**Inner and Outer Sphere Perturbation of Strongly Coupled
Class (III) Mixed-Valence Complexes**

by

Mousa Al-Noaimi

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Department of Chemistry

Ottawa-Carleton Institute

Carleton University

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Abstract

This study involved the investigation of donor-acceptor mixed-valence complexes in order to develop a framework for the future design of highly polarizable non-linear optical materials. Two novel families of Class III mixed-valence complexes, $[\{\text{Ru}(\text{L})(\text{L}')\}_2(\mu\text{-dicyd})]^{2+}$ and $[\{\text{Ru}(\text{L})(\text{L}')\}_2(\mu\text{-adpc})]^{2+}$, where L is 4'-*p*-tolyl-2,2':6',2''-terpyridine (ttp) or 4-*p*-tolyl-2,6-di(2-pyrazinyl)-pyridine (tpz), and L' is 2,2'-bipyrazine (bpz) or 2,2'-bipyridine (bpy), were synthesized and characterized by elemental analysis, IR, ^1H NMR, X-ray crystallography, UV-visible, Near-IR spectroscopies, cyclic voltammetry and IR-spectroelectrochemistry. The main thrust of this investigation was the in depth examination of inner-sphere and outer-sphere perturbations on metal-metal coupling in these delocalized systems.

In order to fully understand the effect of the auxiliary ligand on the electronic perturbation of the Ru-cyanamide chromophore and the Ru(III/II) redox couple, and how these affect the electronic and antiferromagnetic coupling in dinuclear complexes, four novel phenylcyanamide mononuclear complexes, $[\text{Ru}(\text{L})(\text{L}')(2,3,4,5\text{-Cl}_4\text{pcyd})]^+$, were first studied. Oxidation of these complexes by controlled potential electrolysis allowed for the study of inner sphere effects on the LMCT band energy and the redox chemistry of the complexes. These results have been compared to those of $[\text{Ru}(\text{NH}_3)_5\text{L}'']^{2+}$ where L'' is a substituted phenylcyanamide ligand, and the difference was related to a significant increase in Ru(III)-cyanamide covalency which results from the increased stability of the metal $d\pi$ -orbitals due to the weak σ -donor ligands. The Ru(III/II) redox couples of these

mononuclear complexes were used in order to estimate the electronic and antiferromagnetic coupling in the dicyd²⁻ family of dinuclear complexes.

The IR spectra of the mixed-valence complexes $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-dicyd})]^{3+}$ and $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-adpc})]^{3+}$, which represent the two families, and comproportionation data was consistent with a delocalized mixed-valence state. A spectroscopic analysis assuming C_{2h} microsymmetry led to a prediction of multiple MMCT transitions with the lowest energy transition equal to the resonance exchange integral for the mixing of ruthenium donor and acceptor orbitals with a bridging ligand orbital (the preferred superexchange pathway). The solvent dependence of the MMCT band energy that was observed for the 1,4-azodi(phenylcyanamide) family was suggested to be largely due to a ground state perturbation of metal-metal coupling due to a donor-acceptor interaction of solvent molecules with the azo group of the bridging ligand.

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Dedication

To my mother who instilled in me the love of knowledge and self-reliance

*To my wife (Rema) and my children (Hossam and Noura) who gave me all
their love and support*

*To everyone who has played an encouraging role in helping me to accomplish
this work*

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List of Symbols

H_{ad}	Acceptor-donor coupling element (Hush model)
AN	acetone
AC	acetonitrile
Adpc	4,4-azodi(phenylcyanamide
bpz	2,2'-Bipyrazine
bpy	2,2'-Bipyridine
K_c	Comproportionation constant
CV	Cyclic voltammetry
DCE	dichloroethane
DMF	<i>N,N'</i> -dimethylformamide
DMSO	dimethylsulfoxide
dicyd ²⁻	1,4-dicyanamidobenzene
ΔG_e	Electrostatic free energy
E_{it}	Energy of the intervalence transition
ΔG_s	Entropic free energy
ΔG_{ex}	Free energy of antiferromagnetic exchange
ΔG_c	Free energy of comproportionation
ΔG_{IP}	Free energy of ion-pairing
ΔG_r	Free energy of resonance exchange
HOMO	Highest occupied molecular orbital
ΔG_i	Inductive free energy
λ_{inner}	Inner-sphere reorganizational energy
IT	Intervalence transition

IC	interconfigurational band
LMCT	Ligand-to-metal charge transfer
LUMO	Lowest unoccupied molecular orbital
MLCT	Metal-to-ligand charge transfer
MMCT	Metal-to-metal charge transfer
H_{MM}	Metal-metal coupling element (CNS model)
NIR	Near-infrared
NM	nitromethane
NB	nitrobenzene
N.H.E.	Normal hydrogen electrode
NLO	non linear optical material
NMR	Nuclear magnetic resonance
OTTLE	Optically transparent thin layer electrode
f	Oscillator strength
λ_{outer}	Outer-sphere reorganizational energy
pcyd ⁻	Phenylcyanamide
PC	propylene carbonate
tpz	4- <i>p</i> -tolyl-2,6-di(2-pyrazinyl)-pyridine
ttp	4'- <i>p</i> -tolyl-2,2':6',2''-terpyridine
H	Resonance exchange integral
TBAH	Tetrabutylammonium hexafluorophosphate
ΔG_{th}	Thermal energy barrier to electron transfer
terpy	2,2':6',2''-terpyridine

Chapter 1 Introduction

1.1 Non-Linear Optical Materials and Applications

The creation of novel materials that have useful applications such as in video displays and nanoscale electronics is an important goal for many chemists.¹ One of the most important areas of research involves Non-Linear Optical (NLO) materials: a large class of materials that include electro-optic and second harmonic generation materials. These materials are the key elements for future photonic technologies used in many devices such as electro-optical modulators for optical switching, electro-to-optical transduction, and ultrafast analogue-to-digital signal conversion for the optical telecommunication industry.

Second order non-linear optical activity arises from a change in the index of refraction of a material due to the application of a voltage. The influence of an electric field changes the charge distribution within the non-linear optical chromophore by changing the mixing of neutral and charge separated states. This change in charge distribution will alter the velocity of light and cause a phase shift as it propagates through the material. A typical device that can exploit this phenomenon is shown in Figure 1.1.¹ This device acts as an ultrafast shutter impressing electronic data signals onto the laser beam. Light from a laser beam is split and passes through two arms of the optical device, one of which is composed of a NLO material and is under the influence of an electric field. This causes the light passing through the lower arm of the device to change phase relative to the light

in the upper arm. Upon collimation of the two beams of different phase, destructive interference occurs, leading to an amplitude modulation at the output of the device.

Figure 1.1 Electro-optical device configuration.

The effect of an electric field on the optical polarization is key in second order NLO materials. Equation 1 gives the polarization P of a molecule as the sum of the ground-state polarization, P_o , and the induced polarization, P_i (equation 2), which is generated by an external electric field, E , and is expressed as a power series.¹

$$P = P_o + P_i \quad (1)$$

$$P_i = \alpha_{ij} E_j + \beta_{ijk} E_j E_k + \gamma_{ijkl} E_j E_k E_l \quad (2)$$

where the coefficient α is the linear hyperpolarizability, β is the quadratic hyperpolarizability, γ is the cubic hyperpolarizability, and i, j, k and l refer to the molecular coordinate system.¹ The term second-order is derived from the fact that the magnitude of this effect is defined by the second term of the power series expansion in equation 2. Unlike the first- and third-order term of equation 2, there is a symmetry

requirement of the second-terms; namely, that of noncentrosymmetric or acentric symmetry. In order to display non-linear second-order properties, the materials cannot have a center of inversion; otherwise its contribution to induced polarization is zero.

The creation of a non-linear optical material is not a simple task. Organic second-order nonlinear optical materials are those in which dipolar molecules form a noncentrosymmetric lattice. In fact, this is a rare occurrence and the overwhelming preference is for dipolar molecules to organize themselves in a way that cancels out dipole moment (a centrosymmetric lattice). For polymer chemists, organization of dipolar moieties in a polymer material can be induced by the application of a strong electric field (poling) while the polymer is in a glass transition phase (Figure 1.2). The poling process works as follows: An organic thin film is cast into indium tin oxide (ITO) coated glass which is conductive and serves as one of the electrodes in the poling step. Following film preparation, a second electrode is applied by thermal evaporation of gold on top of the electro-optic polymer. A voltage is applied across the thin film while it is heated to its glass transition phase. Cooling the polymer to a solid during poling freezes the alignment of the dipoles and creates the asymmetry required for a non-linear optical material. Whether this material is useful depends upon the magnitude of its electro-optic activity.¹

Figure 1.2 Schematic of an electric field poling set-up.

Electro-optic activity is determined by the nature of the dipolar moiety, the extent of its noncentrosymmetric order in the solid state, and the change in non-linear optical properties of the material with the application of an electric field. The choice of dipolar moiety has centered on organic charge-transfer molecules of the general form D-spacer-A, where D is an electron donor moiety such as an amine, A is the electron acceptor moiety (such as a cyano or nitro group) and the spacer is usually a π conjugated molecule that permits coupling between donor and acceptor. A key property of the charge-transfer molecule is its polarizability. The molecular hyperpolarizability (β) of a charge-transfer molecule is a measure of its second-order non-linear properties and, assuming a two-state charge-transfer process, is described by the equation below:

$$\beta = \frac{(\mu_{ee} - \mu_{gg})}{(\Delta E_{ge})^2} (\mu_{ge})^2 \quad (3)$$

where $\mu_{ee} - \mu_{gg}$ is the difference between dipole moments of the ground and excited states. ΔE_{ge} is the HOMO-LUMO energy gap (a charge transfer transition) and μ_{ge} is the transition matrix element between ground and excited states. The sign of β is a function

of the relative magnitudes of μ_{ee} and μ_{gg} , and generally $\mu_{ee} > \mu_{gg}$ and β is positive.² If an electric field is applied, the mixing of ground and excited charge will change thereby changing the value of β . In the bulk material, the change in hyperpolarizability is additive, and, depending on the extent of noncentrosymmetric order of charge transfer moieties, in total gives the electro-optic activity of the material.^{3,4}

The drive voltage (the applied electric field required to induce an electro-optical effect) which is required for digital-level applications must be compatible with semiconductor electronics (less than 6 V and preferably 1 V). With organic chromophores, this low drive voltage is a difficult goal to obtain and, therefore, chemists have begun to focus on a new class of charge-transfer chromophores suitable for electro-optical applications based on transition metal complexes. A number of studies of organometallic systems and Schiff-base complexes have been published, but for the most part research has centered on organic charge-transfer chromophores probably for reasons of synthetic ease and cost.¹ Mixed-valence complexes with conjugated organic bridging ligands are donor-acceptor systems which make them the promising candidates for electro-optical materials.

To achieve an electro-optical activity comparable to lithium niobate (a well known standard for NLO chromophores), requires molecular $\mu\beta$ product values ca. 2000×10^{-30}

esu D or greater. Only a few hyperpolarizability measurements have been performed on mixed-valence complexes.¹ The $\mu\beta$ product values of the mixed-valence complexes $[(\text{CN})_5\text{Ru}-\mu\text{-CN-Ru}(\text{NH}_3)_5]^-$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2-\mu\text{-CN-Ru}(\text{NH}_3)_5]^{3+}$ are 1040 and 780×10^{-30} esu D, respectively, assuming $\mu = 5$ D in both cases.¹ These are encouraging results as metal-metal separation in mixed-valence complexes can be much greater than 5 Å and suggests that far greater $\mu\beta$ product values are possible.¹

In order to achieve a low drive voltage ($< 1\text{V}$), the electrons involved in the charge transfer must be highly polarizable, which is generally true for mixed-valence complexes. This low voltage might be achieved by coupling the metal ions via the HOMO of the bridging ligand where the polarizability of both metal $d\pi$ and bridging ligand HOMO (such as 1,4-dicyanamidobenzene (dicyd²⁻) and 4,4-azo(diphenylcyanamide) (adpc²⁻) bridging ligand) electrons can play a role in determining electro-optical activity. Unfortunately, with increased polarizability, the susceptibility of the chromophore to oxidization is expected to increase and this may affect the products lifetime. A proper balance between these opposing properties must be found.¹

adpc²⁻ dicyd²⁻

In addition to a large $\mu\beta$ value, the chromophore should exhibit appropriate solubility in spin-casting solvents, be compatible with the host polymer, and possess both thermal and

photochemical stability. The stability and the solubility of the complexes can be achieved by using multidentate ligands with organic substituents (e.g. 4'-*p*-tolyl-2,2':6',2''-terpyridine and 4,4',4''-tri-*tert*-butylterpyridine). Poling temperatures typically lie in the range of 90 to 140 °C and therefore volatile ligands (e.g. NH₃ and CO) should be avoided.

1.2 Donor-Acceptor Systems Based on Ru-Phenylcyanamide Mononuclear Complexes

Mixed-valence complexes could be ideal donor acceptor systems for NLO materials. Firstly, however, a good grasp of the electronic coupling that takes place in the mononuclear complexes is necessary in order to understand the properties of mixed-valence dinuclear complexes. When a Ru(III) metal complex binds to a π -donating ligand such as phenylcyanamide (pcyd⁻), a low energy band assigned to a LMCT (ligand to metal charge transfer) appears in the electronic spectrum. The LMCT event (Figure 1.3) involves the oxidation of the pcyd⁻ ligand and reduction of the Ru(III) ion. The energy of the LMCT can be related to the difference between the metal Ru(III/II) and ligand L(0/-1) redox couples according to equation 4.⁵

$$E_{LMCT} = [L(0/-) - Ru(III/II) + C] + \chi \quad (4)$$

where χ is the energy difference between the zeroth vibrational level and the populated excited vibrational level in the excited state during a Franck-Condon transition. It takes into account the inner and outer sphere organization energy involved in the LMCT event.

C is a “fudge factor” and comes from the impossibility of measuring $E(\text{Ru(III/II)})$ after the ligand is oxidized to $L(0)$.

Figure 1.3 State-to-state potential energy curves for a Ru(III)-pcyd complex.

The ligand-metal coupling element H_{LM} in (cm^{-1}) can be derived from the oscillator strength, (f), of the LMCT band by the following equation.⁶

$$H_{LM} = \frac{303}{R} (E_{LMCT} \cdot f)^{\frac{1}{2}} \quad (5)$$

where f is the oscillator strength and can be experimentally determined from the integral of the molar absorptivity versus energy of the charge transfer band and theoretically from the transition dipole moment length R of the LMCT by the following expression.⁷

$$f = 1.085 \times 10^{-5} G \nu S^2 R^2 \quad (6)$$

where G is degeneracy of states, ν is the transition energy in cm^{-1} , and S is the overlap integral of a ruthenium $d\pi$ orbital with a cyanamide $p\pi$.

In order to maximize β , it is necessary to maximize the absolute value of the induced dipole moment ($\mu_{ee}-\mu_{gg}$) (equation 3). Because of the small dipole moment associated with Ru(II)-phenylcyanamide complexes, these systems are unsuitable for nonlinear optical materials. Mixed-valence complexes with conjugated organic bridging ligands are more promising candidates for electro-optical materials, because of the increased dipole moment of the ground state and the greater dipole moment difference ($\mu_{ee}-\mu_{gg}$) that can lead to larger β values. The length of the conjugated π system is also an important factor since the delocalization of the π -electronic clouds can contribute to the molecular hyperpolarizability (β).

With this understanding of the mononuclear complexes one now has the basis for understanding dinuclear complexes made from the same building blocks.

1.3 Donor-Acceptor Systems Based on Mixed-Valence Complexes

Mixed-valence complexes have been known for many years with the vast majority of studies being performed on symmetric ruthenium valence-trapped systems in which two metal ions are joined by a single bridging ligand (BL).^{8,9} The metals possess identical coordination spheres and differ only by the presence of an extra electron. Metal-metal coupling can occur through two major routes: direct overlap of the metal orbitals or superexchange.⁶ Superexchange describes electron exchange between two metal centers through the orbitals of a bridging ligand. The bridging ligand has a great influence on the coupling and may consist of an extended organic molecule group or a single atom.

Electron transfer between the Ru ions of this complex can be induced thermally or photochemically (metal-to-metal charge transfer (MMCT, E_{op} or E_{IT})) and the conceptual framework needed to understand mixed-valence properties owes much to that which forms the basis of the Marcus theory of electron transfer.^{10,11}

In general, the two metal coordination environments in a mixed-valence complex differ in the lengths and the force constants of the metal-ligand bonds and in the solvation; these factors create a barrier for electron transfer. Thermal electron transfer, the lower pathway in Figure 1.4, does not proceed without prior rearrangement of the inner and outer shell which gives an electron transfer activation barrier. Optical electron transfer,

the upper pathway in Figure 1.4, can be induced when light of the correct energy ($E_{op} = \lambda = h\nu$) is absorbed causing the mixed-valence complex $[M-L-M^+]$ to form in the excited state $^*[M^+-L-M]$. In most cases, the MMCT band lies in the near IR region of electromagnetic radiation.

Figure 1.4 Thermal and optical electron transfer processes in a symmetric dinuclear mixed-valence complex. The sizes of the circles (a) reflect the size of the inner coordination sphere of the metal. d_2 , d_3 and f_2 , f_3 are the metal-ligand bond lengths and the force constants for the two metals (M and M^+), respectively. The symbols a^* represent an activated state.

1.4 Classification of Mixed-Valence Complexes

Mixed-valence complexes are typically classified by Robin and Day into three main categories:¹² (i) Class I: a completely valence-trapped system with no coupling between metal ions, (ii) Class II: a valence-trapped system with weak coupling between metal ions; and (iii) Class III: the valency of the system is completely delocalized due to strong coupling between metal ions. There have been few systematic investigations of the

properties of Class III compared to Class II mixed-valence complexes but this is changing with the need to understand and recognize the transition between Class II and III properties. A recent review by Meyer et al¹⁶ examined this issue and proposed the new classification Class II-III in which the complex is solvent-averaged and electronically localized.

1.5 Timescales and Infrared Spectroscopy

Infrared spectroscopy, with a timescale of the order 10^{-13} s, has been recognized as a powerful means to examine the delocalization in mixed-valence systems.¹³ For weakly coupled mixed-valence systems, the electron transfer rate will be slower than 10^{13} s^{-1} , and separate peaks for a given infrared absorption should be observed. For strongly coupled mixed-valence systems, when the electron transfer rate is $\geq 10^{13} \text{ s}^{-1}$, complete coalescence occurs and only an average peak will be observed.

The cyanamide moiety in symmetric complexes bridged by the 4,4'-azodi(phenylcyanamide) dianion or 1,4-dicyanamidebenzene dianion has an intense infrared absorption band in the region of 2200 to 2000 cm^{-1} . For strongly coupled mixed-valence systems where the two metal centers of the complex have the same average oxidation state, only one $\nu(\text{NCN})$ band should be observed. In the weakly coupled mixed-valence system, the two metal centers of the complex have different oxidation states and the $\nu(\text{NCN})$ band should split into two peaks.¹⁴

1.6 Theoretical Modeling of Metal-Metal Coupling

There are two main models used to describe metal-metal coupling. The first model is the classical two-state model of Hush. This model evaluates metal-metal coupling by assessing the oscillator strength, f , of the IT band. The second model focuses on the superexchange mechanisms by invoking the bridging ligand orbitals in the coupling.

1.6.1 The Hush Two State Model

1.6.1.1 Class II Categorization

The theory of electron transfer in a mixed-valence complex has been discussed in many articles and texts.^{8,15} The classical two-state model is the simplest model used to understand thermal and photoinduced electron transfer. The present discussion is restricted to the symmetric system ($\Delta G^0 = 0$) but it can be extended to asymmetric complexes by considering the net free energy change. Figure 1.5 shows the potential energy-configuration diagram for a classical two-state model. This system consists of only two diabatic states, initial (donor) and final (acceptor). The electron is coupled between the donor and the acceptor by a single oscillator that has the same frequency in both the initial (left-hand curve) and final (right-hand curve) states. In thermal electron transfer, the system moves from left to right (horizontally) along the lower surface and (classically) passes over the barrier of height E_{th} . E_{op} is the vertical transition between the two states and takes place when light of the correct energy makes the system pass vertically from the lower to the upper surface.

Figure 1.5 Potential energy configuration diagram (Class I).

In the absence of any interaction between donor and acceptor metal ions (no splitting at the intersection of the potential energy curves), the resonance exchange integral, H_{ad} , which is a measure of the degree of electronic coupling between donor and acceptor, is zero ($H_{ad} = 0$). Such behaviour is representative of a Class I mixed-valence system (Figure 1.5). When an interaction between donor and acceptor does occur, initial and final states mix causing the curves to split at their intersection by $2H_{ad}$. The thermal activation barrier E_{th} decreases as H_{ad} increases with the onset of donor-acceptor coupling (Figure 1.6).

Electronic coupling is promoted by mixing the electronic donor and acceptor wave functions. As mixing increases, covalency is approached. This decreases the distinction between the formal oxidation states of the local sites and causes the structural differences between sites and local solvent dipole orientations to decrease or to be averaged.

Electronic delocalization can be varied by making changes in the metal, the bridging ligand, the auxiliary ligands, or the solvent. If the geometrical distance between the metal centers is large, the direct overlap between the donor and acceptor wave functions becomes negligible. However, electrostatic perturbation between the electron donor and acceptor makes these waves mix and open a channel for electron tunneling.

Figure 1.6 Potential energy configuration diagram showing the distortion of potential energy curves that result when initial and final states are mixed to give a Class II case.

For weakly coupled symmetric Class II mixed-valence complexes, Hush derived the following relationships for the E_{op} band properties:

$$E_{op} = 4E_{th} \quad (7)$$

The band width at half peak height $\Delta\nu_{1/2}$ (in cm^{-1}) assuming that the IT band is Gaussian, is given by the following equation:

$$\Delta\nu_{1/2} = (2310E_{op})^{1/2} \quad (8)$$

Hush further showed that, for weakly coupled systems, the intensity ϵ_{max} (in $\text{M}^{-1}\text{cm}^{-1}$) and position of band (E_{op}) are related to the extent of coupling H_{ad} (in cm^{-1}) between donor and acceptor:

$$H_{\text{ad}} = (2.06 \times 10^{-2} / R)(E_{\text{op}} \epsilon_{\text{max}} \nu_{1/2})^{1/2} \quad (9)$$

where R is the transition dipole moment length (in Å), representing the charge transfer distance. Equation 9 is simply a modified form of equation 5 described in section 1.2. Importantly, the Hush model allows one to estimate the amount of metal-metal coupling, given that an MMCT band is experimentally observable, and R can be estimated (typically by the metal-metal separation from crystal structure data). However, it should be noted that the actual transfer distance is significantly smaller than the metal-metal separation due to the coupling between the metals.

Dielectric continuum theory, which treats the solvent as structureless, has been successfully applied to the solvent dependence of optical electron transfer for weakly coupled Class II complexes (equation 10). The solvent dependence of the absorption band energies, according to this theory, is characterized by the macroscopic dielectric constants, the static dielectric constant (D_s) and the optical dielectric constant (D_{op}).¹¹

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

$$E_{op} = \lambda_i + \lambda_o + \Delta E' \quad (10)$$

where $\Delta E'$ accounts for any additional energy associated with the excitation such as spin-orbit coupling, and λ_o (the outer sphere reorganization energy) and λ_i (the inner-sphere reorganization energy) are given by equations 11 and 12, respectively.

$$\lambda_o = e^2 \left(\frac{1}{r} - \frac{1}{d} \right) \left(\frac{1}{D_{op}} - \frac{1}{D_s} \right) \quad (11)$$

where r is the molecular trapping site radius and d is the distance between metal centers, or the electron-transfer distance (the distance from metal to metal).

$$\lambda_i = \frac{n(2f_2f_3)(d_2 - d_3)}{f_2 + f_3} \quad (12)$$

where d_2 , d_3 and f_2 , f_3 are the metal-ligand bond lengths and the force constants for the metals in differing oxidation states, respectively (see Figure 1.4). λ_i is assumed to be solvent independent for a given Class II system, thus variations in E_{IT} with solvent should be linearly proportional to the solvent term $\left(\frac{1}{D_{op}} - \frac{1}{D_s} \right)$ found in the expression of λ_o (equation 11).

A mixed-valence-trapped Class II complex is generally recognized by its small comproportionation constant (K_c usually < 1000 , see section 1.7 for definition),⁹ the weak intensity of its MMCT absorption band, a value of $\Delta\nu_{1/2}$ that is greater than the values given by the Hush model, and the MMCT energy that is sensitive to the nature of the solvent. When the experimental $\Delta\nu_{1/2}$ is significantly less than the theoretical $\Delta\nu_{1/2}$, which is obtained from Hush model, Class III or Class II-III behavior is approached. In this case, IR spectroscopy would seem to be among the best methods to unambiguously establish the degree of delocalization.

1.6.1.2 Class II-III Categorization

A recent review by Meyer et al.¹⁶ examined the properties of Class II and Class III and the transition between them (Class II-III). Meyer provided clear spectroscopic evidence for the presence of metal centered transitions arising out of low coordination symmetry in the same region as MMCT transitions. He suggested that the high energy asymmetry in the band envelope that is observed in the MMCT transitions of some strongly coupled complexes is not a result of Class III properties, but of the presence of these metal-centered transitions. For example, mixed-valence complexes with strong metal-ligand interactions and high spin-orbit coupling like Os complexes have three resolved MMCT bands and two IC (interconfigurational) transitions bands. Scheme 1 shows the three IT bands; IT1 has the lowest energy and the remaining other two IT transitions (IT2 and IT3) have higher energy. The two IC bands are $d\pi_2 \rightarrow d\pi_1$ and $d\pi_3 \rightarrow d\pi_1$ (scheme below). Information about delocalization in the ground state can be obtained by analyzing the

lowest energy IT band (IT1). The first and second row transition-metal complexes have low spin-orbit coupling and weak metal-ligand interactions, thus causing the three IT bands to overlap in near-IR spectra.¹⁶ Hush's analysis for calculating the metal-metal coupling elements (H_{ad}) assumes only a single IT band (the combination of the three IT bands) which gives the upper limit to the electronic coupling in the ground-state. This overestimates the coupling within the complex because the actual coupling should be calculated using the only the lowest energy feature, IT(1).

In addition, the effect of the solvent on the mixed-valence properties has often been used to discriminate between Class II or III complexes. However, Meyer¹⁶ points out that if thermal electron transfer between donor and acceptor metal ions is greater than the rate of solvent relaxation (10^{12} s^{-1}), the mixed-valence properties of the complex would appear solvent-independent even though, on the electronic timescale 10^{15} s^{-1} , the odd electron may be still trapped on one metal ion. For such systems at the borderline of Class II and III behaviour and possessing intermediate properties, Meyer¹⁶ proposed a new classification, Class II-III.

Class II-III mixed-valence complexes are characterized by the following experimental criteria: (1) the IT1, the low energy band, is narrow and solvent-independent, (2) direct experimental evidence shows the exchanging electron is localized, i.e. via crystal structure or IR spectroscopy.

For example, the μ -N₂-bridged Os sites are inequivalent in the mixed-valence complex *trans,trans*-[(terpy)(Cl)₂Os(N₂)Os(Cl)₂(terpy)](BF₄) as supported by the X-ray structure which shows an asymmetrically located BF₄⁻ counter ion in the crystal lattice and the intense ν (N₂) at 2007 nm in the Near-IR region.¹⁷ This complex shows three IT bands and two IC band in IR-Near-IR spectrum (Figure 1.7); bands I and II can be assigned to interconfigurational (IC) transitions. They are nominally Laporte forbidden but gain intensity through spin-orbit coupling and metal-ligand mixing. The evidence for localization is clear, but the IT bands are unusually narrow. The band width calculated for IT(I) by using equation 8 is 4000 cm⁻¹ compared to the experimental value of 1120 cm⁻¹. The IT bands are also nearly solvent independent. Because this complex is solvent-averaged yet electronically localized, it may be that this complex is classified as a member of Class II-III.

Figure 1.7 IR-near-IR spectrum in CD_3CN , band assignments are discussed in the text.

1.6.1.3 Class III Categorization

Three criteria are used to distinguish this class. First, the comproportionation constant for mixed-valence complexes should be large. The second criterion is a break down of the Hush theory for the spectral properties of the MMCT. The MMCT band extinction coefficient is large (usually $> 10^3 \text{ M}^{-1}$), ν_{max} is solvent independent; $\Delta\nu_{1/2}$ is smaller than that calculated by the Hush model (equation 8). Third, there must be direct experimental evidence seen in the crystal structure or IR spectroscopy that shows that the exchanging electron is delocalized.

The MMCT band in this class arises from the transition between delocalized electronic levels and not from intramolecular charge transfer.¹⁸ The electronic wave functions Ψ_1 and Ψ_2 (Figure 1.8) for the delocalized levels are constructed from symmetric ($\Psi_a + \Psi_b$) and antisymmetric ($\Psi_a - \Psi_b$) combinations of the initial unperturbed electronic wave functions, respectively.

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interaction between the electron pairs of the solvent and a NH_3 ligand (Figure 1.9) or electron pair donor-acceptor interactions with a CN^- ligand.^{19,20} This interaction has a large influence on the internal electronic structure of the mixed-valence complex. For example, the hydrogen-bonding interactions between the solvent molecules and the ammine ligands in the $[(\text{Ru}(\text{NH}_3)_5)_2(\mu\text{-dicyd})](\text{PF}_6)_4$ complex leads to a transfer of electron density to the ruthenium ion and to an increase in the energy gap between the metal and the π -HOMO orbitals of the bridging ligand.²¹ Thus, the metal-metal coupling is decreased.

Figure 1.9 Schematic representation of the donor-acceptor interaction between coordinated amines and solvent.

Further criteria for Class III behaviour are as follows: The two-state Hush model predicts that the MMCT band shape should have a high-energy tail and display a sharp cut-off at energies lower than $2H_{ad}$ (Figure 1.10), and the extent of metal-metal electronic coupling for the two-state model (Hush model) can be obtained directly from the energy of the intervalence transition by equation 13:

$$H_{ad} = E_{op}/2 \quad (13)$$

Figure 1.10 MMCT band shape prediction from the two-state model; the most probable transition is that of lower energy.

Furthermore, a large MMCT extinction coefficient for complexes that have a large comproportionation constant is expected but this correlation should be made with caution. For example, the complex $[(\text{NH}_3)_4\text{Ru}]_2(\mu\text{-bptz})]^{5+}$ has a large K_c (10^{15}) but only a small ϵ_{max} MMCT ($500 \text{ M}^{-1}\text{cm}^{-1}$).²² In contrast, the complex $[(\text{terpyRu})_2(\mu\text{-tpbp})]^{3+}$ has a relatively small K_c (600) but large ϵ_{max} ($27,000 \text{ M}^{-1}\text{cm}^{-1}$).²³

1.6.2 Superexchange in Mixed-Valence Complexes

The mechanism of electron transfer between two metal centers linked by a bridge is referred to as superexchange. In order for superexchange, (indirect mixing of metal orbitals with the bridge orbitals) to occur, the orbitals of the bridging ligand must have an energy and symmetry match with the donor and acceptor orbitals of the metal centers.²⁴

This can manifest itself in two major ways: An electron-transfer superexchange mechanism or a hole-transfer superexchange mechanism. The dominance of one pathway over the other is determined by the energetics of the system. The two pathways are shown in Figure 1.11.

When the empty bridging ligand orbitals are closest in energy to donor wavefunction, as in the case of heterocyclic bridging ligands (e.g. pyrazine), electron-transfer superexchange via the π^* -LUMO of the bridging ligand is the dominant mechanism for metal-metal coupling. This mechanism involves the transfer of an electron from the $d\pi$ orbital of Ru(II) via the vacant lowest unoccupied molecular orbital (π^* -LUMO) of the bridge and a simultaneous transfer of an electron to the appropriate $d\pi$ on the electron deficient metal (Ru(III)). Essentially, an electron moves from the donor to acceptor orbitals, hence the term electron-transfer (Figure 1.11A).

When filled orbitals of the bridging ligand are closest in energy to the acceptor wave function, as in the case of donating conjugated anion ligands (e.g. dicyd²⁻, Figure 1.12), the hole-transfer superexchange via the π -HOMO of the bridging ligand is the dominant superexchange mechanism (Figure 1.11B). This mechanism involves transfer of an electron from π -HOMO of the bridging ligand to the Ru(III) orbitals and a simultaneous transfer of an electron from the Ru(II) orbitals to the bridging ligands. Essentially, a hole moves from the acceptor to donor orbitals, hence the term hole-transfer (Figure 1.11B).

Figure 1.11 The two superexchange pathways in the mixed-valence ruthenium dinuclear complexes bridged by ligand, L.

Figure 1.12 Diagram showing the interaction of the metal d_{xz} orbitals with the dicyd²⁻ ligand HOMO, the most likely pathway for superexchange.

The superexchange model can be represented by the three-state model as an analogue of the two-state model for Hush. In the three-state model, the electron transfer is mediated by a third state. The mediating third state can be either metal-to-ligand charge transfer (MLCT), or ligand-to-metal charge transfer (LMCT) in nature. Figure 1.13 shows the free-energy curves for a three-state Class III system.²⁵ The dashed lines represent the diabatic states whereas the solid lines represent the adiabatic states.

In 1994, Creutz, Newton, and Sutin (CNS)²⁵ reported a novel derivation to calculate metal-metal coupling for weakly coupled Class II systems from the coupling between the metals and their end of the bridging ligand (Figure 1.14). Unlike the Hush model, the CNS model can be used to calculate metal-ligand coupling elements for any donor-acceptor system provided the overlap is neglected and the charge-transfer transition dipole moment lies along the donor-acceptor bonding axis.

Figure 1.13 Diabatic (dashed lines) and adiabatic (solid lines) free-energy curves for a three-state system (Class III category) from reference.²⁶

In practice, metal-metal coupling elements can then be determined from equation 14 by replacing intervalence spectral data with the corresponding metal-to-ligand or ligand-to-metal charge-transfer spectral data. The general equation for the effective (i.e. indirect) coupling of the metal centers, assuming no direct overlap of the metal orbitals due to their spatial separation, is given by the following equation:

$$H_{MM'} = \frac{H_{ML}H_{M'L}}{2\Delta E_{ML}^{eff}} + \frac{H_{LM}H_{LM'}}{\Delta E_{LM}^{eff}} \quad (14)$$

Figure 1.14 Diabatic (dashed lines) and adiabatic (solid lines) free-energy curves for a three-state system (Class II category) from reference.²⁶

The coupling element $H_{MM'}$ of equation 14 is the effective metal-metal coupling, whereas the coupling elements in the two terms on the right of equation 14 are associated with metal-ligand interactions of the electron-transfer (H_{ML}) and hole-transfer pathways (H_{LM}), respectively. The subscript nomenclature ML refers to the electron-transfer pathway which is associated with the metal-to-ligand charge transfer (MLCT) band in the electronic spectrum of the complex, whereas the subscript LM refers to the hole-transfer pathway associated with ligand-to-metal (LMCT) bands, as shown in Figure 1.3.

For the complexes of this study, the first assumption is that superexchange occurs predominantly via the hole-transfer pathway, and thus the first term in equation 14 can be ignored. The second assumption is that $H_{LM} = H_{LM'}$ ⁶ which simplifies equation 14 to

$$H_{MM'} = \frac{H_{LM}^2}{2\Delta E_{LM}^{eff}} \quad (15)$$

H_{LM} is evaluated from the spectroscopic parameters of the LMCT band by equation 5 and the reduced energy gap for the hole-transfer case is given by the following equation.⁶

$$\Delta E_{LM}^{eff} = \left[0.5 \left(\frac{1}{E_{LMCT}} + \frac{1}{E_{LMCT} - E_{IT}} \right) \right] \quad (16)$$

1.7 Thermodynamics of Mixed-Valence Systems

In order to distinguish between Class II and III mixed-valence complexes, a measure of metal-metal coupling is needed. One such measure is provided by the free energy of comproportionation, ΔG_c , according to the comproportionation equilibrium,²⁷

that also defines the comproportionation constant, K_c . For the sake of simplicity, the mixed-valence state will be denoted as $Ru[III,II]$ for the dinuclear complexes of this study even though a more appropriate Class III designation would be $Ru[II\frac{1}{2},II\frac{1}{2}]$.

ΔG_c may be determined electrochemically by using cyclic voltammetry, where the difference between metal centered redox couple potentials, Ru(III/II), is equal to $\Delta E = Ru_2 - Ru_1$,

The free energy of comproportionation, ΔG_c , and equilibrium constant, K_c , for the comproportionation reaction are related by the Nernst equation (equation 19).

$$\Delta G_{com}^\circ = -RT \ln K_c \quad (19)$$

K_c is usually related to the difference in potential between metal-centered reduction couples (ΔE) by this equation²⁷:

$$K_c = 10^{16.91 \Delta E} \quad (20)$$

For Class III complexes, K_c is very large. This reflects the strong bonding interaction between donor and acceptor wave functions, which results in delocalization of the odd electron. K_c is usually less than 10^3 in Class II complexes²⁷.

It is important to recognize that the magnitude of K_c is not a sufficient criterion for distinguishing between Class II and Class III because factors other than those associated with metal-metal coupling make contributions to K_c . For example, in the case of the mixed-valence dimer $[\{(tpm)(Cl)_2Os\}_2(\mu-N_2)]^+$ (tpm = tris(1-pyrazoyl)methane),¹⁷ $H_{ad} \geq 118 \text{ cm}^{-1}$ (which is only 2% of the 0.61 V, the difference in $\Delta E_{1/2}$)

For the majority of mixed-valence complexes, the magnitude of ΔG_c can be adequately described by four factors,⁶

$$\Delta G_c = \Delta G_s + \Delta G_e + \Delta G_i + \Delta G_r \quad (21)$$

In equation 21, ΔG_s reflects the statistical distribution of the comproportionation equilibrium, ΔG_e accounts for the electrostatic repulsion of the two like-charged metal centers, ΔG_i is an inductive factor dealing with competitive coordination of the bridging ligand by the metal ions, and ΔG_r is the free energy of resonance exchange. A fifth term (ΔG_{ex}) measures the stabilizing influence antiferromagnetic exchange has upon the reactant complex in equation 17, and thus is of opposite sign to the remaining terms in equation 21. In addition, a recent study has shown that ion pairing can have a dramatic influence on comproportionation equilibrium and the ion pairing factor, ΔG_{ip} , either increasing or decreasing its magnitude depending on the charge of the complexes. Including these terms in equation 21 yields.²⁸

$$\Delta G_c = \Delta G_s + \Delta G_e + \Delta G_i + \Delta G_r + \Delta G_{ex} + \Delta G_{ip} \quad (22)$$

It is possible to extract the value of ΔG_r from comproportionation data of strongly coupled mixed-valence complexes and hence determine the free energy of resonance exchange per mixed-valence complex, $\Delta G_r' = 0.5\Delta G_r$.⁶ The actual measure of metal-metal coupling is given by the resonance exchange integral (or metal-metal coupling element) H_{ad} which, for strongly coupled symmetric Class III systems, is related to $\Delta G_r'$ by,²⁹

$$\Delta G_r' = H_{ad} - \Delta G_{th} \quad (23)$$

where ΔG_{th} is the activation energy for thermal electron transfer in the absence of metal-metal coupling. The complexes of this study have similar coordination spheres and charges so that the values of ΔG_s , ΔG_e , ΔG_i , ΔG_{ip} and ΔG_{th} are approximately equivalent between the complexes. This means that differences in ΔG_c between the complexes actually reflect differences in ΔG_r and ΔG_{ex} .

In dealing with magnetic coupling in dinuclear complexes, the concern is with the simplest case in which the metals are in the same oxidation state and they are at low spin (e.g. Ru(III)). Consequently, each Ru(III) has an unpaired electron with the total spin of $S=1/2$. If the two Ru(III) that have $S=1/2$ are antiferromagnetically coupled, a singlet ground state (1S) and a triplet excited state (3S) are separated by $-2J$. By convention when J is negative the coupling is termed antiferromagnetic exchange (when a singlet ground state exists in the dimer) as shown below:

When the metal-metal separation is too large for the Ru(III) ions to interact directly, the antiferromagnetic exchange occurs because of the superexchange mechanism in which

orbitals of the bridging ligand directly participate in electron exchange through an LMCT transition.

In systems where mixed-valence metal-metal coupling occurs through electron transfer superexchange, the energetic mismatch of the ligand LUMO and the metal ion d-orbitals of the Ru[III,III] complex should lead to a small or insignificant magnitude of ΔG_{ex} . In systems involving hole transfer superexchange, the magnitude of ΔG_{ex} is significant and ignoring this term would lead to low estimates of free energy of resonance exchange.

To optimize both the electronic (ΔG_r) and magnetic (ΔG_{ex}) coupling, two important criteria must be considered : (a) the HOMO of the bridging ligand must be close in energy to the metal t_{2g} orbitals. For example, in Ru(III) ions bridged by a planar dicyd²⁻, the HOMO pathway possesses π -symmetry suitable for superexchange with the $d\pi$ of Ru(III) ions.³⁰ A previous study showed that the measurement of antiferromagnetic ($-J$) exchange of the $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-L})]^{4+}$ where $\text{L} = \text{Me}_2\text{dicyd}^{2-}$, dicyd^{2-} , $\text{Cl}_2\text{dicyd}^{2-}$, and $\text{Cl}_4\text{dicyd}^{2-}$ increased with decreasing energy gap between Ru(III) and the HOMO of the bridging ligand.³¹

(b) Planarity: The bridging ligand must be planar to maximize the overlap with electronic and magnetic orbitals of the metals. However, it is important to recognize that planarity and rigidity in the solid state may not be maintained in solution, and that the magnetic and electronic coupling may be changed.

1.8 Selected Studies Showing the Effect of Inner and Outer-Sphere Perturbation on the Coupling of Mixed-valence Complexes

Changes in the inner and outer-sphere of a mixed-valence complex can have a dramatic effect on its metal-metal coupling. The following are a few selected examples of these effects.

Crutchley et al.^{6,14} have presented several studies on dicyd²⁻ bridged systems and the effect of inner and outer-sphere changes on coupling. For example, a recent study using UV-Vis-NIR spectroelectrochemistry systematically changed the auxiliary ligand on a series of mixed-valence ruthenium dimers $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-L})]^{3+}$, *trans,trans*- $[\{\text{Ru}(\text{NH}_3)_4(\text{py})\}_2(\mu\text{-L})]^{3+}$, and *mer,mer*- $[\{\text{Ru}(\text{bpy})(\text{NH}_3)_3\}_2(\mu\text{-L})]^{3+}$, where L is the dicyd²⁻ ligand and its substituted variations. Replacing the strong σ -donor ammine ligand with weaker σ -donor pyridine moieties resulted in an increase in the metal-metal coupling via the hole transfer superexchange mechanism. Outer-sphere changes were also found to affect metal-metal coupling. Changing from a strong donor solvent such as DMSO to a weaker donor solvent like nitromethane also led to increased metal-metal coupling (The donor number of a solvent is the ΔH_f in kcal/mol from the reaction of the solvent with SbCl_5).³² In these examples, removing electron density from the ruthenium centers led to a stabilization of the metal $d\pi$ orbitals and, consequently, provided a better energy match with the π -HOMO of the bridging ligand. These effects were further confirmed in an IR spectroelectrochemistry study of the same family of complexes. Transformations from Class II to Class III behaviour were effected by the same inner and

outer-sphere changes described above. The complex $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-L})]^{3+}$ where $\text{L} = 2,5\text{-dimethyl-1,4-dicyanomidobenzene}$, was shown to be a Class II system in DMSO, but a borderline Class III complex in nitromethane. By replacing two ammine ligands with a 2,2'-bipyridine ligand as in the complex *mer,mer*- $[\{\text{Ru}(\text{bpy})(\text{NH}_3)_3\}_2(\mu\text{-L})]^{3+}$, the result was a complex that displayed Class III behaviour in all solvents, including the strongly donating DMSO.¹⁴

Solvents can not only have a dramatic effect on coupling but can also alter the form of the mixed-valence complex through a specific interaction. An example of this is seen with the mixed-valence complex $[\text{cis}-(\text{bpy})_2(\text{Cl})\text{Os}(\text{pz})\text{Ru}(\text{NH}_3)_5]^{4+}$. It can exist as two oxidation-state isomers, $\text{Os}^{\text{II}}\text{-Ru}^{\text{III}}$ or $\text{Os}^{\text{III}}\text{-Ru}^{\text{II}}$,^{33,35} with the former being a Class II complex and the latter considered to be Class II-III. In lower donor number solvents such as acetonitrile and methanol, the $\text{Os}^{\text{III}}\text{-Ru}^{\text{II}}$ isomer is preferred. Alternatively, in strong donor solvents, such as DMSO and DMF, the $\text{Os}^{\text{II}}\text{-Ru}^{\text{III}}$ form is stabilized by a strong hydrogen bonding interaction between the solvent and $[\text{Ru}(\text{NH}_3)_5]^{3+}$.

Changing the bridging ligand also has a dramatic effect on the coupling within a mixed-valence system. For example, pentaammine dinuclear complexes bridged by 4,4'-azopyridine are more weakly coupled compared with those bridged by 4,4'-dithiodipyridine and this difference is again related to the energy match between the orbitals of the metal and the bridging ligand.³⁶

4,4'-azopyridine

4,4'-dithiodipyridine

1.9 Thesis Outline

The major goals of this thesis are to develop two novel families of Class III mixed-valence ruthenium complexes and to probe the effects of inner and outer-sphere perturbation on metal-metal coupling in these delocalized systems. This study should provide the conceptual framework for the future design of highly polarizable mixed-valence complexes for use in NLO materials. The first step in this study requires the synthesis of a series of mononuclear complexes $[\text{Ru}(\text{L})(\text{L}')(2,3,4,5\text{-Cl}_4\text{pcyd})]^+$ where L is 4'-p-tolyl-2,2':6',2''-terpyridine (ttp) or 4-p-tolyl-2,6-di(2-pyrazinyl)-pyridine (tpz) and L' is 2,2'-bipyrazine (bpz) or 2,2'-bipyridine (bpy) and their in depth characterization using elemental analysis, IR, ^1H NMR, UV-visible Near-IR spectroscopies and cyclic voltammetry. The LMCT (ligand to-metal-charge transfer) band and redox chemistry of these complexes will be compared to their pentammineruthenium(III)phenylcyanamide analogues.

Figure 1.15 The family of the phenylcyanamide mononuclear complexes.

Examining changes in the LMCT band and Ru[III,II] redox couple of these complexes as a result of inner-sphere perturbation provides a basis for understanding these effects in the dinuclear complexes. With this foundation, the synthesis and study of two series of mixed-valence ruthenium complexes $[\{\text{Ru}(\text{L})(\text{L}')\}_2(\mu\text{-dicyd})](\text{PF}_6)_2$ (A) and $[\{\text{Ru}(\text{L})(\text{L}')\}_2(\mu\text{-adpc})](\text{PF}_6)_2$ (B) will be described.

Figure 1.16 The two families of dinuclear complexes A) dicyd²⁻ family B) adpc²⁻ family

The Class III status of these complexes will be confirmed using techniques such as NIR-spectroelectrochemistry, infrared spectroelectrochemistry, and cyclic voltammetry. The effect of inner-sphere perturbation will be examined via the purposeful substitution of the auxiliary ligands from strong σ -donor to weak σ -donor/ π -acceptors, as well as by modification of the bridging ligand. The replacement of strong σ -donor pyridine moieties with weak σ -donor/ π -acceptor ligands like pyrazine is expected to increase the stability of the ruthenium d-orbitals in both the +2 and +3 oxidation state and hence

increase the electronic and magnetic coupling. The outer sphere perturbation will be probed by monitoring changes in the MMCT band of the mixed-valence complexes by electrochemical and chemical studies in solvents of different donor number. The changes in the MMCT band of these Class III complexes can be explained in term of a specific solvent interaction with a functional group of the mixed-valence complex rather than as an indication of valence-trapped status. Furthermore, the shape of the MMCT bands and the multiple MMCT transitions will be rationalized using a spectroscopic analysis assuming C_{2h} microsymmetry for both families.

Chapter 2 Experimental

2.1 Starting Materials

2.1.1 Reagents for Ligand and Metal Complex Synthesis

All of the reagents used were reagent grade: 4,4'-azodianiline (ACROS Organics), tetrabutyl ammonium hexafluorophosphate (TBAH), (Aldrich) twice recrystallized with 1:1 ethanol: water and vacuum dried at 110 °C, ammonium thiocyanate (Fisher), benzoyl chloride (99%, Aldrich), lead acetate trihydrate (Anachemia), sodium hydroxide (Anachemia), glacial acetic acid (99.7%, Anachemia), 2-acetylpyridine (Aldrich), *p*-tolualdehyde (Aldrich), 2-acetylpyrazine (Aldrich), triethylamine 99% (Aldrich), thallium acetate (99.99%, Aldrich), 2,2'-bipyrazine, 2,2'-bipyridine.

2.1.2 Solvents for Synthesis

Chloroform (Fisher), acetonitrile (reagent grade, Caledon labs), 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. N,N'-dimethylformamide (Sigma), toluene (spectro grade, Caledonia Labs) were used as received.

2.1.3 Solvents for NMR Spectroscopy

Chloroform-d₃ and dimethylsulfoxide-d₆ (99.9 atom % D, CDN Isotopes) were used as received.

2.1.4 Solvents for Spectroscopy and Electrochemistry

The organic solvents used for spectroscopy and electrochemistry were distilled under reduced pressure and stored under argon, with the exception of acetone which was used as received (99.9+%, Anachemia). All solvents were dried with an appropriate reagent. Acetonitrile (HPLC grade, Aldrich) was distilled in the presence of phosphorus pentoxide. Dimethylsulfoxide (HPLC grade, Aldrich), nitromethane (HPLC grade, 96+% Sigma) *N,N'*-dimethylformamide and propylene carbonate were dried overnight and distilled in the presence of aluminum oxide (neutral grade) which had been previously activated by heating to 300 °C for 3 h.

2.2 Synthesis Work

2.2.1 Ligand Synthesis

Tl₂[4,4-azodi(phenylcyanamide)], (Tl₂[adpc]), Tl₂[1,4-dicyanamidobenzene], (Tl₂[dicyd]) and Tl[2,3,4,5-Cl₄phenylcyanamide] were prepared according to literature methods^{37,38,39}

2.2.2 Preparation of 4'-p-tolyl-2,2':6',2''-terpyridine

4'-p-tolyl-2,2':6',2''-terpyridine was prepared by the method of Lever, Potvin and et al. with a small modification as follows.⁴⁰ One mL (8.9 mmol) of 2-acetylpyridine was mixed with 0.5 mL (2.49 mmol) of *p*-tolualdehyde in 60 mL (1:1) (methanol/concentrated NH₄OH) and 5 mL of 15 % aqueous KOH. The reaction mixture was stirred for 4 days at room temperature. The precipitate was collected and washed with distilled H₂O until the washes were neutral. The precipitate was dissolved in CHCl₃

and washed with distilled H₂O in a separatory funnel to remove the water-soluble impurities. MgSO₄ then was used to dry the organic phase. The product was collected through rotary evaporation and recrystallized in 1:1 CHCl₃/MeOH. The crystalline product was washed with cold hexane. Yield: 804.0 mg, 40%.

2.2.3 Preparation of 4-*p*-tolyl-2,6-di(2-pyrazinyl)-pyridine.

The procedure is identical to the above synthesis except that 2-acetylpyrazine, 1.08 g, was used instead of 4'-*p*-tolyl-2,2':6',2''-terpyridine, Yield: 707.9 mg, 35%.

2.3 Preparation of Mononuclear Complexes

2.3.1 Preparation of RuCl₂((CH₃)₂SO)₄

Following the literature procedure,⁴¹ RuCl₃·3H₂O (1.0 g, 3.8 mmol) was refluxed in dimethylsulfoxide (5 mL) for 5 min. The volume was reduced to half by rotary evaporation, then 30 mL of acetone were added to precipitate the yellow product RuCl₂((CH₃)₂SO)₄. The final product was washed with acetone and ether, yield 1.02 g, 55%.

2.3.2 Preparation of [Ru(ttp)Cl₃]

Following the literature procedure,⁴² ruthenium trichloride (655 mg, 2.5 mmol) and (808.3 mg, 2.5 mmol) of 4'-*p*-tolyl-2,2':6',2''-terpyridine (ttp) were dissolved in 200 mL of absolute ethanol. The mixture was heated, with stirring, for 4 h. After cooling, the final powdered product was collected and washed with ethanol and ether, and was left to air dry. Yield: 1.123 g, 84%.

2.3.3 Preparation of [Ru(ttp)(bpy)Cl][PF₆] $\cdot$ 2DMF

Ru(ttp)Cl₃ (642 mg, 1.2 mmol) and 2,2'-bipyridine (197 mg, 1.2 mmol) were dissolved in 150 mL of 4:1 water/ethanol, refluxed for 5 h and then LiCl (500 mg) was added. After refluxing for an additional 1 h, NH₄PF₆ (200 mg) was added, the reaction solution volume was reduced to about 50 mL, and the solution was stored in the fridge overnight. The precipitated crude product was filtered out and then purified by column chromatography by using grade III alumina type WA-I (Sigma), with a 2:1 mixture of toluene/acetonitrile as eluent. The main deep purple band was collected and the solvent evaporated to dryness by rotary evaporation. The product was recrystallized by the diffusion of ether into a saturated N,N'-dimethylformamide (DMF) solution of the complex. Yield, 0.62 mg (82%). Elem. Anal. Calcd. for C₃₈H₃₉N₇O₂F₆PClRu: C, 50.31; H, 4.33; N, 10.81. Found: C, 50.15; H, 4.61; N, 11.21. UV-vis in acetonitrile [λ_{max} /nm (ϵ_{max} /M⁻¹cm⁻¹)], 512 (1.0 $\times$ 10⁴). .

2.3.4 Preparation of [Ru(ttp)(bpz)Cl][PF₆]

Ru(ttp)Cl₃ (642 mg, 1.2 mmol) and 2,2'-bipyrazine (189.6 mg, 1.2 mmol) were dissolved in 150 mL of 3:1 (v/v) ethanol/water with 0.1 mL triethylamine. The mixture was refluxed for 5 h at which time an excess amount of LiCl (500 mg) was added. The reaction mixture was heated for an additional hour. The volume was reduced to approximately 30 mL and then 200 mg of NH₄PF₆ were added to precipitate the crude product. The crude product was filtered out and washed with water to remove the excess NH₄PF₆. The crude product was then dried and dissolved in 20 mL (2:1)

dichloromethane/acetonitrile and purified by chromatography on a 50 cm long, 3 cm diameter column containing 250 g grade (III) alumina (Brockman I, weakly acidic 150 mesh). The first pale orange band, thought to be $[\text{Ru}(\text{ttp})_3](\text{PF}_6)_2$, as eluted with (2:1) dichloromethane/acetonitrile. The second deep purple band, which was the $[\text{Ru}(\text{ttp})(\text{bpz})\text{Cl}](\text{PF}_6)$, was eluted with (1:1) dichloromethane/acetonitrile. It was collected, and the solvent was evaporated to dryness by rotary evaporation. Yield: 0.450 g, 49.5%. Elem. Anal. Calcd. for $\text{RuC}_{30}\text{H}_{23}\text{N}_7\text{ClPF}_6$: C, 47.22; H, 3.04; N, 12.85. Found: C, 46.85; H, 3.16; N, 12.92. UV-vis in acetonitrile [$\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{max}}/\text{M}^{-1}\text{cm}^{-1}$)], 518 nm (1.8×10^4).

2.3.5 Preparation of $[\text{Ru}(\text{tpz})(\text{bpy})\text{Cl}][\text{PF}_6]$

$\text{RuCl}_2(\text{CH}_3)_2\text{SO}_4$ (0.5 g, 1.03 mmol) and 4-*p*-tolyl-2,6-di(2-pyrazinyl)-pyridine (334.75 mg, 1.03 mmol) were dissolved in 100 mL of DMF. The yellow solution changed to a black-brown colour after 5 min. of heating. After refluxing for 2 h of 2,2'-bipyridine (156 mg, 1.03 mmol) was added to the solution. The reaction was heated for an additional 4 h at which time an excess amount of LiCl (500 mg) was added. After allowing the reaction mixture to reflux for an additional hour, the volume of the solution was then reduced by rotary evaporation to about 20 mL. The excess aqueous amount of NH_4PF_6 (500 mg in 100 mL H_2O) was added to the DMF solution and the crude product was filtered out and washed with water to remove the excess NH_4PF_6 . The crude product was dried and dissolved in 60 mL of (1:1) acetonitrile/toluene and purified by chromatography on a 50 cm by 3 cm diameter column containing 250 g grade (III) alumina (Brockman I, weakly acidic 150 mesh). The first main purple band, the

mononuclear complex $[\text{Ru}(\text{tpz})(\text{bpy})\text{Cl}](\text{PF}_6)$, was eluted by (1:1) acetonitrile/toluene, collected, and the solvent evaporated to dryness by rotary evaporation. Yield: 0.521 g, 66.7%. Elem. Anal. Calcd. for $\text{RuC}_{30}\text{H}_{23}\text{N}_7\text{ClPF}_6$: C, 47.22; H, 3.04; N, 12.85. Found: C, 46.87; H, 3.26; N, 12.82. UV-vis in acetonitrile [$\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{max}}/\text{M}^{-1}\text{cm}^{-1}$)], 547 nm (7.0×10^3), 497 nm (7.1×10^3).

2.3.6 Preparation of $[\text{Ru}(\text{tpz})(\text{bpz})\text{Cl}](\text{PF}_6)$

$\text{RuCl}_2((\text{CH}_3)_2\text{SO})_4$ (0.5 g, 1.03 mmol) and 4-*p*-tolyl-2,6-di (2-pyrazinyl)-pyridine (335 mg, 1.03 mmol) were dissolved in 100 mL of DMF and the yellow solution changed to a black-brown colour after 5 min. of heating. After refluxing for 2 h, 2,2'-bipyrazine (162.7 mg, 1.03 mmol) was added to the solution. The reaction was refluxed for additional 6 h at which time an excess amount of LiCl (500 mg) was added. The reaction mixture was heated for an additional hour and the volume of the solution was then reduced by rotary evaporation to about 20 mL. An excess amount of aqueous NH_4PF_6 (500 mg in 100 mL H_2O) was added to the DMF solution and the crude product was filtered out and washed with water to remove the excess NH_4PF_6 . The crude product was dried, dissolved in 20 mL acetonitrile and purified by chromatography on a 50 cm $\times$ 3 cm diameter column containing 150 g grade (I) alumina (Brockmann I, weakly acidic 150 mesh). Two bands were eluted with acetonitrile by slowly increasing the amount of methanol up to 20%. It is thought that the composition of the bands was as follows: The first band (orange) was $[\text{Ru}(\text{tpz})_2](\text{PF}_6)_2$, and the second band (purple) was the target complex. It was collected and then dried by rotary evaporation. Yield: 0.150 g, 20%.

Elem. Anal. Calcd. for $\text{RuC}_{28}\text{H}_{21}\text{N}_9\text{ClPF}_6$: C, 43.96; H, 3.06; N, 16.48. Found: C, 44.28, H, 3.06, N, 16.35. UV-vis in acetonitrile [$\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{max}}/\text{M}^{-1}\text{cm}^{-1}$)], 500 nm (1.0×10^4).

2.3.7 Preparation of $[\text{Ru}(\text{ttp})(\text{bpy})(2,3,4,5\text{-Cl}_4\text{pcyd})][\text{PF}_6] \cdot 2\text{DMF}$

$[\text{Ru}(\text{ttp})(\text{bpy})\text{Cl}](\text{PF}_6)$ (0.38 g, 0.51 mmol) was dissolved in 100 mL of DMF in a 250 mL round bottom flask. $\text{Ti}[2,3,4,5\text{-Cl}_4\text{phenylcyanamide}]$ (0.235 g, 0.51 mmol) was added. The deep red solution was refluxed for 18 h and the reaction mixture was then chilled to -20°C . The precipitate, TiCl , was separated from the solution by filtering the reaction mixture through celite. Ether (500 mL) was added to the solution in order to precipitate the crude product, which was then collected by suction filtration. Recrystallization was achieved by the slow diffusion of ether into a saturated solution of the crude complex in DMF. Yield: 0.465 g, 81%. Elem. Anal. Calcd. for $\text{RuN}_9\text{C}_{45}\text{H}_{40}\text{PF}_6\text{O}_2\text{Cl}_4$: C, 48.25; H, 3.66; N, 11.18. Found: C, 48.25; H, 3.79; N, 11.32. UV-vis in acetonitrile [$\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{max}}/\text{M}^{-1}\text{cm}^{-1}$)], 1.26×10^3 , 503 nm (1.2×10^4 , IR: $\nu(\text{NCN})$, 2167 cm^{-1}).

2.3.8 Preparation of $[\text{Ru}(\text{tpz})(\text{bpy})(2,3,4,5\text{-Cl}_4\text{pcyd})][\text{PF}_6] \cdot \text{DMF}$

The procedure is identical to the above synthesis except that $[\text{Ru}(\text{ttp})(\text{bpz})\text{Cl}](\text{PF}_6)$ (0.39g, 0.51 mmol) was used instead of $[\text{Ru}(\text{ttp})(\text{bpy})\text{Cl}](\text{PF}_6)$, and the crude product was purified by dissolving it in 1:1 acetonitrile/toluene and then passing it through 150 g of grade (III) alumina (Brockmann I, weakly acidic 150 mesh). The first pale-purple band (thought to be the solvato complex) was eluted with (1:1) acetonitrile/toluene. The purple target product, which is the second band, was eluted with (2:1) acetonitrile/toluene. Recrystallization was achieved by the slow diffusion of ether into a

saturated solution of the crude complex in DMF. Yield: 200 mg, 40%. Elem. Anal. Calcd. $\text{RuC}_{40}\text{Cl}_4\text{OPF}_6\text{H}_{31}$: C, 45.51; H, 2.96; N, 13.27. Found: C, 45.5; H, 3.11; N, 13.13. UV-vis in acetonitrile [$\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{max}}/\text{M}^{-1}\text{cm}^{-1}$)], 524 (7.5×10^2) 409 (1.2×10^3 , IR: $\nu(\text{NCN})$, 2167 cm^{-1} .

2.3.9 Preparation of $[\text{Ru}(\text{tpz})(\text{bpz})(2,3,4,5\text{-Cl}_4\text{pcyd})][\text{PF}_6]\cdot\text{DMF}$

The procedure is identical to the above synthesis except that $[\{\text{Ru}(\text{tpz})(\text{bpz})\text{Cl}\}(\text{PF}_6)]$ (0.39 g, 0.51 mmol) was used instead of $[\text{Ru}(\text{ttp})(\text{bpy})\text{Cl}](\text{PF}_6)$ and the crude product was purified by dissolving it in acetonitrile, then passing it through silica gel (200-400 mesh, $60\text{ \AA}$) using $0.03\text{ M NH}_4\text{PF}_6$ in acetonitrile as eluent. The first purple band was the target complex whereas the second purple band was $[\text{Ru}(\text{tpz})(\text{bpz})\text{Cl}][\text{PF}_6]$. The first band was recrystallized by slow diffusion of ether into a saturated solution of the crude complex in DMF. Yield, 75 mg, 15%. Elem. Anal. Calcd. for $\text{RuC}_{38}\text{Cl}_4\text{OPF}_6\text{H}_{29}$: C, 43.12; H, 2.86; N, 15.88 Found: C, 42.91; H, 3.11; N, 13.83. UV-vis in acetonitrile [$\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{max}}/\text{M}^{-1}\text{cm}^{-1}$)], 487 (1.2×10^3 , IR: $\nu(\text{NCN})$, 2176 cm^{-1} .

2.3.10 Preparation of $[\text{Ru}(\text{ttp})(\text{bpz})(2,3,4,5\text{-Cl}_4\text{pcyd})][\text{PF}_6]\cdot 2\text{DMF}$

The procedure is identical to the above synthesis except that $\{\text{Ru}(\text{ttp})(\text{bpz})\text{Cl}\}(\text{PF}_6)$ (0.39 g, 0.51 mmol) was used instead of $[\{\text{Ru}(\text{tpz})(\text{bpz})\text{Cl}\}(\text{PF}_6)]$. Yield, 175.5 mg, 35%. Elem. Anal. Calcd. for $\text{RuC}_{43}\text{N}_{11}\text{H}_{38}\text{Cl}_4\text{PF}_6\text{O}_2$: C, 45.76; H, 3.39; N, 13.65 C, 45.23; H, 2.46; N, 12.83 Found C, 45.34; H, 3.50; N, 13.65. UV-vis in acetonitrile [$\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{max}}/\text{M}^{-1}\text{cm}^{-1}$)], 508 (2.08×10^3), IR: $\nu(\text{NCN})$, 2185 cm^{-1} .

2.4 Preparation of Dinuclear Complexes

2.4.1 Synthesis of $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-adpc})](\text{PF}_6)_2$

To a solution of $[\text{Ru}(\text{ttp})(\text{bpy})\text{Cl}][\text{PF}_6]$ (0.673 g, 0.89 mmol) dissolved in 100 mL of DMF was added $\text{Ti}_2(\text{adpc})$ (0.30g, 0.45mmol) and the reaction mixture refluxed for 3 days. The solution was then chilled to $-20\text{ }^\circ\text{C}$ and filtered through cellite to remove the TiCl precipitate. The filtrate was concentrated to 20 mL by rotary evaporation and then 600 mL of ether was added to precipitate the crude product. This was filtered off, dissolved in 60 mL of acetonitrile/toluene (3:1), and purified by chromatography by using a 50 cm $\times$ 3 cm diameter column containing 250 g grade (V) alumina (Brockmann I, weakly acidic 150 mesh). Elution with acetonitrile/toluene (3:1) yielded two bands which were spectroscopically identified as unreacted reagents, $[\text{Ru}(\text{ttp})(\text{bpy})\text{Cl}]^+$ and adpc^{2-} . Elution with acetonitrile and acetonitrile/methanol (4:1) gave the desired dinuclear complex which, after evaporation to dryness, was dissolved in 10 mL dimethylformamide and filtered through cellite. To the filtrate was added excess aqueous NH_4PF_6 , precipitating the dinuclear complex. Recrystallization was achieved by the slow diffusion of ether into saturated solution of the complex in dimethylformamide. Yield after vacuum drying, 470 mg (55 %). Elem. Anal. Calcd. for $\text{C}_{78}\text{H}_{58}\text{N}_{16}\text{F}_{12}\text{P}_2\text{Ru}_2$: C, 54.74; H, 3.42; N, 13.09. Found: C, 54.35; H, 3.36; N, 13.11. UV-vis in DMF [$\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{max}}/\text{M}^{-1}\text{cm}^{-1}$)], 491 (5.98×10^4), IR: $\nu(\text{NCN})$ 2171 cm^{-1} .

2.4.2 Synthesis of $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-dicyd})][\text{PF}_6]_2$

The procedure is identical to the above synthesis except that $\text{Ti}_2(\text{dicyd})$ (242 mg, 0.45 mmol) was used instead of $\text{Ti}_2(\text{adpc})$ and the reaction refluxed under nitrogen. Yield, 364 mg (43%). Elem. Anal. Calcd. for $\text{C}_{72}\text{H}_{54}\text{N}_{14}\text{P}_2\text{F}_{12}\text{Ru}_2$: C, 53.80; H, 3.39; N, 12.20. Found: C, 53.44; H, 3.22; N, 12.24; C, 53.8; H, 3.39; N, 12.20. Found: C, 53.44; H, 3.22; N, 12.24. UV-vis in DMF [$\lambda_{\text{max}}/\text{nm}(\epsilon_{\text{max}}/\text{M}^{-1}\text{cm}^{-1})$], 493 nm 2.4×10^4 , IR: $\nu(\text{NCN})$, 2138 cm^{-1} .

2.4.3 Preparation of $[\{\text{Ru}(\text{tpz})(\text{bpy})\}_2(\mu\text{-adpc})][\text{PF}_6]_2 \cdot \text{H}_2\text{O}$

The procedure is identical to synthesis of $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-adpc})](\text{PF}_6)_2$ except that $[\text{Ru}(\text{tpz})(\text{bpy})\text{Cl}](\text{PF}_6)$ (0.681 g, 0.89 mmol) was used instead of $[\text{Ru}(\text{ttp})(\text{bpy})\text{Cl}][\text{PF}_6]$. Yield: 243 mg, 30%. Elem. Anal. Calcd. for $\text{Ru}_2\text{H}_{56}\text{C}_{74}\text{N}_{20}\text{P}_2\text{F}_{12}\text{O}$: C, 51.27; H, 3.26; N, 16.16. Found: C, 50.94; H, 3.52; N, 16.22. UV-vis in DMF [$\lambda_{\text{max}}/\text{nm}(\epsilon_{\text{max}}/\text{M}^{-1}\text{cm}^{-1})$], 480 (5.9×10^3), IR: $\nu(\text{NCN})$, 2171 cm^{-1} .

2.4.4 Preparation of $[\{\text{Ru}(\text{tpz})(\text{bpy})\}_2(\mu\text{-dicyd})][\text{PF}_6]_2 \cdot 2\text{H}_2\text{O}$

The procedure is identical to the above synthesis except that $\text{Ti}_2(\text{dicyd})$ (242 mg, 0.45 mmol) was used instead of $\text{Ti}_2(\text{adpc})$, grade (I) alumina instead of grade (V) alumina was used for chromatography and the reaction was refluxed under nitrogen. Yield, 179 mg, 25%. Elem. Anal. Calcd. for $\text{Ru}_2\text{C}_{68}\text{H}_{54}\text{N}_{18}\text{P}_2\text{F}_{12}\text{O}_2$: C, 49.58; H, 3.30 N, 15.30. Found: C, 49.40; H, 3.50; N, 15.10. UV-vis in DMF [$\lambda_{\text{max}}/\text{nm}(\epsilon_{\text{max}}/\text{M}^{-1}\text{cm}^{-1})$], 582 (1.25×10^4), IR: $\nu(\text{NCN})$, 2138, 2056 cm^{-1} .

2.4.5 Preparation of $[\{\text{Ru}(\text{ttp})(\text{bpz})\}_2(\mu\text{-adpc})][\text{PF}_6]_2$

The procedure is identical to synthesis of $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-adpc})](\text{PF}_6)_2$ except that $[\{\text{Ru}(\text{ttp})(\text{bpz})\}\text{Cl}](\text{PF}_6)$ (0.681 g, 0.89 mmol) and neutral alumina were used. Yield: 160 mg, 20 %. Elem. Anal. Calcd. for $\text{Ru}_2\text{C}_{74}\text{H}_{54}\text{N}_{20}\text{P}_2\text{F}_{12}$: C, 51.27; H, 3.26; N, 16.16. Found: C, 50.94; H, 3.52; N, 16.22. $[\lambda_{\text{max}}/\text{nm} (\epsilon_{\text{max}}/\text{M}^{-1}\text{cm}^{-1})]$, at $\lambda = 503 \text{ nm}$ (5.82×10^3), IR: $\nu(\text{NCN})$, 2159 cm^{-1} .

2.4.6 Preparation of $[\{\text{Ru}(\text{ttp})(\text{bpz})\}_2(\mu\text{-dicyd})][\text{PF}_6]_2 \cdot 2\text{DMF}$

The procedure is identical to the above synthesis except that $\text{Ti}_2(\text{dicyd})$ (242 mg, 0.45 mmol) was used instead of $\text{Ti}_2(\text{adpc})$, grade (I) alumina instead of neutral alumina and the reaction refluxed under nitrogen. Yield, 107 mg, 15%. Elem. Anal. Calcd. for $\text{Ru}_2\text{C}_{74}\text{H}_{64}\text{N}_{20}\text{P}_2\text{F}_{12}$: C, 50.52; H, 3.91 N, 16.07. Found: C, 50.37; H, 4.09; N, 15.96. UV-vis in DMF $[\lambda_{\text{max}}/\text{nm} (\epsilon_{\text{max}}/\text{M}^{-1}\text{cm}^{-1})]$, 503 (2.43×10^4), IR: $\nu(\text{NCN})$ 2142, 2112 cm^{-1} .

2.5 Physical Measurements**2.5.1 Infrared Spectra**

Infrared spectra were recorded on a Bomem Michelson 120 FTIR spectrophotometer, which was on line to a Hewlett-Packard Color-pro Plotter. All samples were prepared as KBr disks. Reference spectra of air were run prior to all sample spectra.

2.5.2 ^1H NMR Spectra

All the ^1H spectra were recorded on a Bruker AMX-200 or AMX-400 NMR spectrometer at ambient temperature. Normally, 5 mg of samples were dissolved in 0.5 mL of dimethyl sulphoxide- d_6 or $\text{CHCl}_3\text{-d}_3$ in a Norell XR-55 NMR tube. Chemical shifts derived from an internal TMS reference.

2.5.3 Electronic Absorption Spectra

Electronic absorption spectra for samples at room temperature were taken on a Varian Cary 5 UV-Vis-NIR. All samples were run using matching quartz cells of either 1.000 cm or 0.20 cm path length. Background correction was performed before each run at 800 nm/min.

2.5.4 Cyclic Voltammetry

Cyclic voltammograms were recorded using a BAS CV-27 apparatus and BAS X-Y recorders at constant temperature of 25 °C. The electrochemical cell consisted of a double-jacketed glass container, which was charged with approximately 15 mL of solvent. The cell temperature was set at 25 °C by means of a Haake D8-G refrigerated bath and circulator (accuracy 0.02 °C). The cell was fitted with a Teflon cap that had four holes to permit insertion of electrodes and an argon gas bubbler into the cell. Three electrodes were utilized in this system, two platinum-disk working and counter (auxiliary) electrodes (BAS, 1.6-mm diameter), and a silver wire pseudo-reference electrode with ferrocene (0.665 V vs. NHE)⁴³ as an internal reference. The potential was controlled by the BAS CV-27. Tetrabutylammonium hexafluorophosphate (TBAH 0.1

M) was used as supporting electrolyte. TBAH was recrystallized twice from ethanol:water (1:1) and vacuum-dried at 110 °C overnight. The platinum working-electrode was manually cleaned with 1 mM diamond polish before each scan. Solvents used in all cyclic voltammetry experiments were deoxygenated by bubbling with argon for 15 min.

2.5.5 Spectroelectrochemistry

Spectroelectrochemistry of mononuclear and dinuclear complexes was performed using an OTTLE (Optically Transparent Thin Layer Electrochemistry) cell.⁴⁴ The cell had interior dimensions of roughly 1 × 2 cm with a path length of 0.2 cm and was fitted with a Ag/AgCl reference electrode (Figure 2.1). ITO (indium-tin oxide) coated glass served as working and counter

electrodes and was purchased from Delta-Technologies. Spectra were obtained on Cary 5 Spectrophotometer vs. appropriate background of solvent and electrolyte at scan rate of 1800 nm/min. The potential was controlled by the same BAS CV-27 which was used for cyclic voltammetry. At any given potential, the system was allowed to come to equilibrium ($i \approx 0 \mu\text{A}$) before the spectrum was taken.

Figure 2.1 Schematic of the OTTLE cell spacer (left) and the teflon superstructure (right). a = Ag\AgCl wire, b = platinum wire.

2.5.6 Chemical Oxidation

In a small vial, the oxidant $[\text{Fe}(\text{bpy})_3](\text{PF}_6)_3$ was added in increments of 0.3 equivalences to a solution of the dimer complex.⁴⁵ The OTTLE cell, having a path length of 0.2 cm, was charged with the reaction mixture. Spectra were obtained on Cary 5 Spectrophotometer vs. appropriate background of solvent at scan rate of 1800 nm/min.

2.5.7 Infrared Spectroelectrochemistry

An infrared spectroscopic study for $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-dicyd})](\text{PF}_6)_2$ and $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-adpc})](\text{PF}_6)_2$ was performed using the OTTLE cell described above. Gold foil (500 line/inch, 60 % transmittance, Buckbee Mears) was used as the working and counter electrode whereas Ag/AgCl was used as the reference electrode. Infrared spectroelectrochemistry, focusing on the range of the deprotonated cyanamide stretch ($2200\text{-}1950\text{ cm}^{-1}$), were taken at ambient temperature using a Bomem Michelson 120 FTIR spectrophotometer, which was on line to a Hewlett-Packard Colorpro Plotter.

2.5.8 Crystallography

Thin plates of $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-adpc})][\text{PF}_6]_2 \cdot 6\text{DMF}$ were grown by slow diffusion of diethyl ether into a N,N'-dimethylformamide (DMF) solution of complex. The data were collected on a 1K Siemens Smart CCD using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 203(2) K using an ω -scan technique and corrected for absorptions using equivalence reflections.¹⁷ No symmetry higher than triclinic was observed and solution in the centric space group option yielded chemically reasonable and computationally stable results of refinement. The structure was solved by direct methods and refined with full-matrix least-squares procedures. The molecular cation is located at an inversion center. Six molecules of DMF are cocrystallized in the unit cell. Anisotropic refinement was performed on all non-hydrogen atoms. All hydrogen atoms were calculated. Scattering factors are contained in the SHELXTL 5.1 program library.

2.5.9 Elemental Analysis

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

Chapter 3 Results

3.1 Reactant Complexes

The 4'-*p*-tolyl-2,2':6',2''-terpyridine (ttp) and 4'-*p*-tolyl-2,6-di(2-pyrazinyl)-pyridine (tpz) ligands were synthesized by stirring 2 equivalents of 2-acetylpyridine or 2-acetylpyrazine with one equivalent of *p*-tolualdehyde in excess NH_4OH , and 1:1 (CH_3OH :15% KOH) at room temperature for four days according to the scheme below:

Two types of reactions were used to prepare the reactant complexes. The $[\text{Ru}(\text{ttp})(\text{bpy})\text{Cl}](\text{PF}_6)$ and $[\text{Ru}(\text{ttp})(\text{bpz})\text{Cl}](\text{PF}_6)$ mononuclear complexes were synthesized by the reaction of the mononuclear complex $[\text{Ru}(\text{ttp})\text{Cl}_3]$ with 1 equivalent of bpy or bpz using ethanol as a reducing solvent. $[\text{Ru}(\text{tpz})(\text{bpy})\text{Cl}](\text{PF}_6)$ and $[\text{Ru}(\text{tpz})(\text{bpz})\text{Cl}](\text{PF}_6)$ were prepared by refluxing the tpz ligand with $[\text{Ru}(\text{DMSO})_4\text{Cl}_2]$ in

a 1:1 mole ratio in DMF solution for 10 min., followed by the addition of 1 equivalent of bpy or bpz ligand and further reflux for 4 h.

Figure 3.1 synthesis of $[\text{Ru}(\text{tpz})(\text{bpy})\text{Cl}](\text{PF}_6)$ and $[\text{Ru}(\text{tpz})(\text{bpz})\text{Cl}](\text{PF}_6)$

The planar nature of the tpz ligand forces the formation of a single $[\text{Ru}(\text{L})(\text{L}')\text{Cl}](\text{PF}_6)$ product in the above reactions.

The ^1H NMR data for the reactant complexes are summarized in Table 3.1 and their ^1H NMR spectra are shown in Figure 3.2 to Figure 3.9. The tpz and ttp ligands showed seven and six chemical shifts respectively, whereas the 2,2'-bipyridine and 2,2'-bipyrazine ligands having two magnetically inequivalent pyridine and pyrazine moieties showed a total of eight and six chemical shifts, respectively. All the resonances were assigned using COSY (see Figure 3.3, Figure 3.5, Figure 3.7 and Figure 3.9).

Table 3.1 ^1H NMR Spectrum of the Reactant Complexes.

Complex	Ligand Chemical Shifts
$[\text{Ru}(\text{ttp})(\text{bpy})\text{Cl}]^+$	methyl protons at 2.45 (3H, s); ttp and bpy protons at 10.1 (H, d); 9.29 (2H, s); 8.93 (3H, t), 8.64 (H, d); 8.35(H, t); 8.24 (2H, d); 8.06 (H, t); 8.01 (2H, t); 7.77 (H, t); 7.62 (2H, d); 7.51 (2H, d); 7.42 (H, d); 7.38 (2H, t); 7.07 (H, t)
$[\text{Ru}(\text{tpz})(\text{bpy})\text{Cl}]^+$	methyl protons at 2.50 (3H, s); tpz and bpy protons at 10.03 (2H, s); 9.97 (H, d); 9.37 (2H, s); 8.94 (H, d); 8.68 (H, d), 8.54 (2H, d); 8.42 (1H, t); 8.25 (2H, d); 8.09 (H, t); 7.87 (3H, m); 7.54 (2H, d); 7.41(H, d); 7.12 (H, t)
$[\text{Ru}(\text{ttp})(\text{bpz})\text{Cl}]^+$	methyl protons at 2.50 (3H, s); ttp and bpz protons at 10.23 (H, s); 9.96 (H, d); 9.89 (H, s); 9.19 (2H, s); 9.17(H, d); 8.95 (2H, d) , 8.28 (2H, d); 8.19 (H, d); 8.05 (2H, t); 7.67 (H, d), 7.68 (2H, d); 7.52 (2H, d), 7.37 (2H, t)
$[\text{Ru}(\text{tpz})(\text{bpz})\text{Cl}]^+$	methyl protons at 2.50 (3H, s); tpz and bpz protons at 10.26 (H, s); 10.14 (2H, s); 9.99 (H, s); 9.93 (H, d); 9.46 (2H, s); 9.20 (H, d); 8.56 (2H, d); 8.32 (2H, d); 8.26(H, d); 7.95 (3H, m), 7.77 (H, d); 7.52 (H, d)

Data in ppm vs. TMS reference, at 0.00 ppm, s, singlet; d, doublet; t, triplet; m, multiplet

Figure 3.2 ^1H NMR spectrum of $[\text{Ru}(\text{tp})(\text{bpy})\text{Cl}](\text{PF}_6)$ in DMSO-d_6 , (to clarify the integration of the protons in Figure 3.3).

Figure 3.3 400 MHz ^1H NMR COSY of $[\text{Ru}(\text{tp})(\text{bpy})\text{Cl}](\text{PF}_6)$ in DMSO-d_6 showing the tp and bpy hydrogen resonances.

Figure 3.4 ^1H NMR spectrum of $[\text{Ru}(\text{tpz})(\text{bpy})\text{Cl}](\text{PF}_6)$ in $\text{DMSO}-d_6$ (to clarify the integration of the protons in Figure 3.5).

Figure 3.5 400 MHz ^1H NMR COSY of $[\text{Ru}(\text{tpz})(\text{bpy})\text{Cl}](\text{PF}_6)$ in DMSO-d_6 showing the tpz and bpy hydrogen resonances.

Figure 3.6 ^1H NMR spectrum of $[\text{Ru}(\text{ttp})(\text{bpz})\text{Cl}](\text{PF}_6)$, in DMSO-d_6 , (to clarify the integration of the protons in Figure 3.7).

Figure 3.7 400 MHz ^1H NMR COSY of $[\text{Ru}(\text{tp})(\text{bpz})\text{Cl}](\text{PF}_6)$ in DMSO-d_6 showing the tp and bpz hydrogen resonances.

Figure 3.8 ^1H NMR spectrum of $[\text{Ru}(\text{tpz})(\text{bpz})\text{Cl}](\text{PF}_6)$ in DMSO-d_6 , (to clarify the integration of the protons in Figure 3.9).

Figure 3.9 400 MHz ^1H NMR COSY of $[\text{Ru}(\text{tpz})(\text{bpz})\text{Cl}](\text{PF}_6)$ in DMSO-d_6 showing the tpz and bpz hydrogen resonances.

3.2 Electronic Spectra of Reactant Complexes

The electronic absorption data of the reactant complexes are shown in Table 3.2. The [Ru(tpp)(bpy)Cl](PF₆) mononuclear complex in acetonitrile is characterized by a band at 512 nm which was assigned to the metal-to-ligand charge transfer (MLCT) $d\pi \rightarrow \pi^*$ transition. This band is shifted to a lower energy (518 nm) upon replacing the 2,2'-bipyridine with a 2,2'-bipyrazine moiety.

Table 3.2 The Electronic Spectral Data, MLCT λ_{max} (nm), for the Reactant Complexes in Acetonitrile.

Complex	λ_{max} (nm) ($\epsilon \text{ M}^{-1} \text{ cm}^{-1}$)
[Ru(tpp)(bpy)Cl] ⁺	512 (1.0×10^4)
[Ru(tpz)(bpy)Cl] ⁺	495, 547 (7×10^3)
[Ru(tpp)(bpz)Cl] ⁺	518 (1.8×10^4)
[Ru(tpz)(bpz)Cl] ⁺	500 (1.0×10^4)

The [Ru(tpz)(bpy)Cl](PF₆) mononuclear complex in acetonitrile was characterized by two MLCT bands, the low energy band at 547 nm was assigned to $d\pi \rightarrow (\text{tpz})\pi^*$, whereas the high energy band at 495 nm was assigned to $d\pi \rightarrow (\text{bpy})\pi^*$. These two bands merged

to give one band at 500 nm upon replacing the 2,2'-bipyridine with 2,2'-bipyrazine moiety in the mononuclear complex $[\text{Ru}(\text{tpz})(\text{bpz})\text{Cl}](\text{PF}_6)$.

3.3 The Phenylcyanamide Mononuclear Complexes

3.3.1 Synthesis

The mononuclear phenylcyanamide Ru(II) complexes were prepared according to the following metathesis reaction:

Where L = ttp or tpz, L' = bpz or bpy

$[\text{Ru}(\text{ttp})(\text{bpy})(2,3,4,5-\text{Cl}_4\text{pcyd})](\text{PF}_6)$ complex was obtained in sufficient purity by simply diffusing ether into a saturated DMF solution of the reaction product to yield dark brown crystals. The other complexes required purification by column chromatography to ensure purity. Acceptable elemental analyses and clean ^1H NMR spectra were used as indicators of sufficient purity. These complexes were crystallized as deep purple needles in DMF. The solubility of these complexes decreased when pyridine moieties were replaced by pyrazine moieties.

3.3.2 Infrared and Electronic Spectroscopy

Figure 3.10 shows the infrared spectrum of $\text{Ti}(2,3,4,5-\text{Cl}_4\text{pcyd})$. The band located at 2134 cm^{-1} was assigned to $\nu(\text{NCN})$. This band was shifted to a higher energy when the free ligand was coordinated to the electropositive Ru(II) (Figure 3.11). Interpretation of the IR results for phenylcyanamide complexes was taken from a previous study.⁴⁶

The protonated form of the phenylcyanamide ligand shows an infrared stretch with mostly nitrile character, typically around 2250 cm^{-1} .²⁷ The formation of a resonance-stabilized three-atom π -system is caused by deprotonation of the cyanamide ligand (scheme below), in which there are two pairs of non-bonding electrons that can be delocalized over a three-atom system, generating two resonance forms.

Deprotonation of the cyanamide group and coordination of a metal ion will shift the $\nu(\text{NCN})$ to lower energies (2120 cm^{-1}),⁴⁶ but the magnitude of this effect depends on the contribution of each resonance form to the electronic structure of the cyanamide group, as influenced by the nature of the metal ion. As resonance form **A** is similar to an organic carbodiimide, its $\nu(\text{NCN})$ should be within the range of $2100\text{--}2150\text{ cm}^{-1}$.⁴⁶ Resonance form **B** should have a $\nu(\text{NCN})$ that resembles the value for a neutral phenylcyanamide (2250 cm^{-1}). When Dicyd^{2-} derivatives compared to phenylcyanamide ligands, they show the same effect, even so, the $\nu(\text{NCN})$ is typically shifted to lower frequencies by approximately 20 cm^{-1} .⁴⁶ Thus, the shift of $\nu(\text{NCN})$ to higher energy relative to the free ligand must be explained by greater contribution of resonance form **B** to the cyanamide group when the nitrile moiety is coordinated to Ru(II) . Nitrile ligands are π -acceptors, and thus are expected to be favored by the π -donor Ru(II) .

The IR spectrum for $[\text{Ru}(\text{ttp})(\text{bpy})(2,3,4,5\text{-Cl}_4\text{pcyd})](\text{PF}_6)$ as a representative spectrum is shown in Figure 3.11 and the infrared data for these complexes are summarized in Table 3.3. The presence of only one sharp and intense absorption band for the cyanamide stretching frequency in all complexes provides evidence that the cyanamide ligands are equivalent in the solid state. When the cyanamide ligands are inequivalent, multiple $\nu(\text{NCN})$ are observed.³⁹

Table 3.3 Cyanamide Stretching Energies, $\nu(\text{NCN})$ (cm^{-1}), for the Phenylcyanamide Mononuclear Complexes.

Complex ($\text{L}=2,3,4,5\text{-Cl}_4\text{pcyd}$)	$\nu(\text{NCN})$ (cm^{-1})
$[\text{Ru}(\text{ttp})(\text{bpy})\text{L}]^+$	2167
$[\text{Ru}(\text{tpz})(\text{bpy})\text{L}]^+$	2167
$[\text{Ru}(\text{ttp})(\text{bpz})\text{L}]^+$	2176
$[\text{Ru}(\text{tpz})(\text{bpz})\text{L}]^+$	2185

Figure 3.10 Infrared spectrum of the Tl(2,3,4,5-Cl₄pcyd).

Figure 3.11 Infrared spectrum of [Ru(ttp)(bpy)(2,3,4,5-Cl₄pcyd)](PF₆).

The electronic absorption spectral data of the phenylcyanamide mononuclear complexes in acetonitrile are summarized in Table 3.4. These mononuclear complexes show similar absorption spectra compared to that of reactant complexes ($[\text{Ru}(\text{L})(\text{L}')\text{Cl}](\text{PF}_6)$) except that the λ_{max} of all bands are slightly shifted to higher energy.

Table 3.4 The Electronic Spectrum Data, MLCT λ_{max} (nm), for the Phenylcyanamide Mononuclear Complexes in Acetonitrile.

Complex (L=2,3,4,5-Cl ₄ pcyd)	λ_{max} (nm) ($\epsilon \text{ M}^{-1} \text{ cm}^{-1}$)
$[\text{Ru}(\text{ttp})(\text{bpy})\text{L}]^+$	503 (1.2×10^3)
$[\text{Ru}(\text{tpz})(\text{bpy})\text{L}]^+$	524 (750), 409 (1.2×10^3)
$[\text{Ru}(\text{ttp})(\text{bpz})\text{L}]^+$	508 (2.0×10^3)
$[\text{Ru}(\text{tpz})(\text{bpz})\text{L}]^+$	487 (1.2×10^3)

3.3.3 Proton NMR Spectroscopy

Figure 6.1 (see the appendix) shows the ^1H NMR spectra of the free Tl(2,3,4,5-Cl₄pcyd). The singlet peak at 6.94 ppm was assigned to the proton in the benzene ring. Upon coordination, the proton ^1H NMR resonance for 2,3,4,5-Cl₄pcyd in $[\text{Ru}(\text{L})(\text{L}')(2,3,4,5\text{-Cl}_4\text{pcyd})](\text{PF}_6)$ (L is ttp or tpz whereas L' is bpy or bpz) complexes is shifted upfield as

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shown in Figure 6.2 to Figure 6.5 (see the appendix) and in Table 3.5. All other resonances are assigned to those seen in the reactant complexes.

Table 3.5 A Summary of the ^1H NMR Data for Phenylcyanamide Mononuclear Complexes (see the appendix Figure 6.2, Figure 6.3, Figure 6.4 and Figure 6.5).

Complex ($\text{L}=2,3,4,5\text{-Cl}_4\text{pcyd}$)	Phenylcyanamide Proton	Ligand Chemical Shifts
$[\text{Ru}(\text{ttp})(\text{bpy})\text{L}]^+$	5.87	2.48 (3H, s); ttp and bpy protons at 9.64 (H, d); 9.29 (2H, s); 9.06 (2H, d); 8.97 (H, d); 8.71 (H, d); 8.42 (H, t); 8.29 (2H, t); 8.12 (3H, m); 7.88 (H, t); 7.50 (2H, d); 7.58 (H, d); 7.53 (H, d); 7.48 (2H, t); 7.17 (H, t)
$[\text{Ru}(\text{tpz})(\text{bpy})\text{L}]^+$	5.95	methyl protons at 2.48 (3H, s); tpz and bpy protons at 10.14 (2H, s); 9.53 (H, d); 9.45 (2H, s); 8.98 (H, d); 8.71 (H, d); 8.63 (2H, d); 8.46 (H, t); 8.29 (2H, d); 8.12 (H, t); 7.94 (3H, m); 7.54 (3H, m); 7.19 (H, t)
$[\text{Ru}(\text{ttp})(\text{bpz})\text{L}]^+$	5.86	methyl protons at 2.48 (3H, s); 10.22 (H, s); 9.96 (H, d); 9.65 (H, d); 9.32 (2H, s); 9.17 (H, d); 9.07 (2H, d); 8.29 (2H, d); 8.28 (H, d); 8.17 (2H, t); 7.90 (H, d); 7.8 (2H, d); 7.53 (2H, d); 7.46 (2H, t);
$[\text{Ru}(\text{tpz})(\text{bpz})\text{L}]^+$	5.95	methyl protons at 2.48 (3H, s); tpz and bpz protons at 10.24 (H, s); 10.15 (2H, s); 9.98 (H, s); 9.56 (H, d); 9.49 (2H, s); 9.20 (H, d); 8.65 (2H, d); 8.33 (H, d); 8.30 (2H, d); 8.05 (2H, d); 7.83 (H, d); 7.56 (2H, d)

Data in ppm vs. TMS reference, at 0.00 ppm, s, singlet; d, doublet; t, triplet; m, multiplet

3.3.4 Cyclic Voltammetry

The cyclic voltammetry data of the four phenylcyanamide mononuclear complexes are summarized in Table 3.6 and are shown in Figure 3.12 to Figure 3.14. A representative voltammogram of $[\text{Ru}(\text{ttp})(\text{bpy})(2,3,4,5\text{-Cl}_4\text{pcyd})](\text{PF}_6)$ is shown in Figure 3.12. The $\text{Ru}(\text{III}/\text{II})$ couples were determined from the average of the anodic and cathodic peak potential ($E_{1/2}$), where $E_{1/2} = (E_{\text{pa}} + E_{\text{pc}})/2$ at scan rate of 100 mV s^{-1} .

Figure 3.12 Cyclic voltammogram of $[\text{Ru}(\text{ttp})(\text{bpy})(2,3,4,5\text{-Cl}_4\text{pcyd})]^+$ in acetonitrile, data reported in V vs. NHE with scan rate of 0.1 V/s ; 0.1 M TBAH at 25°C .

The $\text{Ru}(\text{III}/\text{II})$ couple occurred at 1.09 V vs. NHE and was quasi reversible with an anodic to cathodic peak separation of 80 mV . This separation was generally invariant at scan rates from 50 to 500 mV/s . Scanning to more positive potential, $\text{L}(0/-1)$ for phenylcyanamide ($2,3,4,5\text{-Cl}_4\text{pcyd}$) appeared at 1.85 V vs. NHE. This couple was much less reversible having large peak-to-peak separation (150 mV). It can also be seen from the voltammogram (Figure 3.13), that three one-electron ligand reduction waves were observed between -1.0 and -2.0 V . The first reduction wave couple occurred at -1.09 V

vs. NHE with cathodic and anodic peak separation of 70 mV. This likely corresponded to the reduction of the coordinated ttp ligand due to the greater stability of ttp orbitals compared to that of bpy.⁴⁷

This was followed by the irreversible reduction of the coordinated bpy ligand,

The maximum cathodic peak of this couple occurred at -1.41 V vs. NHE, whereas the third irreversible reduction wave at -1.74 V (the cathodic peak maximum), likely corresponded to the second reduction of ttp ligand.

From Table 3.6 and the voltammograms in Figure 3.14, it can be seen that the Ru(III/II) redox couple, the L(0/-1) redox couple, and the reduction potential for the auxiliary ligand were shifted to more positive potentials upon replacing the pyridine ligand with the weaker σ -donor pyrazine moieties. The Ru(III/II) redox couple for $[Ru(tpz)(bpz)(2,3,4,5-Cl_4pcyd)]^+$ (Figure 3.14) was quasi reversible, with the cathodic current noticeably smaller compared to the anodic current due to the decrease in the stability of the Ru(III) complex.

Figure 3.13 Cyclic voltammogram showing the reduction of $[\text{Ru}(\text{tp})(\text{bpy})(2,3,4,5\text{-Cl}_4\text{pcyd})](\text{PF}_6)$ in acetonitrile, data reported in V vs. NHE with scan rate of 0.1 V/s; 0.1 M TBAH at 25 $^{\circ}\text{C}$.

Figure 3.14 Cyclic voltammogram of the phenylcyanamide complexes (a) $[\text{Ru}(\text{ttp})(\text{bpy})(\text{L})]^+$, (b) $[\text{Ru}(\text{tpz})(\text{bpy})(\text{L})]^+$, (c) $[\text{Ru}(\text{ttp})(\text{bpz})(\text{L})]^+$, (d) $[\text{Ru}(\text{tpz})(\text{bpz})(\text{L})]^+$ in acetonitrile, data reported in V vs. NHE with scan rate of 0.1 V/s; 0.1 M TBAH at 25 $^{\circ}\text{C}$, $\text{L} = 2,3,4,5\text{-pcyd}^-$.

3.3.5 Spectroelectrochemistry

The electronic spectral data of the $[\text{Ru}(\text{L})(\text{L}')(2,3,4,5\text{-Cl}_4\text{pcyd})](\text{PF}_6)$ (where L is bpy or bpz and L' is ttp or tpz) in acetonitrile solution are summarized in Table 3.6. As a representative example, Figure 3.15 shows the oxidation of $[\text{Ru}(\text{ttp})(\text{bpy})(2,3,4,5\text{-Cl}_4\text{pcyd})](\text{PF}_6)$ in acetonitrile to the fully oxidized Ru(III) complex. Controlled potential electrolysis of $[\text{Ru}(\text{ttp})(\text{bpy})(2,3,4,5\text{-Cl}_4\text{pcyd})]^+$ in acetonitrile was used to generate the absorption spectrum of $[\text{Ru}(\text{ttp})(\text{bpy})(2,3,4,5\text{-Cl}_4\text{pcyd})]^{2+}$. The UV–Visible spectra were taken at various intervals during the course of the experiment. Reversibility was evaluated by the maintenance of the isobestic points in the absorption spectrum for both forward (oxidation) and reverse (reduction) processes. The initial spectrum (Figure 3.15) is that of $[\text{Ru}(\text{ttp})(\text{bpy})(2,3,4,5\text{-Cl}_4\text{pcyd})](\text{PF}_6)$ in acetonitrile. Upon oxidation the MLCT band centered at 500 nm loses intensity and two new bands appear at 1053 nm and at 430 nm (see discussion for more detail). These two bands are assigned to ligand to metal charge transfer (LMCT) $\pi \rightarrow d\pi^*$ transitions associated with Ru(III) cyanamide chromophore. These bands are shifted to lower energy upon perturbation of the metal with weak σ -donor pyrazine moieties (see Figure 3.16 to Figure 3.18).

Figure 3.15 Spectroelectrochemical data for the oxidation of $[\text{Ru}(\text{tp})(\text{bpy})(2,3,4,5\text{-Cl}_4\text{pcyd})](\text{PF}_6)$ in acetonitrile (0.8 to 1.2 V, vs. Ag/AgCl).

Figure 3.16 Spectroelectrochemical data for the oxidation of $[\text{Ru}(\text{tpz})(\text{bpy})(2,3,4,5\text{-Cl}_4\text{pcyd})](\text{PF}_6)$ in acetonitrile, (1.0 to 1.3 V, vs. Ag/AgCl).

Figure 3.17 Spectroelectrochemical data for the oxidation of $[\text{Ru}(\text{tpz})(\text{bpz})(2,3,4,5\text{-Cl}_4\text{pcyd})](\text{PF}_6)$ in acetonitrile, (1.1 to 1.4 V, vs. Ag/AgCl).

Figure 3.18 Spectroelectrochemical data for the oxidation of $[\text{Ru}(\text{tpz})(\text{bpy})(2,3,4,5\text{-Cl}_4\text{pcyd})](\text{PF}_6)$ in acetonitrile, (1.0 to 1.3 V, vs. Ag/AgCl).

Table 3.6 The Redox Couples and E_{LMCT} (cm^{-1}) for the Phenylcyanamide Complexes.^a

Complex L=2,3,4,5-Cl ₄ pcyd	Ru(III/II)	L(0/-1)	L ₁ ^b	L ₂ ^b	L ₃ ^b	E_{LMCT} (V)	ΔE (V) ^c
[Ru(tpp)(bpy)L] ⁺	1.09	1.85	-1.09	-1.41	-1.74	1.177	0.76
[Ru(tpz)(bpy)L] ⁺	1.17	1.83	-0.86	-1.17	-1.44	1.131	0.66
[Ru(tpp)(bpz)L] ⁺	1.31	1.98	-0.66	-1.24		1.128	0.68
[Ru(tpz)(bpz)L] ⁺	1.47	2.12	-0.50	-0.67	-1.19	1.118	0.65

^a versus NHE, platinum working electrode, 0.1 M TBAH electrolyte, at 25 °C

^b the first, second and the third auxiliary ligand reduction couples

^c $\Delta E = L(0/-1) - \text{Ru(III/II)}$

It is known that correlates the ligand-to-metal charge transfer band energy to the difference in redox couples between the centers involved the charge-transfer events (equation 4). The energy of the LMCT band is related to the difference in the oxidation potential of the ligand, L(0/-1) and the reduction potential of the metal, Ru(III/II) which can be found by cyclic voltammetry. A linear relationship (Figure 3.19) is found by plotting the LMCT band energies against the difference between the L(0/-1) and Ru(III/II).

Figure 3.19 Plot of LMCT energy vs. ΔE for the four mononuclear phenylcyanamide complexes, from Table 3.6, equation of line is $E_{\text{LMCT}} = 0.562 \Delta E + 0.748$ $R^2 = 0.985$.

3.4 [$\{\text{Ru}(\text{L})(\text{L}')\}_2(\mu\text{-dicyd})\](\text{PF}_6)_2$ Complexes

3.4.1 Synthesis

The dinuclear complexes [$\{\text{Ru}(\text{L})(\text{L}')\}_2(\mu\text{-dicyd})\](\text{PF}_6)_2 of this study were synthesized by the metathesis reaction of refluxing [$\text{Ru}(\text{L})(\text{L}')\text{Cl}]^+$ where L is ttp and tpz and L' is bpy and bpz with the thallium salts of dicyd²⁻ in DMF solution. The reaction of the reactant mononuclear complexes with $\text{Tl}_2(\text{dicyd})$ produced the labile complex [$\text{Ru}(\text{L})(\text{L}')\text{DMF}]^{2+}$ and the precipitate TlCl . The labile complex was easily bound to the bridging ligand in a reasonable yield according to this reaction:$

The crude product of this reaction was suggested to be a dinuclear dication complex based on the observation of a deprotonated cyanamide $\nu(\text{NCN})$ band in the IR spectrum. Acceptable elemental analyses and clean ¹H NMR spectra were used as an indicator of sufficient purity of the final products. These Ru(II) complexes are air stable. An attempt was made to obtain crystals of the [$\{\text{Ru}(\text{L})(\text{L}')\}_2(\mu\text{-dicyd})\}]^{2+}$ dinuclear complex by using various counter ions and solvent conditions but without success. However crystals of the analogous adpc²⁻ complex were obtained (section 3.5.2).

The crude product of [$\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-dicyd})\](\text{PF}_6)_2$ was purified by column chromatography over alumina *WA-1* grade (V). For [$\{\text{Ru}(\text{ttp})(\text{bpz})\}_2(\mu\text{-dicyd})\](\text{PF}_6)_2$ and [$\{\text{Ru}(\text{tpz})(\text{bpy})\}_2(\mu\text{-dicyd})\](\text{PF}_6)_2$. A more active alumina was required and so alumina *WA-1* grade (I) was used. A mixture of (3:1) acetonitrile/toluene was used to elute both

the unreacted mononuclear complex and the dicyd²⁻ bridging ligand, whereas a mixture of acetonitrile/methanol (4:1) gave the desired dinuclear complex. Upon evaporation to dryness, the desired product was dissolved in dimethylformamide and filtered through cellite to remove the fine particles of alumina. The product was precipitated by adding excess aqueous NH₄PF₆, washed with water to remove the excess NH₄PF₆, and ether, and then left to air dry.

3.4.2 IR and ¹H NMR Spectroscopy

The infrared spectra of these complexes are shown in Figure 3.20 to Figure 3.21 and summarized in Table 3.7. As a representative example, the IR spectrum of [$\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-dicyd})\](PF₆)₂] showed a broad absorption band around 2136 cm⁻¹ (Figure 3.20), which was assigned to anionic cyanamide $\nu(\text{NCN})$. This broad band split into two narrower bands (Figure 3.21) for the [$\{\text{Ru}(\text{ttp})(\text{bpz})\}_2(\mu\text{-dicyd})\](PF₆)₂] and [$\{\text{Ru}(\text{tpz})(\text{bpz})\}_2(\mu\text{-dicyd})\](PF₆)₂] complexes, and may arise from the *syn* and *anti* conformations of these complexes.$$$

Figure 3.20 Infrared spectrum of $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-dicyd})](\text{PF}_6)_2$.

Figure 3.21 Infrared spectrum of $[\{\text{Ru}(\text{ttp})(\text{bpz})\}_2(\mu\text{-dicyd})](\text{PF}_6)_2$.

Table 3.7 Cyanamide Stretching Energies, $\nu(\text{NCN})$ (cm^{-1}), for the $[\{\text{Ru}(\text{L})(\text{L}')\}_2(\mu\text{-dicyd})](\text{PF}_6)_2$ Complexes.

Complex ($\text{L} = (\mu\text{-dicyd})$)	$\nu(\text{NCN})$ (cm^{-1})
$\text{Ti}_2(\text{dicyd})$	2089
$[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2\text{L}](\text{PF}_6)_2$	2137
$[\{\text{Ru}(\text{ttp})(\text{bpz})\}_2\text{L}](\text{PF}_6)_2$	2142, 2112
$[\{\text{Ru}(\text{tpz})(\text{bpy})\}_2\text{L}](\text{PF}_6)_2$	2138, 2056

The ^1H NMR spectra of the dinuclear $[\{\text{Ru}(\text{L})(\text{L}')\}_2(\mu\text{-dicyd})](\text{PF}_6)_2$ complexes are shown in Figure 6.6 to Figure 6.8 (see appendix) and summarized in Table 3.8. The six methyl protons for L occurred around 2.45 ppm, the phenyl proton resonance of the L and L' around between 7.0 and 10.2 ppm and showed the usual splitting pattern for the dinuclear complex. There is a small downfield shift when strong σ -donor pyridine moieties are replaced with weak σ -donor pyrazine moieties. The four phenyl protons around 5.45 to 6.0 ppm, have been assigned to the proton resonance of the bridging ligand.

Table 3.8 A Summary of the ^1H NMR Data for the $[\{\text{Ru}(\text{L})(\text{L}')\}_2(\mu\text{-dicyd})](\text{PF}_6)_2$ Complexes (see appendix Figure 6.6, Figure 6.7 and Figure 6.8).

Complex ($\text{L} = (\mu\text{-dicyd})$)	Ligand Chemical Shifts
$[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2\text{L}](\text{PF}_6)_2$	methyl protons, 2.45 (6H, s); dicyd $^{2-}$ phenyl protons, 5.45 (4H, singlet), ttp and bpy protons, 9.62 (2H, d); 9.16 (4H, s); 8.93 (6H, d); 8.66 (2H, d); 8.36 (2H, t); 8.20 (4H, d); 8.07 (2H, d); 8.01 (4H, t); 7.80 (2H, t); 7.64 (4H, d); 7.46 (6H, t) 7.39 (4H, t); 7.09 (2H, t)
$[\{\text{Ru}(\text{tpz})(\text{bpy})\}_2\text{L}](\text{PF}_6)_2$	methyl protons at 2.45 (6 H, s); phenyl protons for dicyd bridging ligand at 5.51 (4H, s), tpz and bpy protons at 10.03 (4 H, s), 9.52 (2H, d), 9.37 (4H, s), 8.96 (2H, d), 8.71 (2H, d), 8.54 (4H, d), 8.44 (2H, t), 8.20 (4 H, d), 8.10 (2H, t), 7.89 (6H, m), 7.50 (4H, d), 7.45 (2H, d), 7.13 (2H, t)
$[\{\text{Ru}(\text{ttp})(\text{bpz})\}_2\text{L}](\text{PF}_6)_2$	methyl protons at 2.45 (6H, s); phenyl protons for dicyd bridging ligand at 5.48 (4H, s), ttp and bpz protons at 10.19 (2H, s), 9.92 (2H, s, 9.61 (2H, d), 9.21 (4H, s), 9.15 (2H, d), 8.97 (4H, d), 8.22 (6H, m), 8.07 (4H, t), 7.85 (2H, d), 7.69 (4H, d), 7.47 (4H, d), 7.38 (4H, d)

Data in ppm vs. TMS reference, at 0.00 ppm, s, singlet; d, doublet; t, triplet; m, multiplet

3.4.3 Cyclic Voltammetry

Figure 3.23 shows the cyclic voltammograms for $[\{(\text{Ru}(\text{L})(\text{L}'))_2(\mu\text{-dicyd})\}(\text{PF}_6)_2$ complexes in acetonitrile and the redox couples and comproportionation constants for these dinuclear complexes are summarized in Table 3.9. The Ru(III/II) couples in acetonitrile were quasi-reversible with a separation between the cathodic and anodic waves of 70 mV, which was largely independent of the scan rate between 50 to 500 mV/s.

As a representative example, the two waves of Ru(III/II) couple of the $[\{\text{Ru}(\text{ttp})(\text{bpz})\}_2(\mu\text{-dicyd})](\text{PF}_6)_2$ complex in acetonitrile (Figure 3.22) occurred at 0.44 V and 0.88 V vs. NHE. From the differences in Ru(III/II) couples of the dinuclear complex ($\Delta E = 44$ mV), the comproportionation constant (K_c) for the formation of the Ru(III/II) mixed-valence complex was determined to be 2.8×10^7 . This comproportionation constant is approximately the same as that found for the Creutz-Taube ion $[(\text{NH}_3)_5\text{Ru}]_2(\mu\text{-pyrazine})^{5+}$ ($K_c = 8.54 \times 10^6$ in DMF)⁴⁸ and by analogy, is supportive of a Class III assignment for the mixed-valence complex of this study.⁴⁹

Three one electron ligand reduction waves are observed between -1.0 and -2.0 V, in the voltammogram of $[\{\text{Ru}(\text{ttp})(\text{bpz})\}_2(\mu\text{-dicyd})](\text{PF}_6)_2$ (Figure 3.22). The first reduction wave of $[\{\text{Ru}(\text{ttp})(\text{bpz})\}_2(\mu\text{-dicyd})](\text{PF}_6)_2$ occurred at -0.75 V vs. NHE. It was quasi reversible with cathodic and anodic peak separation of 90 mV and this was assigned to a reduction of bpz.

Figure 3.22 Cyclic voltammogram of $[\{Ru(tp)(bpz)\}_2(\mu-dicyd)](PF_6)_2$ in acetonitrile, data reported in V vs. NHE with scan rate of 0.1 V/s; 0.1 M TBAH at 25 °C.

The second reduction wave was irreversible with significant loss of anodic current at scan rates less than 100 mV/s, and this wave was most likely related to the coordinated *ttp* ligand. The maximum cathodic peak of this couple occurred at -1.27 V vs. NHE. This wave overlaps with the third reduction wave, which has a cathodic peak maximum was at -1.47 V, which likely corresponded to the second reduction of *bpz* ligand.

The current of the three ligand reduction couples were twice that of the Ru(III/II) couples. This is due to fact that there was a one-electron ligand reduction at each end of the complex at the same potential compared to one electron oxidation for the metal. Cyclic voltammetry of the free dicyd²⁻ molecule in acetonitrile showed two redox couples corresponding to dicyd^{1-/2-} at -0.215 and dicyd^{0/-} at 0.46 V vs. NHE.⁵⁰ These couples shift to more positive potentials when coordinated to Ru(III). For example, the dicyd^{1-/2-} and dicyd^{0/-} couples occur at 0.83 and 1.29 V vs. NHE in the cyclic voltammogram of [Ru(NH₃)₅]₂(μ-dicyd)]⁴⁺ in acetonitrile²¹. For the complex *trans*-[Ru(NH₃)₄(pyridine)]₂(μ-dicyd)]⁴⁺, the replacement one σ-donor ammine ligand with weak σ-donor pyridine ligand shifted the dicyd^{1-/2-} and dicyd^{0/-} couples to 0.97 V and 1.34 V vs. NHE respectively. More positive shift of these couples occurred when the five ammine were replaced with a very weak σ-donor ligands in [Ru(tpz)(bpy)]₂(μ-dicyd)](PF₆)₂ complex, making the first couple (dicyd^{1-/2-}) appear at 1.85 V. Unfortunately, the second couple (dicyd^{0/-}) was not observed up to 2.2 V, the anodic limit of acetonitrile.

The effect of the inner-sphere perturbation on the coupling of the dinuclear complexes was investigated by replacing strong σ-donor pyridine moieties with weak σ-donor pyrazine moieties (see Figure 3.23 and Table 3.9). The two redox waves of the Ru(III/II) couples for [Ru(tpz)(bpy)]₂(μ-dicyd)](PF₆)₂ and [Ru(tpz)(bpz)]₂(μ-dicyd)](PF₆)₂ were slightly shifted to more positive potential compared to the analogous couples of [Ru(tpz)(bpy)]₂(μ-dicyd)](PF₆)₂ but the difference in the two redox couples, which related to K_c by equation 20, is almost the same (see Chapter 4 for more detail).

Figure 3.23 Cyclic voltammograms of dinuclear complexes with dicyd^{2-} as the bridging ligand (a) $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-dicyd})](\text{PF}_6)_2$ (b) $[\{\text{Ru}(\text{tpz})(\text{bpy})\}_2(\mu\text{-dicyd})](\text{PF}_6)_2$ (c) $[\{\text{Ru}(\text{ttp})(\text{bpz})\}_2(\mu\text{-dicyd})](\text{PF}_6)_2$ in acetonitrile, data reported in V vs. NHE with scan rate of 0.1 V/s; 0.1 M TBAH at 25 °C.

RESULTS

Table 3.9 Redox couples and Comproportionation Constants for Dinuclear Complexes in Acetonitrile. ^a

Complex	Ru ₁ ^b	Ru ₂ ^c	L ₁ ^d	L ₂ ^d	L ₃ ^d	(L ⁻²⁻) ^e	$\Delta E_{1/2}$ ^f	K _c ^g
[{Ru(ttp)(bpy)} ₂ L] ²⁺	0.33	0.79	-0.99	-1.16	-1.53	1.65	0.46	6.0 × 10 ⁷
[{Ru(ttp)(bpz)} ₂ L] ²⁺	0.44	0.88	-0.75	-1.27	-1.47	1.85	0.44	2.8 × 10 ⁷
[{Ru(tpz)(bpy)} ₂ L] ²⁺	0.36	0.80	-0.77	-0.92	-1.55	1.86	0.44	2.8 × 10 ⁷

L=μ-dicyd²⁻

^a versus NHE, platinum working electrode, 0.1 M TBAH electrolyte, at 25 °C

^b Ru₁ = Ru[III,II]/Ru[II,II]

^c Ru₂ = Ru[III,III]/Ru[III,II]

^d auxiliary ligands reduction couples

^e dicyd oxidation couple

^f $\Delta E_{1/2} = Ru_2 - Ru_1$

^g the comproportionation constant $K_c = 10^{16.91\Delta E}$

To investigate the effect of outer-sphere perturbations on the metal-metal coupling in $[\{\text{Ru}(\text{tp})(\text{bpy})\}_2(\mu\text{-dicyd})](\text{PF}_6)_2$, cyclic voltammetry was performed in four solvents of varying donor strength. All cyclic voltammograms were collected at a scan rate of 0.1 V/s with electrochemical reversibility being tested at scan rates between 50 mV to 500 mV. The solvent properties and electrochemical data for $[\{\text{Ru}(\text{tp})(\text{bpy})\}_2(\mu\text{-dicyd})](\text{PF}_6)_2$ are described in Table 3.10.

The small change in separation between Ru(III/II) couples, which was achieved by changing the solvent from nitromethane to DMSO, shows that the magnitude of metal-metal coupling is only slightly perturbed by the nature of the solvent.

Table 3.10 Redox Couples and Comproportionation Constants for $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-dicyd})](\text{PF}_6)_2$ as a Function of Solvent.^a

Solvent	DN ^b	Ru ₁ ^c	Ru ₂ ^d	ΔE ^e	K_c ^f	L ₁ ^g	L ₂ ^g
NM	2.7	0.79	0.35	0.44	2.8×10^7		
AC	17	0.79	0.33	0.46	6.0×10^7	-1.16	-1.53
DMF	26.6	0.80	0.32	0.48	1.30×10^8	-0.875	-1.175
DMSO	29.8	0.79	0.35	0.44	2.8×10^7	-0.90	-1.173

^a versus NHE, platinum working electrode, 0.1 M TBAH electrolyte, at 25 °C.^b donor number³²^c $\text{Ru}_1 = \text{Ru}[\text{III},\text{III}]/\text{Ru}[\text{III},\text{II}]$ ^d $\text{Ru}_2 = \text{Ru}[\text{III},\text{II}]/\text{Ru}[\text{II},\text{II}]$ ^e $\Delta E = \text{Ru}_1 - \text{Ru}_2$ ^f the comproportionation constant $K_c = 10^{16.91\Delta E}$ ^g auxiliary ligands reduction couples

3.4.4 Infrared Spectroelectrochemistry

To determine whether these mixed-valence complexes are delocalized or localized systems, infrared spectroelectrochemistry was performed, as its timescale (10^{-13} s) gives an almost instantaneous view of the state of a fluxional molecule. The infrared spectroelectrochemistry of the dinuclear complex $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-dicyd})](\text{PF}_6)$ complex in DMSO solvent is shown in Figure 3.24 to Figure 3.25. Figure 3.24 shows the initial spectrum of $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-dicyd})]^{2+}$ and the oxidation to the mixed-valence state in DMSO. It is clear that at least two $\nu(\text{NCN})$ bands are present at 2141 and 2107 cm^{-1} . The spectrum of the dicyd^{2-} complexes in the solid state also showed two bands for $\nu(\text{NCN})$. The observation of more than one $\nu(\text{NCN})$ band is unusual for the solution IR spectrum of dicyanamidobenzene complexes,¹⁴ but is often seen in solid state IR spectra where it has been ascribed to different conformations of the complex in the crystal lattice.^{50,51} The majority of crystal structures^{56,52} have shown a preference for the *anti* conformation but the crystal structure of *trans, trans*- $[\{\text{Ru}(\text{NH}_3)_4(\text{pyridine})\}_2(\mu\text{-dicyd})]^{4+}$ showed a planar bridging ligand with the cyanamide groups in a *syn* conformation.⁵³ The presence of two $\nu(\text{NCN})$ in the solution IR spectra of these complexes is an indication that both Ru[II,II] complexes exist in at least two conformations in solution.

Oxidation of both complexes to their mixed-valence form (Figure 3.24) showed a slight blue shift in energy of $\nu(\text{NCN})$ and a loss of intensity. Further oxidation of $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-dicyd})]^{3+}$ (Figure 3.25) to give the Ru[III,III] complex showed an increase in intensity and a slight blue shift in energy. An additional band appears on the

high frequency side of the main $\nu(\text{NCN})$ due to multiple conformations of the complex in solution.

The observation of only one $\nu(\text{NCN})$ band in the IR spectrum of the mixed-valence complex $[\{\text{Ru}(\text{tp})(\text{bpy})\}_2(\mu\text{-dicyd})]^{3+}$ is strong evidence that these complexes are delocalized on the infrared timescale (10^{13} s^{-1}).

Figure 3.24 Infrared spectroelectrochemistry showing the oxidation of the Ru[II,II], $[\{\text{Ru}(\text{tp})(\text{bpy})\}_2(\mu\text{-dicyd})](\text{PF}_6)_2$, in DMSO to the Ru[III,II] complex (0.1 to 0.23 V vs. Ag/AgCl).

Figure 3.25 IR spectrum showing the oxidation of the Ru[III,II], [$\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-dicyd})\](PF₆)₂, in DMSO to the Ru[III,III] complex, (0.25 to 0.61 V vs. Ag/AgCl).$

3.4.5 UV-Vis-NIR Spectroelectrochemistry

As a representative example, Figure 3.26 shows the electronic spectra for the oxidation of dinuclear $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-dicyd})](\text{PF}_6)_2$, $\text{Ru}[\text{II},\text{II}]$, to the mixed-valence $\text{Ru}[\text{III},\text{II}]$ complex in DMF. The absorption spectrum of the $\text{Ru}[\text{II},\text{II}]$ complex (Figure 3.26) shows MLCT band at 478 nm that are typical of $[\text{Ru}(\text{II})(\text{ttp})(\text{bpy})]$ chromophores.^{54,55} Upon oxidation to the mixed-valence $\text{Ru}[\text{III},\text{II}]$ complex, a new band grows at 1100 nm ($\epsilon = 1.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). Only a single set of isosbestic points are seen for these absorbance changes associated with a given oxidation step and these changes are, for the most part, reversible. Further oxidation to the $\text{Ru}[\text{III},\text{III}]$ complex (Figure 3.27) results in a blue shift of this band and a slight increase in intensity. The assignment of this band for the $\text{Ru}[\text{III},\text{III}]$ complexes is straightforward as it is a characteristic of $\text{Ru}(\text{III})$ -cyanamide complexes that they possess two LMCT transitions as does the phenylcyanamide mononuclear complexes. The assignment of the band centered at 1100 nm in the $\text{Ru}[\text{III},\text{II}]$ spectrum (Figure 3.26) is not as simple as it may look. A single $\text{Ru}(\text{III})$ -cyanamide LMCT chromophore would be expected to result in a band of significantly reduced intensity compared to that seen for the $\text{Ru}[\text{III},\text{III}]$ complex. However, there is no significant absorption of the mixed-valence complex in the NIR region (up to 2650 nm). It is suggested that the intervalence transition for this complex has combined with the LMCT transition to give the observed absorption band centered at 1100 nm. This assignment will be discussed in detail in Chapter 4.

The inner-sphere perturbation of coupling of the dinuclear complex was investigated by replacing the strong σ -donor pyridine moieties with weak σ -donor pyrazine moieties.

The UV-Vis-NIR spectroelectrochemistry data for $[\{\text{Ru}(\text{tpz})(\text{bpy})\}_2(\mu\text{-dicyd})](\text{PF}_6)_2$ and $[\{\text{Ru}(\text{ttp})(\text{bpz})\}_2(\mu\text{-dicyd})](\text{PF}_6)_2$ dinuclear complexes in DMF are shown in Figure 3.28 to Figure 3.30. These complexes lose their isobestic point easily when oxidized to $\text{Ru}[\text{III},\text{III}]$ in comparison to $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-dicyd})](\text{PF}_6)_2$.

Figure 3.26 Spectroelectrochemical data for $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-dicyd})](\text{PF}_6)_2$ showing the oxidation of the $\text{Ru}[\text{II},\text{II}]$ complex to the mixed-valence $\text{Ru}[\text{III},\text{II}]$ under increasing anodic potential in DMF, (-0.25 to 0.2 V vs. Ag/AgCl).

Figure 3.27 Spectroelectrochemical data for $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-dicyd})](\text{PF}_6)_2$ showing the oxidation of the Ru[III,II] complex to Ru[III,III] under increasing anodic potential in DMF, (0.41 to 0.62 V vs. Ag/AgCl).

Figure 3.28 Spectroelectrochemical data for $[\{\text{Ru}(\text{tpz})(\text{bpy})\}_2(\mu\text{-dicyd})](\text{PF}_6)_2$ showing the oxidation of $\text{Ru}[\text{II},\text{II}]$ complex to $\text{Ru}[\text{III},\text{II}]$ under increasing anodic potential in DMF, (0.0 to 0.29 V vs. Ag/AgCl).

Figure 3.29 Spectroelectrochemical data for $[\text{Ru}(\text{tpz})(\text{bpy})_2(\mu\text{-dicyd})](\text{PF}_6)_2$ showing the oxidation of the Ru[II,III] complex to Ru[III,III] under increasing anodic potential in DMF, (0.55 to 0.78 V vs. Ag/AgCl).

Figure 3.30 Spectroelectrochemical data for $[Ru(tp)(bpz)_2(\mu\text{-dicyd})](PF_6)_2$ showing the oxidation of the Ru[II,II] complex to Ru[III,II] under increasing anodic potential in DMF, (0 .0 to 0.46 V vs. Ag/AgCl).

Figure 3.31 Spectroelectrochemical data for $[\{\text{Ru}(\text{tp})(\text{bpz})\}_2(\mu\text{-dicyd})](\text{PF}_6)_2$ showing the oxidation of the $\text{Ru}[\text{III},\text{II}]$ complex to $\text{Ru}[\text{III},\text{III}]$ under increasing anodic potential in DMF, (0.55 to 0.78 V vs. Ag/AgCl).

3.5 [$\{Ru(L)(L')\}_2(\mu\text{-adpc})\](PF_6)_2$ Complexes

3.5.1 Synthesis

The dinuclear complexes [$\{Ru(L)(L')\}_2(\mu\text{-adpc})\](PF₆)₂ where (L= bpy or bpz L'= ttp or tpz) were synthesized by the metathesis reaction of [Ru(L)(L')Cl]⁺ with the thallium salts of adpc²⁻ in refluxing DMF.$

The crude products [$\{Ru(tpp)(bpy)\}_2(\mu\text{-adpc})\](PF₆)₂ and [$\{Ru(tpz)(bpy)\}_2(\mu\text{-adpc})\](PF₆)₂ were purified by column chromatography over alumina grade (V), whereas [$\{Ru(tpp)(bpz)\}_2(\mu\text{-adpc})\](PF₆)₂ was purified over neutral alumina. The unreacted mononuclear complex and adpc²⁻ ligand were eluted with acetonitrile/toluene (3:1) whereas the products were eluted using (4:1) acetonitrile/methanol.$$$

3.5.2 X-Ray Crystallography

Deep red-brown plates of the dinuclear Ru(II) complex [$\{Ru(tpp)(bpy)\}_2(\mu\text{-adpc})\](PF₆)₂·6DMF suitable for crystallography were grown by diffusion of ether into a solution of the complex in DMF. Crystallographic data, and bond lengths and angles are reported in Table 3.11 to Table 3.12. ORTEP drawings of the complex are shown in Figure 3.32 to Figure 3.33. The Ru(II) ion occupies a pseudo-octahedral coordination sphere of nitrogen donor atoms where the cyanamide group of the adpc²⁻ bridging ligand is *trans* to a pyridine moiety of the 2,2'-bipyridine ligand. The adpc²⁻ ligand is approximately planar with the cyanamide groups in an *anti*-conformation relative to each$

other with the azo group adopting the more thermodynamically stable *trans* conformation. This conformation of the bridging ligand is essentially identical to that obtained in an earlier study for $[\{\text{Ru}(\text{terpy})(\text{bpy})\}_2(\mu\text{-adpc})][\text{PF}_6]^{36}$ and, indeed, the planar geometry of adpc^{2-} is a common feature of all aromatic cyanamide ligands.^{30,19} The cyanamide group is approximately linear ($172.0(7)^\circ$) as is the coordination of its terminal nitrogen to Ru(II) ($174.3(5)^\circ$). In contrast, the crystal structure of $[\{\text{Ru}(\text{terpy})(\text{bpy})\}_2(\mu\text{-adpc})][\text{PF}_6]$ shows that the coordination of the cyanamide group to Ru(II) was significantly bent with an angle of $164.4(2)^\circ$.³⁸ This difference in the Ru-cyanamide bond angle may indicate that crystal packing forces are sufficient to overcome the weak π -bonding between Ru(II) and the cyanamide group which would be optimized by a linear coordination mode. Furthermore, whereas the complex cation in the solid state possesses an inversion center, it seems likely that the complex in solution will be able to access a range of possible conformations of lower symmetry and this will have relevance to the spectroscopic analysis.

Figure 3.33 Unit cell for the $[\{\text{Ru}(\text{tpb})(\text{bpy})\}_2(\mu\text{-adpc})][\text{PF}_6] \cdot 6\text{DMF}$.

Table 3.11 Crystal Data for [$\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-adpc})\](\text{PF}_6)_2 \cdot 6(\text{DMF})$.

Formula	$\text{C}_{96}\text{H}_{100}\text{F}_{12}\text{N}_{22}\text{O}_6\text{P}_2\text{Ru}_2$
FW	2150.06 g/mol.
crystal system	triclinic
space group	P-1
unit cell dimensions	a, 13.1504(18); b, 13.4147(18); c, 14.3338(18) Å
α, β, γ /degrees	76.176(3), 81.3525(3), 79.954(3)°
volume	2401.9(6) Å ³
Z	1
calculated density	1.486 g/cm ³
crystal dimensions	0.20 x 0.10 x 0.02 mm
θ range	1.58 to 28.96°
limiting indices	$16 \leq h \leq 16, -17 \leq k \leq 17, 0 \leq l \leq 15$
reflections collected	8477
unique reflections	7004
absorption correction	semi-empirical from equivalences
transmission range	1.000000 to 0.757626
R1, wR2 [$I > 2\sigma(I)$] ^a	R1 = 0.0619, wR2 = 0.1325
goodness-of-fit on F ²	1.034

$$^a R1 = \sum \|F_o| - |F_c|\| / \sum |F_o|, wR2 = \left(\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2 \right)^{1/2}$$

Table 3.12 Selected Crystal Structure Data for $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-adpc})](\text{PF}_6)_2 \cdot 6\text{N,N-dimethylformamide}$.

Bond Lengths ^a / Angstroms			
Ru-N(1)	2.074(5)	N(6)-C(33)	1.162(7)
Ru-N(2)	1.971(5)	N(7)-C(33)	1.299(8)
Ru-N(3)	2.081(5)	N(7)-C(34)	1.407(8)
Ru-N(4)	2.073(5)	N(8)-C(37)	1.454(9)
Ru-N(5)	2.040(5)	N(8)-N(8A)	1.234(11)
Ru-N(6)	2.049(5)		
Bond Angles ^a / deg.			
N(1)-Ru-N(2)	79.9(2)	N(4)-Ru-N(5)	78.7(2)
N(1)-Ru-N(5)	88.4(2)	N(6)-C(33)-N(7)	172.0(7)
N(3)-Ru-N(2)	79.02(2)	C(33)-N(6)-Ru	174.3(5)
N(4)-Ru-N(3)	104.55(19)	C(33)-N(7)-C(34)	120.5(6)
N(5)-Ru-N(2)	99.2(2)	N(8A)-N(8)-C(37)	112.7(9)

^a estimated standard deviations are in parentheses.

3.5.3 IR and ^1H NMR Spectroscopy

The infrared spectrum of $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-adpc})](\text{PF}_6)_2$ complex as a representative example is shown in Figure 3.34. The broad absorption band at 2172 cm^{-1} was assigned to the anionic cyanamide $\nu(\text{NCN})$ stretching frequency. This band shifted to lower energy when strong σ -donor pyridine moieties were replaced by weak σ -donor pyrazine moieties (Table 3.13).

Figure 3.34 Infrared spectrum of $[\{\text{Ru}(\text{tp})(\text{bpy})\}_2(\mu\text{-adpc})](\text{PF}_6)_2$.

Table 3.13 Cyanamide Stretching Energies, $\nu(\text{NCN})$ (cm^{-1}), for the $[\{(\text{Ru}(\text{L})(\text{L}'))_2(\mu\text{-adpc})\}(\text{PF}_6)_2]$ Complexes.

Complex ($\text{L}=\mu\text{-adpc}$)	$\nu(\text{NCN})$ (cm^{-1})
$\text{Ti}_2(\text{adpc})$	2156
$[\{(\text{Ru}(\text{ttp})(\text{bpy}))_2\text{L}\}(\text{PF}_6)_2]$	2172
$[\{(\text{Ru}(\text{ttp})(\text{bpz}))_2\text{L}\}(\text{PF}_6)_2]$	2159
$[\{(\text{Ru}(\text{tpz})(\text{bpy}))_2\text{L}\}(\text{PF}_6)_2]$	2163

Figure 6.9 to Figure 6.11 (see appendix) show the ^1H NMR spectra of the $[\{(\text{Ru}(\text{L})(\text{L}'))_2(\mu\text{-adpc})\}(\text{PF}_6)_2]$ dinuclear complexes and the data are summarized in Table 3.14. The six methyl protons for L occurred at 2.45 ppm, the phenyl protons of L and L' proton occurred between 7.0 and 10.2 ppm and showed the usual splitting pattern for the dinuclear $[\{(\text{Ru}(\text{L})(\text{L}'))_2(\mu\text{-adpc})\}(\text{PF}_6)_2]$ complex. The two doublets around 6.00 and 7.10 ppm were assigned to the two unique proton resonances of the bridging ligand..

Table 3.14 A Summary of the ^1H NMR Data for the $[\{(\text{Ru}(\text{L})(\text{L}'))_2(\mu\text{-adpc})\}(\text{PF}_6)_2]$ Complexes (see appendix Figure 6.9, Figure 6.10 and Figure 6.11).

Complex	Ligand Chemical Shifts
$[\{(\text{Ru}(\text{ttp})(\text{bpy}))_2(\mu\text{-adpc})\}(\text{PF}_6)_2]$	methyl protons at 2.45(6H, s); phenyl protons for adpc ²⁻ bridging ligand at 6.03 (4H, d) and 7.19 (4H, d), ttp and bpy protons at 9.66 (2H, d); 9.25 (4H, s); 9.02 (4H, d); 8.96 (2H, d); 8.69 (2H, d); 8.40 (2H, t); 8.26 (4H, d); 8.11 (6H, t); 7.85 (2H, t); 7.69 (4H, m); 7.55 (H, d); 7.49 (H, d); 7.46 (H, d); 7.15 (2H, t)
$[\{(\text{Ru}(\text{tpz})(\text{bpy}))_2(\mu\text{-adpc})\}(\text{PF}_6)_2]$	methyl protons at 2.45(6H, s); phenyl protons for adpc bridging ligand at 6.08 (4H, d) and 7.24 (4H, d), tpz and bpy protons at 10.12 (4H, s), 9.57 (2H, d), 9.45 (4H, s), 9.00 (2H, d), 8.73 (2H, d), 8.63 (4H, d), 8.46 (2H, t), 8.27 (4H, d), 8.14 (2H, t), 7.94 (6H, m), 7.50 (6H, m), 7.18 (2H, t)
$[\{(\text{Ru}(\text{ttp})(\text{bpz}))_2(\mu\text{-adpc})\}(\text{PF}_6)_2]$	methyl protons at 2.50 (6H, s); phenyl protons for adpc bridging ligand at 7.22 (4H, d) and 6.06 (4H, d), ttp and bpz protons at 10.24 (2H, s), 9.97 (2H, s), 9.66 (2H, d), 9.31 (4H, s), 9.19 (2H, d), 9.06 (4H, d), 8.28 (6H, m), 8.17 (4H, t), 7.94 (2H, d), 7.80 (4H, d), 7.52 (4H, d), 7.46 (4H, t)

Data in ppm vs. TMS reference, at 0.00 ppm, s, singlet; d, doublet; t, triplet; m, multiplet

3.5.4 Cyclic Voltammetry

The voltammogram of the $[\{(\text{Ru}(\text{L})(\text{L}'))_2(\mu\text{-adpc})\}(\text{PF}_6)_2]$ complexes in acetonitrile are shown in Figure 3.36. The Ru(III/II) couples of the $[\{(\text{Ru}(\text{L})(\text{L}'))_2(\mu\text{-adpc})\}(\text{PF}_6)_2]$ are generally quasi-reversible with anodic to cathodic waves separated by approximately 80 mV and largely invariant with scan rate. The current of the three ligand reduction couples were twice that of the Ru(III/II) couples for the same reason mentioned in section

3.4.3. Poor reversibility of the most positive Ru(III/II) couple corresponding to Ru[III,III]/Ru[III,II] was noted when the pyridine moieties were replaced with pyrazine moieties, making spectroelectrochemical studies of this couple problematic. From the difference in Ru(III/II) couples of the dinuclear complex, the comproportionation constant (K_c) for the formation of the Ru[III,II] mixed-valence complex can be calculated as summarized in Table 3.15.

As a representative example, Figure 3.35 shows the voltammogram of the $[\{Ru(tp)(bpy)\}_2(\mu-adpc)](PF_6)_2$ complex in acetonitrile. At positive potentials, two quasi-reversible Ru(III/II) redox couples are observed at 0.78 V and 1.52 V vs. NHE. From the difference between Ru(III/II) couples ($\Delta E = 0.76$ V), the comproportionation constant (K_c) for the formation of the Ru[III,II] mixed-valence complex was determined to be 3.2×10^{12} . At negative potentials, irreversible waves are observed. The first wave at -1.19 V vs NHE is reversible if the scan is limited to -1.3 volts. It is suggested that the first wave corresponds to the reduction of *ttp* while the other waves are likely azo and bipyridine centered reduction couples. Reduction of the azo group occurs in this potential range and has been shown to be an irreversible process.³⁸

The second reduction couple at -1.30 V vs. NHE is likely for *bpy* ligand

Figure 3.35 The cyclic voltammogram for $[\{\text{Ru}(\text{tpb})(\text{bpy})\}_2(\mu\text{-adpc})](\text{PF}_6)_2$ in acetonitrile, data reported in V vs. NHE with scan rate of 0.1 V/s; 0.1 M TBAH at 25 °C.

The effect of the inner-sphere perturbation on metal-metal coupling of the $[\{\text{Ru}(\text{L})(\text{L}')\}_2(\mu\text{-adpc})](\text{PF}_6)_2$ was investigated by replacing the strong σ -donor pyridine moieties with weak σ -donor pyrazine moieties. From the data in Table 3.15 and Figure 3.36, the two redox waves of Ru(III/II) couples for $[\{\text{Ru}(\text{tpz})(\text{bpy})\}_2(\mu\text{-adpc})](\text{PF}_6)_2$ and $[\{\text{Ru}(\text{tpb})(\text{bpz})\}_2(\mu\text{-adpc})](\text{PF}_6)_2$ have shifted to more positive potentials compared to the analogous couples of $[\{\text{Ru}(\text{tpb})(\text{bpy})\}_2(\mu\text{-adpc})](\text{PF}_6)_2$.

Figure 3.36 Cyclic voltammogram of dinuclear complexes with adpc^{2-} as the bridging ligand in acetonitrile, data reported in V vs. NHE and scan rate of 0.1 V/s; 0.1 M TBAH at 25 °C. a) $[\{\text{Ru}(\text{tp})(\text{bpy})\}_2(\mu\text{-adpc})](\text{PF}_6)_2$, b) $[\{\text{Ru}(\text{tpz})(\text{bpy})\}_2(\mu\text{-adpc})](\text{PF}_6)_2$, c) $[\{\text{Ru}(\text{tp})(\text{bpz})\}_2(\mu\text{-adpc})](\text{PF}_6)_2$.

Table 3.15 Redox Couples and Comproportionation Constants for the $[\{\text{Ru}(\text{L})(\text{L}')\}_2(\mu\text{-adpc})](\text{PF}_6)_2$ Complexes.^a

Complex	Ru_1^{b}	Ru_2^{c}	ΔE^{d}	L_1^{e}	L_2^{e}	K_c^{f}
$[\{\text{Ru}(\text{ttp})(\text{bpy})_2\text{L}\}(\text{PF}_6)_2]$	0.78	1.52	0.74	-1.16	-1.40	3.2×10^{12}
$[\{\text{Ru}(\text{ttp})(\text{bpz})_2\text{L}\}(\text{PF}_6)_2]$	0.84	1.81	0.97	-0.80	-1.30	2.5×10^{16}
$[\{\text{Ru}(\text{tpz})(\text{bpy})_2\text{L}\}(\text{PF}_6)_2]$	0.86	1.80	0.94	-0.68	-1.11	7.8×10^{15}

$\text{L} = \text{adpc}^{2-}$

^a versus NHE, platinum working electrode, 0.1 M TBAH electrolyte, at 25 °C.

^b $\text{Ru}_1 = \text{Ru}[\text{III}, \text{II}]/\text{Ru}[\text{II}, \text{II}]$

^c $\text{Ru}_2 = \text{Ru}[\text{III}, \text{III}]/\text{Ru}[\text{III}, \text{II}]$

^d $\Delta E = \text{Ru}_2 - \text{Ru}_1$

^e ligand reduction couples

^f the comproportionation constant $K_c = 10^{16.91\Delta E}$

To study the effect of outer-sphere perturbation, cyclic voltammetry data for $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-adpc})]^{2+}$ was obtained in solvents with varying donor number (Table 3.16). Reduced reversibility of the most positive Ru(III/II) couple corresponding to $\text{Ru}[\text{III,III}]/\text{Ru}[\text{III,II}]$ was noted in some solvents making spectroelectrochemical studies of this couple problematic. From the Table 3.16, the two waves for Ru(III/II) couples, particularly the second wave, $\text{Ru}[\text{III,III}]/\text{Ru}[\text{III,II}]$, moved to more negative potential as the donor number increased. The comproportionation constants (K_c) also decreased as the donor number increased.

Table 3.16 Electrochemical Data for $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-adpc})][\text{PF}_6]_2$ in different Solvents.^a

Solvent	Ru_2^{b}	Ru_1^{c}	ΔE^{d}	K_c^{e}	L_1^{f}	L_2^{f}
NM	1.65	0.87	0.78	1.5×10^{13}	-	-
AC	1.52	0.78	0.74	3.2×10^{12}	-1.18	-1.41
PC	1.50	0.77	0.73	2.2×10^{12}	-1.19	-1.46
DMF	1.27	0.58	0.69	4.6×10^{11}	-1.34	-1.64
DMSO		0.51			-1.42	-1.72

^a versus NHE, platinum working electrode, 0.1 M TBAH electrolyte, at 25 °C.

^b $\text{Ru}_2 = \text{Ru}[\text{III},\text{III}]/\text{Ru}[\text{III},\text{II}]$

^c $\text{Ru}_1 = \text{Ru}[\text{III},\text{II}]/\text{Ru}[\text{II},\text{II}]$

^d $\Delta E = \text{Ru}_2 - \text{Ru}_1$

^e the comproportionation constant $K_c = 10^{16.91\Delta E}$

^f ligand reduction couples L_1 and L_2 of terpyridine and 2,2'-bipyridine ligands, respectively

3.5.5 Infrared Spectroelectrochemistry

Infrared spectroelectrochemistry in the region of the $\nu(\text{NCN})$ band for $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-adpc})](\text{PF}_6)_2$ was done in DMF to determine whether the mixed-valence complexes represent delocalized or localized systems. The mixed-valence complex showed poor reversibility in other solvents such as DMSO.

The $\nu(\text{NCN})$ for the $\text{Ru}[\text{II},\text{II}]$ dimer occurred at 2158 cm^{-1} . This band started to lose its intensity (Figure 3.37) when the complex was oxidized to the mixed-valence state. Unfortunately, the $\text{Ru}[\text{III},\text{III}]$ complex $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-adpc})]^{4+}$ is unstable. It is important to note that the observation of only one $\nu(\text{NCN})$ band in the IR spectrum of the mixed-valence complexes $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-adpc})]^{3+}$ is strong evidence that these complexes are delocalized on the infrared timescale (10^{13} s^{-1}).

Figure 3.37 Infrared spectroelectrochemistry showing the oxidation of the Ru[II,II], $[\{\text{Ru}(\text{tp})(\text{bpy})\}_2(\mu\text{-adpc})(\text{PF}_6)_2]$ in DMSO to the Ru[III,II] complex, (0.5 to 1.0 V vs. Ag/AgCl).

3.5.6 Electronic Absorption and Spectroelectrochemistry

The electronic absorption data of the thallium salt adpc^{2-} in DMF showed a strong absorption band around the 500 nm, which was assigned to intraligand charge transfer (from cyanamide to the azo group). This band overlapped with the MLCT of $[\{\text{Ru}(\text{L})(\text{L}')\}_2(\mu\text{-adpc})](\text{PF}_6)_2$ complexes.

As a representative example, Figure 3.38 shows the absorption spectrum of the oxidation of $[\{(\text{Ru}(\text{ttp})(\text{bpy}))_2(\mu\text{-adpc})\}](\text{PF}_6)_2$ to the $\text{Ru}[\text{III},\text{II}]$ in DMF. The absorption spectrum of the $[\text{II},\text{II}]$ complex shows MLCT bands at 494 nm that are typical of $[\text{Ru}(\text{II})(\text{ttp})(\text{bpy})]$ chromophores. Upon oxidation to $\text{Ru}[\text{III},\text{II}]$, three new bands appeared at $\lambda_{\text{max}} = 659$ nm, 827 nm and 2012 nm. The band at 827 nm was assigned to the $\text{Ru}(\text{III})$ -cyanamide LMCT transition as it appears to gain absorptivity with the formation of $\text{Ru}[\text{III},\text{III}]$. The intense absorption band at 2010 nm, which was absent in the $\text{Ru}[\text{II},\text{II}]$ and $\text{Ru}[\text{III},\text{III}]$ complexes, was assigned to the MMCT and the band at 659 nm was assigned to the $\text{Ru}(\text{III})$ -azo chromophore.

Figure 3.38 Spectroelectrochemical data for $[\{\text{Ru}(\text{tp})(\text{bpy})\}_2(\mu\text{-adpc})]^{2+}$ showing the oxidation of the Ru[II,II] complex to the mixed-valence Ru[III,II] complex under increasing the anodic potential in DMF (0.51 to 0.55 V vs. Ag/AgCl). Inset shows the MMCT band.

The inner-sphere perturbation of the coupling of the dinuclear complex was investigated by replacing the strong σ -donor pyridine moieties with weak σ -donor pyrazine moieties. The near-IR spectroelectrochemistry data for $[\{\text{Ru}(\text{tpz})(\text{bpy})\}_2(\mu\text{-adpc})](\text{PF}_6)_2$ and $[\{\text{Ru}(\text{ttp})(\text{bpz})\}_2(\mu\text{-adpc})](\text{PF}_6)_2$ complexes in DMF are shown in Figure 3.39 and Figure 3.40. The MMCT band shifted to higher energy by replacing the strong σ -donor pyridine moieties with weak σ -donor pyrazine moieties and the splitting in the broad MMCT became clearer.

The spectroelectrochemical studies of the oxidation of $[\{\text{Ru}(\text{terpy})(\text{bpy})_2(\mu\text{-adpc})\}]^{2+}$ and that of $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-adpc})]^{2+}$ are not significantly different;⁵⁸ both show a strong MMCT band at approximately 1900 nm. However, the solubility of the latter complex is considerably greater and this has allowed for a solvent dependence study of its MMCT band. In addition to spectroelectrochemical oxidation, the $\text{Ru}[\text{III},\text{II}]$ complex was generated by oxidation with $[\text{Fe}(\text{bpy})_3](\text{PF}_6)_3$.⁵⁶ Table 3.17 summarizes the energy of the MMCT generated by the electrochemical and chemical methods for the $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-adpc})]^{2+}$ (Figure 3.41) and chemical method for $[\{\text{Ru}(\text{tpz})(\text{bpy})\}_2(\mu\text{-adpc})]^{2+}$ (Figure 3.42). The variation of MMCT band oscillator strength that is seen in the adpc^{2-} family should not be regarded as significant because of the instability of the mixed-valence complex in solvents other than DMF.

Figure 3.39 Spectroelectrochemical data for $[\text{Ru}(\text{tpz})(\text{bpy})_2(\mu\text{-adpc})]^{2+}$ showing the oxidation of the Ru[II,II] complex to the mixed-valence Ru[III,II] complex under increasing the anodic potential in DMF (0.7 to 1.2 V vs. Ag/AgCl). Inset shows the MMCT band.

Figure 3.40 Spectroelectrochemical data for $[\{\text{Ru}(\text{tp})(\text{bpy})\}_2(\mu\text{-adpc})]^{2+}$ showing the oxidation of the Ru[II,II] complex to the mixed-valence Ru[III,II] complex under increasing the anodic potential in DMF (0.7 to 1.22 V vs. Ag/AgCl). Inset shows the MMCT band.

Figure 3.41 The oxidation of the $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-adpc})]^{2+}$ complex to mixed-valence $\text{Ru}[\text{III},\text{II}]$ complex by $[\text{Fe}(\text{bpy})_3]^{3+}$ in DMF. Inset shows the MMCT band.

Figure 3.42 The oxidation of the $[\{\text{Ru}(\text{tpz})(\text{bpy})\}_2(\mu\text{-adpc})]^{2+}$ complex to the mixed-valence $\text{Ru}[\text{III,II}]$ complex by $[\text{Fe}(\text{bpy})_3]^{3+}$ in DMF. Inset shows the MMCT band.

Table 3.17 Solvent Dependence of the MMCT Band of $[\text{Ru}\{(\text{ttp})(\text{bpy})\}_2(\mu\text{-adpc})]^{3+}$ and $[\text{Ru}\{(\text{tpz})(\text{bpy})\}_2(\mu\text{-adpc})]^{3+}$.

solvent	$I/D_{\text{op}}-1d/s^a$	Donor number ³²	E_{IT}^b (cm ⁻¹) by oxidant	E_{IT}^c (cm ⁻¹) by electrochem.	MMCT ^d (cm ⁻¹) by oxidant
DMSO	0.4372	29.8	4970	4975	5568
DMF	0.4637	26.6	5107	5181	5701
AC	0.4934	17	5470		5852
PC	0.4811	15.1	5252	5254	
AN	0.5289	14.1	5530	5564	5970
NB	0.3851	4.4	5144		5834
NM	0.4978	2.7	5461	5373	5899
DCE	0.3809		5420		

^a (D_s) the static dielectric constant, (D_{op}) and the optical dielectric constant,^b $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-adpc})]^{3+}$ chemical oxidation using $[\text{Fe}(\text{bpy})_3][\text{PF}_6]_3$ ^c $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-adpc})]^{3+}$ electrochemical oxidation.^d $[\{\text{Ru}(\text{tpz})(\text{bpy})\}_2(\mu\text{-adpc})]^{3+}$ chemical oxidation using $[\text{Fe}(\text{bpy})_3][\text{PF}_6]_3$

Chapter 4 Discussion

4.1 Mononuclear Complexes: Conceptual Framework

Much of the behaviour of Ru(II)-L and Ru(III)-L mononuclear complexes is dominated by the fact that Ru(II) exhibits π -base properties whereas Ru(III) exhibits π -acid properties. The energy of the Ru(II) (donor) and Ru(III) (acceptor) orbitals and the ability of these orbitals to interact with ligand-based orbitals (such as those of pcyd^- , dicyd^{2-} , or adpc^{2-}) can be significantly affected by the nature of the auxiliary ligands which make up the coordination sphere. Strong σ -donor ligands, for example, serve to destabilize Ru $d\pi$ -orbitals, whereas weak σ -donors and π -acceptors stabilize the metal orbitals. The change in $d\pi$ -orbital energy can be measured experimentally using cyclic voltammetry to obtain the potential of the Ru(III,II) couple, which shifts to more positive potentials as the metal orbitals are stabilized. This has been demonstrated, for example, by the replacement of σ -donating ammine ligands with pyridine-type ligands by Crutchley et al.⁵⁸ Comparative electrochemistry of $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$ and $[\text{Ru}(\text{bpy})(\text{tpy})\text{L}]^{2+}$, where tpy = terpyridine and L is a substituted phenylcyanamide ligand, showed a positive shift of 0.8 V in the Ru(III,II) couple of the latter complex.⁵⁸ The same effect is noted when pyridine ligands are replaced by even weaker σ -donor pyrazine ligands. Crutchley and Lever⁵⁷ compared the Ru(III/II) couple of $[\text{Ru}(\text{bpz})_3]^{2+}$ and $[\text{Ru}(\text{bpy})_3]^{2+}$ and observed that the metal and ligand orbitals in the bipyrazine derivative were stabilized by approximately 0.5 V.

Electronic spectroscopy can also be used to understand the relative energies of metal and ligand orbitals. Ru(II) is electron rich in πd (t_{2g} in octahedral symmetry) electron density, which may be delocalized into a ligand (L) that has a low-lying π^* such as an N-aromatic heterocyclic auxiliary ligand (a moderately strong acid) to produce a metal to ligand charge transfer (MLCT) in the visible spectral region (Figure 4.1). The energy of this transition depends on the relative energies of both Ru(II) and L orbitals. For example, in the comparative study of $[\text{Ru}(\text{bpz})_3]^{2+}$ and $[\text{Ru}(\text{bpy})_3]^{2+}$ by Crutchley and Lever,⁵⁷ the MLCT bands of the two systems were of similar energy, despite the apparent 0.5 V stabilization of the ruthenium $d\pi$ orbital in the bipyrazine case as evidenced by its electrochemistry. This meant that the π^* orbital of bipyrazine was also stabilized by approximately 0.5 V relative to that of bipyridine, another strong indication that bipyrazine is a weaker σ -donor than bipyridine.⁵⁷

Figure 4.1 The πd -L- π^* interaction.

When Ru(III) binds to an electron rich (a moderately strong base) ligand such as phenylcyanamide, a ligand to metal charge transfer band (LMCT) at low energy can appear in the visible region. Once again, the energy of this band depends on the relative energy of the corresponding orbitals. The energy of the LMCT band is important as it can be used to calculate the ligand-metal coupling element, H_{LM} , which is necessary in

order to predict the metal-metal coupling through the hole-transfer superexchange mechanism in related mixed-valence complexes.

4.1.1 Cyclic Voltammetry and MLCT Transitions of Ru(II) Mononuclear Complexes

The results of cyclic voltammetry experiments on Ru(II) pyrazine phenylcyanamide mononuclear complexes are presented in Figure 3.14. $E_{1/2}$ values were calculated from the average of the cathodic and anodic potentials. The ratio of the value of the cathodic peak current relative to the anodic peak current (i_{pa}/i_{pc}) demonstrates the stability of the complex on the CV time scale. A value of $i_{pa}/i_{pc} \approx 1$ demonstrates that the complex in this oxidation state is stable at least on the CV time scale. These complexes undergo one-electron reversible oxidation except for $[\text{Ru}(\text{tpz})(\text{bpz})(2,3,4,5\text{-Cl}_4\text{pcyd})]^+$ which has only a partially reversible Ru(III/II) reduction couple in acetonitrile (Figure 3.14). By comparing the electrochemistry results of the $[\text{Ru}(\text{tpz})(\text{bpz})(2,3,4,5\text{-Cl}_4\text{pcyd})]^+$ complexes, where L is ttp or tpz and L' is bpy or bpz, with $[\text{Ru}(\text{NH}_3)_5(2,3,4,5\text{-Cl}_4\text{pcyd})]^+$,³⁹ it can be seen that $[\text{Ru}(\text{tpz})(\text{bpz})(2,3,4,5\text{-Cl}_4\text{pcyd})]^+$ is approximately 1.24 V harder to oxidize relative to the pentaammine analogue. Furthermore, both the metal and ligand oxidation couples in the pyrazine-based mononuclear complexes were shifted positively relative to corresponding couples of $[\text{Ru}(\text{ttp})(\text{bpy})(2,3,4,5\text{-Cl}_4\text{pcyd})]^+$ and the difference between the $d\pi$ and π^* orbitals remained constant as pyridine moieties were replaced by pyrazine moieties. These results all concur with previous studies where the loss of strong σ -donating ligands leads to the stabilization of the ruthenium $d\pi$ -orbitals.

As described in section 4.1, the metal-to-ligand charge transfer (MLCT) band in a Ru(II) mononuclear complex can provide information about the relative energies of the system's metal- and ligand-based orbitals. Figure 4.2 shows the quantitative absorption spectra of the mononuclear chloride complexes in acetonitrile. Clearly, the MLCT band energy is unaffected by the substitution of pyrazine ligands for pyridine ligands (Table 3.2), as was seen previously in the comparison of $[\text{Ru}(\text{bpz})_3]^{2+}$ and $[\text{Ru}(\text{bpy})_3]^{2+}$. Figure 4.3 shows a simplified MO scheme demonstrating that the MLCT band can remain of the same energy if the metal and ligand orbitals are stabilized (or destabilized) by the same amount.⁵⁷ In this MO scheme, only one MLCT band is indicated. In the mononuclear complexes of this study, however, two main MLCT chromophores are available: $d\pi \rightarrow (\text{bpy or bpz})\pi^*$ and $d\pi \rightarrow (\text{tpz or ttp})\pi^*$. For example, the mononuclear complex $[\text{Ru}(\text{tpz})(\text{bpy})\text{Cl}]^+$ clearly has two MLCT bands, one at high energy (497 nm) and the other at low energy at (548 nm), (Figure 4.2). The high energy band at 495 nm was assigned to $d\pi \rightarrow (\text{bpy})\pi^*$, whereas the low energy band at 548 nm was assigned for $d\pi \rightarrow (\text{tpz})\pi^*$. In the other cases, the two MLCT bands merge to form a single broadened band.

Figure 4.2 Quantitative UV-visible spectra for the mononuclear complexes in acetonitrile 1) $[\text{Ru}(\text{tpp})(\text{bpz})\text{Cl}]^+$, 2) $[\text{Ru}(\text{tpz})(\text{bpz})\text{Cl}]^+$, 3) $[\text{Ru}(\text{tpp})(\text{bpy})\text{Cl}]^+$, 4) $[\text{Ru}(\text{tpz})(\text{bpy})\text{Cl}]^+$.

Figure 4.3 Molecular orbital scheme showing the metal-to-ligand charge transfer transitions in an ideal tris(diimine)ruthenium case, assuming octahedral microsymmetry.

The MLCT bands of the phenylcyanamide mononuclear complexes (Figure 4.4, Table 3.4) are very similar to the starting material chloride complexes, except for a slight shift to higher energy. The blue shift in the energy of the MLCT indicates that $pcyd^-$ is a somewhat weaker σ -donor compared to the Cl^- ligand.

Figure 4.4 Quantitative UV-visible spectra for the mononuclear complexes in acetonitrile 1) $[\text{Ru}(\text{tpz})(\text{bpz})\text{L}]^+$, 2) $[\text{Ru}(\text{ttp})(\text{bpz})\text{L}]^+$, 3) $[\text{Ru}(\text{ttp})(\text{bpy})\text{L}]^+$, 4) $[\text{Ru}(\text{tpz})(\text{bpy})\text{L}]^+$, $\text{L} = 2,3,4,5\text{-Cl}_4\text{pcyd}^-$.

4.1.2 LMCT Transitions of Ru(III) Mononuclear Complexes

The electronic properties of the Ru(III)-cyanamide LMCT chromophore have also been probed by varying the nature of auxiliary ligand. Spectroelectrochemistry of the phenylcyanamide complexes was performed in acetonitrile in order to generate the LMCT band which can be used to measure the ligand-metal coupling element H_{LM} from equation 5 which is essential for estimating the coupling in the analogous dinuclear complexes. These mononuclear complexes showed varying degrees of stability upon oxidation to Ru(III), where $[\text{Ru}(\text{ttp})(\text{bpy})(2,3,4,5\text{-Cl}_4\text{pcyd})]^+$ and $[\text{Ru}(\text{tpz})(\text{bpy})(2,3,4,5\text{-Cl}_4\text{pcyd})]^+$ have good reversibility ($> 90\%$), the $[\text{Ru}(\text{tpz})(\text{bpz})(2,3,4,5\text{-Cl}_4\text{pcyd})]^+$ and $[\text{Ru}(\text{ttp})(\text{bpz})(2,3,4,5\text{-Cl}_4\text{pcyd})]^+$ lose the isosbestic point easily, with reversibility of less than 80%. The poor reversibility of these complexes makes the estimation of the real value of the oscillator strength impossible. In addition, the greater covalency in the metal-ligand bond creates a large error in the estimation of the transition dipole moment (R). These two reasons make the calculation of H_{LM} from the CNS model using equation 5 of questionable value.

The oxidation of $[\text{Ru}(\text{L})(\text{L}')(2,3,4,5\text{-Cl}_4\text{pcyd})]^+$ results in the disappearance of the MLCT band centered at 500 nm and the appearance of new bands at 1053 nm and at 430 nm. (Figure 3.15 to Figure 3.18 and Table 3.6). These two bands are assigned to ligand-to-metal charge transfer (LMCT) $\pi \rightarrow d\pi^*$ transitions associated with Ru(III) cyanamide chromophore. These bands are shifted to lower energy upon replacing the strong σ -donor pyridine moieties with weak σ -donor pyrazine moieties (see Table 3.6). The shift to lower energy is explained by the increase of the stability of Ru(III) orbitals relative to

non-bonding orbitals of the phenylcyanamide ligand and thus decreasing the LMCT band energy (see Figure 4.5).

Figure 4.5 qualitative molecular orbital diagram for the LMCT transition (shown by arrow) for phenylcyanamide mononuclear complexes (A) perturbing the metal with weak σ -donor ligand decreases the energy of LMCT band (B).

In earlier studies,²⁴ it was shown the phenylcyanamide $pcyd^-$ ligands are pseudo halides with two π -symmetry molecular orbitals π_{nb2} and π_{nb1} (Figure 4.6), resulting from the delocalization of the two pairs of nonbonding π -electrons on the nitrogen atoms of the cyanamide group as shown by extended Huckel calculation. π_{nb1} has significant antibonding character (it is therefore at higher energy than π_{nb2}) and has the correct symmetry to mix with the bonding π -orbitals of phenyl ring.

Figure 4.6 (a) Resonance forms of the phenylcyanamide anion ligand (b) Hückel π -symmetry orbitals (π_{nb1} is orthogonal to π_{nb2}) resulting from the delocalization of two non-bonding electron pairs.²⁴ The sizes of atomic orbitals approximate their contribution to the molecular orbital.

In order to interpret the LMCT transitions for the complexes of this study, a linear combination of two sets of π_{nb} molecular orbitals and Ru(III) orbitals must be considered. If the Ru(III) complex has C_{2v} microsymmetry, the interaction between the cyanamide π_{nb} orbitals and Ru(III) is suggested to be represented by Figure 4.7 which shows two LMCT transitions, an allowed $b_1 \rightarrow b_1^*$ transition and a formally forbidden $b_2 \rightarrow b_1^*$ transition.

The plot of E_{LMCT} of the $b_1 \rightarrow b_1^*$ transition versus ΔE , (L(0/-)-Ru(III/II)), (Figure 4.8, Table 4.1) for this family of complexes, as well as the $[Ru(NH_3)_5(L)]^{2+}$, and the $[Ru(terpy)(bpy)(L)]^+$ families, where L is the pcyd⁻ substituted derivatives, is nearly linear,⁵⁸ with a slope of 0.97 ($r^2 = 0.997$) and an intercept (which is made up of the outer- and inner-sphere reorganization energy) of 0.46 eV. While a linear relationship is anticipated for each family, it is unexpected, however, that these three families all fall on the same line, especially since their inner coordination spheres differ so dramatically.

The factor χ from equation 4 is made up of both inner-sphere (χ_i) and outer-sphere (χ_o) reorganization energies as shown in equation 24:

$$\chi = \chi_i + \chi_o \quad (35)$$

It may be possible that the difference between the inner-sphere and outer-sphere components of χ for the families are opposing and therefore can cancel.

Figure 4.7 Qualitative molecular orbital diagram for the LMCT transition (shown by arrow) in mononuclear phenylcyanamide complexes resulting from π interaction between phenylcyanamide and Ru(III).

Table 4.1 Electrochemical data and E_{LMCT} for $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$, $[\text{Ru}(\text{terpy})(\text{bpy})\text{L}]^+$ and $[\text{Ru}(\text{L}')(\text{L}'')(2,3,4,5\text{Cl}_4\text{pcyd})]^+$, L = substituted phenylcyanamide, L' = ttp or tpz and L'' = bpy or bpz

$[\text{Ru}(\text{NH}_3)_5(\text{L})]^{2+}$			$[\text{Ru}(\text{terpy})(\text{bpy})(\text{L})]^+$		$[\text{Ru}(\text{L}')(\text{L}'')(2,3,4,5\text{-Cl}_4\text{pcyd})]^+$		
L	$\Delta E^a(\text{v})$	E_{LMCT}	$\Delta E^a(\text{v})$	$E_{\text{LMCT}}(\text{eV})$	(L')(L'')	$\Delta E^a(\text{V})$	$E_{\text{LMCT}}(\text{eV})$
4-Mepcyd ⁻	1.12	1.60	-	-	(ttp)(bpy)	0.76	1.177
3-Clpcyd ⁻	1.35	1.74	-	-	(tpz)(bpy)	0.66	1.13
2,4-Cl ₂ pcyd ⁻	1.29	1.73	0.64	1.08	(ttp)(bpz)	0.68	1.128
2,4,5-Cl ₃ pcyd ⁻	1.34	1.79	0.69	1.16	(tpz)(bpz)	0.65	1.118
2,4,6-Cl ₄ pcyd ⁻	1.37	1.85	0.71	1.16			
2,3,4,5-Cl ₄ pcyd ⁻	1.40	1.83	0.72	1.17			
2,3,5,6-Cl ₄ pcyd ⁻	1.48	1.95	0.7500	1.2288			
Cl ₅ -pcyd ⁻	1.4400	1.9220	0.7600	1.1945

Figure 4.8 LMCT energy versus the energy gap between Ru(II/III) and pcyd(-/0) redox couples (ΔE) for phenylcyanamide mononuclear complexes $[\text{Ru}(\text{terpy})(\text{bpy})\text{L}]^+$ (■)⁵⁸ and $[\text{Ru}(\text{NH}_3)_5\text{L}]^+$ (●)³⁹ and $[\text{Ru}(\text{L}')(\text{L}'')2,3,4,5\text{-Cl}_4\text{pcyd}]^+$ (▲), L = 4-Mepcyd to Cl_5pcyd^- , L' = ttp or tpz, L'' = bpy or bpz.

1, L = 2,3,5,6- Cl_4pcyd	2, L = $\text{Cl}_5\text{-pcyd}$	3, L = 2,4,6- Cl_3pcyd
4, L = 2,3,4,5- Cl_4pcyd	5, L = 2,4,5- Cl_3pcyd	6, L = 3- Clpcyd
7, L = 2,4- Cl_2pcyd	8, L = 4-Mepcyd	9, L = 2,3,5,6- Cl_5pcyd
10, L = Cl_5pcyd	11, L' = ttp and L'' = bpy	12, L = 2,4,5- Cl_3pcyd
13, L = 2,4,6- Cl_3pcyd	14, L = 2,3,5,6- Cl_4pcyd	15, L' = ttp and L'' = bpz
16, L' = tpz and L'' = bpy	17, L', tpz and L'', bpz	18, L = 3- Clpcyd

4.2 Summary of Findings for Mononuclear Complexes

The electronic absorption and electrochemical results of the mononuclear complexes described above confirm several ideas. Firstly, the effect of the replacement of pyridine based ligands with pyrazine based ligands results in a stabilization of the metal $d\pi$ -orbitals as seen in the cyclic voltammetry results. This stabilization, however, does not result in a noticeable shift in the MLCT band energy for the Ru(II) complexes, due to the equivalent stabilization of the pyrazine ligand π^* -orbitals. Secondly, the LMCT band energy of the Ru(III)-pcyd mononuclear complexes was found to be affected by the nature of the auxiliary ligands, through the variation of the metal $d\pi$ -orbital energy. Unfortunately, it was not possible to calculate the ligand-metal coupling elements, H_{LM} , from the LMCT bands because of suspect oscillator strength values and difficulties in estimating R . In any case, these studies have provided a foundation for understanding the effect of inner-sphere perturbation of metal-metal coupling in the following mixed-valence dinuclear complexes.

4.3 Dinuclear complexes

The effect of inner-sphere and outer-sphere perturbation on metal-metal coupling was investigated by comparing two families of dinuclear complexes. Each family has three dinuclear complexes with either dicyd²⁻ or adpc²⁻ as the bridging ligand. The inner sphere of each system was perturbed in a similar fashion as that described for the mononuclear complexes (i.e. replacing pyridine with pyrazine). Outer-sphere perturbations were investigated by varying the donor number of the solvent and by

observing its effect on the coupling for these two families. In general, the degree of metal-metal coupling was investigated by IR spectroelectrochemistry, cyclic voltammetry and NIR-vis spectroelectrochemistry.

4.3.1 Proof of Class III Status

To determine whether these mixed-valence complexes are delocalized or localized systems, infrared spectroelectrochemistry was performed as its timescale (10^{-13} s) is faster than the timescale of solvent relaxation and gives an almost instantaneous view of the state of a fluxional molecule. Interpretation of the IR spectroelectrochemical results requires an understanding of the effect of oxidation state on the energy of the cyanamide group. An earlier study on dinuclear ruthenium polyamine complexes bridged by dicyd²⁻ ligands showed that a single $\nu(\text{NCN})$ band appeared for the delocalized state whereas two bands appeared for the valence-trapped state.¹⁴ The energy of the $\nu(\text{NCN})$ in the delocalized case was found to be the average of the two bands seen in a similar Class II system, but this energy was virtually unchanged relative to the energy of the Ru[III,III] $\nu(\text{NCN})$. This was ascribed to the polarizability of the cyanamide group.¹⁴ The IR spectra of the generation of the mixed-valence complex $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-dicyd})]^{3+}$ (Figure 3.24) and the further oxidation to the Ru[III,III] system (Figure 3.25) are reversible and thus any spectral change cannot be attributed to decomposition. In the mixed-valence spectrum, a single unbroadened $\nu(\text{NCN})$ at the same energy as the $\nu(\text{NCN})$ of the Ru[III,III] system is indicative of a delocalized state on the IR timescale. Similarly, the IR spectrum of the mixed-valence complex $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-adpc})]^{3+}$ shows only one sharp $\nu(\text{NCN})$ (Figure 3.47). These observations are strong evidence that

these two families of complexes should be classified as Class III on the infrared timescale (10^{13} s^{-1}).

4.3.2 MMCT Band Analysis

The MMCT band of $[\{\text{Ru}(\text{tp})(\text{bpy})\}_2(\mu\text{-adpc})]^{3+}$ in Figure 4.9 shows a band shape that is distinctly non-Gaussian with a pronounced high-energy tail and this has been mentioned as a characteristic of the MMCT band for a delocalized complex.⁵⁹ Meyer¹⁷ has recently pointed out, for borderline delocalized mixed-valence complexes, that the asymmetry of the MMCT band may be the result of underlying metal-centered transitions (IC, see text diagram page 19) due to the low symmetry of the metal ion. Other low energy metal-centered transitions have been predicted, which have been observed for osmium mixed-valence complexes but the evidence is not as clear for analogous ruthenium systems, because attempts to find evidence for the presence of these IC transitions in the NIR-IR spectra have been unsuccessful. When one considers the results of the IR spectroelectrochemical study (Figure 3.24, Figure 3.25, and Figure 3.37) and the large comproportionation constants that were observed in Table 3.15 and Table 3.16, it seems probable that $[\{\text{Ru}(\text{tp})(\text{bpy})\}_2(\mu\text{-dicyd})]^{3+}$ and $[\{\text{Ru}(\text{tp})(\text{bpy})\}_2(\mu\text{-adpc})]^{3+}$ are not borderline but are delocalized mixed-valence systems. In this case, it is possible to explain the appearance of multiple MMCT bands in the electronic spectra of these systems by invoking a considerable degree of mixing between the π -symmetry metal orbitals and non-bonding orbitals of the bridging ligand. A spectroscopic analysis on the mixed-valence complexes assuming C_{2h} microsymmetry was performed in this study, and the results are shown in Figure 4.10.

Figure 4.9 The best Gaussian fit of the MMCT band of $[\{\text{Ru}(\text{tp})(\text{bpy})\}_2(\mu\text{-adpc})]^{2+}$.

In Figure 4.10, three MMCT transitions are symmetry allowed $a_u \rightarrow b_g^*$ (ν_1), $b_u \rightarrow b_g^*$ (ν_2), and $a_u \rightarrow b_g^*$ (ν_3); however, ν_1 is nevertheless forbidden because there is no overlap between metal and ligand orbitals. Under conditions of lower symmetry, symmetry restrictions would break down and further transitions to b_g^* would be possible. In addition, IR spectroscopic and crystallographic evidence (Figure 3.32) suggest that the complexes can exist in at least two conformations because of the *syn* and *anti* conformations of the bridging ligand. This alone would result in a doubling of observed MMCT bands. A further consequence of the treatment shown in Figure 4.10, is that the energy of the ν_3 transition is equal to the resonance exchange element H_{ad} for the mixing of donor, acceptor and bridging ligand wavefunctions and is not equal to $2H_{ad}$ as

predicted by the two-state Hush model.^{8,11} Figure 4.10 is applicable to both $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-adpc})]^{3+}$ and $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-dicyd})]^{3+}$; however, the latter complex does not absorb significantly between 1400 to 2600 nm.

Figure 4.10 Qualitative molecular orbital scheme showing the origin of metal-metal transitions for the delocalized case in C_{2h} symmetry. The phenyl rings of the bridging ligands are coplanar with the x-y plane.

There is no reason for the MMCT band of $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-dicyd})]^{3+}$ to be forbidden and its energy can be predicted from comproportionation data and application of equation 23.

The extraction of ΔG_{ex} for the dicyd²⁻ complexes from an experimentally determined CV spectrum is a simple procedure, because each pair of the complexes from the two families (dicyd²⁻ and adpc²⁻) of this study have similar coordination spheres and charges, so that the values of ΔG_{s} , ΔG_{e} , ΔG_{i} , ΔG_{ip} and ΔG_{th} are approximately equivalent. This means that differences in ΔG_{c} between the complexes actually reflect the differences in ΔG_{r} and ΔG_{ex} . It is also possible to extract the value of ΔG_{r} from comproportionation data of strongly coupled mixed-valence complexes and hence determine the free energy of resonance exchange per mixed-valence complex, $\Delta G_{\text{r}}' = 0.5\Delta G_{\text{r}}$.⁶

Figure 4.11 (used as a representative example to calculate ΔG_{ex} for dicyd²⁻ family) shows the cyclic voltammograms of the Ru(III/II) couples of the mononuclear complex [Ru(tp)(bpy)(2,3,4,5-Cl₄pcyd)(PF₆)₂] and the dinuclear complexes [$\{\text{Ru}(\text{tp})(\text{bpy})\}_2(\mu\text{-dicyd})$](PF₆)₂ and [$\{\text{Ru}(\text{tp})(\text{bpy})\}_2(\mu\text{-adpc})$](PF₆)₂, in acetonitrile solution. The Ru(III/II) couples of [$\{\text{Ru}(\text{tp})(\text{bpy})\}_2(\mu\text{-adpc})$](PF₆)₂ are centrosymmetrically disposed about the couple of the mononuclear complex because of the approximately equal stabilization of the mixed-valence state with respect to Ru[III,III] and Ru[II,II] states of the dinuclear complex, the sum of which is the free energy of comproportionation (equation 21). This observation requires that both ΔG_{ex} and ΔG_{ip} are small for this complex. For [$\{\text{Ru}(\text{tp})(\text{bpy})\}_2(\mu\text{-dicyd})$]³⁺, the contribution of ΔG_{ex} must be accounted for because of an antiferromagnetic exchange which stabilizes the Ru[III,III] state relative to the mixed-valence state and causes the Ru[III,III]/Ru[III,II] couple to shift towards more negative potentials. This effect is clearly shown in Figure 4.11 where the Ru(III/II) couples of [$\{\text{Ru}(\text{tp})(\text{bpy})\}_2(\mu\text{-dicyd})$](PF₆)₂ are not symmetrically disposed

about the Ru(III/II) couple of the mononuclear complex, $[\text{Ru}(\text{ttp})(\text{bpy})(2,3,4,5\text{-Cl}_4\text{pcyd})](\text{PF}_6)$. As antiferromagnetic exchange only affects the Ru[III,III] state, the free energy of antiferromagnetic exchange can be estimated by assuming that in the absence of antiferromagnetic exchange, the free energy of comproportionation would be equal to twice the difference between the Ru[III,II]/Ru[II,II] couple of $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-dicyd})](\text{PF}_6)_2$ and the Ru(III/II) couple of the mononuclear complex (ΔE , see Figure 4.11). Subtracting the experimental ΔG_{el} (Figure 4.11) from this calculated value of ΔG_{c} ($2\Delta E$) (see Figure 4.11) leads to a value of ΔG_{ex} ($2\Delta E - \Delta G_{\text{el}}$) = 1.08 V or 8700 cm^{-1} . Experimental values of ΔG_{ex} for pentaamineruthenium dinuclear dicyd²⁻ complexes have approached values of 500 cm^{-1} and so this magnitude of ΔG_{ex} estimated for $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-dicyd})]^{4+}$ must reflect the much greater stabilization of Ru(III) orbitals in a penta-pyridine relative to a pentaammine coordination sphere.^{50,60} The closer in energy Ru(III) orbitals are relative to π non-bonding orbitals of dicyd²⁻, the larger the metal-ligand coupling element will be between Ru(III) and dicyd²⁻. For the representative example and also for all other dicyd²⁻ complexes of this study, see Table 4.2 for the results of these calculations.

Figure 4.11 Cyclic voltammogram of a) $[\text{Ru}(\text{tp})(\text{bpy})(\text{Cl}_4\text{-pcyd})](\text{PF}_6)$, b) $[\{\text{Ru}(\text{tp})(\text{bpy})\}_2(\mu\text{-dicyd})](\text{PF}_6)_2$ and c) $[\{\text{Ru}(\text{tp})(\text{bpy})\}_2(\mu\text{-adpc})](\text{PF}_6)_2$, in acetonitrile, 0.1 M TBAH electrolyte, scan rate 100 mV/s.

Table 4.2 A Summary of the Values of ΔG_{ex} and the Difference in Coupling, ΔH_{ad} , between $[\{\text{Ru}(\text{L})(\text{L}')\}_2(\mu\text{-dicyd})]^{3+}$ and $[\{\text{Ru}(\text{L})(\text{L}')\}_2(\mu\text{-adpc})]^{3+}$ Complexes, $\text{L}=\text{ttp}$, tpz and $\text{L}'=\text{bpy}$ or bpz .

Complex	$2\Delta E^a$ (V)	$\Delta G_{\text{cl}}(\text{V})^b$ $\text{L}=\mu\text{-dicyd}$	ΔG_{ex}^c (V)	$\Delta G_{\text{c}}(\text{V})^d$ $\text{L}=\mu\text{-adpc}$	$\Delta(\Delta G_{\text{r}})^e$ (V)	$\Delta(\Delta G_{\text{r}})^f$ (cm^{-1})
$[\text{Ru}(\text{ttp})(\text{bpy})\}\text{L}]^{2+}$	1.52	0.46	1.06	0.74	0.39	3140
$[\text{Ru}(\text{tpz})(\text{bpy})\}\text{L}]^{2+}$	1.62	0.44	1.18	0.94	0.34	2737
$[\text{Ru}(\text{ttp})(\text{bpz})\}\text{L}]^{2+}$	1.74	0.44	1.30	0.97	0.385	3099

^a $\Delta E = \text{Ru(III/II)}$ (for mononuclear) – $\text{Ru[III/II]/Ru[II/II]}$ (for dicyd²⁻ dinuclear complexes)

^b $\Delta G_{\text{cl}} = \text{Ru[III/III]/Ru[III/II]} - \text{Ru[III/II]/Ru[II/II]}$ for dicyd²⁻ dinuclear complexes

^c $\Delta G_{\text{ex}} = 2\Delta E - \Delta G_{\text{cl}}$

^d $\Delta G_{\text{c}} = \text{Ru[III/III]/Ru[III/II]} - \text{Ru[III/II]/Ru[II/II]}$ for adpc²⁻ dinuclear complexes

^e $2\Delta(\Delta G_{\text{r}}) = 2\Delta E - \Delta G_{\text{c}}$

^f $\Delta(\Delta G_{\text{r}}) \times 8051$

Similar to the spectrum of the mononuclear complex $[\text{Ru}(\text{ttp})(\text{bpy})(2,3,4,5\text{-Cl}_4\text{pcyd})]^{2+}$, the absorption spectrum of the fully oxidized Ru[III,III] system $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-dicyd})]^{3+}$, (Figure 3.27) clearly shows two LMCT bands at 443 nm and 1053 nm. Upon oxidation of Ru[II,III] to Ru[III,III] , some NIR absorbance intensity is lost and this is taken as evidence that the MMCT transition may lie underneath the LMCT transition.

The approximate doubling in intensity of the LMCT band when the complex is fully oxidized to Ru[III,III] relative to Ru[II,III] is of course consistent with the fact that there are two Ru(III)-cyanamide chromophores present.

Returning to our representative example, from the difference in resonance exchange between $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-dicyd})]^{3+}$ and $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-adpc})]^{3+}$, it is possible to estimate the energy of the MMCT band of $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-dicyd})]^{3+}$. Consider the equation for the free energy of resonance exchange for the symmetric delocalized mixed-valence case (equation 23). Both complexes are expected to have the same thermal barrier to electron transfer because of their similar coordination spheres. Subtracting ΔG_c (ΔG_{c2} , Figure 4.11) of $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-adpc})]^{3+}$ from ΔG_c of $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-dicyd})]^{3+}$ in the absence of antiferromagnetic exchange ($2\Delta E_1$) and correcting for the number of moles of mixed-valence complex generated in the comproportionation equilibrium will yield the difference in resonance exchange between the complexes (0.39 V or 3140 cm^{-1}).⁶¹ Adding this energy to the energy of the MMCT band of $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-adpc})]^{3+}$ yields a predicted MMCT energy for $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-dicyd})]^{3+}$ of 8700 cm^{-1} . This places the MMCT band of $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-dicyd})]^{3+}$ under the LMCT band centered at 1000 nm as has been previously assumed.⁵⁰ Indeed, a multiple Gaussian fit of the electronic spectrum of $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-dicyd})]^{3+}$ (Figure 4.12) shows a band centred at approximately 8200 cm^{-1} which is suggested to be the MMCT band. Table 4.3 lists the LMCT and MMCT band energies for the example system as well as for the other members of the adpc^{2-} and dicyd^{2-} families of complexes.

Figure 4.12 The best Gaussian fit of the MMCT band (low energy band) and the LMCT bands (at high energy bands) for $[\{\text{Ru}(\text{tp})(\text{bpy})\}_2(\mu\text{-dicyd})]^{3+}$. The band centred at 8200 cm^{-1} is suggested to be a MMCT transition.

Table 4.3 The Energy of MMCT and LMCT Band for both Families, L = adpc²⁻, L' = dicyd²⁻.

Complex	LMCT (cm ⁻¹) ^a	MMCT (cm ⁻¹) ^b	LMCT – MMCT (cm ⁻¹)
[{Ru(ttp)(bpy)} ₂ L](PF ₆) ₂	12370	5180	7190
[{Ru(ttp)(bpz)} ₂ L](PF ₆) ₂	12560	5930	6630
[{Ru(tpz)(bpy)} ₂ L](PF ₆) ₂	12520	5840	6680
[{Ru(ttp)(bpy)} ₂ L'](PF ₆) ₂	10319	8610	1709
[{Ru(ttp)(bpz)} ₂ L'](PF ₆) ₂	11338	8990	2348
[{Ru(tpz)(bpy)} ₂ L'](PF ₆) ₂	11210	8810	2400

^a E_{LMCT} for adpc²⁻ complexes were calculated from Figure 3.38, Figure 3.39 and Figure 3.40 while for dicyd²⁻ complexes were calculated from Figure 3.27, Figure 3.29 and Figure 3.31

^b MMCT for adpc²⁻ complexes were calculated from Figure 4.14 while for dicyd²⁻ family using method described in text.

The predicted three state model is expected to be valid for both families of complexes.

The increase in the MMCT band energy for dicyd²⁻ complexes relative to the adpc²⁻ family is (see Table 4.3) due to the greater mixing between the donor and the acceptor

wave functions which leads to greater stabilization of the ground state in dicyd²⁻ relative to adpc²⁻ family.

4.3.3 Effect of Inner-Sphere Perturbation on Class III systems

The effect of inner-sphere changes on these Class III complexes was investigated by perturbing the metal with weaker σ -donor ligands. Figure 3.36 shows the cyclic voltammetry for $[\{\text{Ru}(\text{L})(\text{L}')\}_2(\mu\text{-adpc})](\text{PF}_6)_2$, where L is ttp or tpz and L' is bpy and bpz, in acetonitrile solution.

Metal-metal separation is essentially constant through a series that has the same bridging ligand. Any increase in metal-metal coupling must reflect the increasing ability of the Ru(III) and Ru(II) orbitals to interact with the superexchange pathway provided by the bridging ligand. For the series of complexes $[\{\text{Ru}(\text{L})(\text{L}')\}_2(\mu\text{-adpc})](\text{PF}_6)_2$ the increase in metal-metal coupling that is seen (Figure 4.15 and Table 3.15) as pyridine moieties are replaced by pyrazine moieties occurs because both Ru(II) and Ru(III) orbitals are becoming closer in energy to the HOMO of the adpc²⁻ bridging ligand. This is represented schematically in Figure 4.13.

Perturbing the metal with a weak σ -donor auxiliary ligand increases the energy for the MMCT and LMCT bands for both families (Table 4.3). Furthermore, the multiple MMCT bands become more resolved (compare 1 and 3 in Figure 4.14, for example). As the metal $d\pi$ orbitals are stabilized a greater energetic matching of these orbitals will ensue. Henceforth from that point, decreasing the energy gap between the metal and

ligand orbitals will increase their overlap. This will result in an increased splitting of the resultant bonding and antibonding orbitals and thus an increase in E_{LMCT} and E_{IT}

Figure 4.13 Schematic representation of how the weak σ -donor ligand perturbs metal $d\pi$ orbital energy in relation to the π -HOMO of the bridging ligand.

Figure 4.14 The metal-metal charge transfer band of 1) $[\{Ru(tpz)(bpy)\}_2(\mu\text{-adpc})]^{2+}$, 2) $[\{Ru(tpz)(bpz)\}_2(\mu\text{-adpc})]^{2+}$ and 3) $[\{Ru(tpz)(bpy)\}_2(\mu\text{-adpc})]^{2+}$ in DMF.

Alternatively, changes in the inner sphere of the dicyd^{2-} family of Class III complexes appear to have little effect on their metal-metal coupling. The cyclic voltammograms of the Ru(III,II) couples for $[\{\text{Ru}(\text{L})(\text{L}')\}_2(\mu\text{-dicyd})](\text{PF}_6)_2$ dinuclear complexes, where L is ttp or tpz and L' is bpy and bpz, in acetonitrile solution are summarized in Table 3.6 and shown in Figure 3.23. There was a slight positive shift of the two redox Ru(III,II) couples, $\text{dicyd}^{-/2-}$, and the first reduction waves for the auxiliary ligand when pyridine moieties were replaced by pyrazine moieties. The reason for the slight positive shift of two redox Ru(III,II) couples has already been explained, but the difference between the redox couples ($\Delta E = \text{Ru}_2 - \text{Ru}_1$), which reflects the value of K_c , is almost the same in all complexes. The K_c value is not increased by increasing the number of pyrazine moieties, unlike the adpc^{2-} case, because decreasing the energy gap for hole transfer increases the electronic coupling of the ruthenium centers and the antiferromagnetic exchange at the same time. Since ΔG_r and ΔG_{ex} are of opposite sign, these terms cancel (see equation 22), leading to little or no change in ΔG_c (see Table 4.3).

4.3.4 Effect of Outer-Sphere Perturbation on Class III systems

Implicit in the construction of the molecular orbital scheme in Figure 4.10 is that the mixed-valence system is a delocalized case. The classical view of a delocalized system is that it should be largely insensitive to the nature of the solvent, and indeed the comproportionation data of $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-dicyd})](\text{PF}_6)_2$ (Table 3.10) show no clear evidence of solvent dependence. On the other hand, the comproportionation data of $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-adpc})](\text{PF}_6)_2$ (Table 3.16) show a significant solvent dependence as does the MMCT band data in Table 3.17, Figure 4.17 and Figure 4.18. This is surprising

as the IR spectroelectrochemical study (Figure 3.37) shows that the cyanamide groups are equivalent because of an average cyanamide stretching frequency. This requires thermal electron transfer to be greater than the IR timescale (10^{13} s^{-1}) and therefore faster than solvent relaxation rates (10^{12} s^{-1}). In addition, a comparison of MMCT band energies derived from chemical and electrochemical oxidations in various solvents shows little or opposing effects. This is not expected for a valence trapped mixed-valence system in the presence of 0.1 M TBAH electrolyte.⁵⁶ What then is the mechanism by which solvent can influence the properties of $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-adpc})]^{3+}$, which is independent of solvent dynamics? To be consistent with all the evidence, the mechanism must be a ground state perturbation of metal-metal coupling of a delocalized system.

The pyridine moieties of terpyridine and bipyridine ligands are fairly effective at shielding the ruthenium ion from the influence of solvent but this is not true for the bridging adpc^{2-} ligand. Whereas the cyanamide groups of adpc^{2-} are coordinated to ruthenium, the electron-acceptor azo group is exposed to the solvent and its electronic structure can be perturbed by the solvent's electron donor properties. Other researchers have found that reducing the azo group in the bridging ligand, 4,4'-azo-dipyridine, had the effect of eliminating metal-metal coupling in the mixed-valence complex $[\{(\text{NH}_3)_5\text{Ru}\}_2(\mu\text{-4,4'-azo-dipyridine})]^{5+}$ and indeed these authors suggested that this was a demonstration of a molecular switching device.⁶²

Figure 4.15 chemical reduction for the azo group of the bridging ligand, 4,4'-azodipyridine⁶².

The solvent-azo, donor-acceptor interactions are not as extreme as chemical reduction but they also apparently perturb the electronic structure of the azo group and hence the superexchange pathway in a manner that is detrimental to metal-metal coupling. Figure 4.16 shows the calculated symmetry HOMO for adpc^{2-} . As a result of mixing between the donor phenylcyanamide groups and the acceptor azo group, a continuous coupling pathway is generated across the adpc^{2-} ligand. It is therefore evident that a solvent-azo donor-acceptor interaction is in direct competition with this phenylcyanamide-azo interaction, and can serve to interrupt this coupling pathway, leading to the observed solvent effect (Figure 4.16).

Figure 4.16 Ab initio calculation of the highest occupied molecular orbital (HOMO) of adpc^{2-} .

This is illustrated by Figure 4.17 and Figure 4.18 which show the MMCT band energy of $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-adpc})]^{3+}$ decreasing with increasing donor number of the solvent. The correlation is not good and may indicate that other factors other than the donor properties of the solvent are important. In Figure 4.18, the MMCT band energy was affected only very slightly by whether or not the mixed-valence state was generated electrochemically or chemically, and thus ion-pairing has been shown to have little impact on these systems.

Figure 4.17 Solvent dependence of the intervalence band of $[\{\text{Ru}(\text{tp})(\text{bpy})\}_2(\mu\text{-adpc})]^{3+}$ in DMF 1), acetonitrile 2), nitromethane 3), DMSO 4), propylene carbonate 5). The spectra were generated electrochemically, platinum working electrode, 0.1 M TBAH.

Figure 4.18 Solvent dependence of the energy of the MMCT band of $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-adpc})]^{3+}$, electrochemical oxidation (Δ) in the presence of 0.1 M TBAH and chemical oxidation ($\blacktriangle$) using $[\text{Fe}(\text{bpy})_3][\text{PF}_6]_3$

While $[\{\text{Ru}(\text{tpz})(\text{bpy})\}_2(\mu\text{-adpc})](\text{PF}_6)_2$ has been shown to be more strongly coupled than $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-adpc})](\text{PF}_6)_2$, as supported by the high value of the K_c (Table 3.15), and the energy the MMCT band (Figure 4.14), in both cases the sensitivity of this complex to the donor number of the solvent shows the same trend (Figure 4.19). There is no noticeable effect of the solvent on the coupling when the donor number of the solvent is low (< 17), whereas the coupling is significantly affected by solvent with higher donor number.

Figure 4.19 Solvent dependence of the energy of the MMCT band maximum of $[\{Ru(tpz)(bpy)\}_2(\mu\text{-adpc})]^{3+}$ (black circle) and $[\{Ru(tpz)(bpy)\}_2(\mu\text{-adpc})]^{3+}$ (black square) using $[Fe(bpy)_3][PF_6]_3$ oxidant.

4.4 Summary of Findings for Dinuclear Complexes

Two families of dinuclear complexes bridged by either 1,4-dicyanamidobenzene or 4,4-azo(diphenylcyanamide) were prepared and fully characterized. The observation of only one $\nu(NCN)$ band in the IR spectra of the mixed-valence complexes $[\{Ru(tpz)(bpy)\}_2(\mu\text{-$

dicyd)]³⁺ and [$\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-adpc})$]³⁺ is strong evidence that these complexes are delocalized on the infrared timescale (10^{13} s^{-1}). In order to understand the effects of inner-sphere and outer-sphere perturbation on metal-metal coupling in these Class III systems, the auxiliary pyridine ligands about the metal centers were systematically replaced with weaker σ -donor pyrazine moieties. In the simplest sense, increasing the energetic matching between the metal orbitals and the bridging ligands orbitals (by replacing pyridine with pyrazine moieties) increases coupling in the adpc²⁻ family due to an increase of the covalency of the metal-bridging ligand bonding. The K_c value for the dicyd²⁻ family does not increase with increasing pyrazine moieties, unlike the adpc²⁻ family, because decreasing the energy gap for hole transfer increases the electronic coupling of the ruthenium centers and the antiferromagnetic exchange at the same time. Because ΔG_r and ΔG_{ex} are of opposite sign, these terms cancel each other.⁶³

In order to model the coupling in these Class III systems, a minimum requirement is to invoke mixing of the bridging ligand orbital with ruthenium donor and acceptor orbitals. The predicted metal-to-metal transition is formally assigned to a non-bonding to antibonding metal orbital transition and the energy of this transition is equivalent to the resonance exchange integral H_{ad} . This model can result in multiple MMCT transitions by including other metal orbitals, particularly if symmetry constraints are relaxed. In order for a class II-III designation to be confirmed, it is insufficient to rely on the observation of multiple NIR MMCT bands. Low energy IC bands must also be observed (see text diagram page 19).

In addition, this three state model, together with comproportionation data, can be used to predict the energy of MMCT transitions. For example, in the case of $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-dicyd})]^{3+}$, the MMCT transition energy was predicted to be 8700 cm^{-1} which places this transition under the LMCT band envelope centered at 1000 nm. When the two families (adpc^{2-} and dicyd^{2-}) are compared, the difference in the coupling (ΔH_{ad}), and the high energy of the calculated MMCT band for the dicyd^{2-} family indicate that the energy gap (see equation 14) for hole transfer for the dicyd^{2-} family is narrower than for the adpc^{2-} family.

The solvent dependence of MMCT band energy that was observed for the 1,4-azodi(phenylcyanamide) family was also a key finding of this study. Again, solvent dependence of the MMCT band is typically associated with localized Class II status. However, since the IR spectrum of $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-adpc})]^{3+}$ indicated that the complex was delocalized on a faster timescale than that of solvent relaxation, the solvent dependence can only be explained by a ground state perturbation of metal-metal coupling. The mechanism of this perturbation is suggested to involve a donor-acceptor interaction of solvent molecules with the azo group of the bridging ligand.

Chapter 5 Future work

In accordance with these findings, future work could investigate the effect of a strong σ -donor auxiliary ligand such as phpy (η^2 -phenylpyridine) or 2-pyrazine carboxylic acid. These auxiliary ligands are electron rich and they will destabilize the metal orbitals and increase the energy gap for the hole transfer superexchange, and as a result, the coupling should decrease and both the LMCT and the MMCT bands should shift to a higher energy. It would be interesting to note if these complexes would retain their Class III status.

This project is only one step in developing a conceptual framework of donor-acceptor systems that may be used to build highly-polarizable systems for non-linear optical materials. If NLO materials are used telecommunication applications, the chromophore must not significantly absorb at the operating wavelengths of 1.3 and 1.55 μm . This can be a problem for mixed-valence complexes because the intervalence transitions typically (but not always) occur in the NIR region. Careful design of asymmetric mixed-valence complexes is the solution to this problem. Thus, whereas symmetric mixed-valence complexes have intervalence charge-transfer energy approximated by the sum of inner and outer reorganizational energies (λ), for asymmetric systems, an additional term describing the difference between donor and acceptor energy can shift the intervalence band to the visible region. On the other hand, there are other photonic applications that can take advantage of NIR absorption chromophores (memory storage devices, slow switches).

Chapter 6 Appendix

6.1 Appendix A: Supporting Figures

Figure 6.1 ^1H NMR spectrum of the $\text{Tl}(2,3,4,5\text{-Cl}_4\text{pcyd})$ in DMSO-d_6 , resonances at 3.33 and 2.50 are due to solvent.

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Integration values (from left to right): 1.00, 2.27, 2.14, 1.07, 1.05, 2.87, 2.13, 3.35, 4.31, 1.0, 1.7, 1.11, 3.01, 3.72, 3.01.

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Figure 6.6 ^1H NMR spectrum of $[\{\text{Ru}(\text{tp})(\text{bpy})\}_2(\mu\text{-dicyd})](\text{PF}_6)_2$ in DMSO-d_6 , tp and bpy resonances were assigned using COSY of the reactant complex $[\text{Ru}(\text{tp})(\text{bpy})\text{Cl}](\text{PF}_6)$, as shown in Figure 3.3. The singlet peak at 5.45 ppm was assigned to the proton in the dicyd^{2-} ligand.

Figure 6.7 ^1H NMR spectrum of $[\{\text{Ru}(\text{tpz})(\text{bpy})\}_2(\mu\text{-dicyd})](\text{PF}_6)_2$ in DMSO-d_6 , tpz and bpy resonances were assigned using COSY of the reactant complex $[\text{Ru}(\text{tpz})(\text{bpy})\text{Cl}](\text{PF}_6)$, as shown in Figure 3.5. The singlet peak at 5.51 ppm was assigned to the proton in the dicyd^{2-} ligand.

Figure 6.8 ^1H NMR spectrum of $[\{\text{Ru}(\text{tpb})(\text{bpz})\}_2(\mu\text{-dicyd})](\text{PF}_6)_2$ in DMSO-d_6 , tpb and bpz resonances were assigned using COSY of the reactant complex $[\text{Ru}(\text{tpb})(\text{bpz})\text{Cl}](\text{PF}_6)$, as shown in Figure 3.7. The singlet peak at 5.48 ppm was assigned to the proton in the dicyd $^{2-}$ ligand.

Figure 6.9 ^1H NMR spectrum of $[\{\text{Ru}(\text{tp})\}(\text{bpy})_2(\mu\text{-adpc})](\text{PF}_6)_2$ in DMSO-d_6 , , ttp and bpy resonances were assigned using COSY of the reactant complex $[\text{Ru}(\text{tp})(\text{bpy})\text{Cl}](\text{PF}_6)$, as shown in Figure 3.3. The doublet peaks at 6.03 and 7.19 ppm was assigned to the protons in the adpc^{2-} ligand.

Figure 6.10 ^1H NMR spectrum of $[\{\text{Ru}(\text{tp})(\text{bpz})\}_2(\mu\text{-adpc})](\text{PF}_6)_2$ in DMSO-d_6 , ttp and bpz resonances were assigned using COSY of the reactant complex $[\text{Ru}(\text{tp})(\text{bpz})\text{Cl}](\text{PF}_6)$, as shown in Figure 3.7. The doublet peaks at 6.06 and 7.22 ppm was assigned to the protons in the adpc^{2-} ligand.

Figure 6.11 ^1H NMR spectrum of $[\{\text{Ru}(\text{tpz})(\text{bpy})\}_2(\mu\text{-adpc})](\text{PF}_6)_2$ in DMSO-d_6 , tpz and bpy resonances were assigned using COSY of the reactant complex $[\text{Ru}(\text{tpz})(\text{bpy})\text{Cl}](\text{PF}_6)$, as shown in Figure 3.5. The doublet peaks at 6.08 and 7.24 ppm was assigned to the protons in the adpc^{2-} ligand.

Figure 6.12 Cyclic voltammetry of $[\{\text{Ru}(\text{tpz})(\text{bpy})\}_2(\mu\text{-dicyd})]^{2+}$ in acetonitrile, data reported in V vs. NHE with scan rate of 0.1 V/s; 0.1 M TBAH at 25 °C.

Figure 6.13 Cyclic voltammetry of $[\{\text{Ru}(\text{tpz})(\text{bpy})\}_2(\mu\text{-dicyd})]^{2+}$ in nitromethane, data reported in V vs. NHE with scan rate of 0.1 V/s; 0.1 M TBAH at 25 °C.

Figure 6.14 Cyclic voltammetry of $[\{\text{Ru}(\text{tp})(\text{bpy})_2(\mu\text{-dicyd})\}]^{2+}$ in DMF, data reported in V vs. NHE with scan rate of 0.1 V/s; 0.1 M TBAH at 25 °C.

Figure 6.15 Cyclic voltammetry of $[\{\text{Ru}(\text{tp})(\text{bpy})_2(\mu\text{-adpc})\}]^{2+}$ in nitromethane, data reported in V vs. NHE with scan rate of 0.1 V/s; 0.1 M TBAH at 25 °C.

Figure 6.16 Cyclic voltammetry of $[\{\text{Ru}(\text{tp})(\text{bpy})\}_2(\mu\text{-adpc})]^{2+}$ in propylene carbonate, data reported in V vs. NHE with scan rate of 0.1 V/s; 0.1 M TBAH at 25 °C.

Figure 6.17 Cyclic voltammetry of $[\{\text{Ru}(\text{tp})(\text{bpy})\}_2(\mu\text{-adpc})]^{2+}$ in DMF, data reported in V vs. NHE with scan rate of 0.1 V/s; 0.1 M TBAH at 25 °C.

Figure 6.18 Spectroelectrochemical data for $[\{\text{Ru}(\text{tp})(\text{bpy})\}_2(\mu\text{-adpc})]^{2+}$ showing the oxidation of the $\text{Ru}[\text{II},\text{II}]$ complex to the mixed-valence $\text{Ru}[\text{III},\text{II}]$ complex under increasing anodic potential in acetonitrile (0.49 to 0.55 V vs. Ag/AgCl). Inset shows the MMCT band.

Figure 6.19 Spectroelectrochemical data for $[\{\text{Ru}(\text{tp})(\text{bpy})\}_2(\mu\text{-adpc})]^{2+}$ showing the oxidation of the Ru[II,II] complex to the mixed-valence Ru[III,II] complex under increasing anodic potential in DMSO (0.53 to 0.59 V vs. Ag/AgCl). Inset shows the MMCT band.

Figure 6.20 Spectroelectrochemical data for $[\{\text{Ru}(\text{tp})(\text{bpy})\}_2(\mu\text{-adpc})]^{2+}$ showing the oxidation of the $\text{Ru}[\text{II},\text{II}]$ complex to the mixed-valence $\text{Ru}[\text{III},\text{II}]$ complex under increasing anodic potential in nitromethane (0.45 to 0.49 V vs. Ag/AgCl). Inset shows the MMCT band.

Figure 6.21 Spectroelectrochemical data for $[\{\text{Ru}(\text{tp})(\text{bpy})\}_2(\mu\text{-adpc})]^{2+}$ showing the oxidation of the Ru[II,II] complex to the mixed-valence Ru[III,II] complex under increasing anodic potential in propylene carbonate (0.45 to 0.49 V vs. Ag/AgCl). Inset shows the MMCT band.

Figure 6.22 The oxidation of the $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-adpc})]^{2+}$ complex to the mixed-valence $\text{Ru}[\text{III},\text{II}]$ complex by $[\text{Fe}(\text{bpy})_3]^{3+}$ in nitromethane. Inset shows the MMCT band.

Figure 6.23 The oxidation of the $[\{\text{Ru}(\text{tp})(\text{bpy})\}_2(\mu\text{-adpc})]^{2+}$ complex to the mixed-valence $\text{Ru}[\text{III},\text{II}]$ complex by $[\text{Fe}(\text{bpy})_3]^{3+}$ in acetone. Inset shows the MMCT band.

Figure 6.24 The oxidation of the $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-adpc})]^{2+}$ complex to the mixed-valence $\text{Ru}[\text{III},\text{II}]$ complex by $[\text{Fe}(\text{bpy})_3]^{3+}$ in acetonitrile. Inset shows the MMCT band.

Figure 6.25 The oxidation of the $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-adpc})]^{2+}$ complex to the mixed-valence $\text{Ru}[\text{III},\text{II}]$ complex by $[\text{Fe}(\text{bpy})_3]^{3+}$ in dichloromethane. Inset shows the MMCT band.

Figure 6.26 The oxidation of the $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-adpc})]^{2+}$ complex to the mixed-valence $\text{Ru}[\text{III},\text{II}]$ complex by $[\text{Fe}(\text{bpy})_3]^{3+}$ in nitrobenzene. Inset shows the MMCT band.

Figure 6.27 The oxidation of the $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-adpc})]^{2+}$ complex to the mixed-valence $\text{Ru}[\text{III},\text{II}]$ complex by $[\text{Fe}(\text{bpy})_3]^{3+}$ in DMSO. Inset shows the MMCT band.

Figure 6.28 The oxidation of the $[\{\text{Ru}(\text{tp})(\text{bpy})\}_2(\mu\text{-adpc})]^{2+}$ complex to the mixed-valence $\text{Ru}[\text{III},\text{II}]$ complex by $[\text{Fe}(\text{bpy})_3]^{3+}$ in propylene carbonate. Inset shows the MMCT band.

Figure 6.29 Spectroelectrochemical data for $[\{\text{Ru}(\text{tp})(\text{bpy})\}_2(\mu\text{-dicyd})]^{2+}$ showing the oxidation of the $\text{Ru}[\text{II},\text{II}]$ complex to the mixed-valence $\text{Ru}[\text{III},\text{II}]$ complex under increasing anodic potential in DMSO (-0.25 to 0.22 V vs. Ag/AgCl). The wavy pattern seen in the spectra are an artifact, see appendix B for more detail.

Figure 6.30 Spectroelectrochemical data for $[\{Ru(tp)(bpy)\}_2(\mu-dicyd)]^{2+}$ showing the oxidation of the Ru[III,II] complex to Ru[III,III] complex under increasing anodic potential in DMSO, (0.44 to 0.60 V vs. Ag/AgCl).

Figure 6.31 Spectroelectrochemical data for $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-dicyd})]^{2+}$ showing the oxidation of the Ru[II,II] complex to the mixed-valence Ru[III,II] complex under increasing anodic potential in nitromethane (-0.25 to 0.16 V vs. Ag/AgCl).

Figure 6.32 Spectroelectrochemical data for $[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu\text{-dicyd})]^{2+}$ showing the oxidation of the Ru[III,II] complex to the Ru[III,III] complex under increasing anodic potential in nitromethane (0.31 to 0.51 V vs. Ag/AgCl).

Figure 6.33 The oxidation of the $[\{\text{Ru}(\text{tpz})(\text{bpy})\}_2(\mu\text{-adpc})]^{2+}$ complex to the mixed-valence $\text{Ru}[\text{III},\text{II}]$ complex by $[\text{Fe}(\text{bpy})_3]^{3+}$ in nitromethane. Inset shows the MMCT band.

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Figure 6.34 The oxidation of the $[\{\text{Ru}(\text{tpz})(\text{bpy})\}_2(\mu\text{-adpc})]^{2+}$ complex to the mixed-valence $\text{Ru}[\text{III},\text{II}]$ complex by $[\text{Fe}(\text{bpy})_3]^{3+}$ in DMSO. Inset shows the MMCT band.

Figure 6.35 The oxidation of the $[\{\text{Ru}(\text{tpz})(\text{bpy})\}_2(\mu\text{-adpc})]^{2+}$ complex to the mixed-valence $\text{Ru}[\text{III},\text{II}]$ complex by $[\text{Fe}(\text{bpy})_3]^{3+}$ in acetonitrile. Inset shows the MLCT band.

Figure 6.36 The oxidation of the $[\{\text{Ru}(\text{tpz})(\text{bpy})\}_2(\mu\text{-adpc})]^{2+}$ complex to the mixed-valence $\text{Ru}[\text{III},\text{II}]$ complex by $[\text{Fe}(\text{bpy})_3]^{3+}$ in acetone. Inset shows the MMCT band.

Atomic Coordinates ($\times 10^4$) and Equivalence Isotropic.
Table 1:Displacement parameters ($\text{\AA}^2 \times 10^3$) .

U(equation) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
<hr/>				
Ru	2634 (1)	521 (1)	3488 (1)	28 (1)
N (1)	4121 (4)	-276 (4)	3286 (4)	29 (2)
N (2)	3433 (3)	1402 (4)	3927 (4)	25 (1)
N (3)	1459 (3)	1682 (4)	3819 (4)	29 (2)
N (4)	1889 (3)	-435 (4)	2962 (4)	30 (2)
N (5)	2769 (4)	1176 (4)	2043 (4)	28 (2)
N (6)	2396 (4)	-281 (4)	4891 (4)	32 (2)
N (7)	2095 (4)	-1453 (4)	6476 (4)	33 (2)
N (8)	85 (5)	-462 (4)	9981 (5)	45 (2)
C (1)	4443 (5)	-1093 (5)	2892 (5)	36 (2)
C (2)	5484 (5)	-1491 (5)	2711 (5)	37 (2)
C (3)	6232 (5)	-1043 (5)	2973 (6)	43 (2)
C (4)	5922 (4)	-197 (5)	3381 (5)	38 (2)
C (5)	4868 (4)	190 (5)	3537 (5)	27 (2)
C (6)	4473 (4)	1108 (5)	3944 (5)	27 (2)
C (7)	5025 (4)	1670 (5)	4333 (5)	32 (2)
C (8)	4548 (5)	2530 (5)	4699 (5)	31 (2)
C (9)	3462 (4)	2800 (5)	4680 (5)	32 (2)
C (10)	2928 (4)	2230 (5)	4289 (5)	29 (2)
C (11)	1788 (4)	2413 (5)	4201 (5)	31 (2)
C (12)	1119 (5)	3231 (5)	4451 (5)	39 (2)
C (13)	72 (5)	3360 (5)	4309 (5)	43 (2)
C (14)	-262 (5)	2638 (5)	3926 (5)	39 (2)
C (15)	437 (4)	1816 (5)	3706 (5)	38 (2)
C (16)	5148 (5)	3119 (5)	5125 (5)	30 (2)
C (17)	6228 (5)	3040 (5)	4903 (5)	35 (2)
C (18)	6805 (5)	3513 (6)	5364 (6)	45 (3)
C (19)	6343 (5)	4071 (6)	6058 (6)	42 (2)
C (20)	5261 (5)	4182 (5)	6237 (6)	47 (2)
C (21)	4675 (5)	3711 (5)	5783 (6)	37 (2)
C (22)	6973 (6)	4524 (6)	6608 (6)	62 (3)
C (23)	1456 (5)	-1263 (5)	3476 (5)	43 (2)
C (24)	1139 (5)	-1965 (5)	3051 (6)	44 (2)
C (25)	1290 (5)	-1840 (6)	2062 (6)	50 (2)
C (26)	1707 (5)	-980 (6)	1524 (6)	48 (2)
C (27)	1972 (5)	-265 (5)	1976 (6)	35 (2)
C (28)	2401 (5)	683 (5)	1460 (5)	32 (2)
C (29)	2404 (6)	1098 (6)	472 (5)	51 (2)
C (30)	2828 (7)	1977 (6)	63 (6)	59 (3)
C (31)	3247 (6)	2456 (6)	637 (6)	52 (2)

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C(32)	3201 (4)	2042 (5)	1625 (5)	38 (2)
C(33)	2213 (4)	-785 (5)	5661 (5)	29 (2)
C(34)	1610 (4)	-1126 (5)	7318 (6)	31 (2)
C(35)	1359 (5)	-1905 (6)	8132 (5)	38 (2)
C(36)	881 (5)	-1652 (6)	8972 (6)	41 (2)
C(37)	629 (5)	-630 (6)	9057 (5)	39 (2)
C(38)	891 (5)	156 (5)	8257 (6)	38 (2)
C(39)	1362 (4)	-92 (5)	7405 (6)	30 (2)
P	8744 (1)	6367 (2)	2823 (2)	51 (1)
F(1)	8144 (3)	5776 (4)	3802 (3)	71 (2)
F(2)	9339 (4)	6956 (5)	1864 (4)	99 (2)
F(3)	7669 (3)	6722 (4)	2367 (4)	77 (2)
F(4)	9804 (3)	6002 (3)	3306 (4)	78 (2)
F(5)	8922 (3)	5333 (4)	2432 (4)	74 (2)
F(6)	8562 (4)	7387 (3)	3255 (4)	77 (2)
C(40)	4502 (9)	6494 (8)	7710 (7)	88 (3)
C(41)	4465 (9)	4818 (7)	8770 (8)	105 (4)
C(42)	3076 (7)	5571 (8)	7687 (8)	97 (4)
C(43)	4396 (10)	8624 (18)	536 (8)	243 (14)
C(44)	3837 (8)	8871 (8)	-1024 (7)	101 (4)
C(45)	3417 (8)	7218 (8)	41 (8)	101 (4)
C(46)	1434 (8)	4917 (8)	118 (9)	102 (4)
C(47)	1641 (9)	4699 (9)	1767 (8)	106 (4)
C(48)	632 (7)	3583 (7)	1269 (8)	96 (4)
N(9)	4055 (5)	5654 (5)	8044 (5)	66 (2)
N(10)	3865 (5)	8190 (5)	-93 (5)	60 (2)
N(11)	1246 (5)	4430 (6)	984 (6)	67 (2)
O(1)	5309 (6)	6623 (7)	7943 (6)	122 (3)
O(2)	4363 (7)	7667 (9)	1313 (8)	163 (4)
O(3)	1921 (7)	5668 (6)	-130 (6)	129 (3)

Table 2: Bond lengths [Å] and angles [deg].

Ru-N(2)	1.971(5)
Ru-N(5)	2.040(5)
Ru-N(6)	2.049(5)
Ru-N(4)	2.073(5)
Ru-N(1)	2.074(5)
Ru-N(3)	2.081(5)
N(1)-C(1)	1.327(8)
N(1)-C(5)	1.383(7)
N(2)-C(6)	1.358(7)
N(2)-C(10)	1.364(8)
N(3)-C(15)	1.354(7)
N(3)-C(11)	1.388(8)
N(4)-C(23)	1.343(8)
N(4)-C(27)	1.367(8)
N(5)-C(32)	1.351(7)
N(5)-C(28)	1.367(8)
N(6)-C(33)	1.162(7)
N(7)-C(33)	1.299(8)
N(7)-C(34)	1.407(8)
N(8)-N(8)#1	1.234(11)
N(8)-C(37)	1.454(9)
C(1)-C(2)	1.390(9)
C(2)-C(3)	1.377(9)
C(3)-C(4)	1.371(9)
C(4)-C(5)	1.397(8)
C(5)-C(6)	1.469(9)
C(6)-C(7)	1.386(8)
C(7)-C(8)	1.392(9)
C(8)-C(9)	1.414(8)
C(8)-C(16)	1.487(9)
C(9)-C(10)	1.379(8)
C(10)-C(11)	1.496(7)
C(11)-C(12)	1.365(9)
C(12)-C(13)	1.397(8)
C(13)-C(14)	1.382(9)
C(14)-C(15)	1.373(9)
C(16)-C(21)	1.384(9)
C(16)-C(17)	1.398(8)
C(17)-C(18)	1.393(10)
C(18)-C(19)	1.390(10)
C(19)-C(20)	1.395(9)
C(19)-C(22)	1.509(10)
C(20)-C(21)	1.390(9)
C(23)-C(24)	1.385(10)
C(24)-C(25)	1.375(10)
C(25)-C(26)	1.376(10)
C(26)-C(27)	1.393(10)
C(27)-C(28)	1.469(9)
C(28)-C(29)	1.392(9)
C(29)-C(30)	1.358(10)
C(30)-C(31)	1.380(11)
C(31)-C(32)	1.389(9)

C(34)-C(39)	1.400(9)
C(34)-C(35)	1.409(8)
C(35)-C(36)	1.360(10)
C(36)-C(37)	1.384(10)
C(37)-C(38)	1.406(9)
C(38)-C(39)	1.371(9)
P-F(2)	1.581(5)
P-F(5)	1.584(5)
P-F(3)	1.596(4)
P-F(4)	1.599(4)
P-F(6)	1.600(5)
P-F(1)	1.605(5)
C(40)-O(1)	1.210(11)
C(40)-N(9)	1.316(10)
C(41)-N(9)	1.424(10)
C(42)-N(9)	1.487(10)
C(43)-O(2)	1.49(2)
C(43)-N(10)	1.49(2)
C(44)-N(10)	1.427(10)
C(45)-N(10)	1.482(11)
C(46)-O(3)	1.240(11)
C(46)-N(11)	1.267(11)
C(47)-N(11)	1.447(11)
C(48)-N(11)	1.452(10)
N(2)-Ru-N(5)	99.2(2)
N(2)-Ru-N(6)	88.6(2)
N(5)-Ru-N(6)	172.2(2)
N(2)-Ru-N(4)	175.9(2)
N(5)-Ru-N(4)	78.7(2)
N(6)-Ru-N(4)	93.5(2)
N(2)-Ru-N(1)	79.9(2)
N(5)-Ru-N(1)	88.4(2)
N(6)-Ru-N(1)	92.45(19)
N(4)-Ru-N(1)	96.4(2)
N(2)-Ru-N(3)	79.0(2)
N(5)-Ru-N(3)	93.4(2)
N(6)-Ru-N(3)	88.6(2)
N(4)-Ru-N(3)	104.55(19)
N(1)-Ru-N(3)	158.9(2)
C(1)-N(1)-C(5)	117.7(5)
C(1)-N(1)-Ru	129.3(4)
C(5)-N(1)-Ru	112.7(4)
C(6)-N(2)-C(10)	121.2(5)
C(6)-N(2)-Ru	118.6(4)
C(10)-N(2)-Ru	120.0(4)
C(15)-N(3)-C(11)	116.8(5)
C(15)-N(3)-Ru	128.9(5)
C(11)-N(3)-Ru	114.3(4)
C(23)-N(4)-C(27)	117.6(6)
C(23)-N(4)-Ru	127.0(5)
C(27)-N(4)-Ru	114.8(4)
C(32)-N(5)-C(28)	118.1(5)
C(32)-N(5)-Ru	125.3(5)
C(28)-N(5)-Ru	116.6(4)
C(33)-N(6)-Ru	174.3(5)

C(33)-N(7)-C(34)	120.5(6)
N(8)#1-N(8)-C(37)	112.7(9)
N(1)-C(1)-C(2)	123.5(6)
C(3)-C(2)-C(1)	119.2(7)
C(4)-C(3)-C(2)	118.5(6)
C(3)-C(4)-C(5)	120.5(6)
N(1)-C(5)-C(4)	120.6(6)
N(1)-C(5)-C(6)	115.5(5)
C(4)-C(5)-C(6)	123.9(5)
N(2)-C(6)-C(7)	118.9(6)
N(2)-C(6)-C(5)	113.0(5)
C(7)-C(6)-C(5)	128.0(5)
C(6)-C(7)-C(8)	122.1(5)
C(7)-C(8)-C(9)	117.2(6)
C(7)-C(8)-C(16)	121.5(5)
C(9)-C(8)-C(16)	121.3(6)
C(10)-C(9)-C(8)	119.8(6)
N(2)-C(10)-C(9)	120.8(5)
N(2)-C(10)-C(11)	112.3(5)
C(9)-C(10)-C(11)	126.8(6)
C(12)-C(11)-N(3)	121.9(5)
C(12)-C(11)-C(10)	124.0(6)
N(3)-C(11)-C(10)	114.0(5)
C(11)-C(12)-C(13)	120.0(7)
C(14)-C(13)-C(12)	118.5(6)
C(15)-C(14)-C(13)	119.3(6)
N(3)-C(15)-C(14)	123.5(6)
C(21)-C(16)-C(17)	118.1(6)
C(21)-C(16)-C(8)	121.8(6)
C(17)-C(16)-C(8)	120.0(7)
C(18)-C(17)-C(16)	120.3(7)
C(17)-C(18)-C(19)	122.0(7)
C(20)-C(19)-C(18)	116.8(6)
C(20)-C(19)-C(22)	121.1(8)
C(18)-C(19)-C(22)	122.1(7)
C(21)-C(20)-C(19)	121.8(8)
C(16)-C(21)-C(20)	120.9(7)
N(4)-C(23)-C(24)	122.9(7)
C(25)-C(24)-C(23)	119.7(7)
C(24)-C(25)-C(26)	118.0(7)
C(25)-C(26)-C(27)	120.6(8)
N(4)-C(27)-C(26)	120.9(6)
N(4)-C(27)-C(28)	114.8(6)
C(26)-C(27)-C(28)	124.3(7)
N(5)-C(28)-C(29)	121.1(6)
N(5)-C(28)-C(27)	114.2(6)
C(29)-C(28)-C(27)	124.7(7)
C(30)-C(29)-C(28)	120.1(7)
C(29)-C(30)-C(31)	119.4(7)
C(30)-C(31)-C(32)	119.1(7)
N(5)-C(32)-C(31)	122.1(7)
N(6)-C(33)-N(7)	172.0(7)
C(39)-C(34)-N(7)	125.0(6)
C(39)-C(34)-C(35)	118.0(8)
N(7)-C(34)-C(35)	117.1(6)

C(36)-C(35)-C(34)	120.6(7)
C(35)-C(36)-C(37)	121.5(7)
C(36)-C(37)-C(38)	118.6(7)
C(36)-C(37)-N(8)	116.1(7)
C(38)-C(37)-N(8)	125.4(7)
C(39)-C(38)-C(37)	120.3(7)
C(38)-C(39)-C(34)	121.0(7)
F(2)-P-F(5)	91.5(3)
F(2)-P-F(3)	90.6(3)
F(5)-P-F(3)	90.4(3)
F(2)-P-F(4)	90.8(3)
F(5)-P-F(4)	89.9(3)
F(3)-P-F(4)	178.5(3)
F(2)-P-F(6)	90.3(3)
F(5)-P-F(6)	178.0(3)
F(3)-P-F(6)	90.6(3)
F(4)-P-F(6)	89.1(3)
F(2)-P-F(1)	179.4(3)
F(5)-P-F(1)	89.0(3)
F(3)-P-F(1)	89.7(3)
F(4)-P-F(1)	88.8(3)
F(6)-P-F(1)	89.2(3)
O(1)-C(40)-N(9)	124.7(11)
O(2)-C(43)-N(10)	91.4(16)
O(3)-C(46)-N(11)	124.3(12)
C(40)-N(9)-C(41)	121.9(9)
C(40)-N(9)-C(42)	120.0(8)
C(41)-N(9)-C(42)	118.0(8)
C(44)-N(10)-C(45)	116.3(8)
C(44)-N(10)-C(43)	109.9(10)
C(45)-N(10)-C(43)	133.8(10)
C(46)-N(11)-C(47)	120.9(9)
C(46)-N(11)-C(48)	123.8(9)
C(47)-N(11)-C(48)	115.3(8)

Symmetry transformations used to generate equivalence atoms:

#1 -x, -y, -z+2

Table 3: Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$).

The anisotropic displacement factor exponent takes the form:
 $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Ru	25 (1)	34 (1)	28 (1)	-6 (1)	-5 (1)	6 (1)
N (1)	34 (3)	29 (3)	25 (4)	-7 (3)	-5 (2)	-5 (2)
N (2)	28 (2)	28 (3)	22 (4)	-15 (3)	-3 (2)	-3 (2)
N (3)	24 (2)	37 (3)	26 (4)	-9 (3)	-3 (2)	-1 (2)
N (4)	27 (2)	34 (3)	32 (4)	-11 (3)	-5 (2)	-6 (2)
N (5)	32 (3)	32 (3)	25 (4)	-16 (3)	-1 (2)	-6 (2)
N (6)	36 (3)	39 (3)	24 (4)	-8 (3)	-6 (2)	-6 (2)
N (7)	40 (3)	34 (3)	27 (4)	-11 (3)	1 (3)	-7 (2)
N (8)	45 (3)	46 (3)	44 (4)	-9 (4)	-13 (3)	-5 (3)
C (1)	36 (3)	34 (4)	41 (6)	-10 (4)	-8 (3)	-6 (3)
C (2)	45 (4)	31 (4)	40 (5)	-20 (4)	-4 (3)	-4 (3)
C (3)	30 (3)	40 (4)	55 (6)	-11 (4)	-4 (3)	2 (3)
C (4)	26 (3)	43 (4)	47 (6)	-16 (4)	-3 (3)	-3 (3)
C (5)	28 (3)	28 (3)	29 (5)	-10 (3)	-2 (3)	-6 (2)
C (6)	28 (3)	35 (4)	23 (4)	-12 (4)	-5 (3)	-5 (3)
C (7)	27 (3)	36 (4)	35 (5)	-12 (4)	-7 (3)	-2 (3)
C (8)	35 (3)	34 (4)	30 (5)	-16 (4)	-9 (3)	-4 (3)
C (9)	34 (3)	27 (3)	37 (5)	-15 (3)	-8 (3)	3 (3)
C (10)	31 (3)	33 (4)	26 (5)	-9 (4)	-2 (3)	-5 (3)
C (11)	24 (3)	36 (4)	35 (5)	-11 (4)	-4 (3)	-5 (3)
C (12)	31 (3)	46 (4)	43 (5)	-18 (4)	-6 (3)	-2 (3)
C (13)	35 (3)	42 (4)	50 (6)	-15 (4)	-3 (3)	3 (3)
C (14)	25 (3)	47 (4)	44 (5)	-13 (4)	-8 (3)	2 (3)
C (15)	30 (3)	44 (4)	39 (5)	-1 (4)	-6 (3)	-10 (3)
C (16)	31 (3)	32 (3)	30 (5)	-16 (4)	-3 (3)	-1 (3)
C (17)	34 (3)	38 (4)	40 (5)	-23 (4)	-1 (3)	-5 (3)
C (18)	34 (3)	46 (4)	62 (7)	-16 (5)	-15 (4)	-7 (3)
C (19)	46 (4)	36 (4)	52 (7)	-16 (4)	-18 (4)	-8 (3)
C (20)	48 (4)	47 (4)	52 (6)	-24 (4)	-8 (4)	-7 (3)
C (21)	35 (3)	42 (4)	41 (6)	-24 (4)	-6 (3)	0 (3)
C (22)	62 (5)	59 (5)	74 (7)	-18 (5)	-27 (5)	-12 (4)
C (23)	44 (4)	43 (4)	44 (5)	-3 (4)	-11 (3)	-13 (3)
C (24)	45 (4)	41 (4)	53 (6)	-17 (5)	-10 (4)	-18 (3)
C (25)	46 (4)	49 (5)	68 (7)	-31 (5)	-22 (4)	-6 (3)
C (26)	43 (4)	58 (5)	51 (6)	-21 (5)	-16 (4)	-6 (4)
C (27)	33 (3)	43 (4)	36 (5)	-22 (4)	-9 (3)	-3 (3)
C (28)	37 (3)	45 (4)	18 (5)	-16 (4)	-3 (3)	-7 (3)
C (29)	61 (5)	68 (5)	30 (5)	-18 (5)	-9 (4)	-10 (4)
C (30)	80 (6)	75 (6)	24 (5)	-6 (5)	-3 (4)	-24 (5)
C (31)	57 (5)	52 (5)	41 (6)	3 (4)	5 (4)	-15 (4)
C (32)	33 (3)	46 (4)	37 (5)	-8 (4)	-1 (3)	-11 (3)
C (33)	27 (3)	31 (3)	36 (5)	-20 (4)	-9 (3)	0 (2)
C (34)	24 (3)	43 (4)	30 (5)	-13 (4)	-5 (3)	-4 (3)
C (35)	46 (4)	43 (4)	26 (6)	-10 (4)	2 (4)	-9 (3)
C (36)	51 (4)	45 (5)	27 (6)	-13 (5)	2 (4)	-6 (3)
C (37)	32 (3)	62 (5)	21 (5)	-17 (4)	4 (3)	2 (3)
C (38)	38 (3)	36 (4)	40 (6)	-16 (4)	-3 (4)	6 (3)

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C(39)	28(3)	37(4)	27(5)	-18(4)	3(3)	-1(3)
P	42(1)	48(1)	65(2)	-17(1)	-5(1)	-6(1)
F(1)	66(3)	78(3)	66(4)	-11(3)	1(2)	-19(2)
F(2)	102(4)	114(4)	81(4)	-15(4)	15(3)	-49(4)
F(3)	62(3)	80(3)	91(4)	-17(3)	-29(3)	-1(2)
F(4)	47(2)	66(3)	131(5)	-35(3)	-25(3)	-1(2)
F(5)	65(3)	68(3)	104(5)	-53(3)	-6(3)	-6(2)
F(6)	83(3)	47(3)	112(5)	-40(3)	-26(3)	5(2)
C(40)	116(9)	79(7)	73(8)	-10(6)	5(6)	-43(6)
C(41)	138(10)	74(7)	86(8)	7(6)	-9(7)	-6(6)
C(42)	64(6)	111(8)	127(10)	-44(8)	-1(6)	-28(6)
C(43)	106(10)	500(30)	38(8)	-47(13)	-21(7)	176(16)
C(44)	99(8)	103(8)	77(8)	13(7)	-9(6)	2(6)
C(45)	107(8)	81(7)	112(10)	-5(7)	-32(7)	-11(6)
C(46)	96(8)	89(8)	108(10)	18(7)	-11(7)	-28(6)
C(47)	105(9)	129(10)	95(10)	-44(8)	-28(7)	-3(7)
C(48)	67(6)	75(6)	128(10)	14(6)	-3(6)	-20(5)
N(9)	74(5)	63(4)	66(5)	-16(4)	7(4)	-33(4)
N(10)	55(4)	61(4)	61(5)	-7(4)	-13(4)	-7(3)
N(11)	58(4)	75(5)	59(6)	1(5)	-2(4)	-14(4)
O(1)	116(6)	170(8)	112(7)	-45(6)	-6(5)	-94(6)
O(2)	143(8)	199(11)	185(11)	-108(9)	-54(8)	-4(7)
O(3)	150(7)	112(6)	118(7)	6(5)	14(5)	-66(6)

Table 4: Hydrogen coordinates ($\times 10^4$) and isotropicdisplacement parameters ($\text{\AA}^2 \times 10^3$).

	x	y	z	U(eq)
H(1A)	3940	-1420	2727	43
H(2A)	5676	-2060	2413	45
H(3A)	6940	-1311	2874	51
H(4A)	6421	125	3557	46
H(7A)	5744	1464	4351	38
H(9A)	3105	3366	4932	38
H(12A)	1363	3708	4718	46
H(13A)	-394	3925	4471	51
H(14A)	-961	2708	3817	47
H(15A)	193	1320	3464	46
H(17A)	6565	2664	4441	42
H(18A)	7530	3454	5202	54
H(20A)	4919	4585	6676	56
H(21A)	3948	3797	5924	45
H(22A)	7706	4369	6389	93
H(22B)	6847	4225	7294	93
H(22C)	6771	5270	6494	93
H(23A)	1363	-1371	4154	52
H(24A)	823	-2525	3436	52
H(25A)	1113	-2327	1761	60
H(26A)	1814	-873	847	58
H(29A)	2112	770	87	62
H(30A)	2836	2257	-605	71
H(31A)	3560	3054	362	63
H(32A)	3480	2374	2015	46
H(35A)	1524	-2606	8096	46
H(36A)	717	-2184	9506	49
H(38A)	743	854	8306	46
H(39A)	1522	441	6870	36
H(40A)	4171	7032	7258	106
H(41A)	5095	4976	8943	158
H(41B)	4623	4188	8524	158
H(41C)	3957	4721	9337	158
H(42A)	2889	6185	7195	145
H(42B)	2524	5513	8220	145
H(42C)	3176	4961	7413	145
H(43A)	4651	9253	469	291
H(44A)	4151	9477	-1033	151
H(44B)	3121	9085	-1160	151
H(44C)	4221	8513	-1511	151
H(45A)	3484	6811	692	152
H(45B)	3786	6822	-423	152
H(45C)	2688	7385	-59	152
H(46A)	1188	4694	-370	123
H(47A)	2036	5272	1510	159
H(47B)	2088	4104	2092	159
H(47C)	1065	4902	2223	159
H(48A)	398	3462	701	144

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H(48B)	35	3761	1716	144
H(48C)	1054	2960	1581	144

Table 5: Torsion angles [deg].

N(2)-Ru-N(1)-C(1)	-174.7(6)
N(5)-Ru-N(1)-C(1)	-75.0(6)
N(6)-Ru-N(1)-C(1)	97.2(6)
N(4)-Ru-N(1)-C(1)	3.4(6)
N(3)-Ru-N(1)-C(1)	-170.3(5)
N(2)-Ru-N(1)-C(5)	-0.6(4)
N(5)-Ru-N(1)-C(5)	99.1(4)
N(6)-Ru-N(1)-C(5)	-88.7(4)
N(4)-Ru-N(1)-C(5)	177.5(4)
N(3)-Ru-N(1)-C(5)	3.9(8)
N(5)-Ru-N(2)-C(6)	-89.3(4)
N(6)-Ru-N(2)-C(6)	90.1(4)
N(4)-Ru-N(2)-C(6)	-30(3)
N(1)-Ru-N(2)-C(6)	-2.7(4)
N(3)-Ru-N(2)-C(6)	179.0(5)
N(5)-Ru-N(2)-C(10)	96.8(5)
N(6)-Ru-N(2)-C(10)	-83.8(5)
N(4)-Ru-N(2)-C(10)	156(3)
N(1)-Ru-N(2)-C(10)	-176.5(5)
N(3)-Ru-N(2)-C(10)	5.1(4)
N(2)-Ru-N(3)-C(15)	176.7(5)
N(5)-Ru-N(3)-C(15)	77.9(5)
N(6)-Ru-N(3)-C(15)	-94.5(5)
N(4)-Ru-N(3)-C(15)	-1.2(5)
N(1)-Ru-N(3)-C(15)	172.2(5)
N(2)-Ru-N(3)-C(11)	-2.9(4)
N(5)-Ru-N(3)-C(11)	-101.6(4)
N(6)-Ru-N(3)-C(11)	85.9(4)
N(4)-Ru-N(3)-C(11)	179.2(4)
N(1)-Ru-N(3)-C(11)	-7.4(8)
N(2)-Ru-N(4)-C(23)	120(3)
N(5)-Ru-N(4)-C(23)	179.4(6)
N(6)-Ru-N(4)-C(23)	-0.4(5)
N(1)-Ru-N(4)-C(23)	92.4(5)
N(3)-Ru-N(4)-C(23)	-89.9(5)
N(2)-Ru-N(4)-C(27)	-51(3)
N(5)-Ru-N(4)-C(27)	8.1(4)
N(6)-Ru-N(4)-C(27)	-171.8(4)
N(1)-Ru-N(4)-C(27)	-78.9(4)
N(3)-Ru-N(4)-C(27)	98.7(4)
N(2)-Ru-N(5)-C(32)	-6.5(5)
N(6)-Ru-N(5)-C(32)	177.9(13)
N(4)-Ru-N(5)-C(32)	177.1(5)
N(1)-Ru-N(5)-C(32)	-86.0(5)
N(3)-Ru-N(5)-C(32)	72.9(5)
N(2)-Ru-N(5)-C(28)	172.6(4)
N(6)-Ru-N(5)-C(28)	-3.0(18)
N(4)-Ru-N(5)-C(28)	-3.8(4)
N(1)-Ru-N(5)-C(28)	93.1(5)
N(3)-Ru-N(5)-C(28)	-108.0(4)
N(2)-Ru-N(6)-C(33)	178(100)
N(5)-Ru-N(6)-C(33)	-6(6)

N(4)-Ru-N(6)-C(33)	-5(5)
N(1)-Ru-N(6)-C(33)	-102(5)
N(3)-Ru-N(6)-C(33)	99(5)
C(5)-N(1)-C(1)-C(2)	-0.7(9)
Ru-N(1)-C(1)-C(2)	173.2(5)
N(1)-C(1)-C(2)-C(3)	1.8(10)
C(1)-C(2)-C(3)-C(4)	-1.8(10)
C(2)-C(3)-C(4)-C(5)	0.8(10)
C(1)-N(1)-C(5)-C(4)	-0.3(9)
Ru-N(1)-C(5)-C(4)	-175.2(4)
C(1)-N(1)-C(5)-C(6)	178.3(5)
Ru-N(1)-C(5)-C(6)	3.4(6)
C(3)-C(4)-C(5)-N(1)	0.3(10)
C(3)-C(4)-C(5)-C(6)	-178.2(6)
C(10)-N(2)-C(6)-C(7)	-0.4(8)
Ru-N(2)-C(6)-C(7)	-174.2(4)
C(10)-N(2)-C(6)-C(5)	178.9(5)
Ru-N(2)-C(6)-C(5)	5.1(7)
N(1)-C(5)-C(6)-N(2)	-5.5(8)
C(4)-C(5)-C(6)-N(2)	173.0(6)
N(1)-C(5)-C(6)-C(7)	173.8(6)
C(4)-C(5)-C(6)-C(7)	-7.7(10)
N(2)-C(6)-C(7)-C(8)	-0.5(9)
C(5)-C(6)-C(7)-C(8)	-179.8(6)
C(6)-C(7)-C(8)-C(9)	1.4(9)
C(6)-C(7)-C(8)-C(16)	179.3(6)
C(7)-C(8)-C(9)-C(10)	-1.4(9)
C(16)-C(8)-C(9)-C(10)	-179.3(6)
C(6)-N(2)-C(10)-C(9)	0.5(9)
Ru-N(2)-C(10)-C(9)	174.2(4)
C(6)-N(2)-C(10)-C(11)	-179.8(5)
Ru-N(2)-C(10)-C(11)	-6.1(7)
C(8)-C(9)-C(10)-N(2)	0.5(9)
C(8)-C(9)-C(10)-C(11)	-179.3(6)
C(15)-N(3)-C(11)-C(12)	-0.1(9)
Ru-N(3)-C(11)-C(12)	179.5(5)
C(15)-N(3)-C(11)-C(10)	-179.0(5)
Ru-N(3)-C(11)-C(10)	0.7(6)
N(2)-C(10)-C(11)-C(12)	-175.6(6)
C(9)-C(10)-C(11)-C(12)	4.2(10)
N(2)-C(10)-C(11)-N(3)	3.2(7)
C(9)-C(10)-C(11)-N(3)	-177.0(6)
N(3)-C(11)-C(12)-C(13)	-1.0(10)
C(10)-C(11)-C(12)-C(13)	177.7(6)
C(11)-C(12)-C(13)-C(14)	0.8(10)
C(12)-C(13)-C(14)-C(15)	0.6(10)
C(11)-N(3)-C(15)-C(14)	1.6(9)
Ru-N(3)-C(15)-C(14)	-177.9(5)
C(13)-C(14)-C(15)-N(3)	-1.9(10)
C(7)-C(8)-C(16)-C(21)	-156.5(6)
C(9)-C(8)-C(16)-C(21)	21.3(9)
C(7)-C(8)-C(16)-C(17)	20.1(9)
C(9)-C(8)-C(16)-C(17)	-162.1(6)
C(21)-C(16)-C(17)-C(18)	2.4(9)
C(8)-C(16)-C(17)-C(18)	-174.2(6)

C(16)-C(17)-C(18)-C(19)	0.4(10)
C(17)-C(18)-C(19)-C(20)	-3.2(10)
C(17)-C(18)-C(19)-C(22)	175.8(6)
C(18)-C(19)-C(20)-C(21)	3.3(10)
C(22)-C(19)-C(20)-C(21)	-175.7(6)
C(17)-C(16)-C(21)-C(20)	-2.3(9)
C(8)-C(16)-C(21)-C(20)	174.3(6)
C(19)-C(20)-C(21)-C(16)	-0.6(10)
C(27)-N(4)-C(23)-C(24)	3.0(9)
Ru-N(4)-C(23)-C(24)	-168.1(5)
N(4)-C(23)-C(24)-C(25)	1.6(10)
C(23)-C(24)-C(25)-C(26)	-3.3(10)
C(24)-C(25)-C(26)-C(27)	0.4(10)
C(23)-N(4)-C(27)-C(26)	-5.9(9)
Ru-N(4)-C(27)-C(26)	166.3(5)
C(23)-N(4)-C(27)-C(28)	176.9(5)
Ru-N(4)-C(27)-C(28)	-10.9(7)
C(25)-C(26)-C(27)-N(4)	4.4(9)
C(25)-C(26)-C(27)-C(28)	-178.8(6)
C(32)-N(5)-C(28)-C(29)	-4.4(9)
Ru-N(5)-C(28)-C(29)	176.4(5)
C(32)-N(5)-C(28)-C(27)	178.4(5)
Ru-N(5)-C(28)-C(27)	-0.8(7)
N(4)-C(27)-C(28)-N(5)	7.7(8)
C(26)-C(27)-C(28)-N(5)	-169.3(6)
N(4)-C(27)-C(28)-C(29)	-169.3(6)
C(26)-C(27)-C(28)-C(29)	13.6(10)
N(5)-C(28)-C(29)-C(30)	3.6(11)
C(27)-C(28)-C(29)-C(30)	-179.5(7)
C(28)-C(29)-C(30)-C(31)	-0.5(12)
C(29)-C(30)-C(31)-C(32)	-1.6(12)
C(28)-N(5)-C(32)-C(31)	2.3(9)
Ru-N(5)-C(32)-C(31)	-178.6(5)
C(30)-C(31)-C(32)-N(5)	0.7(11)
Ru-N(6)-C(33)-N(7)	70(7)
C(34)-N(7)-C(33)-N(6)	168(4)
C(33)-N(7)-C(34)-C(39)	-10.1(8)
C(33)-N(7)-C(34)-C(35)	170.0(5)
C(39)-C(34)-C(35)-C(36)	0.7(9)
N(7)-C(34)-C(35)-C(36)	-179.4(5)
C(34)-C(35)-C(36)-C(37)	-0.3(10)
C(35)-C(36)-C(37)-C(38)	-0.9(10)
C(35)-C(36)-C(37)-N(8)	177.8(6)
N(8)#1-N(8)-C(37)-C(36)	177.8(7)
N(8)#1-N(8)-C(37)-C(38)	-3.6(10)
C(36)-C(37)-C(38)-C(39)	1.6(9)
N(8)-C(37)-C(38)-C(39)	-176.9(5)
C(37)-C(38)-C(39)-C(34)	-1.2(9)
N(7)-C(34)-C(39)-C(38)	-179.8(5)
C(35)-C(34)-C(39)-C(38)	0.1(8)
O(1)-C(40)-N(9)-C(41)	3.4(17)
O(1)-C(40)-N(9)-C(42)	-178.5(11)
O(2)-C(43)-N(10)-C(44)	-173.6(7)
O(2)-C(43)-N(10)-C(45)	3.8(13)
O(3)-C(46)-N(11)-C(47)	-2.8(17)

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O(3)-C(46)-N(11)-C(48)

176.9(10)

Symmetry transformations used to generate equivalence atoms:
#1 -x, -y, -z+2

6.2 Appendix B: Techniques

6.2.1 ITO Preparation and Etching

Etching of the ITO plate was performed as follows: The ITO plate was first cleaned by soaking the plate in a solution of 20% ethanolamine for 20 minutes. The intact areas of ITO were first protected using nailpolish and the plate was left to dry overnight. The plate was soaked again in a beaker contained an aqueous solution of 20% HCl, 5% HNO₃, and a few drops of liquid detergent. The solution was heated to between 50 and 60 °C for approximately five minutes. The plate is then rinsed in a 10% aqueous solution of Na₂CO₃. The resistance of the etched portions of the plate was then tested

6.2.2 OTTLE Experiment with ITO Electrode: Troubleshooting

An interference pattern is sometimes noted in the UV-vis spectrum when an ITO (on quartz) plate is used in the OTTLE experiment. The appearance of a “rainbow” effect in the cell can be seen and the pattern in the electronic spectrum consists of a wavy line of varying amplitude. This interference pattern could not be removed by background subtraction and was only found to occur when the ITO plate was placed directly on the bottom quartz plate in the OTTLE cell. The bottom quartz plate was removed to avoid this interference pattern and was replaced with same size and thickness of an opening plastic spacer allowing the light to pass through the cell.

6.2.3 Ag/AgCl Reference Electrode Preparation

Two strips of silver wire with known diameter and length were twisted together. The wire was soaked in 3 M HNO_3 for five minutes and rinsed with deionized water. A standard H-cell with working counter, and reference electrodes was set up using the coiled silver wire as the working electrode and 0.1 M HCl as the electrolyte. The current of the cell was adjusted such that the current density is 0.4 mA/cm^2 of silver wire, and the cell was left for twenty minutes. The Ag/AgCl electrode was then rinsed with deionized water and left to dry.

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