)_2]$ (3.73 g, 11 mmol, 66% yield, F.W. 331.33 $\text{g}\cdot\text{mol}^{-1}$) is collected by vacuum filtration and washed with acetone and ether. The product is weighed and transferred to a round-bottomed flask fitted with a condensor column and containing ~10 mL 6 M HCl/0.1 g of *trans*-bisbisulfitetetraammineruthenium(II). This mixture is heated to boiling, at which point all the solid should dissolve, and refluxed for 20 minutes. The colour of the solution will

rapidly darken with heating from a yellow or pale orange colour to a deep orange or orange-brown colour. At the end of the reflux period the solution is refrigerated for several hours, and the resultant orange-brown crystals of *trans*-[Ru(NH₃)₄(SO₂)Cl]Cl (2.36 g, 7.8 mmol - 69% yield, F.W. 304.16 g·mol⁻¹) are collected by vacuum filtration and washed with acetone and ether. (Note: If the solid did not entirely dissolve during the reflux period, the solution should be filtered prior to cooling.)

2.3.3 Triammine-2,2'-dipyridylsulfatoruthenium(III) chloride -

The procedure outlined hereafter is a modification of the method of Curtis²⁹ which was found to be both simpler and to provide an improved yield^a through the elimination of an isolation step.

Bipyridine (1.54 g, 9.6 mmol, F.W. 156.19 g·mol⁻¹) is dissolved in acetone (10 mL) and the volume made up to 100 mL with water. Solid *trans*-[Ru(NH₃)₄(SO₂)Cl]Cl (1.50 g, 4.9 mmol, F.W. 304.16 g·mol⁻¹) is added to the solution which is heated to 50 - 70 °C and stirred for 1.5 hours before being gravity filtered (Whatman #1 filter paper). To the cooled, filtered solution is added 1:1 0.4 M HCl : 30% H₂O₂ (50 mL combined volume, ~50X excess), and the new solution is stirred for 30 minutes to ensure oxidation. After oxidation is complete, the solution is solvent stripped on a rotary evaporator at 55 °C to a

^a Relative to in-house results using the method of Curtis.

total volume of ~25 mL, and the product crashed by addition of 15 volume equivalents of acetone and overnight refrigeration. (Note: because of the presence of peroxide and acid, the solvent stripping is prone to bumping, and the concentrate may effervesce and become hot. Addition of the concentrated solution to the required volume of acetone must be effected immediately subsequent to terminating the solvent stripping.) Recrystallization of the resultant oil is effected by decantation of the supernatant liquid, dissolution of the oil in water (~25 mL), and the slow addition of 8 equivalents of acetone. (A rate of addition of one equivalent of acetone every 10 - 15 minutes will afford a good grade of product.) The mixture should be allowed to sit at room temperature for several hours, and may then be placed in a freezer overnight to maximize the yield of russet-orange flakes of $[\text{Ru}(\text{NH}_3)_3(\text{bipy})(\text{SO}_4)]\text{Cl}$ (1.52 g, 3.5 mmol - 70% yield, F.W. 439.87 g·mol⁻¹) which are collected by vacuum filtration and washed with acetone and ether.

2.3.4 Aquotriammine-2,2'-dipyridylruthenium(II) tetrphenylborate -

The procedure presented here is a modification of that of Curtis²⁹ and uses tetrphenylborate in place of hexafluorophosphate as the counterion. This latter afforded little or no product when used.

$[\text{Ru}(\text{NH}_3)_3(\text{bipy})(\text{SO}_4)]\text{Cl}$ (1.0 g, 2.3 mmol, F.W. 439.87 g·mol⁻¹) is dissolved in water (75 mL), thrice degassed, and transferred to freshly prepared Zn/Hg amalgam (15 g) in an ice

bath. The solution darkens from dark orange to a deep red almost immediately, yet the reduction is allowed to continue for 30 minutes, occasionally venting the solution, to ensure completion. The solution is then transferred to a beaker, and the product precipitated by the pipettewise addition of a solution of NaB(Ph)_4 (3.0 g in 25 mL H_2O). The purple precipitate is collected by vacuum filtration and immediately vacuum dried, yielding $[\text{Ru}(\text{NH}_3)_3(\text{bipy})(\text{H}_2\text{O})][\text{B(Ph)}_4]_2$ (1.99 g, 2.1 mmol - 92% yield, F.W. 964.87 $\text{g}\cdot\text{mol}^{-1}$). (Note: care must be taken to dry the product as much as possible prior during the filtration, as the product initially has a clay-like consistency, retaining quite significant amounts of water. On several occasions, enough water was retained by the product to entirely seal the cold finger of the vacuum manifold with ice during the drying step.)

2.4 Ligand Synthesis

The author would like to thank A. LoFaro for performing the syntheses of $\text{Cl}_2\text{dicydH}_2$ and Cl dicydH_2 .

2.4.1 2,5-dimethyl-1,4-dicyanamidobenzene; 1,4-dicyanamidobenzene; 2,5-dichloro-1,4-dicyanamidobenzene

The syntheses of the ligands 2,5-dimethyl-1,4-dicyanamidobenzene, 1,4-dicyanamidobenzene, and 2,5-dichloro-1,4-dicyanamidobenzene were performed according to the procedure of Naklicki and have been previously reported.^{48,49}

2.4.2 2-Chloro-1,4-phenylenediamine

The method outlined hereafter essentially follows that published by Naklicki.^{48,67}

2-chloro-1,4-phenylenediamine sulfate (20 g, 83 mmol, F.W. 240.67 g·mol⁻¹) was dissolved in an alkaline solution of potassium carbonate (35 g, 250 mmol, F.W. 138.21 g·mol⁻¹) in water (500 mL) and thrice extracted with aliquots of chloroform (250 mL) in a separatory funnel. The brandy-coloured organic phases were combined and solvent stripped using a rotary evaporator, resulting in an oily product which was immediately used for the subsequent reaction.^a

2.4.3 1,4-dicyanamido-2-chlorobenzene

Benzoyl chloride (20.5 g, 146 mmol, F.W. 140.57 g·mol⁻¹) in acetone (150 mL) was added to a boiling solution of ammonium thiocyanate (8.86 g, 116 mmol, F.W. 76.12 g·mol⁻¹) in acetone (150 mL) resulting in the precipitation of ammonium chloride as the reaction progressed. After approximately 10 minutes the formation of NH₄Cl ceases, and the mixture takes on a distinct yellow colour. Dropwise addition of the oil obtained in 2.4.2, 2-chloro-1,4-phenylenediamine (est. 8.3^b g, 58 mmol (*i.e.* as 70%), F.W. 142.59 g·mol⁻¹),

^a To avoid the formation of an oily product, the organic layer should be dried over *e.g.* Mg₂(SO₄).^{48,67}

^b Because of the oily nature of the product, the extraction yield was estimated based upon results from similar extractions, see refs (48) and (67), to determine the stoichiometry of the ligand synthesis.

in acetone (200 mL) to this reaction mixture was effected using a pasteur pipette, and the solution was allowed to boil for 20 minutes after complete addition. The intermediate benzoylthiourea derivative was precipitated from solution, and the NH_4Cl dissolved, by pouring the hot solution into water (1.5 L) with vigorous stirring. The yellow powder was then collected by vacuum filtration, washed copiously with water, and air dried overnight. It was then dissolved in a 2M solution of sodium hydroxide (40 g, 1.0 mol, F.W. 40.00 $\text{g}\cdot\text{mol}^{-1}$) in water (500 mL), and was brought to the boil for 10 minutes. The solution was then cooled to just below 60 °C, and a solution of lead(II) acetate trihydrate (43.69 g, 116 mmol, F.W. 375.30 $\text{g}\cdot\text{mol}^{-1}$) in water (125 mL) was added, resulting in the immediate formation of lead sulfide. The reaction was allowed to proceed (up to a maximum of 5 minutes) until the brown-black initial colour had darkened to pure (anthracite) black, at which time the mixture was filtered through a büchner funnel equipped with a Whatman #1 filter paper, with the filtrate being collected in an ice bath. Glacial acetic acid (60 mL, 1.05 mol, F.W. 60.05 $\text{g}\cdot\text{mol}^{-1}$) was immediately added to neutralize the solution, affording solid 1,4-dicyanamido-2-chlorobenzene (6.8 g, 35 mmol - 60% yield, F.W. 192.61 $\text{g}\cdot\text{mol}^{-1}$), which was collected by vacuum filtration and washed copiously with water until no odour of acetic acid was discernable. The green-hued product was allowed to air-dry and was used without further purification. Elemental Analysis was performed assuming the formula $\text{C}_8\text{H}_5\text{N}_4\text{Cl}$, F.W. 192.61 $\text{g}\cdot\text{mol}^{-1}$: Calcd(%) C, 49.89; H, 2.62; N, 29.09. Found(%) C, 49.42; H, 2.70; N, 29.06. $\nu_{\text{NCN}} = 2228 \text{ cm}^{-1}$.

2.5 Metal Complex Syntheses

2.5.1 The pentaammine complexes $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-L})][\text{PF}_6]_4$

Synthesis of the pentaammine complexes $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-L})][\text{PF}_6]_4$, L = 2,5-dimethyl-1,4-dicyanamidobenzene, 1,4-dicyanamidobenzene, and 2,5-dichloro-1,4-dicyanamidobenzene was performed according to the procedure outlined by Naklicki.⁴⁸

The author thanks C. A. White for assistance with this work.

2.5.2 The tetraammine complexes $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-L})][\text{PF}_6]_4$

Synthesis of the tetraammine complexes $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-L})][\text{PF}_6]_4$, L = 2,5-dimethyl-1,4-dicyanamidobenzene, 1,4-dicyanamidobenzene, 2,5-dichloro-1,4-dicyanamidobenzene, and 2,3,5,6-tetrachloro-1,4-dicyanamidobenzene was performed according to the procedure outlined by Rezvani.⁶⁸ Spectroelectrochemical results in nitromethane and dimethylsulfoxide were obtained upon complexes synthesized by V. V. Kondratiev. Electronic absorption results were all obtained upon complexes synthesized by A. R. Rezvani.

2.5.3 μ -1,4-dicyanamidobenzenebis(triammine-2,2'-dipyridylruthenium(III))

perchlorate - $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-dicyd})][\text{ClO}_4]_4$

1,4-dicyanamidobenzene (0.12 g, 0.78 mmol, F.W. 158.17 g·mol⁻¹) is dissolved in acetone (100 mL) and thrice degassed on a double manifold vacuum line equipped with argon as the inert gas. Solid $[\text{Ru}(\text{NH}_3)_3(\text{bipy})(\text{H}_2\text{O})][\text{B}(\text{Ph})_4]_2$ (1.50 g, 1.55 mmol, F.W. 964.87 g·mol⁻¹) is added (for simplicity, by briefly removing the septum from the rb flask's neck), and the solution degassed one additional time. After 16 - 24 hours stirring under argon, the solution is decanted into an erlenmeyer flask, stirred open to air for an additional 16 - 24 hours, and precipitated by the addition of solid tetrabutylammonium bromide, TBAB, (6 g, ~25X excess, F.W. 322.37 g·mol⁻¹) to the solution, resulting in the precipitation of the mixed-valence complex^a $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-dicyd})]\text{Br}_3$ (0.75 g, 0.74 mmol - 95% yield, F.W. 1012.56 g·mol⁻¹). This crude product was dissolved in water (100 mL), treated with a solution of cerium (IV) ammonium nitrate (0.43 g, 0.74 mmol, F.W. 584.23 g·mol⁻¹) in water (15 mL), and the resultant solution stirred for 20 minutes to ensure complete oxidation. $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-dicyd})][\text{PF}_6]_4$ was precipitated by the addition of solid ammonium hexafluorophosphate (9 g, ~45X excess, F.W. 260.51 g·mol⁻¹), collected by vacuum filtration, and washed sparingly with water. The PF_6^- salt was metathesized by dissolution in acetonitrile^b (30 mL), gravity filtration (Whatman #1), and

^a Redox titrations were performed upon all complexes of this family using cerium(IV) ammonium nitrate to determine the ratio of oxidant required to maximize the intensity of the LMCT band. Results from these titrations indicated the ratio of oxidant required to maximize yields of the III/III complex, in each case. The ratio of 1:1 for this complex implies that the intermediate product is largely the mixed valence II/III form.

^b Once the complex is fully oxidized, it was found to be very sensitive to reduction, and is partially reduced by dissolution in acetone or DMSO, and by $\text{B}(\text{Ph})_4^-$ when used as a counterion.

precipitation by addition of solid TBAB (3 g, ~12X excess). The bromide salt $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-dicyd})]\text{Br}_4$ (0.48 g, 0.44 mmol - 60% yield, F.W. 1092.47) is then dissolved in a minimum of 1 M NaCl (~75 mL), loaded onto a CM Sephadex C25 cation exchanger column (typically 1" diameter and 18" length, prepared with 1 M NaCl), and eluted under pressure with 1 M NaCl. The golden brown product band elutes second after a small reddish band consistent with the mixed-valent complex, and is collected (typical volume ~200 mL). The purified product is precipitated by addition of solid sodium perchlorate (1 g/10 mL of eluate), yielding $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-dicyd})][\text{ClO}_4]_4$ (0.29 g, 0.25 mmol - 55% yield, F.W. 1170.65 g·mol⁻¹) which is collected by vacuum filtration and washed sparingly with cold water. (Note: Perchlorate salts are sensitive and potentially explosive, particularly when dry. Extreme caution must be exercised when handling these salts!) Once dry, the complex is recrystallized from acetonitrile by ether diffusion (first recrystallization in ~20 mL MeCN, with ca. 80% yield). Multiple recrystallizations afford X-ray quality crystals, although the complex is elementally pure after only one or two recrystallizations. Overall (approximate) yield from starting reagents was 30%. Elemental Analysis based upon $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-dicyd})][\text{ClO}_4]_4 \cdot 2\text{H}_2\text{O}$ (as $\text{C}_{28}\text{H}_{42}\text{N}_{14}\text{O}_{18}\text{Cl}_4\text{Ru}_2$), F.W. 1206.69 g·mol⁻¹: Calcd(%) C, 27.87; H, 3.51; N, 16.25. Found(%) C, 27.77; H, 3.43; N, 15.95.

2.5.4 μ -1,4-dicyanamido-2,5-dimethylbenzenebis(triammine-2,2'-dipyridyl-ruthenium(III)) perchlorate - $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{ClO}_4]_4$

This complex was made according to the procedure outlined in 2.5.3, including all molar ratios for the reagents. The neutral ligand, 1,4-dicyanamido-2,5-dimethylbenzene, did not, however dissolve fully in acetone in the first step, and the reaction was performed heterogeneously. Approximate yields for the various steps were as follows: crude $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Me}_2\text{dicyd})]\text{Br}_3$, 100%; $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Me}_2\text{dicyd})]\text{Br}_4$ from the oxidation, 70%; column-purified $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{ClO}_4]_4$, 60%; from the first recrystallization, 90%. Overall (approximate) yield from starting reagents was 40%. Elemental Analysis was performed assuming the formula $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{ClO}_4]_4 \cdot 1.25\text{MeCN}$ (as $\text{C}_{32.5}\text{H}_{45.75}\text{N}_{15.25}\text{O}_{18}\text{Cl}_4\text{Ru}_2$), F.W. 1250.01 $\text{g}\cdot\text{mol}^{-1}$: Calcd(%) C, 31.23; H, 3.69; N, 17.09. Found(%) C, 31.60; H, 3.47; N, 16.75.

2.5.5 μ -1,4-dicyanamido-2,5-dichlorobenzenebis(triammine-2,2'-dipyridyl-ruthenium(III)) perchlorate - $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cl}_2\text{dicyd})][\text{ClO}_4]_4$

This complex was made according to the procedure outlined in 2.5.3, including all molar ratios for the reagents with the exception of cerium (IV) ammonium nitrate. The optimum ratio of oxidant:complex was found to be 0.8:1, and the corresponding molar ratio was used. As with the case for the dimethyl ligand, neutral 1,4-dicyanamido-2,5-

dichlorobenzene did not dissolve fully in acetone in the first step, and the reaction was performed heterogeneously. No trace of unreacted ligand was noticed subsequent to the initial reaction period. Approximate yields for the various steps were as follows: crude $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cl}_2\text{dicyd})]\text{Br}_3$, 95%; $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cl}_2\text{dicyd})]\text{Br}_4$ from the oxidation, 80%; column-purified $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cl}_2\text{dicyd})][\text{ClO}_4]_4$, 35%; from the first recrystallization, 70%. Additionally, the crude bromide salt was purified by metathesis first to a PF_6^- salt and then back to a Br^- salt prior to performing the oxidation. This step had an approximate yield of 70%, and was found to be necessary to avoid over-oxidation of the complex, and the attendant loss of yield during column purification. (The more highly oxidized form(s?) of the complex do not elute from the column.) Overall (approximate) yield from starting reagents was 25%. Elemental Analysis was performed assuming the formula $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cl}_2\text{dicyd})][\text{ClO}_4]_4 \cdot 0.5\text{MeCN}$ (as $\text{C}_{29}\text{H}_{43.5}\text{N}_{14.5}\text{O}_{18}\text{Cl}_6\text{Ru}_2$), F.W. $1260.07 \text{ g}\cdot\text{mol}^{-1}$: Calcd(%) C, 27.64; H, 2.99; N, 16.12. Found(%) C, 27.81; H, 3.07; N, 15.85.

2.5.6 μ -1,4-dicyanamido-2-chlorobenzenebis(triammine-2,2'-dipyridyl-ruthenium(III)) perchlorate - $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cl}\text{dicyd})][\text{ClO}_4]_4$

This complex was made according to the procedure outlined in 2.5.3, including all molar ratios for the reagents with the exception of cerium (IV) ammonium nitrate. The optimum ratio of oxidant:complex was found to be 0.9:1, and the corresponding molar ratio was used. As with the case for the dimethyl ligand, neutral 1,4-dicyanamido-2-

chlorobenzene did not dissolve fully in acetone in the first step, and the reaction was performed heterogeneously. No trace of unreacted ligand was noticed subsequent to the initial reaction period. Approximate yields for the various steps were as follows: crude $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cldicyd})]\text{Br}_3$, 90%; $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cldicyd})]\text{Br}_4$ from the oxidation, 80%; column-purified $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cldicyd})][\text{ClO}_4]_4$, 40%; from the first recrystallization, 80%. Additionally, the crude bromide salt was purified by metathesis first to a PF_6^- salt and then back to a Br^- salt prior to performing the oxidation. This step had an approximate yield of 55%, and was found to be necessary to avoid overoxidation of the complex, and the attendant loss of yield during column purification. (The more highly oxidized form(s?) of the complex do not elute from the column.) Overall (approximate) yield from starting reagents was 15%. Elemental Analysis was performed assuming the formula $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cldicyd})][\text{ClO}_4]_4 \cdot 0.5\text{Et}_2\text{O}$ (as $\text{C}_{30}\text{H}_{42}\text{N}_{14}\text{O}_{18.5}\text{Cl}_5\text{Ru}_2$), F.W. 1242.15 $\text{g}\cdot\text{mol}^{-1}$: Calcd(%) C, 29.01; H, 3.41; N, 15.79. Found(%) C, 29.02; H, 3.10; N, 16.00.

2.6 Physical Measurements

2.6.1 Infrared spectroscopy

Infrared spectroscopy was performed on a Bomem Michelson 120 FTIR spectrometer as KBr mulls. Data was analyzed using Bomem Grams/386 v3.04 Level II software.

2.6.2 NMR spectrometry

All standard 1-D and 2-D (COSY, NOESY) ^1H NMR was performed on a Bruker AMX-400 spectrometer at 300 K using Ultra-Imperial Grade PP-507 sample tubes (Wilmad) and were referenced to solvent resonances or TMS. Evans method experiments were performed using Ultra-Imperial Grade PP-507 sample tubes and Special Stem Coaxial Inserts (Wilmad) and were referenced to TMS. Solvent and reference information are given in sections 2.2.3 and 2.1.5, respectively.

2.6.3 X-ray crystallography

The x-ray structure of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2\mu\text{-dicyd}](\text{ClO}_4)_4$ was performed by Dr. G. P. A. Yap at the Windsor Molecular Structure Centre. The following experimental description was written by Dr. Yap.

Crystallographic data and refinement parameters are detailed in Table 3.3.1. Unit-cell parameters were calculated from reflections obtained from 60 data frames collected at different sections of the Ewald sphere. No symmetry higher than triclinic was evident from the diffraction data and unit-cell parameters. Data was collected on a Siemens SMART CCD diffractometer using a multirun routine which collects two-dimensional data frames with an effective coverage of >80% of the Ewald sphere. The *E*-statistics strongly suggested the centric option and solution in *P*-1 yielded chemically reasonable

and computationally stable results. A trial application of semi-empirical absorption corrections based on redundant data at varying effective azimuthal angles yielded T_{max}/T_{min} at unity and was ignored.

The standard Lorentz polarization correction was applied. The anions were located each statistically disordered with a 50/50 site distribution. Three cocrystallized water molecules of hydration were also located. All non-hydrogen atoms were refined with anisotropic displacement coefficients excepting those atoms on the anions and solvent molecules which were refined isotropically. All hydrogen atoms were treated as idealized contributions excepting those hydrogen atoms on the water molecules which were ignored but included in calculations for intrinsic properties.

The structure was solved by direct methods, completed by subsequent Fourier syntheses and refined with full-matrix least-squares methods.

All scattering factors and anomalous dispersion coefficients are contained in the SHELXTL 5.03 program library (Sheldrick, G. M., Madison, Wi). Further crystallographic details are deposited with the Cambridge Crystallographic Data Centre (<http://www.ccdc.cam.ac.uk>) under the depository number 100738.

2.6.4 Electronic absorption spectroscopy

UV-Vis-NIR spectra were taken on a Varian Cary 5 UV-Vis-NIR Spectrophotometer at ambient temperatures using Quartz cells of either 1.000 cm or 0.200 cm path length from Hellma (Canada) Limited. Runs were done at 600 nm/min vs.

solvent backgrounds, with a data interval of 0.333 nm, a spectral bandwidth of 2.00 nm, and a signal averaging time of 0.033 s. Quantitative spectroscopy on the triammines was done exclusively using solvents prepared according to 2.2.2 as was the nitromethane and dimethyl sulfoxide quantitative spectroscopy performed on the tetraammines, with the exception of the DMSO spectra of $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-dicyd})](\text{PF}_6)_4$ and $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-Cl}_2\text{dicyd})](\text{PF}_6)_4$ which were performed in stock DMSO (Accusolv).

2.6.5 Cyclic voltammetry

Cyclic voltammetry was performed using a BAS CV-27 voltammograph and BAS X-Y recorder at a constant temperature of 25 °C, maintained with a Haake D8-G refrigerated bath and circulator. The cell is configured for a working volume of ~15 mL and is double-hulled to permit temperature control via the water bath. It was fitted with a teflon cap through which the electrodes and argon bubbler were introduced to the cell via pre-drilled holes. The electrodes themselves consisted, for non-aqueous solutions, of platinum disk working and counter electrodes (BAS, 1.6 mm diameter) and a silver wire pseudo-reference electrode with ferrocene ($E^\circ = 0.665 \text{ V vs. NHE in acetonitrile}$)⁶⁹ added as the internal reference and 0.1 M TBAH as the supporting electrolyte. For aqueous solutions the working electrode was a disk of glassy-carbon (BAS, 5 mm diameter), the counter electrode a platinum disk (BAS, 1.6 mm diameter), the reference electrode a saturated calomel electrode (SCE, $E^\circ = 0.224 \text{ V vs. NHE at } 25^\circ\text{C}^{70}$) assembly (Accumet) and 0.1 M KCl was used as the supporting electrolyte. Analyte concentrations were on

the order of 10^{-3} M. In all cases the solutions were deoxygenated by bubbling with argon for 20-30 minutes and an argon blanket was maintained throughout the experiment.

Solvent and internal reference information are given in sections 2.2.2 and 2.1.5, respectively.

2.6.6 Spectroelectrochemistry

Spectroelectrochemistry of the tetraamminepyridine complexes was performed in an H-cell of published design⁷¹ at ambient temperatures using 0.1 M TBAH as the supporting electrolyte, a platinum mesh working electrode (area ≈ 6.65 cm²), a platinum wire counter electrode, and a silver wire pseudo-reference electrode. Analyte concentrations were on the order of 10^{-5} M, and potentials were controlled using the same BAS CV-27 as was used for cyclic voltammetry. Spectroelectrochemistry on the pentaammine and triamminebipyridine complexes was performed using an OTTLE (Optically Transparent Thin Layer Electrochemistry) cell based on the design of Hartl⁷² and using gold-foil (500 line/inch, 60% Transmittance, Buckbee Mears) working and counter electrodes and a Ag/AgCl reference electrode. Spectra were obtained on the same Cary 5 Spectrophotometer as was used for electronic absorption spectroscopy vs. appropriate backgrounds of solvent and electrolyte at a scan rate of 1200 nm/min, and potentials were controlled using the same BAS CV-27 as was used for cyclic voltammetry. At any given potential, the system was allowed to come to equilibrium ($i \approx 0$ μ A) prior to acquisition of the spectrum. Solvent information is given in section 2.2.2.

The backplate of a Wilmad 5321 demountable IR cell was fitted with a custom-made teflon superstructure (see figure 2.6.1 at right*) anchored about the screw posts, and leaving an inner area just large enough to permit insertion of standard 38x19x4 mm IR-quartz plates (Wilmad).

Figure 2.6.1 - Schema of the OTTLE cell spacer (left) and the teflon superstructure (right). The rounded features at top and lower corners anchor the superstructure to the screw-posts of the backplate, while the three squared slots allow the spacer's wires to be anchored to larger diameter conducting wires to which are connected leads from the voltammograph.

A spacer (see figure 2.6.1 at left) was constructed by melt-sealing two 0.1 mm diameter platinum wires (b) and a Ag/AgCl electrode (a) constructed of twinned 0.1 mm diameter silver wires between two sheets of 0.1 mm thick polyethylene (pre-cut to the shape of the teflon spacers provided with the cell), with several centimetres of wire projecting beyond the spacer. The positions of the wires correspond to the positions of the three anchoring slots in the teflon superstructure, each of which is fitted with a brass

* The diagram of the superstructure shown in figure 1 is configured for an older three-post cell design, not the newer four-post design.

screw and whose depth corresponds to the height of a single quartz plate seated upon the rear gasket of the cell. To the screw in each anchoring position is attached a piece of 0.5 mm diameter tin-coated copper wire to allow the cell to be connected to the voltammograph via alligator clips. Most of the length of these connectors are external to the superstructure, excepting a short “post” about which the spacer-electrodes are wrapped to afford contact. While the external length can be any required length, the height of the connection-post must be such that it doesn’t short-circuit the cell by coming in contact with the faceplate after assembly. (This latter stricture is also important for the spacer wires themselves, particularly if they are long). The cell is assembled by anchoring the spacer to the connection-posts and laying the gold mesh electrodes upon the platinum wires. (The area of the working and counter electrodes is somewhat variable, depending upon the spacer’s final shape. An effort should be made to keep their relative areas similar) The upper quartz plate is then put into position, and the cell’s front plate attached. Since the electrodes maintain contact with the platinum conductors due to the pressure of the quartz windows, the final thickness of the spacer is critical. The polyethylene must be thick enough not to rip due to the enclosed wires, but not so thick that the gold electrodes don’t make good contact with the platinum wires. (This latter eventuality is generally apparent since the electrodes will be displaced during introduction of the sample). Because of the small size of the cell, the incident beam of the spectrometer will most likely be larger than the size of the working electrode. It is critical to ensure that the cell is masked (we used electrical tape) so that the incident radiation passes exclusively through the working electrode. Here again, the potentials were

controlled using the BAS CV-27. Samples are introduced to the cell using 2 mL luer-lock syringes via the cell's inlet and outlet ports. Care must be taken to ensure no air bubbles remain in the cell prior to its being sealed with teflon plugs (provided with the cell).

A note on melt-sealing: The temperature of the melt-sealing must be kept very close to 133 °C so that the polyethylene softens but doesn't overly deform. This was accomplished by modifying a standard Black and Decker Toast-R-Oven (TRO) by inclusion of a thermocouple linked to a custom designed "black-box" external temperature control circuit (± 1 °C) (BOX) which provided power to the TRO via a Variac variable amperotransformer (VAT) providing approximately 70 V. Use of the VAT to attenuate the voltage provided to the BOX was found necessary to limit temperature fluctuations. At 120 V, the TRO elements heat too rapidly/vigorously for the BOX circuit to properly control. However, attenuating the voltage much beyond 70 V, while improving temperature fluctuations, led to overheating of the VAT.

2.6.7 Elemental analyses

All elemental analyses were performed by Canadian Microanalytical Services, Ltd. in Delta, B. C., Canada.

2.7 Laboratory Techniques

2.7.1 Recrystallizations

a) Complexes

Initial recrystallization of the complexes by ether diffusion into acetonitrile was effected by dissolving the crude solid in approximately 1-1.5 mL of acetonitrile/10 mg of solid, gravity filtration of the solution to remove most solid residues (Whatman #1), and microfiltration (Gelman 1 μ m Acrodisk disk filters) into a clean, oven-dried beaker (100 or 150 mL) before placement in the diffusion chamber. Subsequent recrystallizations omitted the gravity filtration step. Volumes and glassware sizes were altered to optimize conditions, as required.

b) Electrolytes

Recrystallization of KCl was effected by dissolution in water, with heating to the boil, gravity filtration while hot (Whatman #1), and cooling to room temperature either on the bench or in the freezer. Endothermic dissolution allows for safe washing with cold H₂O after collection by vacuum filtration. Mass:solvent ratio, 1 g:2 mL.

Recrystallization of TBAH was effected by dissolution in ethanol with heating to the boil, gravity filtration while hot (Whatman #1), and careful addition of one half volume

equivalent of hot/boiling water prior to slow cooling to room temperature on the bench.

The product is collected by vacuum filtration and washed liberally with H₂O.

Mass:solvent ratio, 2 g:25 mL ethanol.

Note: Electrolytes should be recrystallized (at least) twice before use.

c) Ligands

Recrystallization of Me₂dicyd is effected in methanol with heating to the boil, gravity filtration of the hot solution (Whatman #1), and careful addition of one volume equivalent of hot/boiling H₂O prior to slow cooling of the solution on the bench. The resultant fine needles were collected by vacuum filtration and washed copiously with water. Mass:solvent ratio, 1 g:150 mL methanol. Yield ~70%.

Recrystallization of dicyd is effected in acetone using the same general technique as, and with similar results to, Me₂dicyd. Mass:solvent ratio, 1 g:35 mL acetone.

2.7.2 Low-pressure distillations

All distillations of solvents for electrochemistry and spectroscopy were effected using an all-glass apparatus connected to a double-manifold vacuum-argon line.

Appropriate drying agents were chosen according to (73). With the exception of DMSO, vacuum was applied sparingly to the solutions until vigorous bubbling (but not bumping) of the solution was afforded. This initial period of evacuation is necessary to ensure no

water vapours remain in the system. Subsequent to the initial degassing of the solution, the bubbling tends to decrease markedly, and the receiver may be cooled in a dewar of liquid nitrogen. After the temperature in the receiver equilibrates, the vacuum is adjusted to ensure vigorous bubbling of the distillation pot, and a reasonable rate of collection. Condensation of the distillate vapours should not occur except at the receiver head. As the distillation progresses, temperature of the distillation pot will need to be maintained. This was effected using a bath of lukewarm water. Excessive or intermittent heating may lead to bumping, and should be avoided. The first fraction (generally ~10% of the total volume, 15% for nitromethane) was discarded. When changing the receiver, it is necessary to flush the system with argon to exclude water vapours. Collection of the second (main) fraction was effected using the same technique as for the initial fraction. Approximately 15% (20% for nitromethane) of the starting volume is sacrificed at the end of the distillation. Prior to stoppering, the receiver is warmed to room temperature under a blanket of argon. The dry, deoxygenated distillate is stored under argon. Distillation of DMSO follows largely the same procedure except that vacuum may be applied continuously, that heating to ca. 50 °C is necessary, and that cooling of the receiver should be effected via ice bath and not liquid nitrogen. This latter requirement helps avoid having the DMSO solidify within (and consequently plug) the receiver head. Heating was effected via a heating mantle on a low setting.

Chapter 3

Results

3.1 Infrared Spectroscopy

Infrared spectroscopy was performed upon the four complexes $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-L})][\text{ClO}_4]_4$, $\text{L} = \text{Me}_2\text{dicyd}^{2-}$, dicyd^{2-} , $\text{Cl}\text{dicyd}^{2-}$, and $\text{Cl}_2\text{dicyd}^{2-}$, and the neutral bridging ligand CldicydH_2 . Data for the ligand are collected in table 3.1.1 and compared with those for the other three ligands, which have been previously published.⁴⁸ Data for the four complexes are collected in table 3.1.2. The spectra themselves are presented as figures 3.1.1 - 3.1.5.

The ligand's spectrum correlates well with published data for compounds of this type (see table 3.1.1). With the exception of the cyanamide moiety's stretch, $\nu(\text{N}=\text{C}=\text{N})$, vibrational energies of all common functionalities fit within literature ranges.⁷⁴ Data for the four complexes are likewise in agreement, both vibrational energies and peak intensities, with analogous spectra for the pentaammine^{48,49,51} and tetraammine^{50,68} complexes and with literature where applicable.⁷⁵ The cyanamide stretching frequency of the dianion ligands, $\nu(\text{N}=\text{C}=\text{N})$, is assigned by analogy with published data for the AsPh_4^- salts of the dianion ligands.^{48,49}

Infrared spectroscopy is used mainly for early characterization of the complexes where it is useful in proving complexation of the ligand to the metal (by virtue of the shift of the nitrile stretch at ca. 2230 cm^{-1} to the cyanamide stretch at ca. $2080 - 2100\text{ cm}^{-1}$).

Table 3.1.1 - Infrared stretching energies (in cm^{-1}) for selected characteristic vibrations of the neutral dicyd ligands.

Ligand	$\nu(\text{C}\equiv\text{N})$	$\nu(?)^a$	$\nu(\text{C}-\text{N})$	$\nu(\text{N}-\text{H})$	$\nu(\text{C}=\text{C})$
$\text{Me}_2\text{dicydH}_2$	2230	1529	1409	3184	1621
dicydH_2	2234	1531	1408	3178	1627
Cl dicydH_2	2228	1519	1401	3159	1622
$\text{Cl}_2\text{dicydH}_2$	2232	1515	1389	3188	1623

^a The peak at ca. 1520 cm^{-1} had been previously assigned as a $\nu(\text{C}=\text{C})$.⁴⁸ The exact nature of this peak, however, has not been definitively proven, and this work prefers not to assign it to a specific mode.

Figure 3.1.1 - Infrared spectrum (as KBr mull) of 2-Chloro-1,4-dicyanamidobenzene

Table 3.1.2 - Infrared stretching energies (in cm^{-1}) for selected characteristic vibrations of the complexes $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-L})][\text{ClO}_4]_4$.

Ligand	$\nu(\text{N}=\text{C}=\text{N})$	$\nu(\text{C}=\text{C})$	$\nu(\text{N-H})$	$\delta(\text{N-H})$	$\nu(\text{Cl-O})$
$\text{Me}_2\text{dicydH}_2$	2088	1467	3331 3270 3200	1626	1087
dicydH_2	2082	1484	3332 3266 3194	1625	1087
Cl dicydH_2	2081	1471	3352 3278 3206	1625	1090
$\text{Cl}_2\text{dicydH}_2$	2083 2064	1468	3347 3267 3202	1627	1095

Figure 3.1.2 - Infrared spectrum of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{ClO}_4]_4$.

Figure 3.1.3 - Infrared spectrum of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-dicyd})][\text{ClO}_4]_4$.

Figure 3.1.4 - Infrared spectrum of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Clidicyd})][\text{ClO}_4]_4$.

Figure 3.1.5 - Infrared spectrum of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cl}_2\text{dicyd})][\text{ClO}_4]_4$.

3.2 Nuclear Magnetic Resonance

Nuclear magnetic resonance experiments were run on the complexes $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-L})][\text{ClO}_4]_4$ ($\text{L} = \text{Me}_2\text{dicyd}^{2-}$, dicyd^{2-} , and $\text{Cl}_2\text{dicyd}^{2-}$) in nitromethane and acetonitrile. The complex $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-dicyd})][\text{ClO}_4]_4$ was also examined in dimethyl sulfoxide. The COSY 2-D technique was used on both the $\text{L} = \text{Me}_2\text{dicyd}^{2-}$ (in nitromethane) and the $\text{L} = \text{Cl}_2\text{dicyd}^{2-}$ (in both solvents) complexes to elucidate through-bond coupling. Through-space (T_1 relaxation) interactions⁷⁶ in these complexes was examined via the NOESY 2-D technique in nitromethane only. Evans method experiments were run on the $\text{L} = \text{dicyd}^{2-}$ and $\text{L} = \text{Cl}_2\text{dicyd}^{2-}$ complexes in acetonitrile to check for paramagnetism.

The chemical shift data for all the 1-D experiments have been placed in table 3.2.1, and selected sections of the spectra themselves are presented (see figures 3.2.2, 3.2.3, and 3.2.6 - 3.2.11). The COSY and NOESY results for the aromatic region of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{ClO}_4]_4$ in nitromethane are also presented (see figures 3.2.4 and 3.2.5). Each 1-D spectrum was run over the range +250 ppm to -250 ppm in order to detect any paramagnetically shifted peaks. No peaks were found beyond the range 0 - 14 ppm in any of the spectra.

Unambiguous assignment of all eight bipyridine hydrogens was possible for $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{ClO}_4]_4$ in nitromethane. Examination of figure 3.2.2 shows that all eight resonances are well separated, and that the peaks are split as expected, with the 3 and 3' and 6 and 6' protons being doublets and the 4 and 4' and 5 and 5' protons being pseudo-triplets (doublets of doublets). Figure 3.2.1 provides the numbering scheme for the ring hydrogens.

Figure 3.2.1 - Schematic representation of the equatorial coordination plane about one ruthenium centre in $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Me}_2\text{dicyd})]^{4+}$ showing the hydrogen numbering scheme for bipyridine. Peaks due to bridging ligand hydrogens (H) or methyl groups (Me) are so labeled.

The strong through-space interaction of the 3 and 3' protons is readily apparent in the NOESY spectrum (figure 3.2.5) and provides a starting point from which the remainder of the hydrogens may be readily assigned from the coupling patterns in the COSY spectrum (figure 3.2.4). Finally, the NOESY spectrum indicates a through-space interaction between the 6 position hydrogen and the equatorial ammine. Differentiation of the 6 and 6' hydrogens allows each hydrogen of bipyridine to be assigned not only to a position on a ring, but to a specific ring.

The acetonitrile spectrum of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{ClO}_4]_4$ (figure 3.2.6) is largely the same as that in nitromethane, although the splittings of the 6 and 4 position protons are no longer resolved. Assignment of the peaks was made by analogy with the nitromethane spectrum, and the identity of the 3 and 3' and 6 and 6' protons were confirmed by their respective J values of 8.1 Hz and 5.6 Hz which were nearly constant (within ± 0.1 Hz) for all three complexes whenever these splittings were resolved.

Assignment of the resonances of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-dicyd})][\text{ClO}_4]_4$ in nitromethane (figure 3.2.7) was made by direct analogy with the nitromethane results for $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{ClO}_4]_4$. The two spectra are quite similar except that the 6 and 6' position resonances overlap in the $\text{L} = \text{dicyd}^{2-}$ complex's spectrum. J values were used to confirm the assignment the 3 and 6 position protons relative to the analogous J values obtained for the $\text{L} = \text{Me}_2\text{dicyd}^{2-}$ complex in nitromethane.

The spectrum of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-dicyd})][\text{ClO}_4]_4$ in acetonitrile (figure 3.2.8) loses much of the resolution of its nitromethane analog. Assignment here was made by recognizing that the rounded resonances are, by analogy with figure 3.2.6, those of

protons 6 and 4 while the J value of the doublet at 8.4 confirmed its identity as the hydrogen 3'.

In the case of the DMSO spectrum of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-dicyd})][\text{ClO}_4]_4$ (figure 3.2.9), assignment of all peaks was made by considering the nitromethane spectrum of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cl}_2\text{dicyd})][\text{ClO}_4]_4$ (figure 3.2.10) which reveals the increasing shielding of the 6 and 6' hydrogens as the systems become less strongly coupled. Thus, these protons were assigned as the most shielded of the bipyridine hydrogens in the DMSO spectrum of the $\text{L} = \text{dicyd}^{2-}$ complex. The remainder of the assignments were kept consistent with the general trend of the 3 protons being more deshielded than the 4 protons, themselves more deshielded than the 5 protons. While the spectra of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cl}_2\text{dicyd})][\text{ClO}_4]_4$ indicate that the 5 and 5' resonances shift relative to the 3 and 4 resonances, the most likely source of error in this strategy is the very real possibility that reduction of the complex by the solvent may introduce trace paramagnetism to the experiment (see section 2.5.1).

As for the $\text{L} = \text{Cl}_2\text{dicyd}^{2-}$ complex itself, its nitromethane spectrum (figure 3.2.10) was assigned as was the nitromethane spectrum of the $\text{L} = \text{Me}_2\text{dicyd}^{2-}$ complex: the 3 and 3' resonances were identified in the NOESY spectrum and the remaining resonances were assigned from the coupling patterns of the COSY spectrum. Because no through space interaction between the 6 position hydrogen and the equatorial ammine was resolved, direct assignment of the protons to a given bipyridine ring (*i.e.* differentiation of the “primed” and “unprimed” rings) was not possible. Assignment of “primes” was made by analogy with the spectrum of the $\text{L} = \text{Me}_2\text{dicyd}^{2-}$ complex in nitromethane.

This is similarly the case for the acetonitrile spectrum of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cl}_2\text{dicyd})][\text{ClO}_4]_4$ (figure 3.2.11), in which hydrogen 3 was identified both by its splitting pattern (and J value of 8.1 Hz) and by its position as the most deshielded bipyridine resonance. The remainder of the assignments follow directly from the coupling patterns of the COSY 2-D spectrum.

In all cases, assignment of the axial (A_{ax}) and equatorial (A_{eq}) amines was made on the basis of their 2:1 relative integration ratios, and the 3:1 absolute integration ratio between the single equatorial ammine's peak and the bipyridine's hydrogens' peaks (except the DMSO spectrum where the amines integrated to only 80% of their expected value, and the acetonitrile spectrum of the $\text{Cl}_2\text{dicyd}^{2-}$ complex where the amines integrated to only 65% of their expected value).

The ligand's ring hydrogens (H on the spectra) were only unambiguously assignable in the nitromethane spectrum of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{ClO}_4]_4$ in which the COSY spectrum indicated coupling to the methyl groups. In the DMSO spectrum of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-dicyd})][\text{ClO}_4]_4$ (figure 3.2.9) assignment was complicated by overlap of the H and 6' resonances and was made on the basis of integration. In the nitromethane spectrum of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cl}_2\text{dicyd})][\text{ClO}_4]_4$ (figure 3.2.10) a broadened resonance near 7.8 ppm was ascribed to H. This broadened resonance provides a clue for locating what may be the bridging ligand's ring's hydrogens' resonances in the nitromethane spectrum of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-dicyd})][\text{ClO}_4]_4$ in which the baseline in the area of 8 ppm has the general shape of a broad, low arch which may represent the "missing" resonance. Since conformational changes on the NMR

timescale may cause such broadening temperature dependent spectra were run on the $L = \text{dicyd}^{2-}$ complex in acetonitrile over the temperature range 245 K - 350 K. No resolution of the missing resonance was evidenced by these efforts, however. This is quite possibly because of the restricted temperature range over which the studies could be carried out. (The complexes are known to decompose at elevated temperatures⁴⁸ and acetonitrile solidifies at 245 K even with the addition of large quantities of TMS to lower the melting point.)

Table 3.2.1 - Chemical shift data for the complexes $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-L})][\text{ClO}_4]_4$ ($L = \text{Me}_2\text{dicyd}^{2-}$, dicyd^{2-} , and $\text{Cl}_2\text{dicyd}^{2-}$) in ppm. Bipyridine hydrogens are represented by the numbers, the bridging ligand hydrogens and methyl groups by L_H and L_{Me} , respectively, and the equatorial and axial amines by $A_{eq.}$ and $A_{ax.}$, respectively. (The equatorial ammine is that in the plane of the bipyridine rings.)

Ligand	$\text{Me}_2\text{dicyd}^{2-}$		dicyd^{2-}			$\text{Cl}_2\text{dicyd}^{2-}$	
Solvent	NM	AN	NM	AN	DMSO	NM	AN
3	8.59	8.56	8.64	8.68	9.71	8.95	9.40
3'	8.47	8.40	8.48	8.40	8.65	8.53	8.27
4	8.24	8.15	8.30	8.16	8.37	8.30	7.40
4'	8.05	7.98	8.04	7.96	8.03	8.04	8.00
5	7.82	7.79	7.87	7.90	7.21	8.12	8.52
5'	7.59	7.51	7.57	7.50	6.81	7.40	6.99
6	9.02	8.80	8.93	~ 8.57	~ 5.66	8.12	5.85
6'	9.16	8.91	8.96	8.59	5.22	7.99	6.20
L_H	7.64	--	~ 8	--	5.61	~ 7.78	--
L_{Me}	2.20	--	N/A	N/A	N/A	N/A	N/A
$A_{eq.}$	3.17	2.97	3.14	2.96	3.89	3.51	3.77
$A_{ax.}$	2.19	2.09	2.42	2.54	13.87	4.63	10.23

NMR spectroscopy allows the magnetic behaviour of the metal centres to be probed based upon the behaviour of the hydrogens surrounding the metal. Paramagnetism tends to significantly affect proton resonances, often by causing dramatic shifts (upfield or

downfield) or line broadening.⁷⁶ For example, in the complex $[\text{Ru}(\text{NH}_3)_4(\text{Im})_2]^{3+}$ the imidazole (Im) proton resonances occur at 10 ppm, 5 ppm, and -35 ppm, respectively.⁷⁷

The absence of such effects is a good indication that the sample being studied is diamagnetic which, in the case of dinuclear Ru(III) complexes, indicates strong antiferromagnetic coupling.

Quantitative determination of paramagnetism is possible through Evans method experiments in which a coaxial capillary containing only the solvent and reference is inserted into the sample. If the sample is paramagnetic, it will shift the reference peak for the reference in the sample, but not for the reference in the capillary tube. Thus, two reference peaks will be seen with the splitting between them dependent upon the degree of paramagnetism of the sample.^{48,78} Evans method data for the two experiments run are available in table 3.2.2.

Table 3.2.2 - Experimental data and results for the Evans method determination of the solution magnetic moments of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-L})][\text{ClO}_4]_4$, L = dicyd²⁻ and Cl₂dicyd²⁻ in acetonitrile.

L	M (mg/mL) ^a	-Δf (Hz) ^b	μ _{eff} (μ _B /Ru ³⁺) ^c	χ _d (x10 ⁶ cgs) ^d
dicyd ²⁻	8.37	0.00	0.000	578
Cl ₂ dicyd ²⁻	8.57	4.70	0.785	619

^a Concentration of sample solution. ^b Separation (in Hz) between the reference and sample TMS peaks.

^c Calculated according to $\mu_{\text{eff}} = \frac{1}{2}[2.83(\chi_M \cdot T)^{1/2}]$ at 300 K. ^d Determined from the atomic Pascal Constants (see text).

Because of the narrow scope of application of this technique, no derivation of the equations will be undertaken herein. Readers with further interest are referred to the

original work by Evans,⁷⁹ and that by Phillips and Poe⁸⁰ for use with high-field NMR instruments. The gram susceptibility, χ_g , of the sample is obtained via eq 3.2.1

$$\chi_g = \frac{-3(\Delta f)}{4\pi(\nu)M} \text{ cm}^3 \cdot \text{g}^{-1} \quad (3.2.1)$$

where Δf is the difference between the frequency of TMS in the reference capillary and that of TMS in the sample solution, ν is the instrument frequency in Hz, and M is the amount of sample per mL of solvent. The mole susceptibility, χ_m , is obtained by multiplying χ_g by the sample's formula weight and is then corrected for the sample's diamagnetic susceptibility according to eq 3.2.2.

$$\chi_m' = \chi_m - \chi_d \quad (3.2.2)$$

from which the sample's effective magnetic moment may be determined according to eq 3.2.3, where T is the temperature at which the experiment was run.

$$\mu_{\text{eff}} = 2.83\sqrt{\chi_m' \cdot T} \quad (3.2.3)$$

The diamagnetic susceptibilities, χ_d , are obtained by summing the atomic Pascal's Constants⁸¹ for all atoms in the system being studied. The numbers presented in table 3.2.1 were obtained by assuming an atomic contribution of -20×10^{-6} cgs for each ruthenium and using a value of -21.6×10^{-6} cgs for each NCN⁻ moiety. This latter value was obtained by taking the value for thiocyanate (SCN⁻), -31.0×10^{-6} cgs,⁸² and correcting for the replacement of the sulfur atom by a nitrogen atom.

The absence of paramagnetic shifting of the reference peak for the $L = \text{dicyd}^{2-}$ complex in acetonitrile suggests, since metal-metal coupling is higher for this complex in nitromethane and for the $L = \text{Me}_2\text{dicyd}^{2-}$ complex in both acetonitrile and nitromethane,

that diamagnetic ground states exist for both $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-dicyd})][\text{ClO}_4]_4$ and $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{ClO}_4]_4$ in acetonitrile and nitromethane at room temperature.

NMR is also used to determine the presence of the associated solvent of recrystallization reported in the elemental analyses. In all cases, singlet resonances for the solvent molecules of recrystallization associated with each complex (see the experimental section) were identified in their NMR spectra.

Figure 3.2.2 - 400 MHz ^1H NMR spectrum of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{ClO}_4]_4$ in NM-d_3 showing the bipyridine (numbered) and $\text{Me}_2\text{dicyd}^{2-}$ ring hydrogen resonances (H).

Figure 3.2.3 - 400 MHz ^1H NMR of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{ClO}_4]_4$ in NM-d_3 showing the axial (A_{ax}) and equatorial (A_{eq}) ammines and $\text{Me}_2\text{dicyd}^{2-}$ methyl group hydrogen resonances (Me). MeCN represents acetonitrile resonances.

Figure 3.2.4 - 400 MHz ^1H NMR COSY of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{ClO}_4]_4$ in NM-d_3 showing the bipyridine and $\text{Me}_2\text{dicyd}^{2-}$ hydrogen resonances.

Figure 3.2.5 - 400 MHz ¹H NMR NOESY of [$\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Me}_2\text{dicyd})\][ClO_4]₄ in NM-d_3 showing the bipyridine and $\text{Me}_2\text{dicyd}^{2-}$ hydrogen resonances.$

Figure 3.2.6 - 400 MHz ^1H NMR spectrum of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{ClO}_4]_4$ in AN-d_3 showing the bipyridine hydrogen resonances.

Figure 3.2.7 - 400 MHz ^1H NMR spectrum of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-dicyd})][\text{ClO}_4]_4$ in NM-d_3 showing the bipyridine hydrogen resonances.

Figure 3.2.8 - 400 MHz ^1H NMR spectrum of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-dicyd})][\text{ClO}_4]_4$ in AN-d_3 showing the bipyridine (numbered), and axial (A_{ax}) and equatorial (A_{eq}) ammine hydrogen resonances.

Figure 3.2.9 - 400 MHz ^1H NMR spectrum of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-dicyd})][\text{ClO}_4]_4$ in DMSO-d_6 showing the bipyridine (numbered), axial (A_{ax}) and equatorial (A_{eq}) ammine hydrogen resonances, and the bridging ligand's ring's hydrogens' resonance, H.

Figure 3.2.10 - 400 MHz ^1H NMR spectrum of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cl}_2\text{dicyd})][\text{ClO}_4]_4$ in NM-d_3 showing the bipyridine (numbered) and $\text{Cl}_2\text{dicyd}^{2-}$ hydrogen resonances (H).

Figure 3.2.11 - 400 MHz ^1H NMR spectrum of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cl}_2\text{dicyd})][\text{ClO}_4]_4$ in AN-d_3 showing the bipyridine (numbered) and axial ammine (A_{ax}) hydrogen resonances.

Data for the $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-L})][\text{ClO}_4]_4$ complexes may be compared with data for other ruthenium complexes containing bipyridine ligands. Because Ru(III) is typically paramagnetic, comparisons must be drawn with Ru(II) complexes. In the ^1H NMR spectrum of a symmetric complex such as $[\text{Ru}(\text{bipy})_3]\text{Cl}_2$, steric interactions between 3 and 3' protons have been cited as having a deshielding effect typically rendering them the most deshielded of the bipy protons, resonating at 8.9 ppm relative to 7.8 ppm for the 6 and 6' protons.^{83,84} With methyl substituents on each bipyridine ring in the 4 or 4' and 5 positions, the resonances are shielded somewhat, occurring at 8.65 and 8.57 ppm respectively in the mono and di substituted bipyridines of $[\text{Ru}(\text{Me}_2\text{bipy})(\text{Me}_4\text{bipy})(\text{bpm})]^{2+}$, bpm = bipyrimidine,⁸⁵ and thus showing the sensitivity of the ring proton resonances to the electronic condition of the ring. The 6 position protons in that complex have also been shown to be quite sensitive to electronic perturbations on the ring, occurring at 9.14 ppm on the bipyrimidine ring, at 7.9 (av.) on the dimethylbipyridine, and at 7.75 on the tetramethylbipyridine. In asymmetric bis-bidentate polypyridyl complexes, the effect of anisotropic magnetic fields upon the 6 position protons causes the 6 and 6' protons to have dramatically different chemical shifts. One of the two protons (say 6') lies within the anisotropic ring field of one ring of the second polypyridine ligand, and may be deshielded by 1.5 - 3 ppm relative to 6, depending on the specific system.⁸⁶⁻⁸⁸ Ligands *cis* to one or the other 6 position proton may also have significant effects, such as is the case for several complexes of the family $[\text{Ru}(\text{bipy})(\text{bquin})\text{LL}']^n$. When L and L' are chlorides, for

example, the 6 position proton is shifted to 9.72 ppm relative to 7.50 ppm for the 6' proton.

It has been shown that pyridyl resonances don't shift significantly ($\leq \sim 1$ Hz relative to the free species) upon coordination to Ru(II).^{84,89} The absolute positions of the resonances of the bipyridine hydrogens for the complexes $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-L})][\text{ClO}_4]_4$, excepting for $\text{L} = \text{dicyd}^{2-}$ in DMSO and $\text{L} = \text{Cl}_2\text{dicyd}^{2-}$ in acetonitrile occur in the same range as those of uncoordinated bipyridine,⁸³ and suggest that the complexes are diamagnetic, with no evidence of significant paramagnetic contact or pseudo-contact shifting in the spectra. This is supported by Evans method data for $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-dicyd})][\text{ClO}_4]_4$ in acetonitrile for which no splitting of the reference peaks was noted and for $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cl}_2\text{dicyd})][\text{ClO}_4]_4$ in acetonitrile which was shown to be slightly paramagnetic ($\mu = .785 \mu_B/\text{Ru}^{\text{III}}$).

The resonances of the 6 position protons and the axial amines are the most variable of position, and their shifting seems to occur in concert. As the systems become less strongly coupled, the 6 position protons are increasingly shielded, while the axial amines become increasingly deshielded. Such behaviour is readily explained in terms of degree of metal-metal coupling. In the very strongly coupled complex $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{ClO}_4]_4$, the 6 position protons resonate at lower field than the 3 position protons, contrary to most data from Ru(II) systems. This is likely due to the more highly deshielding nature of Ru(III) and indicates that the 6 position hydrogens are the most susceptible to the charge on the metal centre. As the complexes become less strongly coupled, solvation effects become more significant^{13,15} and the metal

centre's charge is reduced, causing it to have a less deshielding effect on the 6 position protons.

Meyer has proposed that solvation of ruthenium ammine complexes occurs preferentially at the ammines³⁰ via a mechanism whereby electron density is donated from the solvent to the ruthenium centre via an interaction between the solvent and the ammine hydrogens (see figure 4.2.5). As the interaction between the ammine hydrogens and the solvent is increased, an attendant deshielding of these protons is seen in the NMR spectrum. Thus the same mechanism which explains the increasing shielding of the 6 position protons of bipyridine accounts for the shielding of the ammine protons. That the equatorial ammines are less strongly shielded than the axial ammines may be due to preferential solvation at the less sterically hindered axial sites.

The remaining bipyridine proton resonances occur at similar or slightly deshielded fields relative to those of bipyridines in Ru(II) complexes,^{83,85-88} and exhibit very little shifting from spectrum to spectrum. The J value of 5.6 Hz found for the 6 and 6' protons are similar to the coupling constants reported for $[\text{Ru}(\text{Me}_2\text{bipy})(\text{Me}_4\text{bipy})(\text{bpm})]^{2-}$,⁸⁵ and the value of 8.1 Hz found for the 3 and 3' resonances corresponds well to expected ortho coupling values for aromatic systems.⁷⁶

The DMSO spectrum of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-dicyd})][\text{ClO}_4]_4$ and the acetonitrile spectrum of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cl}_2\text{dicyd})][\text{ClO}_4]_4$ show much more pronounced shifting of both the 6 position hydrogens of bipyridine and (particularly) the axial ammine. In the case of both these systems the magnitude of the shifting is due to paramagnetism, although in the case of the dicyd²⁻ complex this result is non-informative since the solvent

is known to be able to reduce the Ru(III)-Ru(III) complex somewhat to the paramagnetic mixed-valent Ru(III)-Ru(II) complex (see section 2.5.1). In the pentaammine complexes the ammines appeared, in the most strongly coupled case - $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Me}_2\text{dicyd})][\text{PF}_6]_4$ in nitromethane - at 6.92 ppm (*trans*) and 2.96 ppm (*cis*).⁴⁸ This complex, based on determination of its magnetic moment via the Evans method, was shown to be almost diamagnetic. The complex $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-dicyd})][\text{PF}_6]_4$ in DMSO, had corresponding chemical shifts of its *trans* and *cis* ammines of 202 ppm and 52.2 ppm, with the bridging ligand's phenyl ring protons appearing at -8.99 ppm.⁴⁸ For $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-dicyd})][\text{ClO}_4]_4$ in DMSO the corresponding values are 13.87 ppm for the axial ammines, 3.89 for the equatorial ammine, and 5.61 for the hydrogens on the bridging ligand's phenyl ring, suggesting only slight paramagnetism in this system.

3.3 X-Ray Crystallography

X-ray diffraction was performed on a single crystal of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2\mu\text{-dicyd}](\text{ClO}_4)_4$, and the resultant ORTEP is shown in figure 3.3.1.

Figure 3.3.1 - ORTEP structure of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-dicyd})][\text{ClO}_4]_4$.

Of significance is the *anti*- conformation of the cyanamide groups, which was found to be the case for $[\{\text{Ru}(\text{NH}_3)_3\}_2(\mu\text{-dicyd})][\text{OTs}]_4$ ^{4,13} but not for $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-dicyd})][\text{PF}_6]_4$,^{16,30} which adopted a *syn* conformation. With its NCN

moieties in *anti*- conformation, and its bipyridine moieties in *syn*- conformation with respect to the bridging ligand, the structure of $\{[\text{Ru}(\text{NH}_3)_3(\text{bipy})]_2(\mu\text{-dicyd})\}[\text{ClO}_4]_4$ reflects elements of the structures of both its counterparts. Unlike $\{[\text{Ru}(\text{NH}_3)_5]_2(\mu\text{-dicyd})\}[\text{OTs}]_4$, only a single coordination mode of the ligand was found in the crystal structure. Table 3.3.1 contains crystal data and structure refinement information, and table 3.3.2 selected bond lengths and angles from this experiment.

The ruthenium-nitrogen angles for the inner coordination sphere are essentially octahedral, none being more than 4° from right with the exception of a “pinching” effect associated with coordination of bipyridine, resulting in an angle of 174° along the $\text{N}_{(\text{bipy})}\text{-Ru-N}_{(\text{NCN})}$ axis, and an angle of only 79° between the two nitrogens of bipyridine and the ruthenium centre. Near-octahedral bond angles about ruthenium is a feature of all three crystal structures, and the $79.0(3)^\circ$ bite angle for bipyridine is identical to that for the PF_6^- ($n = 2, 3$) and ClO_4^- ($n = 2$) salts of $[\text{Ru}(\text{bipy})_3]^{n+}$.¹⁰³ With the few exceptions listed in table 3.3.2, bond angles and lengths about ruthenium are equivalent between the two centres of $\{[\text{Ru}(\text{NH}_3)_3(\text{bipy})]_2(\mu\text{-dicyd})\}[\text{ClO}_4]_4$ within experimental error. This same holds true for the bond lengths and angles associated with the bipyridine rings, and for the dicyd^{2-} phenyl ring. Table 3.3.2 only presents a minimum data set where only a single example of any bond lengths and angles found to be equivalent within experimental error is presented. The comprehensive data set is available, see section 2.6.3 for details.

The bond angles for the NCN moieties themselves (169° and 174°) and for the NC-N-Ru bonds (174° and 178°) were close to 180° . Such angles are expected, as linear

conformations maximize π -overlap, and hence coupling, in the system. The NCN angle in the free ligand (as a tetraphenylarsonium salt) is 174° .²⁹

Table 3.3.1 - Crystal data and structural refinement information for the x-ray structural determination of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-dicyd})][\text{ClO}_4]_4$.

Empirical formula	$\text{C}_{28}\text{H}_{44}\text{Cl}_4\text{N}_{14}\text{O}_{19}\text{Ru}_2$	
Formula weight	1224.71	
Temperature	298 (2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit Cell dimensions	$a=12.5613$ (1) Å	$\alpha=76.756^\circ$ (1)
	$b=12.8738$ (1) Å	$\beta=83.893^\circ$ (1)
	$c=16.3267$ (2) Å	$\gamma=69.053^\circ$ (2)
Volume	2399.28 (4) Å ³	
Z	2	
Density (calculated)	1.695 Mg/m ³	
Absorption coefficient	0.936 mm ⁻¹	
F (000)	1236	
Crystal size	$0.30 \times 0.20 \times 0.20$ mm	
Theta range for data collection	1.73° to 22.50°	
Limiting indices	$-16 \leq h \leq 16$, $-13 \leq k \leq 16$, $-21 \leq l \leq 21$	
Reflections collected	10023	
Independent reflections	6112 [R (int) = 0.0271]	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	6106/1624/571	
Goodness-of-fit on F^2	1.033	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0568$, $wR2 = 0.1473$	
R indices (all data)	$R1 = 0.0629$, $wR2 = 0.1557$	
Largest diff. peak and hole	0.919 and -0.892 e·Å ⁻³	

Table 3.3.2 - Selected bond lengths and angles for $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-dicyd})][\text{ClO}_4]_4$. Bond lengths are in Å and angles in degrees. Standard deviations are given in parentheses following each listed value. The numbering scheme is available in figure 3.3.1.

Ru(1)-N(12)	1.978 (8)	N(3)-Ru(1)-N(4)	88.9 (3)
Ru(1)-N(2)	2.049 (7)	N(12)-Ru(1)-N(5)	91.7 (3)
Ru(1)-N(1)	2.070 (7)	N(2)-Ru(1)-N(5)	92.5 (3)
Ru(1)-N(3)	2.138 (8)	N(1)-Ru(1)-N(5)	86.5 (3)
Ru(1)-N(4)	2.139 (8)	N(3)-Ru(1)-N(5)	88.8 (3)
Ru(1)-N(5)	2.139 (8)	N(4)-Ru(1)-N(5)	177.6 (3)
N(1)-C(1)	1.357 (13)	N(14)-Ru(2)-N(6)	97.1 (4)
N(1)-C(5)	1.364 (12)	N(14)-Ru(2)-N(7)	177.6 (4)
N(2)-C(6)	1.350 (12)	N(6)-Ru(2)-N(7)	78.8 (4)
N(2)-C(10)	1.362 (12)	N(14)-Ru(2)-N(10)	91.2 (4)
N(11)-C(27)	1.309 (14)	N(6)-Ru(2)-N(9)	88.9 (4)
N(11)-C(26)	1.335 (13)	N(7)-Ru(2)-N(9)	90.3 (4)
N(12)-C(27)	1.172 (12)	N(14)-Ru(2)-N(9)	89.8 (4)
C(1)-C(2)	1.37 (2)	N(6)-Ru(2)-N(9)	92.7 (4)
C(2)-C(3)	1.37 (2)	N(7)-Ru(2)-N(9)	88.9 (3)
C(3)-C(4)	1.38 (2)	N(10)-Ru(2)-N(9)	178.0 (4)
C(4)-C(5)	1.367 (14)	N(14)-Ru(2)-N(8)	87.9 (3)
C(5)-C(10)	1.479 (14)	N(6)-Ru(2)-N(8)	174.3 (4)
C(6)-C(7)	1.38 (2)	N(7)-Ru(2)-N(8)	96.3 (4)
C(7)-C(8)	1.38 (2)	N(10)-Ru(2)-N(8)	88.2 (4)
C(8)-C(9)	1.39 (2)	N(9)-Ru(2)-N(8)	90.1 (4)
C(9)-C(10)	1.387 (14)	C(1)-N(1)-C(5)	118.3 (8)
C(21)-C(22)	1.355 (14)	C(1)-N(1)-Ru(1)	126.4 (7)
C(21)-C(26)	1.426 (14)	C(5)-N(1)-Ru(1)	114.8 (6)
C(22)-C(23)	1.440 (14)	C(27)-N(11)-C(26)	122.6 (9)
C(23)-C(24)	1.426 (14)	C(27)-N(12)-Ru(1)	174.1 (8)
C(24)-C(25)	1.348 (14)	C(28)-N(14)-Ru(2)	178.1 (8)
C(25)-C(26)	1.444 (14)	N(1)-C(1)-C(2)	122.0 (11)
N(12)-Ru(1)-N(2)	95.0 (3)	C(3)-C(2)-C(1)	119.3 (11)
N(12)-Ru(1)-N(1)	173.6 (3)	N(1)-C(5)-N(10)	114.7 (8)
N(2)-Ru(1)-N(1)	79.0 (3)	C(4)-C(5)-N(10)	124.2 (9)
N(12)-Ru(1)-N(3)	88.5 (3)	C(22)-C(21)-C(26)	120.6 (9)
N(2)-Ru(1)-N(3)	176.3 (3)	N(13)-C(23)-C(24)	125.0 (9)
N(1)-Ru(1)-N(3)	97.6 (3)	N(13)-C(23)-C(22)	117.3 (9)
N(12)-Ru(1)-N(4)	88.9 (3)	C(24)-C(23)-C(22)	117.7 (9)
N(2)-Ru(1)-N(4)	89.8 (3)	N(12)-C(27)-N(11)	169.2 (10)
N(1)-Ru(1)-N(4)	93.2 (3)	N(14)-C(28)-N(13)	173.9 (11)

Table 3.3.3 compares the coordination angles of the cyanamide moiety to ruthenium for the pentaammine and tetraamminepyridine complexes with those for the triammine complex. As can be seen, the essential linearity of the entire NCN-Ru moiety is present in all three complexes. Where two different values are presented in the table, they represent the values at each ruthenium centre. Note that the values presented for the pentaammine complex are for its linear coordination isomer. In the bent isomer, $\angle \text{NC-N-Ru}$ is 150° . These values are taken from reference (4). No particular significance should be ascribed to the fact that only a single value is presented for the pentaammine angles, as only selected values are available in literature.

Table 3.3.3 - Comparative bond angles for the cyanamide moiety and the Ru-NCN bond from the X-ray structures of the dicyd²⁻ pentaammine, tetraamminepyridine, and triamminebipyridine ruthenium(III) complexes. Angles have been rounded to the nearest angle.

Complex	$\angle \text{NCN (deg.)}$	$\angle \text{NC-N-Ru (deg.)}$
A5	172	175
A4P	168/176	175
A3B	169/174	174/178

Table 3.3.4 provides data for all three complexes comparing cyanamide (NCN) and various ruthenium-nitrogen bond lengths between the three systems. Just as the NCN and Ru-NCN bond angles in the three complexes are similar, so too are the associated bond lengths, with none changing by more than ca. $0.04 \text{ \AA}$ between the three systems. The Ru-NH₃ bond lengths for all three complexes fall into the range of a large number of Ru^{II} and Ru^{III} complexes, being quite close to those observed for the di-anion bridged Ru^{III} system $[\{\text{Ru}(\text{NH}_3)_4\}_2(\mu_2\text{-(NH}_2)_2)\text{Cl}_4, 2.137(3) \text{ \AA}^{104}$

Table 3.3.4 - Comparative bond lengths (averaged) in Å from the x-ray structures of the dicyd²⁻ pentaammine, tetraamminepyridine, and triamminebipyridine ruthenium(III) complexes, as well as the AsPh₄⁺ salt of the dianion ligand. Standard deviations (averaged) are given in parentheses.

Complex	Ph-NCN	N-CN	NC-N	NCN-Ru	Ru-NH ₃	Ru-N _(py)
A5	1.376 (17)	1.298 (19)	1.151 (19)	1.938 (11)	2.097 (10)	N/A
A4P	1.36 (3)	1.28 (3)	1.19 (3)	1.951 (20)	2.141 (18)	2.061 (18)
A3B	1.333 (13)	1.312 (12)	1.167 (14)	1.978 (8)	2.136 (8)	2.060 (7)
dicyd ²⁻	1.388 (8)	1.299 (10)	1.172 (10)	N/A	N/A	N/A

The Ph-NCN bond is slightly and systematically contracted with pyridine substitution (*e.g.* upon going from the pentaammine system to the tetraammine to the triammine). At the same time, the Ru-NCN bond is lengthening somewhat. The multiple-bond nature of the cyanamide's bonds, however, persists for all three systems. The terminal NC-N bond's length remains close to the value of 1.158 Å³¹ for true nitrile of the form R-C≡N, while the "amide" PhN-CN bond's length is less than that for an aromatic heterocycle's C=N bond (1.352 Å³¹) and the Ph-NCN bond's length only slightly higher than this value. Regardless of small variations in individual bonds, overall Ru(1)-Ru(2) through space separation is unaffected, being 13.1 Å in both [{Ru(NH₃)₅(bipy)}₂(μ-dicyd)][ClO₄]₄ and [{Ru(NH₃)₅}₂(μ-dicyd)][OTs]₄.¹ The much shorter value of 10.9 Å for [{Ru(NH₃)₄(py)}₂(μ-dicyd)][PF₆]₄ is due to the *syn* conformation of its cyanamide moieties.

3.4 Electronic Absorption Spectroscopy

Quantitative UV-Vis-NIR spectra have been collected for all twelve complexes using five solvents (nitromethane, acetonitrile, acetone, dimethyl sulfoxide, and water) spanning a broad range of donor numbers. Data for the pentaammine complexes in all five solvents, obtained by Dr. M. L. Naklicki, have been previously reported and discussed,^{48,53} but are reproduced here to facilitate comparisons. (See tables 3.4.1 - 3.4.4 and figure 3.4.2.)

The tetrammine complexes were initially studied by Dr. A. R. Rezvani in acetonitrile, and those data have likewise been reported elsewhere^{50,68} and are being reproduced here for the sake of completeness and to facilitate comparisons. It should be noted, however, that the tabulated molar absorptivities reported in (68) for $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-dicyd})][\text{PF}_6]_4$ and $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-Cl}_2\text{dicyd})][\text{PF}_6]_4$ were erroneous, and have been corrected in this work. The corrected values may, however, be obtained by analysis of the spectra published in (68). New quantitative data for the tetraammines in dimethyl sulfoxide and nitromethane are now available and are reported herein, although no data has yet been collected in water. Acetone spectra were not attempted since the systems have all been reported to be intractable for study in this solvent.⁶⁸ (See tables 3.4.5 - 3.4.8 and figures 3.4.3 - 3.4.6.) Note that the nitromethane and DMSO spectra reported in figures 3.4.3 - 3.4.6 are qualitative spectra obtained by Dr. V. V. Kondratiev (see section 3.6) normalized using quantitative spectroscopy performed by C. A. White and the author.

As is the case for the pentaammines, spectroscopy was performed on the triammines in all five solvents, and is reported here for the first time. (See tables 3.4.9 - 3.4.12 and figures 3.4.7 - 3.4.10.)

For all three families of complexes, the spectra of the fully oxidized (*i.e.* Ru(III)-Ru(III)) complex was dominated by an intense low energy band assigned as an LMCT transition^{95,96} between the high energy π -HOMO of the dianion ligand and a metal-centred π d orbital, or LCAO of both metals' orbitals.

Figure 3.4.1 - A - Qualitative M.O. diagram for a mononuclear Ru(III)-phenylcyanamide complex showing the LMCT transition (arrow). Labelling is appropriate to C_{2v} symmetry. Adapted from (95). B - Interaction of the metal d_{xz} orbitals with the bridging ligand's π -HOMO in the corresponding dinuclear complex, with labelling appropriate to C_{2h} symmetry.

A qualitative M.O. diagram for a corresponding mononuclear ruthenium(III) complex of phenylcyanamide is provided in figure 3.4.1(A). The mononuclear complex was assigned in C_{2v} microsymmetry,⁹⁵ and the lowest energy LMCT transition of the dinuclear complexes has, by analogy, been labelled $b_1^* \leftarrow b_1$ in previous reports.^{48,49} The idealized geometry of the dinuclear complexes assuming *anti*- conformation of the cyanamide groups is, however, C_{2h} in which symmetry the corresponding assignment would be $b_g^* \leftarrow b_g$ (see figure 3.4.1(B)). As an aside, it should be noted that the magnetic behaviour of a given complex is determined by the thermal populations of the non-bonding a_u and antibonding b_g^* orbitals. As the $b_g^* - a_u$ energy gap increases, paramagnetism will decrease. Due to the complexity of a full M.O. scheme for a Class II dinuclear complex none shall be presented here. Figure 3.4.1(B) deals with the interactions in the dinuclear complex of the metal and ligand orbitals involved in superexchange.

Parameters from the electronic absorption spectra are required for modelling the systems via the CNS model. However, because the band shapes are non-gaussian, calculation of the coupling elements must be effected directly from experimental oscillator strengths.^a These oscillator strengths were determined for each spectrum by modelling the band envelope with multiple gaussian bands using Jandel Scientific's PeakFit™ v3.0 software. The oscillator strengths of the fitting bands were individually determined according to $f = 4.61 \times 10^{-9} (\epsilon_{\max} \nu_{\max})$, and the overall oscillator strength taken as the sum of the contributions of the various fitting bands. No significance was attributed to the number or nature of the fitting bands.

^a For this reason the $\Delta \nu_{\max}$ values reported in (50), which were obtained graphically, are inappropriate for use in calculating oscillator strengths. The oscillator strengths reported in this work are proper, experimental values.

Table 3.4.1 - Electronic absorption spectroscopy data for the LMCT transition of $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-dicyd})][\text{PF}_6]_4$ as a function of solvent.

Solvent ^a	f ^b	ϵ_{max} ^c	$\log(\epsilon_{\text{max}})$	ν_{max} (nm)	ν_{max} (cm^{-1})
NM (2.7)	0.675	6.31×10^4	4.800	1107	9030
AN (14.1)	0.609	4.57×10^4	4.660	1094	9140
AC (17.0)	0.477	2.95×10^4	4.470	1087	9200
DMSO (29.8)	0.351	1.41×10^4	4.149	904	11060
H ₂ O (18.0)	0.351	1.35×10^4	4.130	871	11480

^a Solvent Donor Number in parentheses. ^b Oscillator strength, f , determined using PeakFit software, see text for details. ^c ϵ_{max} has units of $\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$.

Figure 3.4.2 - Electronic absorption spectra of $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-dicyd})][\text{PF}_6]_4$ in nitromethane, acetonitrile, acetone, and dimethyl sulfoxide. Spectra were obtained using the OTTLE cell described in section 2.6.6.

Table 3.4.2 - Electronic absorption spectroscopy data for the LMCT transition of $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Me}_2\text{dicyd})][\text{PF}_6]_4$ as a function of solvent.

Solvent ^a	f^b	ϵ_{max}^c	$\log(\epsilon_{\text{max}})$	ν_{max} (nm)	ν_{max} (cm ⁻¹)
NM (2.7)	0.718	6.76×10^4	4.830	1101	9080
AN (14.1)	0.684	6.46×10^4	4.810	1121	8920
AC (17.0)	0.550	4.27×10^4	4.630	1118	8940
DMSO (29.8)	0.372	1.58×10^4	4.199	1011	9890
H ₂ O (18.0)	0.388	1.55×10^4	4.190	1022	9780

^a Solvent Donor Number in parentheses. ^b Oscillator strength, f , determined using PeakFit software, see text for details. ^c ϵ_{max} has units of L·mol⁻¹·cm⁻¹.

Table 3.4.3 - Electronic absorption spectroscopy data for the LMCT transition of $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Cl}_2\text{dicyd})][\text{PF}_6]_4$ as a function of solvent.

Solvent ^a	f^b	ϵ_{max}^c	$\log(\epsilon_{\text{max}})$	ν_{max} (nm)	ν_{max} (cm ⁻¹)
NM (2.7)	0.537	3.24×10^4	4.511	1089	9180
AN (14.1)	0.468	2.19×10^4	4.340	1006	9940
AC (17.0)	0.400	1.66×10^4	4.220	963	10380
DMSO (29.8)	0.275	1.15×10^4	4.061	791	12640
H ₂ O (18.0)	0.337	1.26×10^4	4.100	794	12590

^a Solvent Donor Number in parentheses. ^b Oscillator strength, f , determined using PeakFit software, see text for details. ^c ϵ_{max} has units of L·mol⁻¹·cm⁻¹.

Table 3.4.4 - Electronic absorption spectroscopy data for the LMCT transition of $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Cl}_4\text{dicyd})][\text{PF}_6]_4$ as a function of solvent.

Solvent ^a	f^b	ϵ_{max}^c	$\log(\epsilon_{\text{max}})$	ν_{max} (nm)	ν_{max} (cm ⁻¹)
NM (2.7)	0.409	1.62×10^4	4.210	953	10490
AN (14.1)	0.366	1.41×10^4	4.149	833	12000
AC (17.0)	0.299	1.17×10^4	4.068	782	12790
DMSO (29.8)	0.223	8.91×10^3	3.950	716	13970
H ₂ O (18.0)	0.209	7.08×10^3	3.850	711	14060

^a Solvent Donor Number in parentheses. ^b Oscillator strength, f , determined using PeakFit software, see text for details. ^c ϵ_{max} has units of L·mol⁻¹·cm⁻¹.

Table 3.4.5 - Electronic absorption spectroscopy data for the LMCT transition of $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{PF}_6]_4$ as a function of solvent.

Solvent ^a	f^b	ϵ_{max}^c	$\log(\epsilon_{\text{max}})$	$\nu_{\text{max}} \text{ (nm)}$	$\nu_{\text{max}} \text{ (cm}^{-1}\text{)}$
NM (2.7)	0.910	7.45×10^4	4.872	1125	8890
AN (14.1)	0.842	7.58×10^4	4.880	1126	8880
AC (17.0)	--	--	--	--	--
DMSO (29.8)	0.439	4.21×10^4	4.624	1174	8520
H ₂ O (18.0)	--	--	--	--	--

^a Solvent Donor Number in parentheses. ^b Oscillator strength, f , determined using PeakFit software, see text for details. ^c ϵ_{max} has units of $\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$.

Figure 3.4.3 - Electronic absorption spectra of $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{PF}_6]_4$ in a number of solvents. Spectra were collected using the H-cell apparatus described in section 2.6.6.

Table 3.4.6 - Electronic absorption spectroscopy data for the LMCT transition of $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-dicyd})][\text{PF}_6]_4$ as a function of solvent.

Solvent ^a	f^b	ϵ_{max}^c	$\log(\epsilon_{\text{max}})$	ν_{max} (nm)	ν_{max} (cm^{-1})
NM (2.7)	0.808	6.95×10^4	4.842	1125	8890
AN (14.1)	0.772	7.54×10^4	4.877	1163	8600
AC (17.0)	--	--	--	--	--
DMSO (29.8)	0.563	4.11×10^4	4.614	1175	8510
H ₂ O (18.0)	--	--	--	--	--

^a Solvent Donor Number in parentheses. ^b Oscillator strength, f , determined using PeakFit software, see text for details. ^c ϵ_{max} has units of $\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$.

Figure 3.4.4 - Electronic absorption spectra of $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-dicyd})][\text{PF}_6]_4$ in a number of solvents. Spectra were collected using the H-cell apparatus described in section 2.6.6.

Table 3.4.7 - Electronic absorption spectroscopy data for the LMCT transition of $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-Cl}_2\text{dicyd})][\text{PF}_6]_4$ as a function of solvent.

Solvent ^a	f^b	ϵ_{max}^c	$\log(\epsilon_{\text{max}})$	ν_{max} (nm)	ν_{max} (cm ⁻¹)
NM (2.7)	0.655	6.33×10^4	4.801	1182	8460
AN (14.1)	0.599	4.24×10^4	4.627	1175	8510
AC (17.0)	--	--	--	--	--
DMSO (29.8)	0.399	1.73×10^4	4.238	1034	9670
H ₂ O (18.0)	--	--	--	--	--

^a Solvent Donor Number in parentheses. ^b Oscillator strength, f , determined using PeakFit software, see text for details. ^c ϵ_{max} has units of L·mol⁻¹·cm⁻¹.

Figure 3.4.5 - Electronic absorption spectra of $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-Cl}_2\text{dicyd})][\text{PF}_6]_4$ in a number of solvents. Spectra were collected using the H-cell apparatus described in section 2.6.6.

Table 3.4.8 - Electronic absorption spectroscopy data for the LMCT transition of $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-Cl}_4\text{dicyd})][\text{PF}_6]_4$ as a function of solvent.

Solvent ^a	f^b	ϵ_{max}^c	$\log(\epsilon_{\text{max}})$	$\nu_{\text{max}} \text{ (nm)}$	$\nu_{\text{max}} \text{ (cm}^{-1}\text{)}$
NM (2.7)	0.602	4.16×10^4	4.619	1135	8810
AN (14.1)	0.578	2.63×10^4	4.420	1070	9350
AC (17.0)	--	--	--	--	--
DMSO (29.8)	0.345	1.36×10^4	4.134	841	11890
H ₂ O (18.0)	--	--	--	--	--

^a Solvent Donor Number in parentheses. ^b Oscillator strength, f , determined using PeakFit software. see text for details. ^c ϵ_{max} has units of $\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$.

Figure 3.4.6 - Electronic absorption spectra of $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-Cl}_4\text{dicyd})][\text{PF}_6]_4$ in a number of solvents. Spectra were collected using the H-cell apparatus described in section 2.6.6.

Table 3.4.9 - Electronic absorption spectroscopy data for the LMCT transition of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{ClO}_4]_4$ as a function of solvent.

Solvent ^a	f^b	ϵ_{max}^c	$\log(\epsilon_{\text{max}})$	$\nu_{\text{max}} \text{ (nm)}$	$\nu_{\text{max}} \text{ (cm}^{-1}\text{)}$
NM (2.7)	0.833	5.17×10^4	4.713	1001	9990
AN (14.1)	0.827	5.53×10^4	4.743	1052	9510
AC (17.0)	0.768	4.91×10^4	4.691	1083	9230
DMSO (29.8)	0.823	7.26×10^4	4.861	1215	8230
H ₂ O (18.0)	0.759	5.00×10^4	4.699	1054	9490

^a Solvent Donor Number in parentheses. ^b Oscillator strength, f , determined using PeakFit software, see text for details. ^c ϵ_{max} has units of $\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$.

Figure 3.4.7 - Electronic absorption spectra of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{ClO}_4]_4$ in acetonitrile. Spectra were obtained quantitatively as described in section 2.6.4.

Table 3.4.10 - Electronic absorption spectroscopy data for the LMCT transition of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-dicyd})][\text{ClO}_4]_4$ as a function of solvent.

Solvent ^a	f^b	ϵ_{max}^c	$\log(\epsilon_{\text{max}})$	ν_{max} (nm)	ν_{max} (cm^{-1})
NM (2.7)	0.876	6.00×10^4	4.778	1069	9350
AN (14.1)	0.894	7.05×10^4	4.848	1119	8940
AC (17.0)	0.780	5.51×10^4	4.741	1146	8730
DMSO (29.8)	0.797	7.40×10^4	4.869	1232	8120
H ₂ O (18.0)	0.811	6.51×10^4	4.814	1148	8710

^a Solvent Donor Number in parentheses. ^b Oscillator strength, f , determined using PeakFit software, see text for details. ^c ϵ_{max} has units of $\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$.

Figure 3.4.8 - Electronic absorption spectra of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-dicyd})][\text{ClO}_4]_4$ in acetonitrile. Spectra were obtained quantitatively as described in section 2.6.4.

Table 3.4.11 - Electronic absorption spectroscopy data for the LMCT transition of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Clidicyd})][\text{ClO}_4]_4$ as a function of solvent.

Solvent ^a	f^b	ϵ_{max}^c	$\log(\epsilon_{\text{max}})$	$\nu_{\text{max}} \text{ (nm)}$	$\nu_{\text{max}} \text{ (cm}^{-1}\text{)}$
NM (2.7)	0.603	3.71×10^4	4.569	1128	8870
AN (14.1)	0.605	4.01×10^4	4.603	1164	8590
AC (17.0)	0.505	3.00×10^4	4.477	1194	8380
DMSO (29.8)	0.455	3.11×10^4	4.493	1230	8130
H ₂ O (18.0)	0.485	3.57×10^4	4.553	1187	8420

^a Solvent Donor Number in parentheses. ^b Oscillator strength, f , determined using PeakFit software, see text for details. ^c ϵ_{max} has units of $\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$.

Figure 3.4.9 - Electronic absorption spectra of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Clidicyd})][\text{ClO}_4]_4$ in acetonitrile. Spectra were obtained quantitatively as described in section 2.6.4.

Table 3.4.12 - Electronic absorption spectroscopy data for the LMCT transition of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cl}_2\text{dicyd})][\text{ClO}_4]_4$ as a function of solvent.

Solvent ^a	f^b	ϵ_{max}^c	$\log(\epsilon_{\text{max}})$	ν_{max} (nm)	ν_{max} (cm^{-1})
NM (2.7)	0.865	7.50×10^4	4.875	1175	8510
AN (14.1)	0.813	7.60×10^4	4.881	1198	8350
AC (17.0)	0.809	8.11×10^4	4.909	1212	8250
DMSO (29.8)	0.566	3.79×10^4	4.579	1202	8320
H ₂ O (18.0)	0.663	5.32×10^4	4.726	1199	8340

^a Solvent Donor Number in parentheses. ^b Oscillator strength, f , determined using PeakFit software, see text for details. ^c ϵ_{max} has units of $\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$.

Figure 3.4.10 - Electronic absorption spectra of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cl}_2\text{dicyd})][\text{ClO}_4]_4$ in acetonitrile. Spectra were obtained quantitatively as described in section 2.6.4.

3.5 Cyclic Voltammetry

Cyclic voltammetry was performed on all twelve complexes in five solvents (nitromethane, acetonitrile, acetone, dimethyl sulfoxide, water) spanning a broad range of solvent donor number. Data from the four complexes $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-L})]^{4+}$, $\text{L} = \text{Me}_2\text{dicyd}^{2-}$, dicyd^{2-} , $\text{Cl}_2\text{dicyd}^{2-}$, $\text{Cl}_4\text{dicyd}^{2-}$, each studied in all five solvents, are the work of Dr. M. L. Naklicki. They have been previously reported^{42,48,51,52} and are reproduced here in tables 3.5.1 - 3.5.4 to facilitate comparison. The data for the non-aqueous spectra have been modified from the values in (48), which were reported vs. NHE but did not consider the variability of the ferrocene-ferrocenium internal reference couple as a function of solvent.^{97,98} Herein, the values are given vs. ferrocene, and should be considered to supercede the older data excepting those in acetonitrile, for which the correct value of $E^{\text{ofc}^+/\text{fc}}$ was used (*e.g.* the data reported in (42) and (52)). Data from the aqueous spectra have similarly been altered from the values in (48), being reported vs. SCE instead of NHE. These values supercede those previously reported in (49), (55), and (90) which were collected using less sensitive instrumentation.

In most cases, the CV spectra of any of the dinuclear complexes indicate four redox events. At more negative potentials are the metal-centred events of eq 1.3.2, with the two couples at higher potentials being formally assigned as the ligand centred events $\text{L}^{0\cdot}$ and $\text{L}^{\cdot 2-}$. Assignment of these bands for the family of complexes $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-L})]^{4+}$ was based upon electrochemical study of the free dicyd^{2-} ligands^{48,90} and a number of mononuclear complexes,^{95,96} and is presented fully in (48). The CV spectra for both the

$[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-L})]^{4+}$ and $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-L})]^{4+}$ families of complexes have the same appearance as those for the pentaammines, and assignment of the four redox events has been made in kind. Note that some argument has been made for assigning the L^{-2-} couple as another essentially metal-centred event producing a mixed-valent Ru(IV)-Ru(III) complex.^{48,51} Since this issue has no impact on the treatment of the data in this work, it will not be further considered.

Table 3.5.1 - Redox couples and comproportionation constants as a function of solvent for $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Me}_2\text{dicyd})][\text{PF}_6]_4$.^a

Solvent ^b	$\text{L}^{0/-}$	L^{-2-}	$\text{E}^\circ_{\text{M}2}$	$\text{E}^\circ_{\text{M}1}$	ΔE^c	K_c^d
NM (2.7)	0.595	0.205	-0.448	-0.816	368	1.7×10^6
AN (14.1)	0.540	0.102	-0.576	-0.916	340	5.6×10^5
AC (17.0)	0.474	0.013	-0.689	-1.014	325	3.1×10^5
DMSO (29.8)	0.385	-0.083	-0.828	-1.026	198	2.2×10^3
H ₂ O (18.0)	0.670	0.297	-0.274	-0.359	85	2.7×10^1

^a Data reported in V vs ferrocene (non-aqueous) or V vs SCE (aqueous); data reproduced from (1).

^b Solvent donor numbers in parentheses. ^c ΔE in mV. ^d $\text{K}_c = \exp[16.91(\Delta\text{E})]$, for ΔE in V.

Table 3.5.2 - Redox couples and comproportionation constants as a function of solvent for $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-dicyd})][\text{PF}_6]_4$.^a

Solvent ^b	$\text{L}^{0/-}$	L^{-2-}	$\text{E}^\circ_{\text{M}2}$	$\text{E}^\circ_{\text{M}1}$	ΔE^c	K_c^d
NM (2.7)	0.741	0.309	-0.412	-0.725	313	2.0×10^5
AN (14.1)	0.627	0.165	-0.534	-0.820	286	6.9×10^4
AC (17.0)	0.593	0.104	-0.652	-0.897	245	1.4×10^4
DMSO (29.8)	0.403	-0.043	-0.809	-0.976	167	6.7×10^2
H ₂ O (18.0)	0.745	0.405	-0.246	-0.349	103	5.5×10^1

^a Data reported in V vs ferrocene (non-aqueous) or V vs SCE (aqueous); data reproduced from (1).

^b Solvent donor numbers in parentheses. ^c ΔE in mV. ^d $\text{K}_c = \exp[16.91(\Delta\text{E})]$, for ΔE in V.

Table 3.5.3 - Redox couples and comproportionation constants as a function of solvent for $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Cl}_2\text{dicyd})][\text{PF}_6]_4$.^a

Solvent ^b	$L^{0/-}$	L^{-2-}	E°_{M2}	E°_{M1}	ΔE^c	K_c^d
NM (2.7)	--	--	-0.342	-0.573	231	8.1×10^3
AN (14.1)	0.790	0.335	-0.473	-0.685	212	3.9×10^3
AC (17.0)	0.711	0.251	-0.613	-0.809	196	2.1×10^3
DMSO (29.8)	--	0.163	-0.845	-0.975	130	1.6×10^2
H ₂ O (18.0)	0.888	0.572	-0.206	-0.284	78	2.1×10^1

^a Data reported in V vs ferrocene (non-aqueous) or V vs SCE (aqueous); data reproduced from (1).

^b Solvent donor numbers in parentheses. ^c ΔE in mV. ^d $K_c = \exp[16.91(\Delta E)]$, for ΔE in V.

Table 3.5.4 - Redox couples and comproportionation constants as a function of solvent for $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Cl}_4\text{dicyd})][\text{PF}_6]_4$.^a

Solvent ^b	$L^{0/-}$	L^{-2-}	E°_{M2}	E°_{M1}	ΔE^c	K_c^d
NM (2.7)	--	--	-0.325	-0.483	158	4.7×10^2
AN (14.1)	0.898	0.447	-0.465	-0.614	149	3.3×10^2
AC (17.0)	0.840	0.363	-0.622	-0.762	140	2.3×10^2
DMSO (29.8)	--	0.301	-0.819	-0.934	115	8.8×10^1
H ₂ O (18.0)	0.790	0.650	-0.244	-0.309	65	1.3×10^1

^a Data reported in V vs ferrocene (non-aqueous) or V vs SCE (aqueous); data reproduced from (1).

^b Solvent donor numbers in parentheses. ^c ΔE in mV. ^d $K_c = \exp[16.91(\Delta E)]$, for ΔE in V.

Data for the four complexes $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-L})][\text{PF}_6]_4$, $L = \text{Me}_2\text{dicyd}^{2-}$, dicyd^{2-} , $\text{Cl}_2\text{dicyd}^{2-}$, $\text{Cl}_4\text{dicyd}^{2-}$, have been previously reported only in acetonitrile and dimethyl sulfoxide, and are the work of Dr. A. R. Rezvani.^{50,68} These data are reproduced here, along with new data for these complexes in nitromethane and water obtained by Dr. V. V. Kondratiev, in tables 3.5.5 - 3.5.8. The complexes have all been previously found to be unsuitable for study in acetone.⁶⁸

Table 3.5.5 - Redox couples and comproportionation constants as a function of solvent for $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-Me}_2\text{dicyd})](\text{PF}_6)_4$.^a

Solvent ^b	$\text{L}^{0/-}$	L^{-2-}	$\text{E}^\circ_{\text{M2}}$	$\text{E}^\circ_{\text{M1}}$	ΔE^c	K_c^d
NM (2.7)	--	--	--	--	375	2.2×10^6
AN (14.1)	0.592	0.268	-0.359	-0.756	397	5.2×10^6
AC (17.0)	--	--	--	--	--	--
DMSO (29.8)	--	0.388	-0.557	-0.832	279	5.2×10^4
H ₂ O (18.0)	--	0.455	-0.057	-0.147	90	3.3×10^1

^a Data reported in V vs ferrocene (non-aqueous) or V vs SCE (aqueous); data for AN taken from (12).

^b Solvent donor numbers in parentheses. ^c ΔE in mV. ^d $\text{K}_c = \exp[16.91(\Delta\text{E})]$, for ΔE in V.

Table 3.5.6 - Redox couples and comproportionation constants as a function of solvent for $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2\mu\text{-dicyd}](\text{PF}_6)_4$.^a

Solvent ^b	$\text{L}^{0/-}$	L^{-2-}	$\text{E}^\circ_{\text{M2}}$	$\text{E}^\circ_{\text{M1}}$	ΔE^c	K_c^d
NM (2.7)	0.788	0.437	-0.218	-0.581	363	1.4×10^6
AN (14.1)	0.676	0.293	-0.320	-0.679	359	1.2×10^6
AC (17.0)	--	--	--	--	--	--
DMSO (29.8)	--	0.440	-0.599	-0.830	230	7.8×10^3
H ₂ O (18.0)	--	0.460	-0.046	-0.154	108	6.7×10^1

^a Data reported in V vs ferrocene (non-aqueous) or V vs SCE (aqueous); data for AN taken from (12).

^b Solvent donor numbers in parentheses. ^c ΔE in mV. ^d $\text{K}_c = \exp[16.91(\Delta\text{E})]$, for ΔE in V.

Table 3.5.7 - Redox couples and comproportionation constants as a function of solvent for $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2\mu\text{-Cl}_2\text{dicyd}](\text{PF}_6)_4$.^a

Solvent ^b	$\text{L}^{0/-}$	L^{-2-}	$\text{E}^\circ_{\text{M2}}$	$\text{E}^\circ_{\text{M1}}$	ΔE^c	K_c^d
NM (2.7)	--	--	--	--	298	1.1×10^5
AN (14.1)	0.830	0.386	-0.236	-0.498	262	2.7×10^4
AC (17.0)	--	--	--	--	--	--
DMSO (29.8)	--	0.199	-0.513	-0.663	150	3.4×10^2
H ₂ O (18.0)	--	0.604	0.009	-0.069	78	2.1×10^1

^a Data reported in V vs ferrocene (non-aqueous) or V vs SCE (aqueous); data for AN taken from (12).

^b Solvent donor numbers in parentheses. ^c ΔE in mV. ^d $\text{K}_c = \exp[16.91(\Delta\text{E})]$, for ΔE in V.

Table 3.5.8 - Redox couples and comproportionation constants as a function of solvent for $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2\mu\text{-Cl}_4\text{dicyd}](\text{PF}_6)_4$.^a

Solvent ^b	$\text{L}^{0/-}$	L^{-2-}	$\text{E}^\circ_{\text{M2}}$	$\text{E}^\circ_{\text{M1}}$	ΔE^c	K_c^d
NM (2.7)	--	--	--	--	212	3.9×10^3
AN (14.1)	--	0.502	-0.237	-0.406	169	7.2×10^2
AC (17.0)	--	--	--	--	--	--
DMSO (29.8)	--	0.348	-0.451	-0.619	128	1.5×10^2
H ₂ O (18.0)	--	--	0.008	-0.040	48	6.5×10^0

^a Data reported in V vs ferrocene (non-aqueous) or V vs SCE (aqueous); data for AN taken from (12).

^b Solvent donor numbers in parentheses. ^c ΔE in mV. ^d $\text{K}_c = \exp[16.91(\Delta\text{E})]$, for ΔE in V.

Cyclic voltammetry has been performed on each of the four complexes

$[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-L})][\text{ClO}_4]_4$, $\text{L} = \text{Me}_2\text{dicyd}^{2-}$, dicyd^{2-} , Clidicyd^{2-} , $\text{Cl}_2\text{dicyd}^{2-}$, in all five solvents, and the results tabulated in tables 3.5.9 - 3.5.12. The spectra themselves are also reproduced in their entirety as figures 3.5.1 - 3.5.21 to safeguard the integrity of the tabulated data. All spectra were collected according to the procedures outlined in section 2.6.5. The spectra presented here were all obtained at a scan rate of 0.100 V/s, with electrochemical reversibility being tested at scan rates ranging from 0.050 to 0.500 V/s.

Table 3.5.9 - Redox couples and comproportionation constants as a function of solvent for $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{ClO}_4]_4$.^a

Solvent ^b	$\text{L}^{0/-}$	L^{-2-}	$\text{E}^\circ_{\text{M2}}$	$\text{E}^\circ_{\text{M1}}$	ΔE^c	K_c^d
NM (2.7)	0.693	0.524	-0.194	-0.604	410	8.6×10^6
AN (14.1)	0.633	0.439	-0.203	-0.624	421	1.3×10^7
AC (17.0)	0.524	0.328	-0.265	-0.713	448	3.8×10^7
DMSO (29.8)	--	0.131	-0.330	-0.695	365	1.5×10^6
H ₂ O (18.0)	--	0.562	0.019	-0.089	108	6.7×10^1

^a Data reported in V vs ferrocene (non-aqueous) or V vs SCE (aqueous). ^b Solvent donor numbers in parentheses. ^c ΔE in mV. ^d $\text{K}_c = \exp[16.91(\Delta\text{E})]$, for ΔE in V.

Table 3.5.10 - Redox couples and comproportionation constants as a function of solvent for $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-dicyd})][\text{ClO}_4]_4$.^a

Solvent ^b	$L^{0/-}$	L^{-2-}	E°_{M2}	E°_{M1}	ΔE^c	K_c^d
NM (2.7)	0.825	0.561	-0.103	-0.500	397	5.7×10^6
AN (14.1)	0.699	0.446	-0.138	-0.550	412	9.3×10^6
AC (17.0)	0.597	0.329	-0.218	-0.639	421	1.3×10^7
DMSO (29.8)	--	0.171	-0.315	-0.630	315	2.1×10^5
H ₂ O (18.0)	--	0.575	0.103	-0.025	128	1.5×10^2

^a Data reported in V vs ferrocene (non-aqueous) or V vs SCE (aqueous). ^b Solvent donor numbers in parentheses. ^c ΔE in mV. ^d $K_c = \exp[16.91(\Delta E)]$, for ΔE in V.

Table 3.5.11 - Redox couples and comproportionation constants as a function of solvent for $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cl-dicyd})][\text{ClO}_4]_4$.^a

Solvent ^b	$L^{0/-}$	L^{-2-}	E°_{M2}	E°_{M1}	ΔE^c	K_c^d
NM (2.7)	0.837	0.555	-0.031	-0.398	367	1.6×10^6
AN (14.1)	0.757	0.456	-0.080	-0.441	361	1.3×10^6
AC (17.0)	0.649	0.362	-0.159	-0.514	355	1.0×10^6
DMSO (29.8)	--	0.232	-0.293	-0.524	231	8.1×10^3
H ₂ O (18.0)	--	0.581	0.170	0.025	145	2.8×10^2

^a Data reported in V vs ferrocene (non-aqueous) or V vs SCE (aqueous). ^b Solvent donor numbers in parentheses. ^c ΔE in mV. ^d $K_c = \exp[16.91(\Delta E)]$, for ΔE in V.

Table 3.5.12 - Redox couples and comproportionation constants as a function of solvent for $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cl}_2\text{-dicyd})][\text{ClO}_4]_4$.^a

Solvent ^b	$L^{0/-}$	L^{-2-}	E°_{M2}	E°_{M1}	ΔE^c	K_c^d
NM (2.7)	0.796	0.497	-0.049	-0.397	348	7.7×10^5
AN (14.1)	0.830	0.511	0.001	-0.327	328	3.5×10^5
AC (17.0)	0.665	0.357	-0.144	-0.469	325	3.1×10^5
DMSO (29.8)	--	0.286	-0.254	-0.460	206	3.0×10^3
H ₂ O (18.0)	--	0.405	0.216	0.058	158	4.7×10^2

^a Data reported in V vs ferrocene (non-aqueous) or V vs SCE (aqueous). ^b Solvent donor numbers in parentheses. ^c ΔE in mV. ^d $K_c = \exp[16.91(\Delta E)]$, for ΔE in V.

Figure 3.5.1 - Cyclic voltammogram of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{ClO}_4]_4$ in nitromethane.

Figure 3.5.2 - Cyclic voltammogram of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{ClO}_4]_4$ in acetonitrile.

Figure 3.5.3 - Cyclic voltammogram of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{ClO}_4]_4$ in acetone.

Figure 3.5.4 - Cyclic voltammogram of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{ClO}_4]_4$ in dimethyl sulfoxide.

Figure 3.5.5 - Cyclic voltammogram of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{ClO}_4]_4$ in water.

Figure 3.5.6 - Cyclic voltammogram of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{ClO}_4]_4$ in dimethyl sulfoxide showing the $\text{bipy}^{0/-}$ reduction couple.

Figure 3.5.7 - Cyclic voltammogram of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-dicyd})][\text{ClO}_4]_4$ in nitromethane.

Figure 3.5.8 - Cyclic voltammogram of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-dicyd})][\text{ClO}_4]_4$ in acetonitrile.

Figure 3.5.9 - Cyclic voltammogram of $[\{Ru(NH_3)_3(bipy)\}_2(\mu-dicyd)][ClO_4]_4$ in acetone.

Figure 3.5.10 - Cyclic voltammogram of $[\{Ru(NH_3)_3(bipy)\}_2(\mu-dicyd)][ClO_4]_4$ in dimethyl sulfoxide.

Figure 3.5.11 - Cyclic voltammogram of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-dicyd})][\text{ClO}_4]_4$ in water.

Figure 3.5.12 - Cyclic voltammogram of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cldicyd})][\text{ClO}_4]_4$ in nitromethane.

Figure 3.5.13 - Cyclic voltammogram of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cldicyd})][\text{ClO}_4]_4$ in acetonitrile.

Figure 3.5.14 - Cyclic voltammogram of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cldicyd})][\text{ClO}_4]_4$ in acetone.

Figure 3.5.15 - Cyclic voltammogram of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Clidicyd})][\text{ClO}_4]_4$ in dimethyl sulfoxide.

Figure 3.5.16 - Cyclic voltammogram of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Clidicyd})][\text{ClO}_4]_4$ in water.

Figure 3.5.17 - Cyclic voltammogram of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cl}_2\text{dicyd})][\text{ClO}_4]_4$ in nitromethane.

Figure 3.5.18 - Cyclic voltammogram of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cl}_2\text{dicyd})][\text{ClO}_4]_4$ in acetonitrile.

Figure 3.5.19 - Cyclic voltammogram of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cl}_2\text{dicyd})][\text{ClO}_4]_4$ in acetone.

Figure 3.5.20 - Cyclic voltammogram of $[\{Ru(NH_3)_3(bipy)\}_2(\mu-Cl_2dicyd)][ClO_4]_4$ in dimethyl sulfoxide.

Figure 3.5.21 - Cyclic voltammogram of $[\{Ru(NH_3)_3(bipy)\}_2(\mu-Cl_2dicyd)][ClO_4]_4$ in water.

In general, the metal-centred couples were well separated in non-aqueous solutions, although insufficiently to allow proper measurement of the peak currents using standard methods.⁹⁹⁻¹⁰¹ Peak currents for the L^{-2-} and L^{0-} couples were similarly difficult to resolve. In all cases, however, the metal centred couples (E_{M1}° and E_{M2}°) and the ligand centred couple L^{-2-} had the appearance of unity or near unity $i_{pc}:i_{pa}$ current ratios, and thus of chemical reversibility. Of notable exception are the E_{M1}° couples for $[\{Ru(NH_3)_3(bipy)\}_2(\mu-Cldicyd)][ClO_4]_4$ for which the absolute peak currents were noticeably less than those of the corresponding E_{M2}° and L^{-2-} couples. This effect is most noticeable in nitromethane (figure 3.5.12) but exists in all solvents, and suggests this couple is chemically irreversible.

In water, the metal-centred couples were not separated, overlapping each other so as to appear as either a single broad couple or as a couple with a pronounced shoulder. Because of this, determination of the $E_{1/2}$ values required special treatment, and the discussion of $E_{pa}-E_{pc}$ values in water is thus conducted separately.

Anodic-cathodic peak to peak ($E_{pa}-E_{pc}$) separations for the metal-centred couples E_{M1}° and E_{M2}° (in non-aqueous solvents) and for the ligand centred couple L^{-2-} (in all solvents) for $[\{Ru(NH_3)_3(bipy)\}_2(\mu-dicyd)][ClO_4]_4$ were all ca. 60 mV at a scan rate of 0.100 V/s, and largely invariant as a function of scan rate. This suggests that the couples for the $L = dicyd^{2-}$ complex are electrochemically reversible as well as chemically reversible.

Results for E_{M1}° , E_{M2}° , and L^{-2-} for $[\{Ru(NH_3)_3(bipy)\}_2(\mu-L)][ClO_4]_4$, $L = Me_2dicyd^{2-}$, were also close to electrochemical reversibility, with $E_{pa}-E_{pc}$ values for the

metal-centred couples of ca. 70 mV and variabilities as a function of scan rate of ca. 10 mV over the range 0.050 V/s - 0.500 V/s for all solvents except acetone for which the range was 100 mV. For L^{-2-} the $E_{pa}-E_{pc}$ values were 60 mV at 0.100 V/s in nitromethane and DMSO, 65 mV in acetonitrile, and 80 mV in acetone and water. The value of $E_{pa}-E_{pc}$ for this couple was invariant with scan rate in water, while it increased by ca. 10 mV in nitromethane and acetonitrile over the range of scan rates, by 20 mV in DMSO, and by 100 mV in acetone.

For $L = Cl_2dicyd^{2-}$ the value of $E_{pa}-E_{pc}$ for the metal-centred couples was ca. 75 mV, varying by ca. 75 mV over the range of scan rates. The L^{-2-} couple had $E_{pa}-E_{pc}$ values of ca. 80 mV varying by 80-100 mV in non-aqueous solvents, and 100 mV varying by 100 mV in water. The $L = Cl_2dicyd^{2-}$ couples must thus be characterized as electrochemically irreversible.

Results for the $L = Cl dicyd^{2-}$ were generally the least reversible, with the metal-centred couples having $E_{pa}-E_{pc}$ values of ca. 100 mV varying by 100 mV over the range of scan rates and the L^{-2-} couples having $E_{pa}-E_{pc}$ values of 100 mV in nitromethane and acetonitrile, 85 mV in acetone, 80 mV in DMSO, and 90 mV in water. Variability as a function of scan rate for this couple ranged from 75 mV in nitromethane to well over 100 mV in DMSO and water.

In all cases, the couple L^{0-} tended to appear quite close to the solvent limit, and was often ill-defined and chemically irreversible. In DMSO and aqueous solutions, this couple wasn't seen at all. For $L = Cl dicyd^{2-}$, accurate values of its $E_{1/2}$ were difficult to obtain, and no meaningful analysis of the peak profile was possible. Results for the other

three ligands loosely mirrored their respective trends for the other three couples, with the best results being obtained for the more strongly coupled complexes.

All the peaks were characterized as one-electron events, and this assignment is supported by the measurement of a bipy-centred redox event in the DMSO spectrum of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2\mu\text{-Me}_2\text{dicyd}](\text{ClO}_4)_4$ (figure 3.5.6). This couple had peak currents roughly twice as large as those of the other couples in the spectrum, representing the one electron events occurring at each ruthenium centre. Its value of $(E_{\text{pa}} - E_{\text{pc}})$ varied by ca. 12 mV over the range of scan rates 0.050 - 0.500 V/s, and had a value of 73 mV at 0.100 V/s.

The E° values of the various couples were taken as the average of E_{pa} and E_{pc} for all couples in which the peaks were fully resolved. This method actually yields $E_{1/2}$ values, which are related to E° via eq. 3.5.1.^{101,102}

$$E^\circ = E_{1/2} - \left(\frac{RT}{nF} \right) \ln \left[\left(\frac{D_R}{D_O} \right)^{1/2} \left(\frac{f_O}{f_R} \right) \right] \quad (3.5.1)$$

As long as all the species associated with the couples remain in solution, their diffusion and activity coefficients (D and f values respectively, where the subscripts refer to the Oxidized and R-educed species of each couple) tend to be similar, and the second term negligible.¹⁰¹ For a 10% difference in D_R and D_O , the second term has a value of approximately 3 mV, for example.¹⁰² Thus it is safe to take $E^\circ = E_{1/2}$ within the reading error of the spectra.

In the case of aqueous spectra, a single broad peak was seen, instead of two individual peaks. As the systems became more strongly coupled, definite shoulders were

seen, but in no case was the separation sufficient to allow for direct measurement of either E° value. Instead, the overall ($E_{pa} - E_{pc}$) value was measured, between the anodic peak of E°_{M2} and the cathodic peak of E°_{M1} , and the actual ΔE value determined graphically. The technique used was developed by Polcyn and Shain¹⁰³ for polarographic techniques, and modified for use with cyclic voltammetry by Richardson and Taube¹⁰² who expanded the limited data of Myers and Shain¹⁰⁴ with data for a number of pentaammine complexes. This expanded data set, covering ΔE values up to 200 mV (whereas the Myers and Shain data only covered ΔE values up to 50 mV) was plotted by Aquino⁹⁰ as ΔE vs. ($E_{pa} - E_{pc}$) plots from which the results herein presented were obtained.

3.6 Spectroelectrochemistry

Spectroelectrochemical study of the twelve complexes was performed selectively in four solvents: nitromethane, acetonitrile, acetone, and dimethyl sulfoxide. Results for the complexes [$\{Ru(NH_3)_5\}_2(\mu-L)]PF_6)_4$ and [$\{Ru(NH_3)_4(py)\}_2(\mu-L)]PF_6)_4$ ($L = Me_2dicyd^{2-}$, $dicyd^{2-}$, Cl_2dicyd^{2-} , and Cl_4dicyd^{2-}) in acetonitrile are the work of Dr. M. L. Naklicki and Dr. A. R. Rezvani, respectively, and have been previously published.^{48,50,52,68} These data are presented along with new data in tables 3.6.1 and 3.6.2. New studies on the complex [$\{Ru(NH_3)_5\}_2(\mu-L)]PF_6)_4$, $L = dicyd^{2-}$ were performed in nitromethane, acetonitrile, acetone, and dimethyl sulfoxide. The $L = Me_2dicyd^{2-}$ complex was studied in acetone and dimethyl sulfoxide, and the $L = Cl_2dicyd^{2-}$ complex was studied in acetone.

Selection of solvents was not made arbitrarily; experiments were done on those complexes sufficiently soluble in a given solvent to afford a suitably intense absorbance band for study. All studies were carried out using the OTTLE cell described in section 2.6.6, with the acetonitrile experiment on $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-dicyd})][\text{PF}_6]_4$ having been carried out to compare the OTTLE cell's behaviour to that of the H-cell.

Additional studies of the four complexes $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-L})][\text{PF}_6]_4$ ($\text{L} = \text{Me}_2\text{dicyd}^{2-}$, dicyd^{2-} , $\text{Cl}_2\text{dicyd}^{2-}$, and $\text{Cl}_4\text{dicyd}^{2-}$) were performed by Dr. V. V. Kondratiev in nitromethane and dimethyl sulfoxide using the H-cell described in section 2.6.6. No attempt was made to study these systems in acetone.

Lastly, the complexes $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-L})][\text{ClO}_4]_4$ ($\text{L} = \text{Me}_2\text{dicyd}^{2-}$, dicyd^{2-} , $\text{Cl}_4\text{dicyd}^{2-}$, and $\text{Cl}_2\text{dicyd}^{2-}$) were all studied in acetonitrile with the $\text{L} = \text{Cl}_2\text{dicyd}^{2-}$ complex being further studied in nitromethane, acetone, and dimethyl sulfoxide, and the $\text{L} = \text{dicyd}^{2-}$ complex further studied in dimethyl sulfoxide. All studies were effected using the OTTLE cell described in section 2.6.6 and the data placed in table 3.6.3.

The technique of spectroelectrochemistry couples electronic absorption spectroscopy with electrochemistry. Thus, considering the complexes of this study, the Ru(III)-Ru(III) complex may be electrochemically reduced in a stepwise fashion and the electronic absorption spectrum monitored at each step once the system comes to equilibrium at a given potential.

In all cases, reduction of the Ru(III)-Ru(III) complex to the Ru(III)-Ru(II) complex was accompanied by a decrease in the intensity of the LMCT band and the appearance of a low energy band (or shoulder in the spectra of the more strongly coupled

systems) which increased in intensity as the LMCT band decreased. This low energy shoulder was assigned as a metal-metal charge transfer (MMCT) band (also commonly called an intervalence transition (IT) band since the charge transfer occurs between metals of differing oxidation states).^{48,52,53} In acetonitrile, the reduction of the pentaammines to the Ru(III)-Ru(II) state was reversible, with the Ru(III)-Ru(III) spectrum being regained upon oxidation.^{48,52} Reversibility was greatest in acetonitrile, with the degree of reversibility in other solvents seemingly following the general trend of coupling, with the more strongly coupled systems exhibiting more reversibility. This is likely due to the fact that, with diminishing separation of the redox couples, some Ru(II)-Ru(II) complex is generated upon reduction. This latter complex is expected to be labile with respect to ligand substitution and hence results in irreversible behaviour. Attempts to purposefully generate a pentaamine Ru(II)-Ru(II) complex were uniformly unsuccessful.

The assignment of the low energy band as an IT band is supported by work on the triamine complexes $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-L})][\text{ClO}_4]_4$ where nearly reversible generation of the Ru(II)-Ru(II) complex was possible. Reduction of the Ru(III)-Ru(II) complex caused the loss of the LMCT-IT isosbestic points, and a decrease in the intensity of the IT band to vanishing (or very nearly vanishing). This is consistent with expectations for a Ru(II)-Ru(II) complex. Upon re-oxidation, the proper band shape of the Ru(III)-Ru(III) complex is, in all cases, regenerated, although the intensity tended to return to only ca. 95% of its initial value. This latter result was anticipated from the experimental observation of residual currents at highly reducing potentials. Such currents are

indications of decomposition - of the system not coming to equilibrium - and were prevalent in the spectroelectrochemical reductions of the pentaammine complexes.

In all examples for the twelve complexes under consideration, the IT band overlapped the corresponding LMCT band to some extent. Analysis of these systems via the CNS and especially the Hush models requires specific parameterization of the IT bands. The experimental IT bands thus had to be deconvoluted from the band envelope of the mixed-valence complex. This was accomplished using the same peak-fitting protocol discussed in section 3.4. For each IT band, the corresponding LMCT band for the Ru(III)-Ru(III) complex was modelled by fitting it with a number of gaussian bands. Assuming that the profiles of the LMCT transitions were largely unaffected by reduction, the ν_{max} and $\Delta\nu_{\text{vib}}$ values and relative intensities of the gaussian fitting bands were used, along with a single additional gaussian band to represent the IT band, to fit the band profiles of the mixed-valence complexes. This technique allowed the low energy side of the mixed-valence complexes to be well modelled,^{48,52} although the fitting of the high-energy side was poorer, and became progressively worse as the modelled systems became more strongly coupled. Thus, while this technique worked exceptionally well for the relatively more weakly coupled pentaammines, the discrepancies for fitting the high energy tail of the band became more prominent for the tetraammines and triammines. This problem can be rationalized by realizing that in the pentaammines an isosbestic point exists at ca. 500 - 600 nm (see figures 3.6.1 - 3.6.8) whereas in the triammines the analogous isosbestic point is >700 nm (see figures 3.6.17 - 3.6.24). That for the more strongly coupled complexes the "high-energy tail" begins to gain intensity at a lower energy may

explain the reduced amenity of curve-fitting the spectrum of the mixed-valence complex. Simply, the high energy tail may contain oscillator strength from the band occurring at ca. 500 nm (see any of figures 3.6.1 - 3.6.24). The fitting of the IT bands, thus, is not expected to be overly perturbed by difficulties in fitting the high energy tail of the band envelope. Such errors are not expected to be any larger than those associated with fitting the low energy side of the band envelope when the IT band cannot be fully sampled due to solvent cutoff. The reader is recommended to (52) in which are published examples of the multiple-gaussian fits of the band envelopes of Ru(III)-Ru(III) and Ru(III)-Ru(II) complexes.

Table 3.6.1 - Spectroelectrochemical IT data for $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-L})][\text{PF}_6]_4$.^a

L	Solvent^b	ϵ_{max}	ν_{max}	$\nu_{1/2}$
$\text{Me}_2\text{dicyd}^{2-}$	AN (14.1)	1.98×10^4	7100	2430
$\text{Me}_2\text{dicyd}^{2-}$	AC (17.0)	1.64×10^4	6930	2350
$\text{Me}_2\text{dicyd}^{2-}$	DMSO (29.8)	9.26×10^3	6890	3760
dicyd^{2-}	NM (2.7)	2.06×10^4	6980	2430
dicyd^{2-}	AN (14.1)	2.00×10^4	6890	2760
dicyd^{2-}	AC (17.0)	1.62×10^4	6750	2760
dicyd^{2-}	DMSO (29.8)	7.59×10^3	7500	4250
$\text{Cl}_2\text{dicyd}^{2-}$	AN (14.1)	1.58×10^4	6910	3390
$\text{Cl}_2\text{dicyd}^{2-}$	AC (17.0)	1.06×10^4	7080	3790
$\text{Cl}_2\text{dicyd}^{2-}$	DMSO (29.8)	5.88×10^3	7950	5720
$\text{Cl}_4\text{dicyd}^{2-}$	AN (14.1)	7.78×10^3	7320	3890

^a Data in units of cm^{-1} except ϵ_{max} which has units of $\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$. ^b Solvent donor number in parentheses.

Table 3.6.2 - Spectroelectrochemical IT data for $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-L})][\text{PF}_6]_4$.^a

L	Solvent ^b	ϵ_{max}	ν_{max}	$\nu_{1/2}$
$\text{Me}_2\text{dicyd}^{2-}$	NM (2.7)	1.69×10^4	7390	2200
$\text{Me}_2\text{dicyd}^{2-}$	AN (14.1)	2.14×10^4	7480	1920
$\text{Me}_2\text{dicyd}^{2-}$	DMSO (29.8)	1.85×10^4	6540	2380
dicyd^{2-}	NM (2.7)	1.57×10^4	7340	2000
dicyd^{2-}	AN (14.1)	2.41×10^4	7230	2090
dicyd^{2-}	DMSO (29.8)	2.24×10^4	6460	2830
$\text{Cl}_2\text{dicyd}^{2-}$	NM (2.7)	2.45×10^4	6580	2240
$\text{Cl}_2\text{dicyd}^{2-}$	AN (14.1)	2.13×10^4	6690	2700
$\text{Cl}_2\text{dicyd}^{2-}$	DMSO (29.8)	1.00×10^4	6910	3750
$\text{Cl}_4\text{dicyd}^{2-}$	NM (2.7)	2.13×10^4	6260	2980
$\text{Cl}_4\text{dicyd}^{2-}$	AN (14.1)	1.70×10^4	6580	3350
$\text{Cl}_4\text{dicyd}^{2-}$	DMSO (29.8)	6.09×10^3	7670	4530

^a Data in units of cm^{-1} except ϵ_{max} which has units of $\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$. ^b Solvent donor number in parentheses.

Table 3.6.3 - Spectroelectrochemical IT data for $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-L})][\text{ClO}_4]_4$.^a

L	Solvent ^b	ϵ_{max}	ν_{max}	$\nu_{1/2}$
$\text{Me}_2\text{dicyd}^{2-}$	AN (14.1)	1.18×10^4	7970	1760
dicyd^{2-}	AN (14.1)	1.82×10^4	7550	1700
dicyd^{2-}	DMSO (29.8)	2.26×10^4	6670	2340
$\text{Cl}_2\text{dicyd}^{2-}$	AN (14.1)	1.20×10^4	7230	2160
$\text{Cl}_2\text{dicyd}^{2-}$	NM (2.7)	2.40×10^4	7000	2290
$\text{Cl}_2\text{dicyd}^{2-}$	AN (14.1)	2.80×10^4	6910	2440
$\text{Cl}_2\text{dicyd}^{2-}$	AC (17.0)	3.11×10^4	6780	2140
$\text{Cl}_2\text{dicyd}^{2-}$	DMSO (29.8)	2.53×10^4	6400	3440

^a Data in units of cm^{-1} except ϵ_{max} which has units of $\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$. ^b Solvent donor number in parentheses.

Figure 3.6.1 - Spectroelectrochemical data for $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Me}_2\text{dicyd})][\text{PF}_6]_4$ in acetone showing the reduction of the Ru(III)-Ru(III) complex to the mixed-valent Ru(III)-Ru(II) complex.

Figure 3.6.2 - Spectroelectrochemical data for $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Me}_2\text{dicyd})][\text{PF}_6]_4$ in dimethyl sulfoxide showing the reduction of the Ru(III)-Ru(III) complex to the mixed-valent Ru(III)-Ru(II) complex.

Figure 3.6.3 - Spectroelectrochemical data for $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-dicyd})][\text{PF}_6]_4$ in nitromethane showing the reduction of the Ru(III)-Ru(III) complex to the mixed-valent Ru(III)-Ru(II) complex.

Figure 3.6.4 - Spectroelectrochemical data for $[\{Ru(NH_3)_5\}_2(\mu\text{-dicyd})][PF_6]_4$ in acetonitrile showing the reduction of the Ru(III)-Ru(III) complex to the mixed-valent Ru(III)-Ru(II) complex.

Figure 3.6.5 - Spectroelectrochemical data for $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-dicyd})][\text{PF}_6]_4$ in acetone showing the reduction of the Ru(III)-Ru(III) complex to the mixed-valent Ru(III)-Ru(II) complex.

Figure 3.6.6 - Spectroelectrochemical data for $[\{Ru(NH_3)_5\}_2(\mu-dicyd)][PF_6]_4$ in dimethyl sulfoxide showing the reduction of the $Ru(III)-Ru(III)$ complex to the mixed-valent $Ru(III)-Ru(II)$ complex.

Figure 3.6.7 - Spectroelectrochemical data for $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Cl}_2\text{dicyd})][\text{PF}_6]_4$ in acetone showing the reduction of the Ru(III)-Ru(III) complex to the mixed-valent Ru(III)-Ru(II) complex.

Figure 3.6.8 - Spectroelectrochemical data for $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Cl}_2\text{dicyd})][\text{PF}_6]_4$ in dimethyl sulfoxide showing the reduction of the Ru(III)-Ru(III) complex to the mixed-valent Ru(III)-Ru(II) complex.

Figure 3.6.9 - Spectroelectrochemical data for $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{PF}_6]_4$ in nitromethane showing the spectra of the Ru(III)-Ru(III) complex and the mixed-valent Ru(III)-Ru(II) complex.

Figure 3.6.10 - Spectroelectrochemical data for $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{PF}_6]_4$ in dimethyl sulfoxide showing the spectra of the Ru(III)-Ru(III) complex and the mixed-valent Ru(III)-Ru(II) complex.

Figure 3.6.11 - Spectroelectrochemical data for $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-dicyd})][\text{PF}_6]_4$ in nitromethane showing the spectra of the Ru(III)-Ru(III) complex and the mixed-valent Ru(III)-Ru(II) complex.

Figure 3.6.12 - Spectroelectrochemical data for $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-dicyd})][\text{PF}_6]_4$ in dimethyl sulfoxide showing the spectra of the Ru(III)-Ru(III) complex and the mixed-valent Ru(III)-Ru(II) complex.

Figure 3.6.13 - Spectroelectrochemical data for $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-Cl}_2\text{dicyd})][\text{PF}_6]_4$ in nitromethane showing the reduction of the Ru(III)-Ru(III) complex to the mixed-valent Ru(III)-Ru(II) complex.

Figure 3.6.14 - Spectroelectrochemical data for $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-Cl}_2\text{dicyd})][\text{PF}_6]_4$ in dimethyl sulfoxide showing the spectra of the Ru(III)-Ru(III) complex and the mixed-valent Ru(III)-Ru(II) complex.

Figure 3.6.15 - Spectroelectrochemical data for $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-Cl}_4\text{dicyd})][\text{PF}_6]_4$ in nitromethane showing the spectra of the Ru(III)-Ru(III) complex and the mixed-valent Ru(III)-Ru(II) complex.

Figure 3.6.16 - Spectroelectrochemical data for $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-Cl}_4\text{dicyd})][\text{PF}_6]_4$ in dimethyl sulfoxide showing the spectra of the Ru(III)-Ru(III) complex and the mixed-valent Ru(III)-Ru(II) complex.

Figure 3.6.17 - Spectroelectrochemical data for $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{ClO}_4]_4$ in acetonitrile showing the reduction of the Ru(III)-Ru(III) complex to the mixed-valent Ru(III)-Ru(II) complex and the spectrum of the fully reduced Ru(II)-Ru(II) complex.

Figure 3.6.18 - Spectroelectrochemical data for $[\{\text{Ru}(\text{NH}_3)_5(\text{bipy})\}_2(\mu\text{-dicyd})][\text{ClO}_4]_4$ in acetonitrile showing the reduction of the Ru(III)-Ru(III) complex to the mixed-valent Ru(III)-Ru(II) complex.

Figure 3.6.19 - Spectroelectrochemical data for $[\{\text{Ru}(\text{NH}_3)_2(\text{bipy})\}_2(\mu\text{-dicyd})][\text{ClO}_4]_4$ in dimethyl sulfoxide showing the reduction of the Ru(III)-Ru(III) complex to the mixed-valent Ru(III)-Ru(II) complex and the spectrum of the fully reduced Ru(II)-Ru(II) complex.

Figure 3.6.20 - Spectroelectrochemical data for $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cldicyd})][\text{ClO}_4]_4$ in acetonitrile showing the reduction of the Ru(III)-Ru(III) complex to the mixed-valent Ru(III)-Ru(II) complex and the spectrum of the fully reduced Ru(II)-Ru(II) complex.

Figure 3.6.21 - Spectroelectrochemical data for $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cl}_2\text{dicyd})][\text{ClO}_4]_4$ in nitromethane showing the reduction of the Ru(III)-Ru(III) complex to the mixed-valent Ru(III)-Ru(II) complex and the spectrum of the fully reduced Ru(II)-Ru(II) complex.

Figure 3.6.22 - Spectroelectrochemical data for $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cl}_2\text{dicyd})][\text{ClO}_4]_4$ in acetonitrile showing the reduction of the Ru(III)-Ru(III) complex to the mixed-valent Ru(III)-Ru(II) complex and the spectrum of the fully reduced Ru(II)-Ru(II) complex.

Figure 3.6.23 - Spectroelectrochemical data for $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cl}_2\text{dicyd})][\text{ClO}_4]_4$ in acetone showing the reduction of the Ru(III)-Ru(III) complex to the mixed-valent Ru(III)-Ru(II) complex and the spectrum of the fully reduced Ru(II)-Ru(II) complex.

Figure 3.6.24 - Spectroelectrochemical data for $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cl}_2\text{dicyd})][\text{ClO}_4]_4$ in dimethyl sulfoxide showing the reduction of the Ru(III)-Ru(III) complex to the mixed-valent Ru(III)-Ru(II) complex and the spectrum of the fully reduced Ru(II)-Ru(II) complex.

Chapter 4

Discussion

Previous work by this group has examined certain aspects of outer- and inner-sphere perturbations to metal-metal coupling in dinuclear complexes. Complexes incorporating bridging ligands of the family dicyd²⁻, 1,4-dicyanamidobenzene dianion, allowed for the study of bridging-ligand centred inner-sphere perturbations by altering the substituents on the bridging ligand's phenyl ring. Thus, four main ligands of the dicyanamidobenzene family, Me₂dicyd²⁻, dicyd²⁻, Cl₂dicyd²⁻, and Cl₄dicyd²⁻ have been incorporated in dinuclear ruthenium complexes of the form [$\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-L})$][PF₆]₄^{42,48,49,52,53,55} and [$\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-L})$][PF₆]₄^{50,68} where L represents one of the four dicyd bridging ligands, to study the effects of ligand-centred inner-sphere perturbations. Outer-sphere (solvent) perturbations to the metal-metal coupling of the pentaammine complexes have also been studied.^{42,48,50,52,53,68}

With the successful synthesis of a third family of complexes, the triammine complexes [$\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-L})$][ClO₄]₄, the last of the electronic perturbations - inner-sphere based on metal spectator ligands - can be properly addressed. Unfortunately, attempts to synthesize [$\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cl}_4\text{dicyd})$][ClO₄]₄ proved unsuccessful, and thus only the complexes of Me₂dicyd²⁻, dicyd²⁻, and Cl₂dicyd²⁻ may be compared for the three types of metal coordination spheres. Four complexes of the type [$\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-L})$][ClO₄]₄ were, however, synthesized: L = Me₂dicyd²⁻, dicyd²⁻,

Cldicyd²⁻, and Cl₂dicyd²⁻. The “fourth”, [$\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cldicyd})\][ClO₄]₄, was intended to provide additional support of outer- and inner-sphere perturbation trends within the triammines, and has no analogues for the other two metal coordination spheres.$

The data under consideration herein are, thus, for the four new triammine complexes, for the pentaammine complexes (most of which, with the exception of analysis via the CNS model and spectroelectrochemistry in solvents other than acetonitrile, have been previously published in a number of venues), and for the tetraammines. Although certain of the data for the tetraammines have been previously published, a significant amount of new spectral, electrochemical, and spectroelectrochemical data is now available (see results sections 3.4, 3.5, and 3.6 for details).

The emphasis of this chapter will be on the electronic absorption, cyclic voltammetry, and spectroelectrochemical results for the three families of complexes, as these techniques give the greatest insight into metal-metal coupling and allow for quantification. In conjunction with the Hush and CNS models of metal-metal coupling, these three techniques provide insight into the nature of the complexes' mixed-valence (*i.e.* Ru(III)-Ru(II) states). ¹H NMR results probing the degree of coupling in the Ru(III)-Ru(III) state by sampling paramagnetism (*i.e.* Evans method experiments) will be discussed although the technique was not explicitly dealt with elsewhere in the thesis. This is because only two Evans experiments were run on the triammines, and the majority of the data (*i.e.* that for the pentaammines and tetraammines) have thus already been published.^{48,50,68,78}

4.1 Characterization of the Triammine Complexes

Elemental analyses, IR spectroscopy, NMR spectrometry, and X-ray crystallography were performed upon the four complexes of the triammine family, $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-L})][\text{ClO}_4]_4$, $\text{L} = \text{Me}_2\text{dicyd}^{2-}$, dicyd^{2-} , $\text{Cl}\text{dicyd}^{2-}$, and $\text{Cl}_2\text{dicyd}^{2-}$, to fully characterize the systems. Solvent of recrystallization invoked to fit the elemental analyses have been found in the NMR spectra of the corresponding complexes with the exception of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cl}\text{dicyd})][\text{ClO}_4]_4$ upon which NMR was not performed. The two Evans method experiments (run in acetonitrile) suggest very strong antiferromagnetic coupling (diamagnetic behaviour) for the $\text{L} = \text{dicyd}^{2-}$ complex and only slight paramagnetism for the $\text{L} = \text{Cl}_2\text{dicyd}^{2-}$ complex. By extension, the acetonitrile result for the $\text{L} = \text{dicyd}^{2-}$ complex implies diamagnetism in nitromethane, and also for the $\text{L} = \text{Me}_2\text{dicyd}^{2-}$ complex in both acetonitrile and nitromethane. The significance of the various chemical shifts, as they do not pertain to the main thrust of this thesis, has been discussed in the appropriate results section, and will not be covered further. It is believed that the nitromethane 1-D spectrum of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{ClO}_4]_4$, showing eight distinct resonances for the hydrogens of bipyridine bound to Ru(III) yet effectively in a diamagnetic environment, is unique in the literature.

A crystal structure of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-dicyd})][\text{ClO}_4]_4$, the only complex of the four whose solvent of recrystallization was water, was performed. Comparison with the crystal structure of the analogous pentaammine complex, $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-dicyd})][\text{OTf}]_4$, in which the NCN moieties of the ligand were similarly in an *anti*

conformation, revealed quite similar structures, with the Ru(1)-Ru(2) through-space separation being 13.1 Å in both systems. Although the crystal structure of the related tetraammine complex, $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-dicyd})][\text{PF}_6]_4$, showed the NCN moieties to be in a *syn* arrangement, modelling upon the ligand suggests a low barrier to rotation.⁷⁸ Thus, for the purposes of all theoretical modelling reported hereafter, it has been assumed that in solution the through-space Ru(1)-Ru(2) separation in all three families of complexes is 13 Å.

When dealing with very strongly coupled systems, questions arise as to the formal oxidation states of the ruthenium centres.^{13,15} Of particular significance, however, is the oxidation state of the ligand.¹⁷ If the ligand is behaving non-innocently, it may significantly alter the behaviour of the system. Kaim, for example, noted paramagnetism in a tetranuclear TCNE complex formally containing only Ru(II) centres and the TCNE ligand due to partial oxidation of the metal centres.¹⁹ The oxidation states of both the metal centres and the ligand may be deduced via the NMR spectrometry and IR spectroscopy of the complexes in question. In the very weakly coupled complex $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Cl}_4\text{dicyd})]^{4+}$ there is not expected to be any significant covalency in the bonding, and this is supported by the fact that the complex's coupling and IT band properties may be predicted from the Hush model (see section 4.5). The solution magnetic moment of this complex in water ($1.86 \mu_B/\text{Ru}^{\text{III}}$ obtained via the Evans method) approaches the experimental range (1.9 - 2.1 μ_B) for a number of low spin Ru(III) complexes,¹⁰⁵ and strongly suggests that this complex is best viewed as containing a dianion ligand and Ru(III) centres. Further, none of the NMR spectra indicates

asymmetry associated with two separate valencies of metal. The response of metal-metal coupling in the pentaammine complexes to inner- and outer-sphere perturbations is consistent with hole-transfer superexchange,⁶¹ and this in turn implies that the formal oxidation states of metal and ligand are not changing within the series of complexes and conditions. (Superexchange in a complex containing Ru(II) bound to the oxidized, dicyanoquinonediimide, DCNQI, form of the ligand would typically occur via the electron-transfer pathway). Further in support of the ligand's oxidation state are the cyanamide stretching frequencies, ν_{NCN} , which occur over the range 2085 - 2110 cm^{-1} for the four complexes of each family, and are consistent with the dianion form of the ligand.⁴⁸ The related vibration for the fully oxidized form of the ligand occurs at 2170 cm^{-1} ,¹⁰⁶ much closer to nitrile-like ν_{NCN} of the protonated ligands (see table 3.1.1).

Response of metal-metal coupling to metal centred inner-sphere perturbations, increasing metal-metal coupling as the metals' πd orbitals are stabilized, is similarly in accordance with a hole-transfer pathway and at odds with an electron-transfer pathway. Thus the behaviour of all three families of complexes is consistent with the presence of Ru(III) centres and a dianion bridging ligand. The apparent diamagnetism of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-dicyd})][\text{ClO}_4]_4$ and $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{ClO}_4]_4$ in nitromethane and acetonitrile can then be said to be indicative of very strong antiferromagnetic coupling in these complexes. Use of "apparent" to describe the diamagnetism is necessary since the Evans method experiment only shows the absence of paramagnetism to a certain threshold, and not the presence of diamagnetism. That the complexes are diamagnetic, however, is supported by their 1-D and 2-D NMR spectra.

4.2 Electronic Absorption Spectroscopy

Electronic absorption spectroscopy provides insights into the nature of metal-metal coupling and metal-ligand interactions through the response of the electronic absorption spectra to outer- and inner-sphere electronic perturbations. Particularly important are the dramatic solvation effects which arise from specific (non-continuum) solvation (see section 1.2). The nature of solvated ammine complexes should be discussed in greater detail to aid in understanding why such dramatic effects occur. Meyer has studied complexes of the type $[(\text{bipy})_2\text{ClOs}(\text{L})\text{Ru}(\text{NH}_3)_5][\text{PF}_6]_4$, where the bridging ligand L is either 4,4'-bipyridine or pyrazine.¹⁰⁷ Preferential solvation of the ammines at the ruthenium centre was sufficient to induce electron transfer in the mixed-valence complex such that the Os(III)-Ru(II) complex which exists in weakly donating solvents becomes the Os(II)-Ru(III) complex in more strongly donating solvents.^{30,31} The cause of such dramatic solvation effects is the preferential solvation of the ammines,²⁹ a schematic representation of the mechanism, as proposed by Meyer,²⁵ is presented in figure 4.2.1.

Figure 4.2.1 - Schematic representation of the donor-acceptor interaction between coordinated ammines and solvent.

This has the effect of stabilizing the Ru(III) oxidation state and providing a solvent barrier to electron transfer from Os(II).^{30,31} In the complexes of our study there will always be a π symmetry d-orbital on ruthenium which can accept electron density from the N-H σ -bond as a result of solvent-amine donor-acceptor interactions.

Figure 4.2.2 provides a simple M.O. diagram for an LMCT transition in a Ru(III)-Ru(III) complex bridged by a π -donor ligand like dicyd²⁻.

Figure 4.2.2 - Qualitative M.O. diagram for the LMCT transition (shown by arrow) in a dinuclear Ru(III)-Ru(III) complex bridged by a ligand with a high energy π -HOMO (A). Decreasing the π -HOMO to π d energy gap (B) decreases E_{LMCT} , and increases the interaction between the metal and ligand orbitals. C_{2h} symmetry has been assumed, as it is appropriate for the complexes of this study.

One can see that as the metal $d\pi$ orbitals are stabilized, or the ligand π -HOMO destabilized, a greater energetic matching of these orbitals will ensue. This will lower the LMCT transition energy (shown by the arrows in figure 4.2.2) and allow for a greater interaction between the metal and ligand orbitals which would be expected to increase the transition's oscillator strength. For a given complex, the perturbation between A and B in figure 4.2.2 (*i.e.* stabilization of the metal π d orbitals) can be effected by solvent. As

electron density on the metal centre is increased by interactions with solvent, the energy of the $d\pi$ orbitals is increased. (The Ru(III) becomes more like a Ru(II), see figure 1.2.1). Thus, the less donating the solvent, the greater the expected oscillator strength. (Here, as was mentioned in section 1.2, the ability of a solvent to donate electron density will be given by its Gutmann donor number (D.N.)). Thus, the trend $f_{\text{NM}} > f_{\text{AN}} > f_{\text{AC}} > f_{\text{DMSO}}$ is expected for the LMCT oscillator strength. Since oscillator strength is a function of molar absorptivity (see eq 1.4.9), the same solvent trend is expected for ϵ_{max} as for f . The trend in E_{LMCT} is expected to be opposite that for either f or ϵ_{max} .

This is exactly what is seen in the results for the pentaammine complexes, relatively speaking the most weakly coupled herein being studied. Considering the spectral data for non-aqueous solvents (see tables 3.4.1 - 3.4.4), the oscillator strength and molar absorptivity for each complex is highest in nitromethane (lowest donor number) and lowest in DMSO (highest donor number).

Further, if the trend between ligands is considered, the oscillator strength in any given solvent is highest for $L = \text{Me}_2\text{dicyd}^{2-}$ and lowest for $L = \text{Cl}_4\text{dicyd}^{2-}$. In terms of the M.O. diagram given in figure 4.2.2, this ligand centred perturbation may be understood as the stabilization of the π -HOMO by removing electron donating substituents (the methyl groups) and replacing them with electron withdrawing substituents (the chlorides). This causes a decrease in the energetic matching of the metal and ligand orbitals and the energy of the LMCT transition, E_{LMCT} , is thus expected to follow the trend $\text{Me}_2\text{dicyd}^{2-} < \text{dicyd}^{2-} < \text{Cl}_2\text{dicyd}^{2-} < \text{Cl}_4\text{dicyd}^{2-}$. The trends in oscillator strength and molar absorptivity are expected, again, to be opposite that of E_{LMCT} . The results for the variation of ϵ_{max} as a

function of ligand-centred perturbations are presented graphically in figure 4.2.4 in acetonitrile.

The sole exception to the expected trends as a function of ligand-centred perturbations is that E_{LMCT} for $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Me}_2\text{dicyd})][\text{PF}_6]_4$ in nitromethane, $E_{\text{LMCT}}(\text{NM})$, is slightly higher than $E_{\text{LMCT}}(\text{AN})$ (9080 cm^{-1} vs 8920 cm^{-1}) and than $E_{\text{LMCT}}(\text{NM})$ for $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-dicyd})][\text{PF}_6]_4$ (9030 cm^{-1}). This seemingly unexpected result can be attributed to increasing covalency of the ruthenium-cyanamide bond in $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Me}_2\text{dicyd})][\text{PF}_6]_4$. The M.O. diagrams corresponding to this effect are given in figure 4.2.3.

Figure 4.2.3 - Qualitative M.O. diagram for the LMCT transition (shown by arrow) in a dinuclear Ru(III)-Ru(III) complex bridged by a ligand with a high energy π -HOMO in C_{2h} symmetry (A). At some threshold, decreasing the energy gap between the π -HOMO and the π^* orbitals (B) causes an increase in E_{LMCT} due to increasing covalency of the metal-bridge bond.

In figure 4.2.3 covalency is increased upon going from A to B. When the bonding in the complex is purely (or predominantly) ionic, decreasing the energy gap between metal and ligand orbitals increases their interaction. At some threshold, however, significant overlap (covalency) will manifest itself in the metal-ligand bonding. Henceforth

from that point, decreasing the energy gap between the metal and ligand orbitals will increase their overlap. This will result in increased splitting of the resultant bonding and antibonding orbitals (see figure 4.2.3, transition from A to B) and thus an increase in E_{LMCT} .

Figure 4.2.4 - Electronic absorption spectra of $[\{Ru(NH_3)_5\}_2(\mu-L)][PF_6]_4$ in acetonitrile as a function of ligand. Spectra were obtained using the H-cell (for $L = Cl_n dicyd^{2-}$) and OTTLE cell during spectroelectrochemistry as described in section 2.6.6. The sharp peak at ca. 1850 nm^{-1} is due to a large solvent background absorption.

The analogous plot to 4.2.4, spectra of $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-dicyd})][\text{PF}_6]_4$ as a function of solvent, is given in the results section as figure 3.4.1 and illustrates the dramatic solvent dependence of the molar absorptivities (and oscillator strengths) of these systems.

Perturbation of the metal πd orbitals, discussed for the pentaammines in terms of solvation, can also be effected via the metal's spectator ligands. Upon substituting a strongly σ -donating ammine with a pyridine moiety - both a weaker σ -donor and potentially a π -acid, the metal πd orbital energy is lowered, decreasing the energy gap between itself and the ligand π -HOMO (see figure 4.2.2). In the absence of covalency effects, this has the same effect as the analogous solvent perturbations, lowering E_{LMCT} and increasing oscillator strengths. Such a perturbation, however, shouldn't affect the trends due to the ligand-centred and solvent perturbations, and should simply cause f to be larger (and E_{LMCT} smaller) for a given tetraammine complex in a given solvent relative to the analogous pentaammine complex.

Examination of the data in tables 3.4.5 - 3.4.8 gives a different story, however. The expected trend in E_{LMCT} - lowest in nitromethane and highest in DMSO - exists only for $\text{L} = \text{Cl}_2\text{dicyd}^{2-}$ and $\text{Cl}_4\text{dicyd}^{2-}$. For $\text{L} = \text{Me}_2\text{dicyd}^{2-}$ and dicyd^{2-} , the trend is reversed, with E_{LMCT} being lowest in DMSO and highest in nitromethane! This trend of increasing LMCT energy with decreasing πd - π -HOMO energy gap is attributed to increasing covalency of the Ru-NCN bond (according to figure 4.2.3). Similarly, the trends in ϵ_{max} for $\text{Cl}_2\text{dicyd}^{2-}$ and $\text{Cl}_4\text{dicyd}^{2-}$ are those expected in the absence of significant covalency - highest extinction coefficient in nitromethane, lowest in DMSO. For both $\text{Me}_2\text{dicyd}^{2-}$ and

dicyd²⁻, however, $\epsilon_{\max}$ is slightly higher in acetonitrile than in nitromethane, though significantly lower in DMSO than in either other solvent. Interestingly, the oscillator strength trend is, for all four ligands, exactly that anticipated without considering covalency effects. Thus, for each ligand, f is highest in nitromethane and lowest in DMSO. This effect indicates the importance of bearing in mind that oscillator strength is a function (see eq 1.4.9) of both molar absorptivity and bandwidth.

In terms of trends as a function of ligand, the oscillator strength and extinction coefficient trends follow expectation, both quantities being, in any given solvent, highest for $L = \text{Me}_2\text{dicyd}^{2-}$, and lowest for $L = \text{Cl}_4\text{dicyd}^{2-}$. Here again, however, the trends in E_{LMCT} are muddled. Only in DMSO is the expected trend (lowest for $L = \text{Me}_2\text{dicyd}^{2-}$, highest for $L = \text{Cl}_4\text{dicyd}^{2-}$) even approximately present. (In fact, for this solvent $E_{\text{LMCT}}(\text{Me}_2\text{dicyd}^{2-})$ is equal to $E_{\text{LMCT}}(\text{dicyd}^{2-})$ within experimental error). Although E_{LMCT} is larger in all solvents for $L = \text{Cl}_4\text{dicyd}^{2-}$ than for $L = \text{Cl}_2\text{dicyd}^{2-}$, the values of E_{LMCT} in acetonitrile and nitromethane are lowest for $L = \text{Cl}_2\text{dicyd}^{2-}$, increasing for $L = \text{dicyd}^{2-}$ and again for $L = \text{Me}_2\text{dicyd}^{2-}$. Here again, increasing covalency of the Ru-NCN bond is invoked to rationalize the results. Clearly, the nature of the “discontinuities” in the expected trends indicates that covalency is significantly affecting the behaviour only of the two most strongly coupled complexes, and only in the less decoupling solvents.

Compared to the pentaammines, where only the most strongly coupled complex exhibited significant covalency in the least decoupling solvent, the presence of covalency effects at higher donor number (*i.e.* in acetonitrile as well as nitromethane) and for $L = \text{dicyd}^{2-}$ as well as $L = \text{Me}_2\text{dicyd}^{2-}$ demonstrates that stabilizing the metal πd orbitals by

replacing a σ -donor ammine ligand with a π -acceptor pyridine ligand has brought the metal and ligand orbitals sufficiently close in energy to make the onset of significant covalency (*i.e.* perturbations as per figure 4.2.3) occur more generally.

Figure 4.2.5 - Electronic absorption spectra of $[\{Ru(NH_3)_4(py)\}_2(\mu-L)][PF_6]_4$ in acetonitrile as a function of ligand. Spectra were obtained using the H-cell described in section 2.6.6, and are the initial runs of their respective experiments.

For each ligand, plots of the spectra as a function of solvent are given in figures 3.4.2 - 3.4.5. A direct comparison, in acetonitrile, of the effect of ligand substitution (*i.e.* the analogous plot to figure 4.2.4 for the pentaammines) is given in figure 4.2.5. Note

how, in contrast to the case for the pentaammines, the molar absorptivities for $L = \text{Me}_2\text{dicyd}^{2-}$ and $L = \text{dicyd}^{2-}$ are nearly identical.

For the most strongly coupled systems, the triammines $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-}L)][\text{ClO}_4]_4$, $L = \text{Me}_2\text{dicyd}^{2-}$, dicyd^{2-} , $\text{Cl}\text{dicyd}^{2-}$, and $\text{Cl}_2\text{dicyd}^{2-}$, the “ionic” trends due to ligand-centred and solvent perturbations (*i.e.* according to figure 4.2.2) vanish entirely. With only one exception ($L = \text{Cl}_2\text{dicyd}^{2-}$), E_{LMCT} for a given ligand is highest in nitromethane and lowest in DMSO - the same trend seen for the $L = \text{Me}_2\text{dicyd}^{2-}$ and $L = \text{dicyd}^{2-}$ tetraammines. For $L = \text{Cl}_2\text{dicyd}^{2-}$ the trend holds for nitromethane, acetonitrile, and acetone, but E_{LMCT} increases from 8250 cm^{-1} in acetone to 8320 cm^{-1} in DMSO, slightly lower than its value in acetonitrile of 8350 cm^{-1} . Molar absorptivity “trends” vanish entirely. Considering the data in tables 3.4.9 - 3.4.12, one can extract only one constant - that in all cases ϵ_{max} is lower in nitromethane than in acetonitrile. Examining figures 3.4.6 - 3.4.9, the jumbled and inconstant nature of ϵ_{max} is evident. The oscillator strength data is somewhat more tractable, however. For $L = \text{Cl}_2\text{dicyd}^{2-}$, f is highest in nitromethane and lowest in DMSO even though ϵ_{max} is highest in acetone, dropping off slightly with donor number upon going to acetonitrile and nitromethane, and significantly lower in DMSO. E_{LMCT} is astonishingly constant for this series of spectra, varying by a mere 260 cm^{-1} from 8510 cm^{-1} in nitromethane to 8250 cm^{-1} in acetone. For $L = \text{Cl}\text{dicyd}^{2-}$, f follows nearly the same trend as it does for $\text{Cl}_2\text{dicyd}^{2-}$, although the value in nitromethane (0.603) is marginally smaller than the value in acetonitrile (0.605). The molar absorptivity is correspondingly highest in acetonitrile for this complex. For $L = \text{dicyd}^{2-}$ the trend in f is entirely jumbled, being $f_{\text{AC}} < f_{\text{DMSO}} < f_{\text{NM}} < f_{\text{AN}}$ while the analogous

trend in $\epsilon_{\max}$ is AC<NM<AN<DMSO! For $L = \text{Me}_2\text{dicyd}^{2-}$, f follows the trend $f_{\text{AC}} < f_{\text{DMSO}} < f_{\text{AN}} < f_{\text{NM}}$ and $\epsilon_{\max}$ the same AC<NM<AN<DMSO trend as for $L = \text{dicyd}^{2-}$.

Before any comparisons between the various complexes in given solvents are attempted the particular case of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Clidicyd})][\text{ClO}_4]_4$ must be considered. It is believed that the molar absorptivities and oscillator strengths of this complex have been significantly attenuated relative to its symmetric analogs. Because of the asymmetry in the bridging ligand, the solvation of the complex is expected to be similarly asymmetric. This may allow for significant solvent trapping of the valence electron on one metal centre relative to the other (see section 1.2), and consequently disrupt the CT interactions (symmetric and antisymmetric combinations in a dinuclear complex of the CT's associated with the corresponding mononuclear complex) discussed by Solomon.¹⁰⁸ Thus the values of f and $\epsilon_{\max}$ for $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Clidicyd})][\text{ClO}_4]_4$ may be more representative of mononuclear LMCTs than dinuclear LMCTs. Naklicki⁴⁸ noted an approximate doubling in the extinction coefficient of $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Me}_2\text{dicyd})]^{4+}$ relative to its mononuclear analog $[\text{Ru}(\text{NH}_3)_5(\text{Me}_2\text{dicyd})]^+$ (a factor of 1.8). Application of this rough factor would bring the extinction coefficients of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Clidicyd})][\text{ClO}_4]_4$ into registry with expected values based on the corresponding results for the $L = \text{dicyd}^{2-}$ and $L = \text{Cl}_2\text{dicyd}^{2-}$ complexes. Such a set of rough assumptions, of course, are not to be taken at face value. A theoretical study of this system is planned to be carried out as soon as the requisite software is available.* Until

* Spartan software (containing metal basis sets) was released in September, 1997, and will be used for these calculations.

such a study is completed, however, the results for the $L = \text{Cl}_2\text{dicyd}^{2-}$ complex will not be compared with those for the remaining three triammines.

Comparing the data for $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-L})][\text{ClO}_4]_4$ for $L = \text{Me}_2\text{dicyd}^{2-}$, dicyd^{2-} , and $\text{Cl}_2\text{dicyd}^{2-}$, the “expected” trend of highest oscillator strength for $L = \text{Me}_2\text{dicyd}^{2-}$ and lowest for $L = \text{Cl}_2\text{dicyd}^{2-}$ is present only in DMSO. The values of f in nitromethane, acetonitrile, and acetone are slightly higher for the $L = \text{dicyd}^{2-}$ complex than the $L = \text{Me}_2\text{dicyd}^{2-}$ complex and, with the exception of acetone, are lower for the $L = \text{Cl}_2\text{dicyd}^{2-}$ complex than for the $L = \text{Me}_2\text{dicyd}^{2-}$ complex. In acetone, f for the $L = \text{Cl}_2\text{dicyd}^{2-}$ complex is higher than for the $L = \text{dicyd}^{2-}$ complex. With the exception of DMSO, ϵ_{max} values are highest for the $L = \text{Cl}_2\text{dicyd}^{2-}$ complex and lowest for the $L = \text{Me}_2\text{dicyd}^{2-}$ complex. In DMSO the $L = \text{Cl}_2\text{dicyd}^{2-}$ complex has the lowest value, followed by the $L = \text{Me}_2\text{dicyd}^{2-}$ complex and the $L = \text{dicyd}^{2-}$ complex. The trend in E_{LMCT} follows the reverse trend in nitromethane, acetonitrile, and acetone, being highest for the $L = \text{Me}_2\text{dicyd}^{2-}$ complex and lowest for the $L = \text{Cl}_2\text{dicyd}^{2-}$ complex. In DMSO, E_{LMCT} is highest for the $L = \text{Cl}_2\text{dicyd}^{2-}$ complex and lowest for the $L = \text{dicyd}^{2-}$ complex.

These results can be largely rationalized by assuming significant covalency effects for the $L = \text{Me}_2\text{dicyd}^{2-}$ and $L = \text{dicyd}^{2-}$ complexes in the three least decoupling solvents, and some covalency effects for the $L = \text{Cl}_2\text{dicyd}^{2-}$ complex in these solvents and for at least the $L = \text{Me}_2\text{dicyd}^{2-}$ complex in DMSO. A graphical representation of the ϵ_{max} trend in acetonitrile as a function of ligand is given in figure 4.2.6. Note that this trend, as previously discussed, is entirely opposite that seen for the pentaammine complexes, and a

logical extension (as a function of increasing covalency of the Ru-NCN bonding) of the trend seen for the tetraammines.

Figure 4.2.6 - Electronic absorption spectra of $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-L})][\text{ClO}_4]_4$ in acetonitrile as a function of ligand. Spectra were obtained according to the procedure outlined in section 2.6.4.

To this stage, only results in non-aqueous solvents have been discussed. It has been long known that water behaves quite differently from other solvents, and that results in water don't generally fit into donor number trends. This has been ascribed to long-range order or high-frequency librations,¹⁰⁹ but may, at least in the case of dicyd

complexes, be attributed to the ability of water to act both an electron donor as outlined in figure 4.2.1 and as an electron acceptor. This latter behaviour takes place between the water's protons and the amide nitrogen of each cyanamide moiety. Electron donation from the amide nitrogen to the protons of water is analogous to protonation of the ligand (to a lesser extent). As the ligand donates electron density to the solvent it increasingly behaves as its neutral (protonated) form, losing planarity as the amide nitrogen rehybridizes from sp^2 to sp^3 geometry. Stabilization of the cyanamide's π -donor orbitals causes poorer energetic matching with the metal πd orbitals, and a consequent loss of oscillator strength. Thus whenever aqueous spectroscopy is considered, the band properties are considerably attenuated with regards to the values to be expected due to water's donor number. Because aqueous spectroscopy is not available for the tetraammines a comparison of the behaviour between the three families of complexes is impossible. The data for the pentaammines have been fully covered elsewhere,⁴⁸ and it is sufficient, therefore, to discuss the results for the triammines in relative isolation. E_{LMCT} follows the trend of being highest for the $L = Me_2dicyd^{2-}$ complex and lowest for the $L = Cl_2dicyd^{2-}$ complex, consistent with the most electron rich ligand being the best donor to water, and hence being the most stabilized. Oscillator strength and molar absorptivity are highest for the $L = dicyd^{2-}$ complex, with f lowest for the $L = Cl_2dicyd^{2-}$ complex and ϵ_{max} lowest for the $L = Me_2dicyd^{2-}$ complex.

Overall, electronic absorption results indicate that the pentaammine complexes' transitions behave as typical charge transfer events and may be rationalized almost exclusively in terms of ionic metal-ligand interactions. The exception to this is

$[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Me}_2\text{dicyd})][\text{PF}_6]_4$ for which covalency seems to play a role in nitromethane. Perhaps significantly, Evans method experiments on $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Me}_2\text{dicyd})][\text{PF}_6]_4$ in nitromethane showed the complex to be almost diamagnetic, the only such result for a pentaammine. As the overall (starting-point) metal-ligand energy separations are decreased through the inner-sphere perturbations, covalency effects become increasingly prevalent. By the triammines, expected solvent dependence of E_{LMCT} on donor number has entirely vanished. For $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cl}_2\text{dicyd})][\text{ClO}_4]_4$ the near-absence of solvent dependence of the “LMCT” band is reminiscent of bonding-antibonding transitions.

4.3 Cyclic Voltammetry

The potentials at which each of the four redox events of a given complex of our study (*i.e.* $\text{L}^{0/-}$, L^{-2-} , $E^\circ_{\text{M}2}$, $E^\circ_{\text{M}1}$) occur are expected to reflect the electronic condition of the complexes. As the electron density on the metal centres increases as a function of its spectator ligands, bridging ligand, and the solvent in which it is dissolved, the metal-centred couples should occur at increasingly negative potentials. The couples formally assigned as being ligand centred should likewise occur at less positive potentials as the ligand becomes more polarizable. Generally speaking these anticipated trends in redox potential are observable in the experimental data.

For the pentaammines (see data in tables 3.5.1 - 3.5.4), the trends hold absolutely for all four complexes as a function of solvent, excluding water from consideration for the

moment. In each case the most positive redox potentials are found for a given complex in nitromethane and the most negative for that complex in DMSO. Similarly, comparing values in a given solvent as a function of bridging ligand, the potential of a given couple is most negative for the $L = \text{Me}_2\text{dicyd}^{2-}$ complex and becomes increasingly positive as the bridging ligand become less electron rich. The sole exception to this latter trend is that for $E^\circ_{\text{M}_2}$ in DMSO (see tables 3.5.1 - 3.5.4) for which an immediate explanation is not forthcoming.

Results in water must be considered separately, though the numerical values listed in the tables cannot be compared directly, in any event, as the aqueous data are referenced vs. SCE whereas all other data are referenced vs. Ferrocenium/Ferrocene. Even with suitable correction for referencing, it has been noted that water behaves uniquely as a solvent, and that spectroscopic and electrochemical results for this solvent cannot be generally compared to results in other solvents.^{109,110} The expected trends for the four complexes in water do hold to a large extent. An apparently anomalous result for L^{0-} for $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Cl}_4\text{dicyd})][\text{PF}_6]_4$ is based on an irreversible couple, and cannot be considered stringent. For the metal centred couples, the trend holds with the exception of the anomalously negative results for $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Cl}_4\text{dicyd})][\text{PF}_6]_4$. Again, no explanation for this occurrence is forthcoming.

Sketchy data hamper such comparisons for the tetraammines (see data in tables 3.5.5 - 3.5.8). Due to experimental error, absolute (referenced) potentials are available in nitromethane only for $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-dicyd})][\text{PF}_6]_4$. Further, the L^{0-} couple was only resolved in acetonitrile (and nitromethane), and not for the $L = \text{Cl}_4\text{dicyd}^{2-}$ complex.

The potentials for the other three redox couples as a function of solvent for each complex do follow the trend of becoming less positive going from nitromethane to DMSO with one exception - L^{-2-} for $[\{Ru(NH_3)_4(py)\}_2(\mu\text{-dicyd})][PF_6]_4$ in DMSO is at higher potential than in nitromethane or acetonitrile. In acetonitrile, the trend as a function of ligand also holds for all three couples, but in DMSO the trend holds only for E°_{M1} . In water, the trend as a function of ligand holds for the three resolved couples with the exception of the E°_{M1} couple for $[\{Ru(NH_3)_4(py)\}_2(\mu\text{-dicyd})][PF_6]_4$ which is slightly more negative than the corresponding couple for $[\{Ru(NH_3)_4(py)\}_2(\mu\text{-Me}_2\text{dicyd})][PF_6]_4$. The small magnitude of this discrepancy may indicate that it is artifactual due to the deconvolution of the $2e^-$ event using the graphical analysis described in section 3.5.

For the triamines, the trends for each complex as a function of solvent hold with the exception of the DMSO results for the $L = Me_2dicyd^{2-}$ and $L = dicyd^{2-}$ complexes, and the data for $[\{Ru(NH_3)_3(bipy)\}_2(\mu\text{-Cl}_2\text{dicyd})][ClO_4]_4$ in acetonitrile for which the referencing seems off. (None of the redox potentials for this complex fit within the expected trends!) Trends between the four complexes in a given solvent (*i.e.* as a function of ligand) are also absolute, although the results for L^{-2-} in acetone contain a "discrepancy". The magnitude of this discrepancy, however, is within graphical reading error and can therefore be disregarded. In water the trends for the three resolved couples exist with one anomaly - the potential of L^{-2-} for $[\{Ru(NH_3)_3(bipy)\}_2(\mu\text{-Cl}_2\text{dicyd})][ClO_4]_4$ is ca. 0.2 V less positive than its expected value.

Similar trends might be expected to hold between the families of complex, and in fact, for E°_{M2} , comparing results for a given ligand and solvent between the three families,

the potential is highest for the most stable metal orbitals (the triammine), and becomes increasingly negative as the metal orbitals become less stable. In acetonitrile and DMSO, where sufficient data exist to allow a comparison between all three families, the potentials for $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Cl}_4\text{dicyd})][\text{PF}_6]_4$ are more negative than the potentials for $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{PF}_6]_4$. Similarly, the potentials for $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-Cl}_4\text{dicyd})][\text{PF}_6]_4$ are more negative than those for $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{ClO}_4]_4$. Thus, there is no overlap between the pentaammine with the most positive redox potentials and the tetraammine with the most negative, or the tetraammine with the most positive potentials and the triammine with the most negative. For E°_{MI} and L^{-2-} , however, such trends are not in general evidence although one isolated example, L^{-2-} in DMSO, does exist.

Cyclic voltammetry provides the most direct measure of the stability of a mixed-valence state via the comproportionation constant, K_c , as described in section 1.3. Any equilibrium constant may, of course, be converted into a free energy using well known thermodynamic relationships. Thus, a free energy of comproportionation may be obtained from K_c according to $\Delta G_c = -RT\ln(K_c)$ or directly from ΔE according to $\Delta G_c = -nF(\Delta E)$. Knowing that K_c will always be greater than one, or similarly that ΔE is always positive, it can be recognized that ΔG_c will always be negative, and the sign may be dispensed with for convenience. Although the extraction of a free energy of comproportionation from an experimentally determined CV spectrum is a simple procedure, the resultant energy is not, in fact, directly a measure of metal-metal coupling. This is because the comproportionation constant is composed of four terms,¹¹¹

$$\Delta G_c = \Delta G_s + \Delta G_e + 2\Delta G_i + 2\Delta G_r \quad (4.3.1)$$

where ΔG_c is the free energy of comproportionation, ΔG_s reflects the statistical distribution of eq 1.3.1, ΔG_e accounts for the electrostatic repulsion of the two like-charged metal centers, ΔG_i is an inductive factor dealing with competitive coordination of the bridging ligand by the metal ions, and ΔG_r is the free energy of resonance exchange; the only component of ΔG_c which represents “actual” metal-metal coupling. The prefactor 2 for the ΔG_i and ΔG_r terms stems from those energies being defined per mole of mixed-valence complex, while ΔG_s and ΔG_e are defined in terms of the comproportionation equilibrium itself.

While Sutton and Taube have shown that all four terms can contribute significantly to ΔG_c for the weak coupling case,¹¹² in the case of the strongly coupled systems of this study, the resonance exchange term dominates ΔG_c .¹³ A theoretical evaluation of certain of the terms composing ΔG_c is possible. The value of ΔG_s may be determined by recognizing that it stems directly from the statistical distribution of the comproportionation equilibrium which implies $K_c = 4$ for a symmetrical system, which relates to a ΔG_s of ca. 36 mV.²⁰ ΔG_e may be evaluated according to eq 4.3.2 which assumes the medium in which the ionic metal centres are found can be treated as a dielectric continuum, and that there is a unit difference in ionic charge between the two centres.¹¹³

$$\Delta G_e = \frac{1}{4\pi\epsilon\epsilon_0 R_{12}} \quad (4.3.2)$$

Here R_{12} represents the separation of the metal centres, ϵ the solvent's static dielectric, and ϵ_0 the permittivity of free space. Practically, this equation is better served by first evaluating a constant allowing one to input R_{12} in Å and obtain a value for ΔG_e in mV.

This conversion factor, K_{CF} , is evaluated according to eq 4.3.3

$$K_{CF} = \frac{e}{4\pi\epsilon_0 \times 10^{-10}} \quad (4.3.3)$$

and results in eq 4.3.4 for ΔG_e .

$$\Delta G_e = \frac{14,400}{\epsilon R_{12}} \quad (4.3.4)$$

Data obtained by evaluating eq 4.3.4 for the solvents of this study are collected in table

4.3.1. A value for R_{12} of 13.1 Å, that found in the crystal structures of both $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-dicyd})][\text{OTs}]_4$ and $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-dicyd})][\text{ClO}_4]_4$, has been chosen as appropriate for describing the solvated complexes (see section 3.3).

Table 4.3.1 - ΔG_e contributions to ΔG_e for the five solvents of this study evaluated according to eq 4.3.4 for $R_{12} = 13.1$ Å.

Solvent	ϵ^a	ΔG_e (mV)
Nitromethane	35.87	30.6
Acetonitrile	35.94	29.3
Acetone	20.56	53.1
Dimethyl Sulfoxide	46.45	23.6
Water	78.36	14.0

^aData @ 25 °C except NM @ 30°C; ref 10

The values so determined must be acknowledged to be approximate insofar as the assumption of dielectric continuum is unlikely to be rigorously true and that significant

coupling within the complex will tend to delocalize the metals' charges, reducing R_{12} significantly.

Clearly, however, ΔG_s and ΔG_c will contribute significantly to ΔG_e only in very weakly coupled complexes. For example, $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Cl}_4\text{dicyd})]^{3+}$ in aqueous solution (the most weakly coupled complex in the most decoupling solvent), was found to have $K_c = 13$ or $\Delta G_c = 520 \text{ cm}^{-1}$. The contributions of ΔG_s (36 mV) and ΔG_c (14 mV - see table 4.3.1, above) account for roughly 75% of ΔE (50 of 65 mV). In such a weakly coupled complex the contribution of ΔG_r to ΔG_e is expected to be very small, and the inductive term, $2\Delta G_i$, thus to account for the remaining 15 mV of splitting.

Unfortunately, there is currently no methodology for quantifying the magnitude of ΔG_i . Using the conceptual approach of Curtis, however, a crude approximation of its magnitude is possible.²⁰ Consider a mononuclear Ru(III) complex containing a π -donor bridging ligand and which has a metal-centred redox event at a potential E . In the related mixed-valence dinuclear complex the analogous reduction potential occurs at a more negative potential E' . One argues that the presence of a Ru(II) centre at the opposite end of the bridging ligand, essentially a π -donor despite its electrostatic charge, inductively increases the electron density at the remaining Ru(III) centre, causing it to be more difficult to reduce. Thus the quantity $E - E'$ crudely represents the magnitude of ΔG_i . For example, the [(III)-(II)]/[(II)-(II)] reduction couple for $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Me}_2\text{dicyd})][\text{PF}_6]_4$ in acetonitrile occurs at -0.816 V vs. ferrocene while the (III)/(II) couple for its mononuclear analogue, $[\text{Ru}(\text{NH}_3)_5(\mu\text{-Me}_2\text{dicyd})][\text{PF}_6]$, in acetonitrile occurs at -0.778 V resulting in an $E - E'$ estimate of the magnitude of ΔG_i of 38 mV. Similarly, one might

compare the [(III)-(II)]/[(II)-(II)] couples for $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-L})][\text{PF}_6]_4$ and $[\text{Ru}(\text{NH}_3)_5(\mu\text{-L})\text{Cu}(\text{bpil})]$, bpil = 1,3-bis(2-pyridylimino)isoindolinato,¹¹⁴ in a given solvent. The heteronuclear complex provides a Ru(III/II) couple in the presence of Cu(II), while the homonuclear complex provides a Ru(III/II) couple in the presence of Ru(II). For $\text{L} = \text{Cl}_2\text{dicyd}^{2-}$ the couple in acetonitrile is at -0.685 V vs. ferrocene for the homonuclear complex and at -0.606 V vs. ferrocene for the heteronuclear complex. The difference of 80 mV between the two couples reflects in part inductive (*e.g.* π -donor) effects associated with the Ru^{II} centre and not the Cu^{II} centre. A similar comparison, again in acetonitrile, for the $\text{L} = \text{dicyd}^{2-}$ complex (couples, respectively, at -0.820 V and -0.710 V vs. ferrocene) yields 110 mV separation between the two couples.

While such numerical exercises may yield (at best?) order of magnitude ideas about ΔG_i , all the factors contributing to ΔG_c are affected in concert by any perturbation to the system. Even the statistical contribution may vary from its maximum value of 36 mV if the system loses its redox symmetry.²⁰ A suitable estimate of the contribution of the non-resonance terms to ΔG_c is therefore required. Given our reasonable assumption that there is no significant contribution to ΔG_c from ΔG_r for $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Cl}_4\text{dicyd})]^{3+}$ in water, ΔG_c for this complex is thus $\Delta G_{nr} = \Delta G_s + \Delta G_c + 2\Delta G_i = 520 \text{ cm}^{-1}$. This value will then be used as our estimate of the contribution of the non-resonance terms to ΔG_c for the remainder of the complexes of the study. The free energy of resonance exchange, $\Delta G_r = 0.5(\Delta G_c - \Delta G_{nr})$, should then provide an acceptable experimental value of the metal-metal coupling element (H_{ad} or H_{NMR}) for comparison with that derived from any given theoretical model.

Tables 4.3.2 - 4.3.4 present the free energies of comproportionation for the complexes of the three families as a function of ligand and solvent. The estimated ΔG_c values will be presented alongside modelling predictions in the appropriate sections to facilitate direct comparison.

Table 4.3.2 - Free energies of comproportionation, ΔG_c , as a function of solvent for the complexes $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-L})][\text{PF}_6]_4$.^a

Solvent ^b	$\text{Me}_2\text{dicyd}^{2-}$	dicyd^{2-}	$\text{Cl}_2\text{dicyd}^{2-}$	$\text{Cl}_4\text{dicyd}^{2-}$
NM (2.7)	2970	2520	1860	1270
AN (14.1)	2740	2310	1710	1200
AC (17.0)	2620	1980	1580	1130
DMSO (29.8)	1600	1350	1050	930
H ₂ O (18.0)	690	830	630	520

^a Calculated according to $\Delta G_c = RT\ln(K_c)$ in cm^{-1} . ^b Solvent Donor Numbers in parentheses.

Table 4.3.3 - Free energies of comproportionation, ΔG_c , as a function of solvent for the complexes $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-L})][\text{PF}_6]_4$.^a

Solvent ^b	$\text{Me}_2\text{dicyd}^{2-}$	dicyd^{2-}	$\text{Cl}_2\text{dicyd}^{2-}$	$\text{Cl}_4\text{dicyd}^{2-}$
NM (2.7)	3020	3070	2400	1710
AN (14.1)	3200	2900	2110	1360
AC (17.0)	--	--	--	--
DMSO (29.8)	2250	1860	1210	1030
H ₂ O (18.0)	730	870	630	390

^a Calculated according to $\Delta G_c = RT\ln(K_c)$ in cm^{-1} . ^b Solvent Donor Numbers in parentheses.

Table 4.3.4 - Free energies of comproportionation, ΔG_c , as a function of solvent for the complexes $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-L})][\text{ClO}_4]_4$.^a

Solvent ^b	$\text{Me}_2\text{dicyd}^{2-}$	dicyd^{2-}	$\text{Cl}\text{dicyd}^{2-}$	$\text{Cl}_2\text{dicyd}^{2-}$
NM (2.7)	3310	3200	2960	2810
AN (14.1)	3400	3320	2910	2650
AC (17.0)	3610	3400	2860	2620
DMSO (29.8)	2940	2540	1860	1660
H ₂ O (18.0)	870	1030	1170	1270

^a Calculated according to $\Delta G_c = RT\ln(K_c)$ in cm^{-1} . ^b Solvent Donor Numbers in parentheses.

As was discussed in the section on electronic absorption spectroscopy, as energy matching of the metal and ligand orbitals is increased, metal-metal coupling is anticipated to increase concurrently owing to increased interactions of each metal centre with the bridging ligand. Generally speaking, then, ΔG_c is expected to be greatest for complexes of $\text{L} = \text{Me}_2\text{dicyd}^{2-}$, decreasing as the bridging ligand becomes less electron donating. Further, ΔG_c should be affected by solvent such that it is greatest for a given complex in nitromethane, and least in DMSO (not considering water). These trends, in fact, hold absolutely for the pentaammines, as is evidenced by the data in table 4.3.2. In water, however, the trend as a function of ligand is lost, with the $\text{L} = \text{dicyd}^{2-}$ complex having the largest free energy of comproportionation.

For the more strongly coupled tetraammines (table 4.3.3) the same trends continue to apply with one very significant exception. For $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{PF}_6]_4$, $\Delta G_c(\text{NM}) < \Delta G_c(\text{AN})$ and also lower than $\Delta G_c(\text{NM})$ for $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-dicyd})][\text{PF}_6]_4$. Thus this single value fits neither the solvent trend nor the ligand perturbation trend. Electronic absorption data for $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{PF}_6]_4$ foreshadows this possibility for, although $f_{\text{NM}} > f_{\text{AN}}$, ϵ_{max} of the LMCT band was lower in

nitromethane than in acetonitrile. These same oscillator strength and molar absorptivity trends exist for $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-dicyd})][\text{PF}_6]_4$, but in this case $\Delta G_e(\text{NM}) > \Delta G_e(\text{AN})$ as expected. Greater insight into the cause of such “inverted” behaviour is necessary, and can be gleaned through consideration of the data for the triammines (table 4.3.4).

For the two least strongly coupled triammines, the complexes with $\text{L} = \text{Clidicyd}^{2-}$ and $\text{L} = \text{Cl}_2\text{dicyd}^{2-}$, the trends hold both as a function of solvent for a given complex and as a function of ligand between the two complexes (again temporarily ignoring water). For the two more strongly coupled complexes, however, the inverted behaviour is more manifest. For both the $\text{L} = \text{Me}_2\text{dicyd}^{2-}$ and $\text{L} = \text{dicyd}^{2-}$ complexes ΔG_e attains its highest value in acetone, and drops off slightly with decreasing donor number in acetonitrile and again in nitromethane. Accepting that the behaviour of $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{PF}_6]_4$ in nitromethane is analogous, a single explanation should clarify the situation.

As the complexes become more and more strongly coupled, eventually they will become fully delocalized (Class III according to the Robin and Day classifications⁸). It is suggested that for each complex ΔG_r will reach a maximum possible value, and will thence be constant for that complex, when the complex is fully delocalized. Under such a circumstance, the influence of the non-resonant terms of ΔG_e could once again be manifest, just as they are in very weakly coupled complexes where the value of ΔG_r is equivalently constant (albeit by virtue of being negligibly small). The difference in ΔE for $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-dicyd})][\text{ClO}_4]_4$ between acetone and nitromethane, for example, is 24 mV, the same as the difference in ΔG_e anticipated for those solvents according to eq

4.3.4 (see table 4.3.1). That these numbers are equivalent is almost unavoidably coincidental, but it is significant that their magnitudes are similar.

Let us go one step further. It has been shown for the pentaammines that trends in metal-metal coupling are analogous for the mixed-valent and fully oxidized complexes.⁴⁸ Thus, as superexchange increases in the mixed-valent complex,⁴² so too does antiferromagnetic coupling in the Ru(III)-Ru(III) complex.^{48,78} This is not unexpected as Solomon¹⁰⁸ has evaluated $-2J$ terms, where $-2J$ represents the triplet-singlet state energy difference which increases as antiferromagnetic coupling increases,¹¹⁵ as being proportional to $h_{d\pi}$, which is essentially a metal-ligand coupling element, and inversely proportional to Δ , which is an energy difference. Thus the CNS treatment of metal-metal interactions in the mixed-valent state and Solomon's treatment of metal-metal interactions in the homovalent state are directly analogous.

Given that ΔG_r seems to have reached a maximum value for $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-L})][\text{ClO}_4]_4$, $\text{L} = \text{Me}_2\text{dicyd}^{2-}$ and $\text{L} = \text{dicyd}^{2-}$, in nitromethane and acetonitrile, and that, under the same conditions these same complexes are diamagnetic (see sections 3.2 and 4.1), a connection might be implied between the behaviours of the complexes in the two oxidation states such that when the metal-ligand interactions are sufficiently strong, Class III behaviour in the [Ru(III)-Ru(II)] complex and room temperature diamagnetism in the [Ru(III)-Ru(III)] complex are reached jointly.

4.4 Spectroelectrochemistry

As was mentioned in section 3.6, the IT bands for each of the complexes had to be deconvoluted from the band envelope of the Ru(III)-Ru(II) complex using a procedure which assumed the LMCT band profile of the Ru(III)-Ru(III) complex was maintained upon reduction to the Ru(III)-Ru(II) complex. Such an assumption is supported by the band profile of the Ru(III)-dicyd LMCT in $[(\text{NH}_3)_5\text{Ru}(\mu\text{-dicyd})\text{Cu}(\text{L})]^{2+}$, where L = 1,3-bis(2'-pyridylimino)isoindolinato,¹¹⁴ which is nearly identical to that of the Ru(III)-dicyd LMCT in $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-dicyd})][\text{PF}_6]_4$.^{48,52} The assumption of gaussian bandshape for the IT band is assumed implicitly by the nature of the fitting. Similar fitting of IT bands by single gaussian bands has been accomplished both for single¹¹⁶ and multiple⁴³ transition systems, and very acceptable fits of the mixed-valence band profiles of the pentaammines were obtained using the multiple-gaussian peak technique.^{48,52} As the systems become more strongly coupled, however, the fits obtained by considering the mixed-valence spectrum as a composite of the bands composing the LMCT plus a single low energy gaussian band representing the IT become less and less acceptable. The breakdown occurs on the high energy side of the band envelope where a series (typically two or three) of low intensity high energy bands need to be included to properly model the high energy trace (particularly the tail) of the band profile. This is rationalized in greater detail in the results section 3.6.

Any errors due to the assumptions of the fitting procedure have the potential of introducing fairly substantial uncertainty to the Hush modelling of the complexes; the CNS

model will be far less susceptible to such vagaries since only the energy of the IT band is required. Since the latter model is primarily the one of interest here, the IT deconvolution results should prove adequate.

The parameters obtained for the IT bands of the complexes of this study (table 3.6.1) perhaps reflect, through the absence of consistent trends, the approximate nature of the fitting protocol. For example, E_{IT} for $[\{Ru(NH_3)_5\}_2(\mu-Me_2dicyd)][PF_6]_4$ decreases as solvent donor number increases but for $[\{Ru(NH_3)_5\}_2(\mu-Cl_2dicyd)][PF_6]_4$ the trend is reversed, with E_{IT} increasing with increasing solvent donor number. In the case of $[\{Ru(NH_3)_5\}_2(\mu-dicyd)][PF_6]_4$, the initial trend is a decrease in E_{IT} with increasing donor number for nitromethane, acetonitrile, and acetone while in DMSO E_{IT} increases dramatically, confounding the trend. In contrast, the trend in ϵ_{max} is constant for all three complexes, paralleling that seen for their LMCT bands; *i.e.* decreasing as a function of increasing solvent donor number. For $\Delta\nu_{1/2}$, the bandwidth at half peak height, the $L = dicyd^{2-}$ and $L = Cl_2dicyd^{2-}$ complexes exhibit consistent trends of the narrowest bandwidth occurring in the least decoupling (lowest donor number) solvent and increasing with increasing solvent donor number. For $L = Me_2dicyd^{2-}$, however, the bandwidth is lower in acetone than in acetonitrile, thence increasing in DMSO. Because acetonitrile and acetone have very similar donor numbers the 80 cm^{-1} decrease (in acetone relative to acetonitrile) might be considered within the (unquantified) “experimental” error of the fitting procedure.

The data for the tetraammines (table 3.6.2), have the interesting feature of exhibiting consistent trends in E_{IT} , ϵ_{max} , and $\Delta\nu_{1/2}$ for the complexes $[\{Ru(NH_3)_4(py)\}_2(\mu-$

Cl₂dicyd)][PF₆]₄ and [{Ru(NH₃)₄(py)}₂(μ-Cl₄dicyd)][PF₆]₄, but no trends in any of the three parameters for [{Ru(NH₃)₄(py)}₂(μ-Me₂dicyd)][PF₆]₄ and inconsistent trends for [{Ru(NH₃)₄(py)}₂(μ-dicyd)][PF₆]₄. For the L = Cl₂dicyd²⁻ and Cl₄dicyd²⁻ complexes, E_{IT} and Δν₁ increase with increasing donor number while ε_{max} decreases with increasing donor number. These trends are consistent with those seen for [{Ru(NH₃)₅}₂(μ-Cl₂dicyd)][PF₆]₄, and with the trends seen for the LMCT bands. The L = dicyd²⁻ complex exhibits the expected trend in Δν₁ but its trend in E_{IT} is the reverse of that seen for the L = Cl₂dicyd²⁻ and Cl₄dicyd²⁻ complexes, *i.e.* decreasing with increasing donor number. No trends exist for the remaining parameters for the L = dicyd²⁻ or Me₂dicyd²⁻ complexes.

For the triammines, only the L = Cl₂dicyd²⁻ complex (see table 3.6.3) was studied in a full range of solvents. Its E_{IT} trend is the same as that for [{Ru(NH₃)₄(py)}₂(μ-dicyd)][PF₆]₄, highest in nitromethane and decreasing steadily to DMSO, while ε_{max} increases with increasing donor number from nitromethane to acetone, then drops sharply in DMSO. Its Δν₁ values increase with solvent donor number excepting the value in acetone which is lower than that in nitromethane.

The results obtained using spectroelectrochemistry are required for modelling the complexes using the Hush and CNS models, and the discussion of their significance is thus reserved for the sections dedicated to each theoretical treatment.

4.5 The Hush Model

Hush's treatment of metal-metal coupling in a mixed-valence complex assumes (not unreasonably) that the experimentally determined IT band contains, via its overall oscillator strength, information about the magnitude of the donor-acceptor interaction. Thus, evaluation of the Hush metal-metal "donor-acceptor" coupling element, H_{ad} , is effected via eq 1.4.11, which utilizes the spectroscopic parameters of the IT band and the donor-acceptor separation exclusively. A prediction of the experimental IT bandwidth, $\Delta\nu_{1/2}$, for one-electron homonuclear electron transfer in a symmetric complex, is possible via eq 1.4.6, $\Delta\nu_{1/2} = (2310\nu_{\max})^{1/2} \text{ cm}^{-1}$.

Table 4.5.1 - Metal-metal coupling elements, H_{ad} , and predicted bandwidths, $\Delta\nu_{1/2}$, for the IT bands of the complexes $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-L})][\text{PF}_6]_4$ as a function of solvent, determined via the Hush model. Experimental ΔG_r and $\Delta\nu_{1/2}$ values are provided for comparative purposes.^a

L	Solvent ^b	$\Delta\nu_{1/2}$	$\Delta\nu_{1/2}$ (Hush)	H_{ad}	ΔG_r
$\text{Me}_2\text{dicyd}^{2-}$	AN (14.1)	2430	4050	930	1110
$\text{Me}_2\text{dicyd}^{2-}$	AC (17.0)	2350	4000	820	1050
$\text{Me}_2\text{dicyd}^{2-}$	DMSO (29.8)	3760	3990	780	540
dicyd^{2-}	NM (2.7)	2430	4020	940	1000
dicyd^{2-}	AN (14.1)	2760	3990	980	900
dicyd^{2-}	AC (17.0)	2760	3950	870	730
dicyd^{2-}	DMSO (29.8)	4250	4160	780	420
$\text{Cl}_2\text{dicyd}^{2-}$	AN (14.1)	3390	4000	960	600
$\text{Cl}_2\text{dicyd}^{2-}$	AC (17.0)	3790	4040	850	530
$\text{Cl}_2\text{dicyd}^{2-}$	DMSO (29.8)	5720	4290	820	270
$\text{Cl}_4\text{dicyd}^{2-}$	AN (14.1)	3890	4110	750	340

^a All data in cm^{-1} . ^b Solvent donor numbers listed in parentheses. ^c Hush predicted bandwidths calculated according to $\Delta\nu_{1/2} \text{ (Hush)} = (2910\nu_{\max})^{1/2} \text{ cm}^{-1}$.

Examination of the data in table 4.5.1 shows that the Hush model predicts $\Delta\nu_{1/2}$ reasonably well for the more weakly coupled complexes ($[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Cl}_4\text{dicyd})][\text{PF}_6]_4$ and $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Cl}_2\text{dicyd})][\text{PF}_6]_4$) and provides reasonably good predictions in DMSO for all four complexes, in which solvent they are all at their most weakly coupled. As the complexes become more strongly coupled, however, the estimated $\Delta\nu_{1/2}$ values match their experimental counterparts less and less well. Predictions of the metal-metal coupling element, H_{ad} , are erratic, dramatically overestimating the experimental ΔG_r values for the most weakly coupled complexes, while giving more reasonable estimates for the remaining complexes. Most telling, however, is the poor correlation of H_{ad} to the experimental ΔG_r values, as is demonstrated in figure 4.5.1.

Figure 4.5.1 - "Shotgun" plot of metal-metal coupling elements, H_{ad} , determined via the Hush model vs. ΔG_r obtained from electrochemical data (see section 4.3).

Notable features of discrepancy include the predicted value of H_{ad} for $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-dicyd})]^{3+}$ in acetonitrile being larger than the predicted value for that complex in nitromethane, contrary to the experimental results. Similarly, ΔG_r for $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-dicyd})]^{3+}$ changes by over a factor of two between DMSO and nitromethane. The corresponding H_{ad} results, meanwhile, have a range of only 160 cm^{-1} , making the nitromethane result a scant 20% larger than the DMSO result. The overall range of H_{ad} considering all complexes in all solvents spans a mere 230 cm^{-1} while the equivalent range in ΔG_r values, 840 cm^{-1} , is quite nearly four times larger.

IT bandwidth is often used as a benchmark for the degree of metal-metal coupling, and the $\Delta\nu_{IT}$ values for the most weakly coupled pentaammine complexes, ca. 4000 cm^{-1} , are consistent with other Class II complexes.²⁰ These values narrow in a fairly consistent manner as the systems become more strongly coupled (see table 4.5.1), and the inability of the Hush model to properly predict this behaviour is indicative of its inapplicability to more strongly coupled systems. Given that the Hush model's predictions of H_{ad} are inconsistent, one might attempt to qualitatively assign the degree of coupling in a given complex based on its IT bandwidth, and the Hush model's ability to predict this feature. Thus, the pentaammines change their behaviour, as a function of bridging ligand and solvent, from "weakly coupled" to "strongly coupled" as delineated by the increasing discrepancy between the experimental and predicted IT bandwidths as the systems become, as determined electrochemically, more strongly coupled.

Given that the tetraammines and triammines are demonstrably more strongly coupled than their pentaammine counterparts, it is utterly unsurprising to find (see tables

4.5.2 and 4.5.3) that significant disagreement between predicted and experimental $\Delta\nu_{1/2}$ values occurs even in the most weakly coupled of the tetraammines (the $L = Cl_4dicyd^{2-}$ complex in NM), and that the degree of disagreement for the more strongly coupled complexes is even more significant than for the pentaammines. Where a rough correlation between H_{ad} and ΔG_r existed for the pentaammines, even this has vanished in the case of the tetraammines and triammines. For the complex $[\{ Ru(NH_3)_4(py) \}_2(\mu-dicyd)]^{3+}$, the Hush model predicts the opposite trend in H_{ad} to that seen experimentally, and this is essentially true of $[\{ Ru(NH_3)_3(bipy) \}_2(\mu-Cl_2dicyd)]^{3+}$, as well.

Table 4.5.2 - Metal-metal coupling elements, H_{ad} , and predicted bandwidths, $\Delta\nu_{1/2}$, for the IT bands of the complexes $[\{ Ru(NH_3)_4(py) \}_2(\mu-L)][PF_6]_4$ as a function of solvent, determined via the Hush model. Experimental ΔG_r and $\Delta\nu_{1/2}$ values are provided for comparative purposes.^a

L	Solvent ^b	$\Delta\nu_{1/2}$	$\Delta\nu_{1/2}$ (Hush)	H_{ad}	ΔG_r
Me ₂ dicyd ²⁻	NM (2.7)	2200	4130	830	1250
Me ₂ dicyd ²⁻	AN (14.1)	1920	4160	880	1340
Me ₂ dicyd ²⁻	DMSO (29.8)	2380	3890	850	870
dicyd ²⁻	NM (2.7)	2000	4120	760	1280
dicyd ²⁻	AN (14.1)	2090	4090	960	1190
dicyd ²⁻	DMSO (29.8)	2830	3860	1010	670
Cl ₂ dicyd ²⁻	NM (2.7)	2240	3900	950	940
Cl ₂ dicyd ²⁻	AN (14.1)	2700	3930	980	800
Cl ₂ dicyd ²⁻	DMSO (29.8)	3750	4000	810	350
Cl ₄ dicyd ²⁻	NM (2.7)	2980	3800	1000	600
Cl ₄ dicyd ²⁻	AN (14.1)	3350	3900	970	420
Cl ₄ dicyd ²⁻	DMSO (29.8)	4530	4210	730	260

^a All data in cm⁻¹. ^b Solvent donor numbers listed in parentheses. ^c Hush predicted bandwidths calculated according to $\Delta\nu_{1/2}$ (Hush) = $(2910\nu_{max})^{1/2}$ cm⁻¹.

Given the nature of the correlation between experimental and predicted IT bandwidths for these complexes, it is somewhat surprising that a better correlation does

not exist for the H_{ad} values, particularly in the case of the more weakly coupled complexes, and especially as regards those for which good estimates of $\Delta\nu_{1/2}$ are afforded by the Hush model.

Table 4.5.3 - Metal-metal coupling elements, H_{ad} , and predicted bandwidths, $\Delta\nu_{1/2}$, for the IT bands of the complexes $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-L})][\text{ClO}_4]_4$ as a function of solvent, determined via the Hush model. Experimental ΔG_r and $\Delta\nu_{1/2}$ values are provided for comparative purposes.^a

L	Solvent ^b	$\Delta\nu_{1/2}$	$\Delta\nu_{1/2}$ (Hush)	H_{ad}	ΔG_r
Me ₂ dicyd ²⁻	AN (14.1)	1760	4290	640	1440
dicyd ²⁻	AN (14.1)	1700	4180	770	1400
dicyd ²⁻	DMSO (29.8)	2340	3930	940	1010
Cl ₁ dicyd ²⁻	AN (14.1)	2160	4090	690	1200
Cl ₂ dicyd ²⁻	NM (2.7)	2290	4020	980	1150
Cl ₂ dicyd ²⁻	AN (14.1)	2440	4000	1090	1070
Cl ₂ dicyd ²⁻	AC (17.0)	2140	3960	1060	1050
Cl ₂ dicyd ²⁻	DMSO (29.8)	3440	3840	1180	570

^a All data in cm⁻¹. ^b Solvent donor numbers listed in parentheses. ^c Hush predicted bandwidths calculated according to $\Delta\nu_{1/2}$ (Hush) = $(2910\nu_{\text{max}})^2$ cm⁻¹.

The very strongly coupled systems of our study are clearly unsuitable for analysis by the Hush model. Only vague implications may be drawn about their coupling from the extent to which Hush model treatment fails to conform to their electrochemical data.

4.6 The CNS Model

The CNS model approaches the question of metal-metal coupling in dinuclear complexes from the perspective of the superexchange mechanism. Thus, since the metals interact with each other via the bridging ligand, it is their individual interactions with the

ligand which ultimately govern the magnitude of their effective (indirect) coupling.

Depending upon whether superexchange occurs via the hole-transfer or electron-transfer pathways (or both), LMCT or MLCT data (or both) are used to determine the effective coupling element H_{LM} .

As was discussed in section 4.2, the LMCT bandshape is not gaussian for any of the complexes of this study. Thus the parameters required for eq 1.4.11 to evaluate the various H_{LM} are not available. (Eq 1.4.11 assumes gaussian bandshape, see section 1.4.) Eq 4.6.1 is used in place of eq 1.4.11 to solve for the various H_{LM} .

$$H_{LM} = \frac{3.03 \times 10^2}{r} (\nu_{\max} \cdot f)^{1/2} \quad (4.6.1)$$

The terms all have their standard meanings (see sections 1.4, 3.4) and eq 4.6.1 is obtained simply by substituting eq 1.4.9 into eq 1.4.11. Note that f in eq 4.6.1 is half the oscillator strength for the observed band, $f = 0.5(f_{LMCT})$, since the overall LMCT oscillator strength arises from two equivalent Ru(III)-NCN chromophores and the metal-ligand coupling elements reflect the coupling between one metal centre and its end of the bridging ligand.

Results of CNS evaluation (see section 1.5) of the pentaammines, tetraammines, and triammines are presented in tables 4.6.1 - 4.6.3, respectively. In accordance with figure 4.2.2, the reduced energy gap, ΔE_{LM} , would be expected to be smallest for the highest energy π -HOMO and in the least electron donating solvents. The results for the pentaammines, $[\{Ru(NH_3)_5\}_2(\mu-L)][PF_6]_4$, reflects this expectation exactly, with ΔE_{LM} being, for each complex, lowest in nitromethane and highest in DMSO, while in acetonitrile ΔE_{LM} is lowest when $L = Me_2dicyd^{2-}$ and highest when $L = Cl_4dicyd^{2-}$. As was

discussed in section 4.2, as the energy difference between the ruthenium πd orbitals and the ligand π -HOMO is decreased their interaction is expected to be increased. Thus H_{LM} for each complex, reciprocally, is expected to be, and is, highest in nitromethane and lowest in DMSO, and in acetonitrile is highest when $L = \text{Me}_2\text{dicyd}^{2-}$ and lowest when $L = \text{Cl}_4\text{dicyd}^{2-}$.

Table 4.6.1 - Metal-ligand coupling elements, H_{LM} , and reduced energy gaps, ΔE_{LM} , and effective metal-metal coupling elements, $H_{MM'}$, for the complexes $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-L})][\text{PF}_6]_4$ as a function of solvent, evaluated according to the CNS Model. ΔG_r values are provided for comparative purposes.^a

L	Solvent ^b	H_{LM} ^c	ΔE_{LM} ^d	$H_{MM'}$ ^e	ΔG_r
$\text{Me}_2\text{dicyd}^{2-}$	AN (14.1)	2570	3020	2190	1110
$\text{Me}_2\text{dicyd}^{2-}$	AC (17.0)	2310	3280	1630	1050
$\text{Me}_2\text{dicyd}^{2-}$	DMSO (29.8)	2000	4600	870	540
dicyd^{2-}	NM (2.7)	2570	3340	1980	1000
dicyd^{2-}	AN (14.1)	2460	3610	1680	900
dicyd^{2-}	AC (17.0)	2180	3870	1230	730
dicyd^{2-}	DMSO (29.8)	2050	5390	780	420
$\text{Cl}_2\text{dicyd}^{2-}$	AN (14.1)	2250	4640	1090	600
$\text{Cl}_2\text{dicyd}^{2-}$	AC (17.0)	2120	5010	900	530
$\text{Cl}_2\text{dicyd}^{2-}$	DMSO (29.8)	1940	6840	550	270
$\text{Cl}_4\text{dicyd}^{2-}$	AN (14.1)	2180	6730	710	340

^a All data reported in cm^{-1} . ^b Solvent donor numbers given in parentheses. ^c Calculated according to eq 4.6.1. ^d Calculated according to eq 1.5.8. ^e Calculated according to eq 1.5.7.

That these results fit the expected pattern is gratifying, and indicates that the CNS model is properly accounting for the behaviour of the complexes with respect to the interaction of each metal centre with the bridge. The more important test, however, is the correlation between $H_{MM'}$ and ΔG_r , which is shown in figure 4.6.1. Importantly, contrary to the H_{ad} predictions of the Hush model (see section 4.5), $H_{MM'}$ has a linear ($r^2 = 0.943$) relationship

with the electrochemically determined ΔG_r . The slope (0.52) is reasonably close to unity and the intercept (36 cm^{-1}) reasonably close to zero.

Figure 4.6.1 - Plot of ΔG_r vs. H_{ML} for the complexes $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-L})][\text{PF}_6]_4$ in all solvents. The line has a slope of 0.52, an intercept of 36 cm^{-1} , and $r^2 = 0.943$. ● = $\text{Me}_2\text{dicyd}^{2-}$, ■ = dicyd^{2-} , ▲ = $\text{Cl}_2\text{dicyd}^{2-}$, ▼ = $\text{Cl}_4\text{dicyd}^{2-}$. Data may be found in table 4.6.1.

Were the model entirely predictive, the slope and intercept would be one and zero, respectively. The analogous plot of ΔG_r vs. H_{ML} for the tetraammines,

$[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-L})][\text{PF}_6]_4$, is given as figure 4.6.2.

Here the slope (0.37) and intercept (85 cm^{-1}) are farther from the values they would hold were the model predictive, and fitting to the best line poorer ($r^2 = 0.883$) than was the case for the pentaammines.

Table 4.6.2 - Metal-ligand coupling elements, H_{LM} , and reduced energy gaps, ΔE_{LM} , and effective metal-metal coupling elements, $H_{MM'}$, for the complexes $[\{Ru(NH_3)_4(py)\}_2(\mu-L)][PF_6]_4$ as a function of solvent, evaluated according to the CNS Model. ΔG_r values are provided for comparative purposes.^a

L	Solvent ^b	H_{LM} ^c	ΔE_{LM} ^d	$H_{MM'}$ ^e	ΔG_r
Me ₂ dicyd ²⁻	NM (2.7)	2960	2570	3410	1250
Me ₂ dicyd ²⁻	AN (14.1)	2850	2420	3360	1340
Me ₂ dicyd ²⁻	DMSO (29.8)	2020	3210	1270	870
dicyd ²⁻	NM (2.7)	2790	2640	2950	1280
dicyd ²⁻	AN (14.1)	2690	2360	3070	1190
dicyd ²⁻	DMSO (29.8)	2280	3300	1580	670
Cl ₂ dicyd ²⁻	NM (2.7)	2450	3080	1950	940
Cl ₂ dicyd ²⁻	AN (14.1)	2350	3000	1840	800
Cl ₂ dicyd ²⁻	DMSO (29.8)	2050	4290	980	350
Cl ₄ dicyd ²⁻	NM (2.7)	2400	3960	1450	600
Cl ₄ dicyd ²⁻	AN (14.1)	2420	4270	1370	420
Cl ₄ dicyd ²⁻	DMSO (29.8)	2110	6230	710	260

^a All data reported in cm⁻¹. ^b Solvent donor numbers given in parentheses. ^c Calculated according to eq 4.6.1. ^d Calculated according to eq 1.5.8. ^e Calculated according to eq 1.5.7.

Table 4.6.3 - Metal-ligand coupling elements, H_{LM} , and reduced energy gaps, ΔE_{LM} , and effective metal-metal coupling elements, $H_{MM'}$, for the complexes $[\{Ru(NH_3)_3(bipy)\}_2(\mu-L)][ClO_4]_4$ as a function of solvent, evaluated according to the CNS Model. ΔG_r values are provided for comparative purposes.^a

L	Solvent ^b	H_{LM} ^c	ΔE_{LM} ^d	$H_{MM'}$ ^e	ΔG_r
Me ₂ dicyd ²⁻	AN (14.1)	2920	2650	3220	1440
dicyd ²⁻	AN (14.1)	2950	2410	3610	1400
dicyd ²⁻	DMSO (29.8)	2650	2460	2850	1010
Cl ₂ dicyd ²⁻	AN (14.1)	2380	2350	2410	1200
Cl ₂ dicyd ²⁻	NM (2.7)	2830	2560	3130	1150
Cl ₂ dicyd ²⁻	AN (14.1)	2720	2460	3010	1070
Cl ₂ dicyd ²⁻	AC (17.0)	2690	2500	2890	1050
Cl ₂ dicyd ²⁻	DMSO (29.8)	2260	3120	1640	570

^a All data reported in cm⁻¹. ^b Solvent donor numbers given in parentheses. ^c Calculated according to eq 4.6.1. ^d Calculated according to eq 1.5.8. ^e Calculated according to eq 1.5.7.

Figure 4.6.2 - Plot of ΔG_r vs. H_{MLF} for the complexes $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-L})][\text{PF}_6]_4$ in all solvents. The line has a slope of 0.37, an intercept of 85 cm^{-1} , and $r^2 = 0.883$. ● = $\text{Me}_2\text{dicyd}^{2-}$, ■ = dicyd^{2-} , ▲ = $\text{Cl}_2\text{dicyd}^{2-}$, ▼ = $\text{Cl}_4\text{dicyd}^{2-}$. Data may be found in table 4.6.2.

Considering immediately the ΔG_r vs. H_{MLF} plot for the triammines, $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-L})][\text{ClO}_4]_4$, given as figure 4.6.3, the slope (0.44) is intermediate between that for the pentaammines and that for the tetraammines while the intercept (-190 cm^{-1}) is farther from zero than that for the tetraammines. That the slope for the triammines is closer to one than that for the tetraammines is somewhat surprising, if the model is believed to break down to a greater extent as the systems become more strongly coupled. The behaviour of the intercept, however, would support such a conclusion, becoming steadily farther from zero as the systems become more strongly coupled.

Figure 4.6.3 - Plot of ΔG_r vs. H_{MML} for the complexes $[\{Ru(NH_3)_3(bipy)\}_2(\mu-L)][ClO_4]_4$ in all solvents. The line has a slope of 0.44, an intercept of -190 cm^{-1} , and $r^2 = 0.889$. ● = Me_2dicyd^{2-} , ■ = $dicyd^{2-}$, ▲ = Cl_2dicyd^{2-} . Data may be found in table 4.6.3.

The existence of such a breakdown of the CNS model as the systems becomes more strongly coupled would be understandable in terms of one of the assumptions made for the use of eq. 1.5.7, namely that H_{LM} be “much smaller” than E_{LMCT} .⁴⁰ Note that while “much smaller” wasn’t explicitly quantified by CNS, the ratio between H_{LM} and E_{LMCT} ranges from 1:6 to 1:4 for the pentaamines and drops to not much better than 1:3 for certain of the tetraamines and most of the triamines.

The other assumption expected to be violated at some point is that overlap between the metal and ligand orbitals can be neglected. (*i.e.* $S_{LM} \approx 0$). As the systems

become more strongly coupled, covalency effects, as has been noted (see sections 4.2 and 4.3), become more pronounced.

In section 1.8 the relationship between f_{LMCT} and ΔG_r was postulated. Figure 4.6.4 provides such a plot composed of data for the complexes of this study.

Figure 4.6.4 - Plot of f_{LMCT} vs. ΔG_r for the complexes $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-L})][\text{PF}_6]_4$ (●), $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-L})][\text{PF}_6]_4$ (■) and $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-L})][\text{ClO}_4]_4$ (▲), $\text{L} = \text{Me}_2\text{dicyd}^{2-}$, dicyd^{2-} , $\text{Cl}_2\text{dicyd}^{2-}$, and $\text{Cl}_4\text{dicyd}^{2-}$ (where applicable) in nitromethane, acetonitrile, acetone, and dimethylsulfoxide. Data from tables 3.4.1 - 3.4.10, 3.4.12, and 4.3.2 - 4.3.4 as $0.5(\Delta G_c - 520) \text{ cm}^{-1}$.

Data from the complex $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Cl}_2\text{dicyd})][\text{ClO}_4]_4$ have been omitted for the reasons discussed in section 4.2.

The curve of the f vs ΔG_r plot has the expected shape, and the region in which increasing energetic matching of the metal and ligand orbitals corresponds to decreasing

oscillator strength coincides with data for the complexes $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-L})][\text{ClO}_4]_4$, $\text{L} = \text{Me}_2\text{dicyd}^{2-}$ and dicyd^{2-} , in acetone, acetonitrile, and nitromethane. These data points are exactly those points for which the behaviour of ΔG_c became “inverted” (thus that the electrochemical ΔE , and hence ΔG_c , decreased as a function of decreasing solvent donor number - see section 4.3.), and the curvature of the f vs. ΔG_r plot is more clearly seen in figure 4.6.5, containing only data for the triammine complexes.

Figure 4.6.5 - Plot of f_{LMCT} vs. ΔG_r for the complexes $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-L})][\text{ClO}_4]_4$ (▲), $\text{L} = \text{Me}_2\text{dicyd}^{2-}$, dicyd^{2-} , and $\text{Cl}_2\text{dicyd}^{2-}$ in nitromethane, acetonitrile, acetone, and dimethylsulfoxide. Data from tables 3.4.9, 3.4.10, 3.4.12 and 4.3.4 as $0.5(\Delta G_c - 520) \text{ cm}^{-1}$.

This inversion of behaviour, also seen for the complex $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{PF}_6]_4$ in acetonitrile vs nitromethane, has been ascribed to optimization of ΔG_r , and hence to full delocalization (Class III behaviour) in the systems (see section 4.3).

(Recall that $\Delta G_r \propto H_{MM'} \propto \nu_{\max}(\text{IT})$. Thus if ΔG_r is constant, so too is $\nu_{\max}(\text{IT})$, which is an important criterion for Class III behaviour). Excluding the data corresponding to these complexes, figures 4.6.2 and 4.6.3 may be recast containing data only for the Class II tetraammine and triammine complexes as figures 4.6.6 and 4.6.7, respectively.

Figure 4.6.6 - Plot of ΔG_r vs. $H_{MM'}$ for the complexes $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-L})][\text{PF}_6]_4$ in all solvents. The line has a slope of 0.44, an intercept of -51 cm^{-1} , and $r^2 = 0.951$. ■ = dicyd^{2-} , ▲ = $\text{Cl}_2\text{dicyd}^{2-}$, ▼ = $\text{Cl}_4\text{dicyd}^{2-}$. Data may be found in table 4.6.2.

Figure 4.6.7 - Plot of ΔG_r vs. H_{NMR} for $[\{Ru(NH_3)_3(bipy)\}_2(\mu-Cl_2dicyd)][ClO_4]_4$ as a function of solvent. The line has a slope of 0.38, an intercept of -54 cm^{-1} , and $r^2 = 0.997$. Data may be found in table 4.6.3.

In both plots, significant improvement in the fit of data to a best line, in slope, and in intercept are seen. A consistent trend now exists for the slopes of the three families, being highest for the pentaammines (0.52), and decreasing for the tetraammines (0.44) and again for the triammines (0.38). The intercepts, -51 cm^{-1} for the tetraammines and -54 cm^{-1} for the triammines, are significantly closer to zero for both systems while the fits to the best line, 0.951 for the tetraammines and 0.997 for the triammines, are dramatically improved.

Plots of ΔG_r vs. H_{NMR} exist in literature^{42,50} for the pentaammine and tetraammine complexes in a single solvent (acetonitrile) showing metal-metal coupling as a function of the bridging ligand. Those spectra will not be reproduced here, nor will the analogous

plot be attempted for the triammines, since the $L = \text{dicyd}^{2-}$ and $\text{Me}_2\text{dicyd}^{2-}$ complexes seem to be too strongly coupled for the CNS model to be appropriate. However, a comparative plot of the three $L = \text{Cl}_2\text{dicyd}^{2-}$ complexes as a function of solvent is presented here (figure 4.6.8) showing how the CNS modelled behaviour of the complexes change as a function of the metals' inner coordination spheres.

Figure 4.6.8 - Plot of ΔG_r vs. H_{MMF} for the three complexes incorporating the bridging ligand $\text{Cl}_2\text{dicyd}^{2-}$ as a function of metal inner coordination sphere and solvent. ● = pentaammine, $m = 0.63$, $b = -65$, $r^2 = 0.977$, ■ = tetraammine, $m = 0.58$, $b = -220$, $r^2 = 0.984$ ▲ = triammine, $m = 0.38$, $b = -54$, $r^2 = 0.997$. (For lines of the type $y = mx + b$). Data from tables 4.6.1 - 4.6.3.

Here again, as in the more general case including all Class II examples for each family, the slope of the ΔG_r vs H_{MMF} for each $L = \text{Cl}_2\text{dicyd}^{2-}$ complex is closest to one for the pentaammine complex (0.63), and decreases for the tetraammine (0.58) and triammine

(0.38) complexes. This is perhaps indicative that as H_{LM} becomes closer in magnitude to ΔE_{LM} , and the requirement " H_{LM} much smaller than E_{LMCT} " thus less distinct, that CNS treatment becomes less valid. It is significant that the model still gives linear correlations with electrochemical data, and the model doesn't actually seem to break down fully until the system being studied exhibits Class III behaviour.

One of the assumptions made during analysis of data via the CNS model is that R , the transition dipole moment, approximated by r , the donor-acceptor separation, is constant. That the slopes are not unity may be due to variations in R as coupling is varied in the complexes, and this possibility may be tested by electroabsorption (Stark) spectroscopic analysis of the complexes (see section 1.5).⁴⁵

4.7 Conclusions and Future Studies

The ability to study three full families of complexes based on ligands of the dicyanamidobenzene family has allowed for elucidation of the electronic factors affecting superexchange due to ligand and metal centred inner-sphere perturbations and outer-sphere perturbations. In broadest terms, the simplistic view that increasing the energetic matching between metal and ligand orbitals will increase their interaction has been borne out. Coupling was systematically increased upon going from the pentaammine complexes to the tetraammines to the triammines, with a concurrent increase in the degree of covalency in the bonding.

The effect of covalency upon both the simplistic energy matching view and the theoretical models of metal-metal coupling was demonstrated, with the electronic absorption and especially the electrochemical data culminating in the assignment of $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{PF}_6]_4$ in nitromethane and of both $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-dicyd})][\text{ClO}_4]_4$ and $[\{\text{Ru}(\text{NH}_3)_3(\text{bipy})\}_2(\mu\text{-Me}_2\text{dicyd})][\text{ClO}_4]_4$ in nitromethane, acetonitrile, and acetone as being valence delocalized (Class III) systems.

The range of coupling over the three families of complexes ranges from near statistical (very weakly Class II) for $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-Cl}_4\text{dicyd})]^{4+}$ in water to Class III for the systems and conditions mentioned above, and may serve as evidence that the “sharp transition” between Class II and Class III behaviour postulated by Broo and Larsson¹¹⁷ does not, at least for polarizable systems, exist.

The onset of Class III behaviour was shown to coincide with breakdown of the CNS model - the point at which it ceased to give linear correlations with experimental data. That the model gave linear correlations for all complexes of this study other than those categorized as Class III may suggest that the CNS model is broadly applicable to all Class II systems, and that the degree of overlap required for Class III behaviour violates the requirement that overlap be ignored attendant to eq 1.4.11.

Evans method (magnetic moment) experiments further suggest that the onset of complete diamagnetism of the ground state occurs in the the fully oxidized ($[\text{Ru(III)}\text{-Ru(III)}]$) complexes under the same conditions for which the corresponding mixed-valence ($[\text{Ru(III)}\text{-Ru(II)}]$) complexes become valence delocalized. Whether this is

coincidental or an indication that the threshold metal-ligand coupling required for both behaviours is the same should certainly be the subject of a future study.

A number of other studies are also proposed to elucidate the findings of this thesis. The simplest of these is the collection of further IT data (via OTTLE spectroelectrochemistry) for the triammine complexes. Data showing that the IT band energies of the $L = \text{Me}_2\text{dicyd}^{2-}$ and $L = \text{dicyd}^{2-}$ complexes are solvent independent, particularly for the solvents in which their behaviour was inverted (nitromethane, acetonitrile, acetone) will help solidify their assignment as Class III. Similarly, more Evans method experiments should be conducted to test the limits at which no paramagnetism is apparent. Solid state magnetic studies might also be valuable for comparative purposes with those previously conducted on the pentaammine and triammine systems.

The most stringent test of delocalization has been said to be the identification of IR bands associated with the delocalized state.¹³ Such a study should be carried out, and the OTTLE cell described herein (see section 2.6.6) is suitable for performing the requisite spectroelectrochemical studies in the IR region to find such a band.

Curtis^{20,21} has also suggested a technique through which redox asymmetry may be used to determine the extent of metal-metal coupling through evaluation of α , the diabatic wavefunction mixing parameter. Such a study could be undertaken on complexes of dicyanamidobenzene ligands bridged by ruthenium centres with inequivalent inner-spheres.

Asymmetric ruthenium complexes pose an interesting problem for the CNS model. Since it is claimed that $H_{\lambda\lambda'}$ may be determined using data from a mononuclear

complex,⁴⁰ an asymmetric complex would allow three experimental determinations of H_{MCT} from the electronic absorption spectra of mononuclear complexes based on each end of the asymmetric complex and of the asymmetric dinuclear complex itself. This would serve to probe the effect two potentially interacting chromophores may have on the metal-ligand coupling elements, and hence on H_{MCT} .

As mentioned in the discussion of the CNS model, R may be evaluated experimentally using Stark (electroabsorption) spectroscopy. Whether R is changing from complex to complex, and the magnitude of R , would both be helpful in understanding the results of CNS analysis, and should be determined.

Lastly, further investigation into f vs ΔG plots is probably merited. In the case of the complexes of this study, f_{LMCT} seemed to reach a plateau, but didn't significantly decrease in a predictable fashion. Much of the "inverted" behaviour stemmed from optimization of ΔG_r . Perhaps a better candidate system will lend itself to elucidation of the expected relationship between these two quantities. In fact, although our correction of ΔG_c to yield ΔG_r is linear, in general it would seem more appropriate to plot f vs. ΔG_c itself. Comparison of such a plot with a f vs. ΔG_r plot would then elucidate whether the inversion is due to optimization of ΔG_r or f .

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