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**Mononuclear and Dinuclear (2,2'-Bipyridine)(2,2':6',2''-
Terpyridine)Ruthenium(II) Complexes With Phenylcyanamide Ligands**

Peter J. Mosher

**A thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfillment of the requirements for the degree of
Master of Science**

**Department of Chemistry
Carleton University
Ottawa, ON Canada
September 2001**

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Terpyridine)Ruthenium(II) Complexes With Phenylcyanamide Ligands**

submitted by Peter J. Mosher
in partial fulfillment of the requirements for
the degree of Master of Science

Chair, Department of Chemistry, Dr. Gerald Buchanan

Thesis Supervisor, Dr. Robert J. Crutchley

Abstract

[Ru(bpy)(trpy)L]PF₆ complexes, where trpy is 2,2':6',2''-terpyridine, bpy is 2,2'-bipyridine and L is 4-methyl-, 3-chloro-, 2,4-dichloro-, 2,4,5-trichloro-, 2,4,6-trichloro-, 2,3,4,5-tetrachloro- 2,3,5,6-tetrachloro-or pentachlorophenylcyanamido, have been prepared and characterized by elemental analysis, IR, ¹H-NMR, and electronic absorption spectroscopies, and cyclic voltammetry. A crystal structure of [Ru(bpy)(trpy)(2,4-dichlorophenylcyanamido)]PF₆ showed the cyanamide group coordinated to Ru(II) by its nitrile nitrogen. Crystal structure data are space group = P-1, with a, b, and c = 11.681(4), 12.240(5) and 15.017(5) Å, respectively, α, β, and γ = 68.00(2), 70.05(3), and 78.55(2)°, respectively, V = 1865(1) Å³, and Z = 2. The structure was refined by using 4848 independent reflections with $I > 2\sigma(I)$ to a final R factor of 0.0722. Spectroelectrochemistry was used to generate the electronic absorption spectra of the Ru(III) complexes, [Ru(bpy)(trpy)L]²⁺ in acetonitrile solution. The spectral data associated with the Ru(III)-cyanamido LMCT chromophore were compared to those derived from their pentaammineruthenium(III) analogues in order to gain a greater understanding of the influence of spectator ligands on the nature of the Ru(III)-cyanamido bond. The data supports greater covalency in the Ru(III)-cyanamide bond of [Ru(bpy)(trpy)L]²⁺ complexes compared to their pentaammineruthenium analogues.

The novel mononuclear and dinuclear complexes, [Ru(trpy)(bpy)(apc)][PF₆], [{Ru(trpy)(bpy)}₂(adpc)][PF₆]₂ (bpy = 2,2'-bipyridine, trpy = 2,2':6',2''-terpyridine, apc⁻ =

4-azo(phenylcyanamido)benzene and $\text{adpc}^{2-} = 4,4'$ -azodi(phenylcyanamido) were synthesized and characterized by ^1H NMR, UV-vis, and cyclic voltammetry. Crystallography showed that the dinuclear Ru(II) complex crystallizes from N,N-dimethylformamide/ether solution as $[\{\text{Ru}(\text{trpy})(\text{bpy})\}_2(\text{adpc})][\text{PF}_6]_2 \cdot 2(\text{ether}) \cdot 2\text{DMF}$. Crystal structure data are crystal system = triclinic, space group = P-1, with a, b, and c = 12.480(2), 13.090(3) and 14.147(3) Å, respectively, α , β , and γ = 79.792(3), 68.027(3), and 64.447(3)°, respectively, V = 1933.3(6) Å³, and Z = 1. The structure was refined to a final R factor of 0.0421. The mixed-valence complex with metal ions separated by a through space distance of 19.5 Å, is a Class III system, having a comproportionation constant $K_c = 1.3 \times 10^{13}$ and an intervalence band at 1920 nm ($\epsilon_{\text{max}} = 10,000 \text{ M}^{-1} \text{ cm}^{-1}$), in dimethylformamide solution. The results of this study strongly suggest that the bridging ligand adpc^{2-} can mediate metal-metal coupling through both hole-transfer and electron-transfer superexchange mechanisms.

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Contents

	Page
Glossary of Acronyms	7
List of Figures	8
List of Tables	10
1. Introduction	11
2. Experimental	24
2.1 Equipment	24
2.2 Solvents	25
2.3 Reagents	25
2.4 Synthetic Work	25
2.5 Crystallography	31
2.6 Oscillator Strength Calculation	32
2.7 Molecular Modeling	33
3. Ru(bpy)(trpy) Phenylcyanamide Complexes	34
3.1 Results	34
3.2 Discussion	48
4. Ru(bpy)(trpy) Azo Complexes	57
4.1 Results	57
4.2 Discussion	73
5. Conclusions and Future Studies	78

	Page
6. References	83
Appendix A. X-ray Crystallographic Data for	
[Ru(bpy)(trpy)(2,4-Cl₂pcyd)][PF₆]·DMF	A0
Appendix B. X-ray Crystallographic Data for	
[{Ru(bpy)(trpy)}₂(μ-adpc)][PF₆]₂·2(ether)·2(DMF)	B0

Glossary of Acronyms

bpy	2,2'-Bipyridine
DMF	N,N-Dimethyl Formamide
$\epsilon_{\max}$	Molar Absorptivity at Maximum Absorption in M^{-1}
E_{LMCT}	LMCT Charge Transfer Energy
f	Oscillator Strength
H_{LM}	Ru(III) Ligand-Metal Coupling Element
H_{ML}	Ru(II) Metal-Ligand Coupling Element
$H_{\text{MM'}}$	Metal-Metal Coupling Element
HOMO	Highest Occupied Molecular Orbital
ILCT	Intraligand Charge Transfer
LMCT	Ligand to Metal Charge Transfer
LUMO	Lowest Unoccupied Molecular Orbital
MeCN	Acetonitrile
MeNO ₂	Nitromethane
MLCT	Metal to Ligand Charge Transfer
MMCT	Metal to Metal Charge Transfer
ν	Band Energy at $\epsilon_{\max}$ in cm^{-1}
$\nu_{1/2}$	Bandwidth at $1/2\epsilon_{\max}$ in cm^{-1}
pcyd	Phenylcyanamide
trpy	2,2':6',2''-Terpyridine

List of Figures

Figure	Page
1. Schematic of conducting polymer chain incorporating metal-cyanamide linkage.	12
2. State to state potential energy curves for a ruthenium(III)-pcyd complex.	13
3. The phenylcyanamido ligands (L) used in $[\text{Ru}(\text{bpy})(\text{trpy})(\text{L})]^+$ complexes.	15
4. Several polythiophenes and their respective band gaps.	16
5. Superimposed potential energy surfaces for the MMCT band	19
6. Electronic spectrum of $[\text{Ru}(\text{bpy})(\text{trpy})(2,3,4,5\text{-Cl}_4\text{pcyd})]^{2+}$ showing the best fit of three gaussian curves used for the calculation of oscillator strength.	33
7. ^1H NMR spectra of $[\text{Ru}(\text{bpy})(\text{trpy})(2,4\text{-Cl}_2\text{pcyd})][\text{PF}_6]$ and $\text{Ti}[2,4\text{-Cl}_2\text{pcyd}]$.	36
8. ORTEP drawing of $[\text{Ru}(\text{bpy})(\text{trpy})(2,4\text{-Cl}_2\text{pcyd})]\text{PF}_6 \cdot \text{DMF}$.	37
9. Cyclic voltammogram of $[\text{Ru}(\text{bpy})(\text{trpy})(2,4\text{-Cl}_2\text{pcyd})][\text{PF}_6]$.	42
10. Quantitative electronic spectrum of $[\text{Ru}(\text{bpy})(\text{trpy})(2,4\text{-Cl}_2\text{pcyd})][\text{PF}_6]$.	45
11. OTTLE cell electronic spectra of $[\text{Ru}(\text{bpy})(\text{trpy})(2,3,4,5\text{-Cl}_4\text{pcyd})]^{1+/2+}$	47
12. LMCT energy verses ΔE for various $[\text{Ru}(\text{bpy})(\text{trpy})(\text{pcyd})]^-$ complexes.	50
13. LMCT energy verses ΔE for various $[\text{Ru}(\text{bpy})(\text{trpy})\text{L}]^{2+}$ and $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$ complexes.	51
14. Oscillator strength, f verses LMCT energy for various $[\text{Ru}(\text{bpy})(\text{trpy})\text{L}]^{2+}$ and $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$ complexes.	53
15. ORTEP drawing of $[\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-adpc})][\text{PF}_6]_2$.	58

16. ^1H NMR spectra of $\text{Ti}_2[\text{adpc}]$ and $[\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-adpc})][\text{PF}_6]_2$	62
17. Cyclic voltammograms of $[\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-adpc})][\text{PF}_6]_2$ and $[\text{Ru}(\text{bpy})(\text{trpy})(\text{apc})][\text{PF}_6]$ in acetonitrile.	65
18. Cyclic voltammograms of $[\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-dicyd})][\text{PF}_6]_2$ and $[\text{Ru}(\text{bpy})(\text{trpy})(2,4\text{-Cl}_2\text{pcyd})][\text{PF}_6]$ in acetonitrile.	65
19. OTTLE cell vis-NIR spectra of $[\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-adpc})]^{2+}$.	68
20. Spectroelectrochemical oxidation of $[\text{Ru}(\text{bpy})(\text{trpy})(\text{apc})]^+$ in DMF.	69
21. Metal-metal charge transfer band of $[\{\text{Ru}(\text{trpy})(\text{bpy})\}_2(\mu\text{-adpc})]^{3+}$ in DMF.	71
22. Superexchange pathways in a dinuclear mixed valence ruthenium complex.	74
23. <i>Ab initio</i> calculation of the HOMO and LUMO of adpc^{2-} and dicyd^{2-}.	76
24. Proposed superexchange pathways utilized by $[\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-adpc})]^{3+}$.	77
25. A rotaxane formed by the association of a cyclodextrin ring with $[\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-adpc})]^{2+}$.	81

List of Tables

Table	Page
1. Crystal Data and Structure Refinement for [Ru(bpy)(trpy)(2,4-Cl ₂ pcyd)]PF ₆ ·DMF.	38
2. Selected crystal structure data for [Ru(bpy)(trpy)(2,4-Cl ₂ pcyd)]PF ₆ ·DMF.	39
3. Electrochemical data ^a for [Ru(bpy)(trpy)L] ⁺ and [Ru(NH ₃) ₅ L] ²⁺ complexes in acetonitrile.	41
4. Electronic spectroscopy data ^a for [Ru(bpy)(trpy)L] ⁺ complexes and the Ru(III) LMCT spectral data of the [Ru(bpy)(trpy)L] ²⁺ complexes in acetonitrile.	44
5. LMCT oscillator strengths ^a and metal-ligand coupling elements ^b derived from the b ₁ →b ₁ [*] LMCT transition of bipyridine(terpyridine)ruthenium(III) and pentaammineruthenium(III) phenylcyanamide (pcyd ⁻) complexes.	54
6. Crystal data for [{Ru(bpy)(trpy)} ₂ (μ-adpc)][PF ₆] ₂ ·2(ether)·2(DMF).	59
7. Selected crystal structure data for [{Ru(trpy)(bpy)} ₂ (μ-adpc)][PF ₆] ₂ ·2(ether)·2(DMF).	60
8. Cyclic voltammetry data ^a of azo ligands and complexes with Ru(bpy)(trpy).	64
9. Electronic spectral data ^a for apc ⁻ , adpc ²⁻ and their Ru(II) and Ru(III) complexes.	67
10. Electrochemical and MMCT band spectral data for [{Ru(trpy)(bpy)} ₂ (μ-adpc)] ³⁺ in various solvents.	72

1. Introduction

A fundamental understanding of intramolecular electron transfer is of key importance to the design of molecular devices such as low impedance molecular wires, molecular switches, as well as the creation of novel materials with useful magnetic or optical properties. Such devices could find applications in a variety of areas such as nanoscale electronics, biological probes, magnetic shields, and video displays.

Much effort has gone into the development of conducting polymers on one hand, while others have focused on electron transfer in metal complexes. Bridging the two fields to create hybrid materials requires a firm understanding of the electronic architecture of the metal-ligand bond. There has been a great deal of focus on ruthenium complexes in particular. The coordination chemistry of ruthenium (II) and (III) has been well developed due to their ability to form stable complexes with a wide range of organic ligands. In addition to this, a close energy and symmetry match between ruthenium $d\pi$ and terminal nitrogen $p\pi$ orbitals of cyanamide ligands ($\text{N}=\text{C}=\text{N}-\text{R}$) has been shown.^{1,2} The cyanamide group could act as an energy bridge to conducting polymer chains which are less suitable for coordination to ruthenium. This arrangement may yield desirable properties for the delocalized π systems required in metal-hybrid molecular wires as depicted in Figure 1.

Figure 1. Schematic of conducting polymer chain incorporating metal-cyanamide linkage.

When ruthenium(III) is bound to π -donating ligands such as phenylcyanamides (pcyd) there arises a low energy ligand-to-metal charge transfer (LMCT) band in the electronic spectrum.^{1,3} The LMCT event involves the oxidation of the pcyd⁻ ligand and reduction of the Ru(III) ion and so the energy of this band (E_{LMCT}) is related to the difference between the metal (Ru(III/II)) and ligand (L(0/-1)) redox couples (ΔE).⁴ Figure 2 illustrates this qualitatively, while the expression for E_{LMCT} is given by :

$$E_{\text{LMCT}} = [E(\text{Ru}^{\text{III/II}}) - E(\text{L}^{0/-1}) - C] + \chi \quad (1)$$

where C is a fudge factor to account for the impossibility of measuring $E(\text{Ru}^{\text{III/II}})$ after the ligand is oxidized to $\text{L}(0)$, and χ represents the inner and outersphere reorganizational energies involved in the LMCT event.

The ligand-metal coupling element⁵ H_{LM} can be derived from the oscillator strength (f) of

Figure 2. State to state potential energy curves for a ruthenium(III)-pcyd complex illustrating the relationship between ΔE and E_{LMCT} .

the LMCT band. Oscillator strength can be experimentally derived from the integral of the molar absorptivity verses energy of the charge transfer band, and it can be calculated theoretically from the transition dipole moment (M) of the LMCT by the expression:⁶

$$f = (1.085 \times 10^{11}) G \cdot E_{LMCT} M^2 \quad (2)$$

where G is degeneracy of states and M is approximately given by:

$$M \approx reS_{ad} \quad (3)$$

where r is the transition dipole moment length, e is the electronic charge, and S_{ad} is the overlap integral between the donor and acceptor wavefunctions. Creutz, Newton and Sutin's (CNS) method for deriving coupling elements⁷ from charge transfer band oscillator strengths assumes that the transition dipole moment lies along the bonding axis and that the overlap between metal and ligand orbitals is equal to zero. For a ligand-to-metal charge transfer (LMCT) band, the expression for the metal-ligand coupling element H_{LM} in cm^{-1} is:

$$H_{LM} = \frac{303}{r} (E_{LMCT} \cdot f)^{1/2} \quad (4)$$

where r is the transition dipole moment length in Å, E_{LMCT} is the LMCT band energy in cm^{-1} at ϵ_{max} and f is the oscillator strength of the LMCT band. This expression is identical in form to that derived by Hush to determine metal-metal coupling elements from metal-to-metal charge transfer (MMCT) band oscillator strengths.⁸

It has been shown in previous studies of dinuclear pentaammine, tetraammine and triammine ruthenium(III) complexes, that the Ru(III)-cyanamide LMCT chromophore is remarkably sensitive to the nature of the solvent.⁹ Simply by changing the donor strength of the solvent, the energy and oscillator strength of the LMCT band varies dramatically in a manner that can be related to the ligand-metal π -coupling element H_{LM} . These coupling elements were then used to predict metal-metal coupling in the mixed-valence complexes. The agreement between experiment and theory was quite reasonable and strongly

supported the relationship between coupling elements and charge transfer band oscillator strengths.

It should be possible to purposefully construct a series of complexes in which the assumptions of equation 2 can be tested. In this regard, a series of $[\text{Ru}(\text{bpy})(\text{trpy})\text{L}]^+$ complexes were synthesized and characterized, where trpy is 2,2':6',2''-terpyridine, bpy is 2,2'-bipyridine, and L is the phenylcyanamido anion ligands depicted in Figure 3. Spectroelectrochemical oxidation to the Ru(III) complexes permitted an analysis of their LMCT spectral properties in comparison to their pentaammineruthenium(III) analogues.¹⁰

Figure 3. The phenylcyanamido ligands (L) used in $[\text{Ru}(\text{bpy})(\text{trpy})(\text{L})]^+$ complexes.

The creation of hybrid polymeric materials that possess useful optical, magnetic and/or electronic properties requires multidisciplinary research and is a very active field.¹¹ These properties depend upon the degree of conjugation between the units making up the polymer chain. One way of achieving a high degree of extended conjugation, and hence a narrow band gap, has been to synthesize polythiophenes made up of alternating donor/acceptor repeat units¹². For example, poly(diamino/dinitro)thiophene has a band gap of 1.1 eV while that of the parent polythiophene is about 2 eV¹³ (Figure 4). Alternatively, increasing the quinoid character of the polythiophene backbone has been found to have a similar effect.¹⁴ For example, polyisothianaphthene exhibits a band gap of only 1.0 eV.

Figure 4. Several polythiophenes and their respective band gaps.

Band gap energy is a macroscopic property but at the molecular level it is analogous to the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The use of an oligomer as a bridging ligand in a dinuclear mixed-valence complex would provide information about its electronic structure. This is because the mediation of electronic interactions by a bridging molecule can be quantitatively modeled by the Marcus-Hush theory for mixed-valence systems.¹⁵ Thus, the study of mixed-valence complexes can provide the knowledge to purposefully synthesize novel polymeric materials.

There has been much study of electron transfer in dinuclear mixed-valence complexes such as Ru(II)-L-Ru(III), in which L is a bridging ligand. Robin and Day classifies these complexes in terms of the extent of delocalization of the odd electron¹⁶. Class I represents species in which the electron is valence trapped, Class III is fully delocalized (shared by both metals), and Class II is an intermediate case.

A mixed valence complex can be produced in solution by a one-electron oxidation:

It exists in solution according to the following equilibrium:

with an equilibrium constant, K_c (the comproportionation constant).

Cyclic voltammetry of the complex in solution provides a measure of the free energy of comproportionation (ΔG_c) via the Nernst equation:

$$\Delta G_c = -nF \Delta E \quad (7)$$

where ΔE is the difference between the redox couples of the two metal centres and F is Faraday's constant. This allows one to calculate K_c from

$$K_c = \exp[-\Delta G_c/RT] \quad (8)$$

where R is the gas constant and T is temperature.

Figure 5 shows a potential energy diagram of a symmetrical mixed valence system. $\Delta G_r'$ represents the lowering in energy of a delocalized wavefunction compared to the localized Class (I) system. For the Class (III) case $\Delta G_r'$ is a major component of ΔG_c , the free energy of comproportionation. It is this stabilization energy which is the driving force to the formation of a mixed valence state. ΔG_c is made up of the following free energy terms:¹⁷

$$\Delta G_c = \Delta G_s + \Delta G_e + \Delta G_i + \Delta G_r + \Delta G_{AF} \quad (9)$$

Figure 5. Superimposed potential energy surfaces for the metal-to-metal charge transfer band (MMCT) of a symmetric Class III complex (black) and Class I (grey). E_{MMCT} is the optical energy of the MMCT band, $H_{MM'} = \frac{1}{2}E_{MMCT}$ is the resonance exchange integral, ΔG_{th} is the thermal electron-transfer barrier, and $\Delta G_r' = H_{MM'} - \Delta G_{th}$ is the free energy of resonance exchange. Note that $\Delta G_r = 2\Delta G_r'$ because of the factor of 2 in equation (6).

where ΔG_s reflects the statistical distribution of the comproportionation equilibrium ($K_{\text{statistical}} = 4$), 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, ΔG_r is the free energy of resonance exchange and ΔG_{AF} is the free energy of antiferromagnetic exchange. Of all the terms making up ΔG_C , only ΔG_{AF} serves

to lower its magnitude. ΔG_{AF} becomes important when antiferromagnetic exchange between the two metals is strong. This has the effect of stabilizing the [III,III] complex, thus shifting the equilibrium to the left in equation 6. When metal-metal coupling is very strong, the resonance exchange term ΔG_r largely determines the magnitude of ΔG_c .⁹

The MMCT band can be produced in solution by spectroelectrochemical oxidation of the [II,II] complex to form the mixed valence [III,II] species. For weakly coupled Class II materials the metal-metal coupling element $H_{MM'}$ can be calculated directly from the band energy and oscillator strength¹⁸ by equation 10:

$$H_{MM'} = \frac{303}{r} (E_{MMCT} \cdot f)^{1/2} \quad (10)$$

or related to the MLCT and LMCT band energies and coupling elements^{19,5} by equation 11, which also applies to more strongly coupled cases.

$$H_{MM'} = \frac{H_{ML} H_{M'L}}{2\Delta E_{ML}} + \frac{H_{LM} H_{LM'}}{\Delta E_{LM}} \quad (11)$$

Here H_{LM} is calculated from equation (4) using the LMCT band from the electronic spectrum of the [III,III] complex, while H_{ML} is calculated similarly from the MLCT band seen in the [II,II] complex. Since $H_{M'L}$ and $H_{LM'}$ cannot be experimentally determined they

are assumed to be equivalent to H_{ML} and H_{LM} respectively. ΔE_{ML} and ΔE_{LM} are the reduced MLCT and LMCT band energies respectively, calculated from:

$$\Delta E_{LM} = \left[0.5 \left(\frac{1}{E_{LMCT}} + \frac{1}{E_{LMCT} - E_{MMCT}} \right) \right]^{-1} \quad \Delta E_{ML} = \left[0.5 \left(\frac{1}{E_{MLCT}} + \frac{1}{E_{MLCT} - E_{MMCT}} \right) \right]^{-1}$$

Pentaammineruthenium dinuclear complexes incorporating various bridging ligands have played an important role in understanding how medium influences coupling in mixed-valence systems.^{20,21} For example, $[\{Ru(NH_3)_5\}_2(\mu\text{-}4,4'\text{-bpy})]^{5+}$, where 4,4'-bpy is:

is a Class II system having $K_c = 20$ and a MMCT band centered at 1030 nm ($\epsilon = 920 \text{ M}^{-1} \text{ cm}^{-1}$).²² Its solvent dependent properties are largely consistent with the predictions of Hush theory.¹³ Inserting an azo group between the pyridine groups of the bridging ligand does not appear to dramatically effect coupling. Thus, $[\{Ru(NH_3)_5\}_2(\mu\text{-}4,4'\text{-azopyridine})]^{5+}$:

is also Class II system having $K_c = 40$ and a MMCT band centered at 1400 nm ($\epsilon = 500 \text{ M}^{-1} \text{ cm}^{-1}$).²³ However, if the azo group is replaced by disulfide, coupling dramatically increases. $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-4,4'-disulfidebipyridine})]^{5+}$:

is a strongly coupled Class II system having $K_c = 8 \times 10^4$ and a MMCT band centered at 1500 nm ($\epsilon = 4300 \text{ M}^{-1} \text{ cm}^{-1}$).²⁴ Note that pyridine possesses low energy π^* orbitals that permit it to act as a π -acceptor ligand and disulfide is expected to be a π donor. This suggests that alternating donor and acceptor groups in a bridging ligand might lead to strong metal-metal coupling just as alternating donor and acceptor groups leads to a narrow band gap in polythiophenes.

In this study, the above rationale was applied to previous work²⁵ on the weakly coupled ($K_c = 16$) mixed-valence complex, $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-bp})]^{3+}$, where bp^{2-} is:

Since the cyanamide end groups act as π donors, it was desirable to insert a π acceptor in between to see its effect on metal-metal coupling. For this reason, the novel bridging ligand 4,4'-azodi(phenylcyanamide) dianion, adpc^{2-} was synthesized:

The Ru(II) dinuclear complex, $[\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-adpc})][\text{PF}_6]_2$ (bpy = 2,2'-bipyridine, trpy = 2,2':6',2''-terpyridine and adpc^{2-} = 4,4'-azodi(phenylcyanamido)), was also synthesized and characterized by ^1H NMR, UV-vis, cyclic voltammetry and x-ray crystallography. One electron oxidation of this complex yields a mixed valence system whose properties are consistent with Class III behavior-despite metal ions separated by 19.5 Å. The nature of the bridging ligand adpc^{2-} was investigated by *ab initio* methods to understand its effectiveness at mediating metal-metal coupling.

2. Experimental

2.1 Equipment

UV-vis spectroscopy was performed on a CARY 5 UV-vis-NIR spectrophotometer. IR spectra were taken with a BOMEM Michelson-100 FT-IR spectrophotometer (KBr disks). ^1H -NMR data from dimethylsulfoxide- d_6 solutions were obtained by using a Bruker AMX-400 spectrometer or a Varian Gemini 200 spectrometer. Cyclic voltammetry was performed using a BAS CV-27 voltammograph, and plotted on a BAS XY recorder. The sample cell consisted of a double walled glass crucible with an inner volume of ~ 15 mL which was fitted with a Teflon lid incorporating a three-electrode system and argon bubbler. The cell temperature was maintained at $(25.0 \pm 0.1)^\circ\text{C}$ by means of a HAAKE D8 re-circulating bath. BAS 2013 Pt electrodes (1.6 mm diameter) were used as the working and counter electrodes. A silver wire functioned as a pseudo-reference electrode. Ferrocene ($E^\circ = 0.665$ V versus NHE) and cobaltocenium hexafluorophosphate ($E^\circ = -0.664$ V versus NHE) were used as internal references.²⁶ An OTTLE cell was used to perform the spectroelectrochemistry.²⁷ The cell had interior dimensions of roughly 1 x 2 cm with a path length of 0.2 mm and was fitted with gold foil working and counter electrodes, and a silver \ silver chloride reference electrode. OTTLE work done in DMF used ITO (indium-tin oxide) coated glass for the working and counter electrodes. ITO glass plates were purchased from Delta-Technologies. Elemental analyses were performed by Canadian Microanalytical Services.

2.2 Solvents

Acetonitrile (Caledon Labs, reagent grade), N,N-Dimethylformamide (Sigma, ACS reagent), Anhydrous Diethyl Ether (Caledon Labs, ACS reagent), Acetone^a (Caledon Labs, laboratory grade), Toluene (Caledon Labs, spectro grade).

^aAcetone was distilled from glass prior to use.

2.2.1 Solvents for electrochemistry

Acetonitrile (Aldrich, HPLC grade) was dried over P₂O₅ and vacuum distilled.

Nitromethane (Anachemia, spec. grade) and N,N-dimethylformamide (Accusolv, spec. grade) were dried with anhydrous alumina and vacuum distilled.

2.3 Reagents

All of the reagents used were reagent grade or better. 4,4'-azodianiline was purchased from ACROS Organics and used as received. Tetrabutylammonium hexafluorophosphate (TBAH), purchased from Aldrich, was twice recrystallized from 1:1 ethanol:water and vacuum dried at 110 °C. Synthesis of [Ru(bpy)(trpy)Cl][PF₆] has been previously described.²⁸ The phenylcyanamide ligands were prepared from established methods.¹

2.4 Synthetic work

2.4.1 Preparation of [Ru(bpy)(trpy)(4-Mepcyd)][PF₆] $\cdot$ DMF. [Ru(bpy)(trpy)Cl][PF₆] (0.34 g, 0.51 mmol) was dissolved in 25 mL N,N'-dimethylformamide (DMF) in a 50 mL round bottom flask. Tl⁺[4-Mepcyd]⁻ (0.17 g, 0.51 mmol) was added and the deep red solution was refluxed for 18 hours. The reaction mixture was then chilled to -20°C and filtered to remove a fine white TlCl precipitate. The crude product precipitated as a deep

red-brown solid with the addition of 500 mL ether to the filtrate, and was collected by suction filtration. Recrystallization was achieved by the slow diffusion of ether into a saturated solution of the crude complex in DMF. Yield: 0.29g (76%). (NCN): 2156 cm^{-1} ; ^1H NMR (400 MHz, DMSO-d_6): 9.63(1)d, 8.87(1)d, 8.80(2)d, 8.68(2)d, 8.61(1)d, 8.35(1)t, 8.23(1)t, 8.03(3)m, 7.80(1)t, 7.68(2)d, 7.41(3)m, 7.11(1)t, 6.58(2)d, 5.82(2)d. Anal. Calcd for $[\text{Ru}(\text{bpy})(\text{trpy})(4\text{-Mepcyd})][\text{PF}_6]\cdot\text{DMF}$ ($\text{C}_{36}\text{H}_{33}\text{N}_8\text{OPF}_6\text{Ru}$): C, 51.49; H, 3.96; N, 13.34. Found: C, 51.03; H, 3.95; N, 13.22.

2.4.2 $[\text{Ru}(\text{bpy})(\text{trpy})(3\text{-Clpcyd})][\text{PF}_6]\cdot\text{H}_2\text{O}$ was prepared in the same manner as above. Yield: 0.28g (68%). (NCN): 2174, 2132 cm^{-1} ; ^1H NMR (400 MHz, DMSO-d_6): 9.63(1)d, 8.94(1)d, 8.88(2)d, 8.76(2)d, 8.67(1)d, 8.39(1)t, 8.30(1)t, 8.06(3)m, 7.84(1)t, 7.71(2)d, 7.43(3)m, 6.79(1)t, 6.45(1)d, 5.95(1)d, 5.83(1)s. Anal. Calcd for $[\text{Ru}(\text{bpy})(\text{trpy})(3\text{-Clpcyd})][\text{PF}_6]\text{H}_2\text{O}$ ($\text{C}_{32}\text{H}_{25}\text{N}_7\text{OPClF}_6\text{Ru}$): C, 47.74; H, 3.13; N, 12.18. Found: C, 48.33; H, 3.18; N, 12.05.

2.4.3 $[\text{Ru}(\text{bpy})(\text{trpy})(2,4\text{-Cl}_2\text{pcyd})][\text{PF}_6]\cdot\text{DMF}$ was prepared in the same manner as above. Yield: 0.38 g (89%). (NCN): 2167 cm^{-1} ; ^1H NMR (400 MHz, DMSO-d_6): 9.63(1)d, 8.94(1)d, 8.87(2)d, 8.75(2)d, 8.67(1)d, 8.39(1)t, 8.31(1)t, 8.08(3)m, 7.84(1)t, 7.71(2)d, 7.44(3)m, 7.14(1)t, 7.08(1)d, 6.75(1)m, 5.73(1)d. Anal. Calcd for $[\text{Ru}(\text{bpy})(\text{trpy})(2,4\text{-Cl}_2\text{pcyd})][\text{PF}_6]\cdot\text{DMF}$ ($\text{C}_{35}\text{H}_{29}\text{N}_8\text{OPCl}_2\text{F}_6\text{Ru}$): C, 46.99; H, 3.27; N, 12.53. Found: C, 46.86; H, 3.34; N, 12.47.

2.4.4 $[\text{Ru}(\text{bpy})(\text{trpy})(2,4,5\text{-Cl}_3\text{pcyd})][\text{PF}_6]\cdot\text{DMF}$ was prepared in the same manner as above. Yield: 0.32g (74%). (NCN): 2181 cm^{-1} ; ^1H NMR (400 MHz, DMSO-d_6): 9.61(1)d, 8.94(1)d, 8.90(2)d, 8.77(2)d, 8.68(1)d, 8.39(1)t, 8.33(1)t, 8.08(3)m, 7.85(1)t, 7.72(2)d,

7.45(3)m, 7.29(1)s, 7.14(1)t, 5.80(1)s. Anal. Calcd for $[\text{Ru}(\text{bpy})(\text{trpy})(2,4,5\text{-Cl}_3\text{pcyd})][\text{PF}_6]\text{DMF}$ ($\text{C}_{35}\text{H}_{28}\text{N}_8\text{OPCl}_3\text{F}_6\text{Ru}$): C, 45.25; H, 3.04; N, 12.06. Found: C, 45.28; H, 3.25; N, 12.09.

2.4.5 $[\text{Ru}(\text{bpy})(\text{trpy})(2,4,6\text{-Cl}_3\text{pcyd})][\text{PF}_6]\cdot 1/5(\text{toluene})$ was prepared in the same manner as above, but required further purification. The crude product (0.16 g) was dissolved in 25 mL of 1:1 MeCN:toluene, filtered, and purified by chromatography on a 50 cm x 3 cm diameter column containing ~250 g grade III alumina (Brockmann I, weakly acidic, 150 mesh) using 1:1 MeCN:toluene as the eluent. Three bands separated out on the column. The first band was eluted in ~100 mL and contained the target complex, which crystalized from the solution upon evaporation of the MeCN.

Yield: 0.03g (10%). (NCN): 2169 cm^{-1} ; ^1H NMR (400 MHz, DMSO- d_6): 9.62(1)d, 8.93(1)d, 8.87(2)d, 8.74(2)d, 8.67(1)d, 8.34(2)m, 8.09(3)m, 7.83(1)t, 7.69(2)d, 7.42(2)t, 7.34(d), 7.12(1)t, 7.06(2)s; Anal. Calcd for $[\text{Ru}(\text{bpy})(\text{trpy})(2,4,6\text{-Cl}_3\text{pcyd})][\text{PF}_6]\cdot 1/5(\text{toluene})$ ($\text{C}_{33.4}\text{H}_{22.6}\text{N}_7\text{PCl}_3\text{F}_6\text{Ru}$): C, 45.89; H, 2.61; N, 11.21. Found: C, 45.91; H, 2.68; N, 11.04.

2.4.6 $[\text{Ru}(\text{bpy})(\text{trpy})(2,3,4,5\text{-Cl}_4\text{pcyd})][\text{PF}_6]$ was prepared in the same manner as above. Yield: 0.35 g (78%). (NCN): 2167 cm^{-1} ; ^1H NMR (400 MHz, DMSO- d_6): 9.60(1)d, 8.95(1)d, 8.90(2)d, 8.78(2)d, 8.68(1)d, 8.39(1)t, 8.34(1)t, 8.08(3)m, 7.86(1)t, 7.72(2)d, 7.45(3)m, 7.15(1)t, 5.81(1)s. Anal. Calcd for $[\text{Ru}(\text{bpy})(\text{trpy})(2,3,4,5\text{-Cl}_4\text{pcyd})][\text{PF}_6]$ ($\text{C}_{32}\text{H}_{20}\text{N}_7\text{PCl}_4\text{F}_6\text{Ru}$): C, 43.17; H, 2.26; N, 11.01. Found: C, 42.80; H, 2.45; N, 10.95.

2.4.7 $[\text{Ru}(\text{bpy})(\text{trpy})(2,3,5,6\text{-Cl}_4\text{pcyd})][\text{PF}_6]$ was prepared in the same manner as above, and purified by column chromatography. Yield: 0.04 g (9%). (NCN): 2181 cm^{-1} ; ^1H NMR

(400 MHz, DMSO- d_6): 9.60(1)d, 8.93(1)d, 8.88(2)d, 8.75(2)d, 8.67(1)d, 8.39(1)t, 8.32(1)t, 8.12(1)t, 8.07(2)t, 7.83(1)t, 7.70(2)d, 7.43(2)t, 7.35(1)t, 7.13(1)t, 7.01(1)s. Anal. Calcd for [Ru(bpy)(trpy)(2,3,5,6-Cl₄pcyd)][PF₆] (C₃₂H₂₀N₇PCl₄F₆Ru): C, 43.17; H, 2.26; N, 11.01. Found: C, 42.83; H, 2.25; N, 10.70.

2.4.8 [Ru(bpy)(trpy)(Cl₅-pcyd)][PF₆]·1/3(toluene) was prepared in the same manner as above, and purified by column chromatography. Yield: 0.06 g (20%). (NCN): 2184 cm⁻¹; ¹H NMR (400 MHz, DMSO- d_6) 9.60(1)d, 8.93(1)d, 8.88(2)d, 8.75(2)d, 8.67(1)d, 8.39(1)t, 8.33(1)t, 8.12(1)t, 8.07(2)t, 7.84(1)t, 7.71(2)d, 7.44(2)t, 7.35(1)d, 7.14(1)t. Anal. Calcd for [Ru(bpy)(trpy)(Cl₅-pcyd)][PF₆]·1/3(toluene) (C_{34.3}H_{21.7}N₇PCl₅F₆Ru): C, 43.16; H, 2.29; N, 10.26. Found: C, 43.52; H, 2.41; N, 10.30.

2.4.9 Preparation of 4,4'-azodi(phenylcyanamide)·H₂O (H₂adpc). Ammonium thiocyanate (1.5 g, 20 mmol) was dissolved in 20 mL of acetone and brought to a boil. To this, a solution of benzoyl chloride (2.8 g, 20 mmol) in 20 mL of acetone was added dropwise, and the mixture was refluxed for an additional 15 minutes. 4,4'-azodianiline (2.1 g, 9.9 mmol) was dissolved in 150 mL of boiling acetone, then slowly added to the refluxing mixture above. The mixture was refluxed for 1 hour then poured into a beaker containing 800 mL of water. The brown benzoyl-thiourea precipitate was removed by suction filtration and dissolved in 300 mL of boiling 2M NaOH. The resulting deep red solution was boiled for 5 minutes, then cooled to 60 °C. Lead acetate (7.5 g, 20 mmol) was dissolved in 20 mL of water and added to the thiourea solution. The temperature was maintained at 60 °C for 15 minutes forming a black PbS precipitate, then filtered by suction into an ice cooled flask. The filtrate was acidified to pH 5 with the addition of 25 g of glacial acetic acid and a green precipitate was removed by suction filtration. Re-

crystallization from 700 mL of boiling acetone afforded a greenish-gold solid. Yield: 1.3 g, 51%. Anal. Calcd for $C_{14}H_{12}N_6O$: C 59.99; H 4.32; N 29.98. Found: C 59.70; H 4.39; N 29.76. IR (NCN): 2225 cm^{-1} ; ^1H NMR (400 MHz): 10.63 (2H, broad singlet), 7.89 (4H, doublet), 7.13 (4H, doublet) ppm. Mpt. 200-205 °C (decomposition)

2.4.10 Preparation of $\text{Th}_2[\text{adpc}]$. 0.25 g (0.95 mmol) of H_2adpc was dissolved in 300 mL of boiling 2:1 acetone/water solution. To this a 50 mL 2:1 acetone/water solution of thallium acetate (0.53 g, 2.0 mmol) was added. An orange precipitate quickly formed with the addition of 1 mL of triethylamine. The mixture was boiled for 2 minutes longer then slowly cooled to $-20\text{ }^\circ\text{C}$. Filtration afforded a bright orange microcrystalline solid which was washed with cold water and acetone. Yield: 0.53 g, 83%. Anal. Calcd for $C_{14}H_8N_6\text{Th}_2$: C 25.13; H 1.21; N 12.56. Found: C 25.51; H 1.31; N 12.57. IR $\nu(\text{NCN})$: 2078 and 2042 cm^{-1} ; ^1H NMR (200 MHz): 7.41 (4H, doublet), 6.62 (4H, doublet) ppm. Mpt (decomposition): 200-205 °C.

2.4.11 Preparation of $\{[\text{Ru}(\text{bpy})(\text{trpy})]_2(\mu\text{-adpc})\}[\text{PF}_6]_2\cdot\text{ether}$. $[\text{Ru}(\text{bpy})(\text{trpy})\text{Cl}][\text{PF}_6]$ (0.60 g, 0.89 mmol) was dissolved in 100 mL of DMF in a 250 mL round bottom flask. $\text{Th}_2[\text{adpc}]$ (0.30 g, 0.45 mmol) was added and the deep red solution was refluxed for 48 hours. The reaction mixture was then chilled to $-20\text{ }^\circ\text{C}$ and filtered to remove a fine white ThCl precipitate. The filtrate was then concentrated to 30 mL by rotary evaporation, and 600 mL of ether was added to precipitate the crude product, which was then collected by suction filtration (0.56 g). The crude product (0.3 g) was dissolved in 60 mL of 1:1 MeCN:toluene, filtered, and purified by chromatography on a 50 cm x 3 cm diameter column containing ~250 g grade III alumina (Brockmann I, weakly acidic, 150 mesh). Three bands containing starting material and a mononuclear complex were eluted with 1:1

MeCN:toluene. A fourth band was eluted with 500 mL 3:1 MeCN:toluene and contained the target complex which crystallized from the solution upon evaporation of the MeCN.

Re-crystallization was achieved by the slow diffusion of ether into a saturated solution of the complex in MeCN. Yield: 0.16 g (43%). Anal. Calcd for $C_{68}H_{56}N_{16}OP_2F_{12}Ru_2$: C, 50.88; H, 3.52; N, 13.96. Found: C, 50.81; H, 3.33; N, 14.04.

IR (NCN): 2161 cm^{-1} ; ^1H NMR (400 MHz): 9.65 (2H, doublet), 8.96 (2H, doublet), 8.90 (4H, doublet), 8.78 (4H, doublet), 8.69 (2H, doublet), 8.40 (2H, triplet), 8.32 (2H, triplet), 8.09 (6H, multiplet), 7.85 (2H, triplet), 7.73 (4H, doublet), 7.46 (6H, multiplet), 7.27 (4H, doublet), 7.15 (2H, triplet), 6.02 (4H, doublet) ppm.

2.4.12 Preparation of 4-azo(phenylcyanamide)benzene- $\frac{1}{2}\text{H}_2\text{O}$ (Hapc). The same procedure as that for H_2adpc was followed. Re-crystallization from acetone/water (3:1) gave orange needles and crystalline flakes of the product. Yield: 60%. Anal Calcd for $C_{13}H_{11}N_4O_{0.5}$: C 67.52; H 4.79; N 24.23. Found: C 67.55; H 4.79; N 24.66. IR (NCN): 2222 cm^{-1} . ^1H NMR (400 Mz): 10.71 (H, broad singlet), 7.95 (2H, doublet), 7.87 (2H, doublet), 7.58 (3H, multiplet), 7.17 (2H, doublet) ppm. Mpt: 154-157 °C.

2.4.13 Preparation of $\text{Ti}[\text{apc}]$. An identical procedure to that used to synthesize $\text{Ti}_2[\text{adpc}]$ was used. Orange crystalline flakes were isolated directly from the reaction solution. Yield: 73%. Anal Calcd for $C_{13}H_9N_4\text{Ti}$: C 36.69; H 2.13; N 13.16. Found: C 36.53; H 2.14; N 13.29. IR (NCN): 2075 and 2042 cm^{-1} .

2.4.14 Preparation of $[\text{Ru}(\text{bpy})(\text{trpy})(\text{apc})][\text{PF}_6]$. The mononuclear complex was synthesized in the same manner as the dinuclear above except that only a 1:1 ratio of $[\text{Ru}(\text{bpy})(\text{trpy})\text{Cl}]^+$ and ligand was used. Yield: 53%. Anal. Calcd for $C_{38}H_{28}N_9F_6\text{PRu}$: C, 53.27; H, 3.29; N, 14.71. Found: C, 53.48; H, 3.42; N, 14.41. IR $\nu(\text{NCN})$: 2161 cm^{-1} . ^1H

NMR (400 MHz): 9.65 (1H, doublet), 8.95 (1H, doublet), 8.91 (2H, doublet), 8.79 (2H, doublet), 8.69 (1H, doublet), 8.40 (1H, triplet), 8.34 (1H, triplet), 8.10 (3H, multiplet), 7.86 (1H, triplet), 7.72 (4H, multiplet), 7.46 (8H, multiplet), 7.15 (1H, triplet), 6.08 (2H, doublet) ppm.

Most of these complexes required the addition of a solvent of crystallization to their molecular formulae. While the crystal structure of $[\text{Ru}(\text{bpy})(\text{trpy})(2,4\text{-Cl}_2\text{pcyd})][\text{PF}_6]\cdot\text{DMF}$ clearly established the presence of DMF, the presence of toluene or DMF solvent of crystallization for the other complexes was demonstrated by ^1H -NMR spectroscopy. The cyclic voltammograms of these complexes showed no evidence of redox active impurities.

2.5 Crystallography

Crystals of $[\text{Ru}(\text{bpy})(\text{trpy})(2,4\text{-Cl}_2\text{pcyd})][\text{PF}_6]\cdot\text{DMF}$ and $[\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-adpc})][\text{PF}_6]_2\cdot 2(\text{ether})\cdot 2(\text{DMF})$ were grown by ether diffusion into DMF solutions of the complex. The data were collected on a 1K Siemens Smart CCD using Mo-K α radiation ($\lambda=0.71073$ Å) at 203(2) K using an ω -scan technique and corrected for absorptions using equivalent reflections.²⁹ 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 structures were solved by direct methods and refined with full-matrix least-squares procedures. 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. Tables giving a complete listing of all bond lengths and angles have been placed in Appendix A and B.

2.6 Oscillator Strength Calculation

Because the LMCT bands are non-gaussian, the use of the equation for oscillator strength:³⁰

$$f = 4.61 \times 10^{-9} \varepsilon_{\max} \Delta \nu \quad (12)$$

where $\varepsilon_{\max}$ is the maximum extinction coefficient in $M^{-1}cm^{-1}$ and $\Delta \nu$ is the band width at one-half peak height in cm^{-1} , would give an inexact value. Instead, the LMCT band envelope was fitted by using *PeakFit* software and multiple gaussian peaks. The LMCT band oscillator strength was then calculated according to equation 13, which gives the sum of the contribution to the oscillator strength from each gaussian band

$$f = 4.61 \times 10^{-9} \sum_i \varepsilon_i \Delta \nu_i \quad (13)$$

Figure 6 shows the fitting procedure on the low energy LMCT band of $[Ru(bpy)(trpy)(2,3,4,5-Cl_4pcyd)]^{2+}$. In this treatment, the number of gaussian bands does not necessarily reflect electronic transitions or vibrational features.

Figure 6. Electronic spectrum of $[\text{Ru}(\text{bpy})(\text{trpy})(2,3,4,5\text{-Cl}_4\text{pcyd})]^{2+}$ showing the best fit of three gaussian curves (dashed lines) used for the calculation of oscillator strength.

2.7 Molecular Modeling

Molecular modeling was performed on a Silicon Graphics workstation using *Spartan* version 5.0.1. The *ab-initio* calculations used the Hartree-Fock model with the 6-31G** basis set and geometry optimization.

3. Ru(bpy)(trpy) Phenylcyanamide Complexes

3.1 Results

The mononuclear Ru(II) complexes were synthesized in generally good yields according to the following metathesis reaction, in refluxing DMF

Although ruthenium(II) should be able to coordinate to either nitrogen of the ligand, the crystal structure (see below) indicates binding to only the nitrile (end) nitrogen. This is also indicated by the ^1H NMR of the complexes, which do not show the presence of any structural isomers. A previous ^1H -NMR study, of the reaction of phenylcyanamide ligands with Ru(II)2,6-bis(1-methylbenzimidazol-2-yl)pyridine complexes,³¹ indicated that the amide bound linkage isomer formed initially but at ambient temperatures slowly converted to the nitrile nitrogen bound linkage isomer. It seems reasonable to suggest that the nitrile nitrogen linkage isomer is more stable because of a reduction in steric hindrance.

A previous³ study of pentammineruthenium(III) complexes with many different phenylcyanamide ligands provided a basis for the ligands chosen here. It was hoped that the ligands which gave a reversible oxidation couple in cyclic voltammetry of their

pentaammineruthenium complexes would form comparably stable Ru(bpy)(trpy)L complexes.

Some of the complexes of this study were obtained in sufficient purity by simply diffusing ether into a saturated DMF solution of the reaction product to yield dark brown crystals. Acceptable elemental analyses and clean ^1H NMR spectra were used as an indicator of sufficient purity. Complexes of the polychloro substituted phenylcyanamide ligands required a column chromatography step to insure purity.

The proton NMR spectrum of [Ru(bpy)(trpy)(2,4-Cl₂pcyd)]PF₆ in DMSO-d₆ (Figure 7A) is typical of all the Ru(bpy)(trpy)L complexes studied. The bipyridine and terpyridine resonances occur between 7 and 10 ppm and have the same splitting pattern found in the starting material, [Ru(bpy)(trpy)Cl][PF₆]. The uncomplexed cyanamide ligand 2,4-Cl₂pcyd is shown in Figure 7B. Note the shifts in the pcyd peaks upon coordination with ruthenium in Figure 7A.

Deep brown, almost black crystalline shards of [Ru(bpy)(trpy)(2,4-Cl₂pcyd)]PF₆·DMF were grown by DMF/ether diffusion. Crystal data and selected bond lengths and angles appear in Tables 1 and 2, respectively. An ORTEP drawing of the complex is shown in Figure 8. The full x-ray data can be found in Appendix A.

Figure 7. ^1H NMR spectra of A, $[\text{Ru}(\text{bpy})(\text{trpy})(2,4\text{-Cl}_2\text{pcyd})][\text{PF}_6]$; and B, $\text{Tl}[2,4\text{-Cl}_2\text{pcyd}]$; in DMSO-d_6 .

Figure 8. ORTEP drawing of $[\text{Ru}(\text{bpy})(\text{trpy})(2,4\text{-Cl}_2\text{pcyd})]\text{PF}_6 \cdot \text{DMF}$. The counter ion and solvent of crystallization have been omitted for clarity.

Table 1. Crystal Data and Structure Refinement for [Ru(bpy)(trpy)(2,4-Cl₂pcyd)]PF₆·DMF.

Empirical Formula	C ₃₅ H ₂₉ F ₆ Cl ₂ N ₈ OPRu
Formula Weight	894.60
Temperature	238(2) K
Wavelength	0.71073 Å
Crystal System	Triclinic
Space Group	P-1
Unit Cell Dimensions	a = 11.681(4) Å alpha = 68.00(2)° b = 12.240(5) Å beta = 70.05(3)° c = 15.017(5) Å gamma = 78.55(2)°
Volume, Z	1865(1) Å ³ , 2
Density (calculated)	1.593 Mg/m ³
Absorption Coefficient	0.678 mm ⁻¹
F (000)	900
Crystal Size	0.10 x 0.08 x 0.05 mm
Theta range for data collection	1.86 to 26.37 °
Limiting Indices	-13 ≤ h ≤ 14, -13 ≤ k ≤ 15, 0 ≤ l ≤ 14
Reflections Collected	9530
Independent Reflections	4848 [R(int) = 0.0570]
Absorption Correction	Semi-empirical from equivalents
Max. and Min. Transmission	0.928077 and 0.407972
Refinement Method	Full-matrix Least-squares on F ²
Data / Restraints / Parameters	4848/51/450
Goodness-of-fit on F ²	1.100
R1 ^a	0.0722
wR2 ^b	0.2122

$$^a R1 = \sum \|F_o| - |F_c|\| / \sum |F_o|$$

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

Table 2. Selected crystal structure data for [Ru(bpy)(trpy)(2,4-Cl₂pcyd)]PF₆·DMF.

Bond Lengths^a / angstroms			
Ru-N(1)	2.076 (8)	Ru-N(6)	2.088 (7)
Ru-N(2)	1.962 (9)	N(6)-C(26)	1.132 (10)
Ru-N(3)	2.084 (8)	N(7)-C(26)	1.288 (10)
Ru-N(4)	2.035 (6)	N(7)-C(32)	1.437 (10)
Ru-N(5)	2.076 (8)		
Bond Angles^a / deg.			
N(1)-Ru-N(2)	79.7 (4)	N(4)-Ru-N(5)	78.7 (3)
N(1)-Ru-N(5)	98.8 (3)	N(6)-C(26)-N(7)	171.5 (10)
N(2)-Ru-N(3)	79.4 (3)	C(26)-N(7)-C(32)	119.6 (8)
N(3)-Ru-N(4)	91.4 (3)	C(26)-N(6)-Ru	169.0 (6)

^a Estimated percent standard deviations are in parenthesis.

The Ru(II) ion occupies a pseudo-octahedral coordination sphere of nitrogen donor atoms where the cyanamide group of the phenylcyanamide ligand is trans to a pyridine moiety of the bipyridine ligand. The cyanamide group is approximately linear ($171.5(10)^\circ$) as is the angle describing the coordination of its terminal nitrogen to Ru(II) ($169.0(6)^\circ$). Similar bond angles have been observed when phenylcyanamides coordinate to Ru(III) ions.^{3,32} The Ru(II)-NCN bond length was measured at 2.088 (7) Å, slightly longer than that found in the crystal structure of trans-[Ru(pyridine)₄(2-Clpcyd)₂], which has Ru(II)-cyanamide bond lengths of 2.041 and 2.060 Å.³³ The Ru(II)-cyanamide bond is considerably longer than the average Ru(III)-cyanamide bond length of 1.97 (2) Å that was derived from six Ru(III)-cyanamide structures.^{3,34} The shorter bond lengths of the Ru(III) complexes can be attributed to the greater electronegativity of the Ru(III) ion.

Cyclic voltammetry data for the [Ru(bpy)(trpy)L]⁺ complexes are given in Table 3 and a representative voltammogram of [Ru(bpy)(trpy)(2,4-Cl₂pcyd)]PF₆ appears in Figure 9. The Ru(III/II) couples are quasi-reversible and generally possess invariant anodic to cathodic peak separations of 80 mV at scan rates from 50 to 500 mV/s in acetonitrile. The phenylcyanamide L(0/-) couples are significantly less reversible having much larger peak-to-peak separations (Figure 9) and greater sensitivity to scan rate. Nonetheless, the L(0/-) voltammogram for the majority of the complexes gave equal anodic and cathodic currents. In contrast, for [Ru(bpy)(trpy)L]PF₆, where L = 4-Mepcyd⁻ and 3-Clpcyd⁻, the L(0/-) couples could not be determined because their Ru(III/II) couples were irreversible, showing only the anodic wave (Table 3). At negative potential, waves associate with the

Table 3. Electrochemical data^a for [Ru(bpy)(trpy)L]⁺ and [Ru(NH₃)₅L]²⁺ complexes in acetonitrile.

L	[Ru(bpy)(trpy)L] ⁺					[Ru(NH ₃) ₅ L] ^{2+c}	
	Ru(III/II)	L(0/-)	bpy or trpy Couples			Ru(III/II)	L(0/-1)
4-Me ₃ pcyd ⁻	0.81 ^b	----	-1.10	-1.38	-1.57	0.04	1.16
3-Cl ₃ pcyd ⁻	0.93 ^b	----	-1.11	-1.36	-1.59	0.12	1.47 ^b
2,4-Cl ₂ pcyd ⁻	1.00	1.64	-1.10	-1.36	-1.61	0.15	1.44
2,4,5-Cl ₃ pcyd ⁻	1.06	1.75	-1.06	-1.31	-1.57	0.20	1.54
2,4,6-Cl ₃ pcyd ⁻	1.03	1.74	-1.03	-1.28	-1.64	0.13	1.50
2,3,4,5-Cl ₄ pcyd ⁻	1.09	1.81	-1.09	-1.29	-1.59	0.23	1.63
2,3,5,6-Cl ₄ pcyd ⁻	1.08	1.83	-1.06	-1.31	-1.56	0.21	1.69 ^b
Cl ₅ pcyd ⁻	1.09	1.85	-1.10	-1.37	-1.66	0.23	1.67

^a in volts vs. NHE at 25 °C and a scan rate of 0.1 V/s; 0.1M TBAH; ferrocene (Fc⁺/Fc = 0.665 V vs. NHE) was used as an internal reference.

^b irreversible wave, anodic peak only.

^c from reference 5 and corrected for an old calibration value of Fc⁺/Fc = 0.400 V vs. NHE.

Figure 9. Cyclic voltammogram of $[\text{Ru}(\text{bpy})(\text{trpy})(2,4\text{-Cl}_2\text{pcyd})][\text{PF}_6]$ (1 mM in acetonitrile) at a scan rate of 75 mV/s; 0.1M TBAH; ferrocene ($E^\circ = 0.665$ V vs. NHE) was used as an internal reference.

reduction of bpy and trpy ligands overlap (Figure 9 and Table 3) making assignment difficult. Despite that, the trpy reduction wave has been suggested to occur at the more positive potential because of the greater stability of its π^* orbitals.³⁵

The electronic spectral data of the $[\text{Ru}(\text{bpy})(\text{trpy})\text{L}]\text{PF}_6$ complexes in acetonitrile solution are given in Table 4. Figure 10 shows the absorption spectrum of $[\text{Ru}(\text{bpy})(\text{trpy})(2,4\text{-Cl}_2\text{pcyd})][\text{PF}_6]$ in acetonitrile. Spectroscopic assignments were made by comparison to the literature.³⁶ The broad absorption band at approximately 500 nm that appears in the complexes' spectra is assigned to a metal-to-ligand charge transfer (MLCT) transition. The two strong absorptions appearing at approximately 285 and 313 nm are assigned to $\pi \rightarrow \pi^*$ transitions of the bipyridine and terpyridine ligands, respectively. The slight decrease in MLCT energy as the substituents on the phenylcyanamide ligand vary from electron withdrawing to electron donating is an indication of the donor ability of the phenylcyanamide ligand and its influence on Ru(II) ion stability. This has been comprehensively quantified for many ligands by Lever's ligand electrochemical series.³⁷

Spectroelectrochemistry was performed on these complexes in order to generate the Ru(III) spectra and in turn allow the study of the spectral data associated with the Ru(III)-cyanamide LMCT chromophore. A representative visible spectrum showing the electrochemical generation of the $[\text{Ru}(\text{trpy})(\text{bpy})(2,3,4,5\text{-Cl}_4\text{pcyd})]^{2+}$ ion in acetonitrile solution is given in Figure 11 and the low energy LMCT band data have been placed in Table 4. A previously published spectroscopic analysis^{38,39} of the Ru(III)-cyanamide

Table 4. Electronic spectroscopy data^a for [Ru(bpy)(trpy)L]⁺ complexes and the Ru(III) LMCT spectral data of the [Ru(bpy)(trpy)L]²⁺ complexes in acetonitrile.

L	$\pi \rightarrow \pi^*$	MLCT	LMCT
4-Mepcyd ⁻	239 (3.32), 278 (4.78), 291 (4.25), 315 (3.41)	496 (0.736)	N/A
3-Clpcyd ⁻	237 (3.23), 281 (5.09), 290 (4.65), 314 (3.76)	494 (0.839)	N/A
2,4-Cl ₂ pcyd ⁻	237 (3.22), 282 (5.22), 290 (5.29), 314 (3.96)	492 (0.835)	1144
2,4,5-Cl ₃ pcyd ⁻	282 (4.89), 291 (5.37), 314 (4.10)	489 (0.844)	1073
2,4,6-Cl ₃ pcyd ⁻	282 (4.62), 292 (5.19), 315 (4.18)	495 (0.859)	1071 (0.913)
2,3,4,5-Cl ₄ pcyd ⁻	282 (4.67), 291 (5.20), 313 (4.37)	487 (0.866)	1058 (1.16)
2,3,5,6-Cl ₄ pcyd ⁻	220 (5.80), 282 (4.26), 292 (4.85), 315 (4.33)	490 (0.859)	1009 (0.811)
Cl ₅ pcyd ⁻	224 (6.15), 282 (4.37), 291 (5.00), 314 (4.39)	489 (0.849)	1038 (0.826)

^a λ_{max} in nm; $\epsilon / 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ in parenthesis.

Figure 10. Quantitative electronic spectrum of $[\text{Ru}(\text{bpy})(\text{trpy})(2,4\text{-Cl}_2\text{pcyd})][\text{PF}_6]$ (6.17×10^{-5} M in acetonitrile).

LMCT chromophore of $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$ assumed C_{4v} microsymmetry about Ru(III) and is applicable to the $[\text{Ru}(\text{trpy})(\text{bpy})\text{L}]^{2+}$ complexes of this study. Accordingly, in Figure 11, the low energy LMCT band at 1058 nm is assigned to the $b_1 \rightarrow b_1^*$ transition while the high energy LMCT band at 430 nm is assigned to the formally forbidden $b_2 \rightarrow b_1^*$ transition. The Ru(III) complexes showed varying degrees of stability and none were stable for periods greater than 10 minutes in solution. The stability of the Ru(III) complexes of 2,4-dichloro- and 2,4,5-trichlorophenylcyanamide ligands was so poor that isosbestic points could not be observed. The 2,4,6-trichlorophenylcyanamide complex gave well-defined isosbestic points however reversibility was no better than 80%. Both the penta- and tetrachloro substituted derivatives showed very good reversibility (>95%) in regenerating the Ru(II) spectra.

Figure 11. OTTLE cell electronic spectra of $[\text{Ru}(\text{bpy})(\text{trpy})(2,3,4,5\text{-Cl}_4\text{pcyd})]^{1+/2+}$ in acetonitrile under increasing oxidation potentials. 0.1 M TBAH; gold foil working and counter electrodes; silver wire pseudo-reference electrode.

3.2 Discussion

The cyclic voltammetry data for $[\text{Ru}(\text{bpy})(\text{trpy})\text{L}]^+$ and $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$ complexes have been compiled in Table 3. Looking within each family of complexes it is apparent that increasing the number of electron withdrawing substituents on the pcyd ligand results in increased redox potentials for both the Ru(III/II) and the L(0/-) couples. This is due to an electron inductive effect of the chlorides on the pcyd ligand and in turn on the metal. This causes them to become more electropositive and thus harder to oxidize. This effect is small when compared to the effect on the redox couples of changing the inner coordination sphere. Switching from ammine to pyridine ligands gives an increase of about 0.8 volts to the Ru(III/II) reduction couples. This is due to the stabilization of Ru(III) by the σ -donating ammines, and also by the stabilization of Ru(II) by the π -accepting pyridines. Switching from ammine to pyridine ligands also has a small effect ($\sim +0.2$ V) on the pcyd ligand reduction couples, L(0/-) . This is because the pyridine moieties cause Ru(III) to be more electropositive, which in turn draws electron density away from the pcyd⁻ ligand, making it more difficult to oxidize.

It has been known for many years that it is possible to correlate charge transfer band energies to the difference in redox couples between the centers involved in the charge transfer event. The LMCT event involves the oxidation of the pcyd⁻ ligand and reduction of the Ru(III) ion. This is equivalent to the difference between the L(0/-) and Ru(III/II) reduction couples which can be found by cyclic voltammetry. The expression⁴⁰ for this is linear (recall equation 1), where E_{LMCT} is the energy of the LMCT band.

$$E_{LMCT} = [L^{(0/-)} - Ru^{(III/II)} - C] + \chi \quad (1)$$

Since it is impossible to measure the Ru(III/II) couple while the ligand is in the oxidized L^0 state the factor 'C' is added to the equation. C should remain constant for a similar group of complexes in a common solvent. The ' χ ' term is used to account for excited vibrational levels of the LMCT excited state which would raise the energy of the charge transfer over that predicted from $L(0/-)$ and Ru(III/II) couples alone. χ is also expected to be constant for a similar group of compounds. Plots of E_{LMCT} versus $L(0/-)$ -Ru(III/II) for both the Ru(bpy)(trpy)L complexes and the Ru(NH₃)₅L complexes are nearly linear as seen in Figures 12 and 13. What is unexpected however, is that the 2 sets of data have nearly the same slope and intercept. This is illustrated in Figure 13, which gives a slope of 1.01, intercept of 0.45, and r^2 of 0.99 using the data from both sets of complexes together. This is difficult to rationalize from the components of equation 1. Although C is expected to be approximately equal for both families of complexes (as it is the effect on Ru(III/II) by the oxidation state of the same ligand), χ should not be since the inner coordination sphere of Ru(NH₃)₅L is quite different from Ru(bpy)(trpy)L. χ is made up of both inner and outersphere reorganizational energies⁴ so coincidentally, it may be possible that the difference between the outer and innersphere reorganizational energies of the two families cancels out.

Figure 12. LMCT energy verses the energy gap between Ru(II/III) and pcyd(-1/ 0) redox couples (ΔE) for various $[\text{Ru}(\text{bpy})(\text{trpy})(\text{pcyd})]^-$ complexes. The equation of the line of best fit is $y = (1.05)x + 0.418$; $r^2 = 0.891$

Figure 13. LMCT energy verses the energy gap between Ru(II/III) and pcyd(-1/ 0) redox couples (ΔE) for various [Ru(bpy)(trpy)L]²⁺ and [Ru(NH₃)₅L]²⁺ complexes. The equation of the line of best fit is $y = (1.01)x + 0.455 \text{ eV}$; $r^2 = 0.984$.

L1	2,4,6-Me ₃ pcyd	L7	2-Clpcyd	L13	2,4,5-Cl ₃ pcyd
L2	3,5-Me ₂ pcyd	L8	3-Clpcyd	L14	2,4,6-Cl ₃ pcyd
L3	(4-Me)pcyd	L9	4-Clpcyd	L15	2,3,4,5-Cl ₄ pcyd
L4	3,4,5-(OMe) ₃ pcyd	L10	2,3-Cl ₂ pcyd	L16	2,3,5,6-Cl ₄ pcyd
L5	3,5-(OMe) ₂ pcyd	L11	2,4-Cl ₂ pcyd	L17	Cl ₅ pcyd
L6	pcyd	L12	2,6-Cl ₂ pcyd		

To prove this would require a solvent-effect study on the LMCT energies of both sets of complexes. Changing solvent properties such as polarity would affect the outersphere reorganizational energies of the two complex types differently since amines are much smaller than pyridines. This type of study was attempted, however the Ru(bpy)(trpy)L complexes proved only sparingly soluble in all but the most dielectric solvents. In addition to this, the working redox range of the solvents was also a stumbling block since the L(0/-) couples of the Ru(bpy)(trpy)L complexes were so anodic. For these reasons a definitive statement on the outersphere contributions to χ was unattainable. Nonetheless, it can be stated with confidence that by changing the inner coordination sphere from ammine to pyridine moieties, the Ru(III)-cyanamide LMCT chromophore energy has decreased by approximately 0.6 volts, and this is in agreement with the changes seen in the Ru(III/II) and L(0/-) redox couples.

Decreasing the energy difference between ligand and metal orbitals would be expected to increase the amount of ligand-metal coupling. This was certainly observed for dinuclear pentaammineruthenium, tetraamminepyridineruthenium, and triammine-bipyridineruthenium complexes where both metal-ligand and metal-metal coupling increased as ammine ligands were replaced with pyridine moieties.⁹ However, the metal-ligand coupling elements (H_{LM}) calculated for the complexes studied here were not in agreement with these results.

Figure 14 shows a plot of oscillator strength, f verses the energy of the LMCT band, E_{LMCT} for both the Ru(bpy)(trpy)L complexes and the pentaammines.

Figure 14. Oscillator strength, f verses LMCT energy for various $[\text{Ru}(\text{bpy})(\text{trpy})\text{L}]^{2+}$ and $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$ complexes.

Table 5. LMCT oscillator strengths^a and metal-ligand coupling elements^b derived from the $b_1 \rightarrow b_1^*$ LMCT transition of bipyridine(terpyridine)ruthenium(III) and pentaammineruthenium(III) phenylcyanamide (pcyd⁻) complexes.

L	[Ru(bpy)(trpy)L]²⁺		[Ru(NH₃)₅L]²⁺	
	<i>f</i>	<i>H_{LM}</i>	<i>f</i>	<i>H_{LM}</i>
2,4-Cl ₂ pcyd ⁻			0.156	2540
2,4,5-Cl ₃ pcyd ⁻			0.148	2520
2,4,6-Cl ₃ pcyd ⁻	0.152	2050	0.128	2380
2,3,4,5-Cl ₄ pcyd ⁻	0.183	2270	0.119	2280
2,3,5,6-Cl ₄ pcyd ⁻	0.153	2120	0.111	2270
Cl ₅ pcyd ⁻	0.178	2260	0.126	2410

^a in acetonitrile solutions, oscillator strength *f* was calculated using equation 13.

^b calculated by using equation 4, $r = 5.56 \text{ \AA}$ and E_{LMCT} from Table 4, in cm^{-1} .

The CNS theory would predict a linear relationship here, but instead the slope appears to taper off in the case of the Ru(bpy)(trpy)L complexes. This result is reflected in the H_{LM} values since they were calculated from the oscillator strength. Table 5 shows the H_{LM} values for the Ru(bpy)(trpy)L and Ru(NH₃)₅L complexes calculated by equation 4. Note that H_{LM} for the Ru(bpy)(trpy)L complexes is considerably smaller than that for the Ru(NH₃)₅L complexes. This would seem to indicate that ruthenium-cyanamide d π -p π bonding is weaker in the Ru(bpy)(trpy)L complexes. It may be that the Ru(III) d π orbitals have shrunk as a result of stabilization from the pyridine moieties (π acceptors) causing a decrease in π overlap with the cyanamide ligand. This however, is not consistent with other studies. For example the mixed valence complex [{Ru(bpy)(trpy)}₂(μ -dicyd)]³⁺, where dicyd is:

was found to be a Class III^{16,2} system, while the pentammine analog, [{Ru(NH₃)₅}₂(μ -dicyd)]³⁺ was only Class II.^{32c} A Class III system has strong metal-metal coupling, and since this occurs through the bridging ligand then the metal-ligand coupling must also be very strong. In other words metal-ligand coupling was found to be much greater for Ru(bpy)(trpy) than for Ru(NH₃)₅L complexes with a phenylcyanamide ligand.

Why then is H_{LM} smaller for the $Ru(bpy)(trpy)L$ complexes in this case?

Examining equation 4 one can see that the length chosen for r (the transition dipole moment length) will have a large effect on the value of H_{LM} . For these calculations r was assumed to be $5.56 \text{ \AA}^{39}$ for both sets of complexes, but this may be not the case. In fact greater covalency in the metal-ligand bond would cause a reduction in the length of the dipole moment, and hence an underestimation in the calculated value of H_{LM} using equation 4. This is reasonable for $Ru(bpy)(trpy)L$ since the LMCT energies and also ΔE (Figure 16) are much lower than for the $Ru(NH_3)_5L$ complexes. As $Ru(III)$ $d\pi$ and $pcyd$ $p\pi$ bonding orbitals get closer in energy, the bond becomes less polarized towards the ligand and hence there is a more equal sharing of the bonding electrons. This results in a reduced dipole length for the LMCT since the electron has less distance to travel. Electron absorption spectroscopy can give an experimental estimate of r , however it is a difficult experiment to perform and is not available at Carleton University. Nevertheless it is an experiment that should be attempted in the future. Also, an assumption used in the derivation⁷ of equation 4 was that the overlap integral is small enough to be ignored, but this might not be reasonable for the $Ru(bpy)(trpy)L$ complexes. As a result, equation 4 may no longer be applicable.

4. Ru(bpy)(trpy) Azo Complexes

4.1 Results

The complexes of this study were synthesized by the metathesis reaction of $[\text{Ru}(\text{bpy})(\text{trpy})\text{Cl}]^+$ with the thallium salts of apc^- or adpc^{2-} in refluxing DMF. Purification by column chromatography was required but reasonable yields of the complexes were still obtained. Photoinduced *cis-trans* isomerization of the azo group⁴¹ was attempted, but not observed. These studies were preliminary and it may be that isomerization back to the more stable *trans* isomer is too rapid⁴² to detect. Both Ru(II) complexes are air-stable and can be readily recrystallized. Preparation of the analogous pentaammineruthenium(III) dinuclear azo complex had previously been attempted by Dr. Crutchley's lab group but they were unsuccessful in obtaining a product that gave a reasonable elemental analysis.

Deep red-brown needles of the dinuclear Ru(II) complex, $[\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-adpc})]^{2+}$ that were suitable for crystallography were grown by diffusion of ether into a solution of the complex in DMF. Crystallography data including selected bond lengths, and angles are reported in Table 6 and 7. An ORTEP drawing of the complex cation is shown in Figure 15, while the full crystallography data has been placed in Appendix B. The Ru(II) ion occupies a pseudo-octahedral coordination sphere of nitrogen donor atoms where the cyanamide group of the phenylcyanamide ligand is *trans* to a pyridine moiety of the bipyridine ligand. The bridging adpc^{2-} ligand is approximately planar with the cyanamide groups in an *anti*-conformation relative to each other and the azo group adopting the more thermodynamically stable *trans* conformation. The planar geometry of the adpc^{2-} bridging ligand is suggested to allow for a more effective delocalization of the cyanamide groups with phenyl and azo groups. This rationale has also been used to

Table 6. Crystal data for [$\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-adpc})][\text{PF}_6]_2 \cdot 2(\text{ether}) \cdot 2(\text{DMF})$.

formula	$\text{C}_{76}\text{H}_{72}\text{F}_{12}\text{N}_{18}\text{O}_2\text{P}_2\text{Ru}_2$
fw	1761.60 g/mol.
crystal system	triclinic
space group	P-1
unit cell dimensions	a, 12.480(2); b, 13.090(3); c, 14.147(3) Å
α, β, γ /degrees	79.792(3), 68.027(3), 64.477(3)°
volume	1933.3(6) Å ³
Z	1
calculated density	1.513 g/cm ³
crystal dimensions	0.30 x 0.15 x 0.04 mm
θ range	1.72 to 28.83°
limiting indices	-15 ≤ h ≤ 16, -17 ≤ k ≤ 17, 0 ≤ l ≤ 18
reflections collected	8763
unique reflections	8763
absorption correction	semi-empirical from equivalents
transmission range	0.928078 to 0.690280
R1, wR2 [$I > 2\sigma(I)$] ^a	R1 = 0.0421, wR2 = 0.0682
goodness-of-fit on F ²	1.044

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

Table 7. Selected crystal structure data for
 $[\{\text{Ru}(\text{trpy})(\text{bpy})\}_2(\mu\text{-adpc})][\text{PF}_6]_2 \cdot 2(\text{ether}) \cdot 2(\text{DMF})$.

Bond Lengths^a / Angströms			
Ru-N(1)	2.041(2)	N(6)-C(26)	1.164(3)
Ru-N(2)	2.069(2)	N(7)-C(26)	1.281(4)
Ru-N(3)	2.065(2)	N(7)-C(27)	1.394(3)
Ru-N(4)	1.964(2)	N(8)-C(30)	1.420(3)
Ru-N(5)	2.062(2)	N(8)-N(8A)	1.274(4)
Ru-N(6)	2.046(2)		
Bond Angles^a / deg.			
N(1)-Ru-N(2)	78.98(9)	N(4)-Ru-N(5)	79.50(10)
N(1)-Ru-N(5)	91.37(9)	N(6)-C(26)-N(7)	173.1(3)
N(3)-Ru-N(2)	99.81(9)	C(26)-N(6)-Ru	164.4(2)
N(4)-Ru-N(3)	79.75(9)	C(26)-N(7)-C(27)	118.7(2)
N(5)-Ru-N(2)	100.94(9)	N(8A)-N(8)-C(30)	114.0(3)

^a estimated standard deviations are in parentheses.

explain the planar conformation of 1,4-dicyanamidobenzene dianion and its derivatives, observed in crystal structures of tetraphenylarsonium salts⁴³ and Ru(III) complexes.³² The cyanamide group is approximately linear ($173.1(3)^\circ$) as expected while the angle describing the coordination of its terminal nitrogen to Ru(II) ($164.4(2)^\circ$) is significantly bent. In contrast, four crystal structures of Ru(III)-cyanamide complexes showed a much straighter average Ru(III)-cyanamide bond angle of 174.6° .^{3,32} It has been suggested⁴⁴ that the π bonding between Ru(III) and cyanamide is optimized when this angle is linear, a condition which evidently relaxed when π bonding is less expressed.

The ^1H NMR spectra of the dinuclear $[\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-adpc})]^{2+}$ complex and adpc^{2-} ligand are shown in Figure 16. The bipyridine and terpyridine proton resonances occur between 7 and 10 ppm and show the usual splitting pattern for Ru(bpy)(trpy)L complexes. The doublets at 6.0 and 7.2 ppm can be unambiguously assigned to the complexed azo ligand.

Cyclic voltammetry data for the thallium salts of apc^- and adpc^{2-} and the two complexes have been placed in Table 8. Figure 17 shows the cyclic voltammograms of the complexes. Oxidation of apc^- is irreversible showing no cathodic wave in the cyclic voltammogram. The CV of $\text{Ti}_2[\text{adpc}]$ shows two closely spaced redox couples which are only partially reversible-the reduction waves being of lower current than the oxidation waves. The Ru(III/II) couple of $[\text{Ru}(\text{bpy})(\text{trpy})(\text{apc})]^+$ in acetonitrile is partially reversible and occurs at a potential of 0.966 V vs. NHE. Scanning to more positive potentials resulted in decomposition of the complex and loss of the cathodic wave for the Ru(III/II) couple. The voltammogram of the dinuclear complex $[\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-adpc})]^{2+}$ in acetonitrile shows two Ru(III/II) oxidation waves occurring at 1.570 and 0.784 V versus NHE. The Ru(III/II) couples were quasi-reversible with the separation between cathodic

Figure 16. 400 MHz ^1H NMR spectra of $\text{Tl}_2[\text{adpc}]$ (top) and $[\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-adpc})][\text{PF}_6]_2$ in DMSO-d_6 . The arrows in the lower spectrum indicate the adpc resonances.

and anodic waves dependent upon the scan rate. Using equation 8 and the difference between the two Ru(III/II) couples of $[\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-adpc})]^{3+}$ yields a comproportionation equilibrium constant of $K_c = 1.3 \times 10^{13}$. This high K_c value implies strong metal-metal coupling in the mixed-valence complex.

The waves in the -1 to -2 volt range were assigned to trpy and bpy reduction couples by analogy to the Ru(bpy)(trpy)(pcyd) complexes described above. The first reduction wave is assigned³⁵ to trpy (0/-1) and shows some reversibility. Reduction of the azo group is also expected to appear in this range, and in the case of the dinuclear complex, results in loss of reversibility-the appearance of a cathodic spike at -1.44 V vs. NHE is evidence of electrode deposition. This chemistry was not pursued.

Table 8, gives the Ru(III/II) couples⁴⁵ of $[\text{Ru}(\text{bpy})(\text{trpy})(2,4\text{-Cl}_2\text{pcyd})]^+$ and $[\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-dicyd})]^{2+}$ for comparison with the analogous complexes of apc^- and adpc^{2-} ligands. Since the ruthenium ions of the mononuclear and dinuclear complexes have similar coordination spheres, a shift in the Ru(III/II) couples of the dinuclear complex compared to that of the mononuclear Ru(III/II) couple should approximate the stabilization energy due to resonance exchange occurring in the mixed valence dinuclear complex. Put another way, the Ru(III/II) couple of the mononuclear ruthenium complex approximates the energy of a ruthenium ion that is not stabilized by resonance exchange. Qualitatively, it is expected that, for a dinuclear complex, the Ru(III/II) couple forming the [III,II] complex should be more positive of this value while the Ru(III/II) couple forming the [II,II] complex should be more negative of this value. Thus, in Figure 17, the Ru(III/II) couples of the apc^- and adpc^{2-} complexes approximately follow the expected behavior but the pcyd⁻ and dicyd²⁻ complexes (Figure 18) do not. The reason for this is that antiferromagnetic exchange in $[\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-dicyd})]^{4+}$ stabilizes the [III,III]

Table 8. Cyclic voltammetry data^a of azo ligands and complexes with Ru(bpy)(trpy).

Ligand/Complex	Ru(III/II)	L(-1/-2)	L(0/-1)
Tl[apc]			0.857 ^{b,d}
Tl ₂ [adpc]		0.492 ^b	0.667 ^b
[{Ru(trpy)(bpy)(apc)}] ⁺	0.964 ^c		
	1.057 ^b		
[{Ru(trpy)(bpy)} ₂ (μ-adpc)] ²⁺	0.794, ^c 1.570 ^c		
	0.911, ^b ≈1.6 ^b		
[{Ru(trpy)(bpy)(2,4-Cl ₂ pcyd)}] ^{+e}	1.00 ^b		
[{Ru(trpy)(bpy)} ₂ (μ-dicyd)] ^{2+,f}	0.690, ^b 0.250 ^b		

^a in volts vs. NHE at 25 °C, scan rate of 0.1 V/s; and 0.1 M TBAH electrolyte; ferrocene (Fc⁺/Fc = 0.665 V vs. NHE) or cobalticenium hexafluorophosphate (E° = -0.664 V vs. NHE) were used as internal references.

^b in DMF

^c in MeCN

^d anodic wave only

^e data from ref. 32

^f data from ref. 33

Figure 17. Cyclic voltammograms of $[\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-adpc})][\text{PF}_6]_2$ (lower trace) and $[\text{Ru}(\text{bpy})(\text{trpy})(\text{apc})][\text{PF}_6]$ (upper trace), in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate, scan rate = 100 mV/s.

Figure 18. Cyclic voltammograms of $[\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-dicyd})][\text{PF}_6]_2$ (lower trace) and $[\text{Ru}(\text{bpy})(\text{trpy})(2,4\text{-Cl}_2\text{pcyd})][\text{PF}_6]$ (upper trace), in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate, scan rate = 100 mV/s.

complex relative to the mixed-valence complex thereby shifting the corresponding Ru(III,II) couple to more negative potential.⁴⁶ This implies that antiferromagnetic exchange is not important in $[\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-adpc})]^{4+}$. Unfortunately, the instability of this [III,III] complex prevented solid state magnetic measurements.

The electronic absorption data of the thallium(I) salts of apc^- and adpc^{2-} and their Ru(II) and Ru(III) complexes in DMF have been placed in Table 9. The anionic ligands in DMF show a strong visible absorption, which we have assigned to a cyanamide-to-azo group intra-ligand charge transfer (ILCT). When these ligands are incorporated into the Ru(II) complex, this transition is still observed but it is now approximately coincident in energy with metal-to-ligand charge transfer (MLCT) transitions of the Ru(II)-bpy and Ru(II)-trpy chromophores.

The spectroelectrochemistry of the [II,II] complex in DMF to generate [III,II] and [III,III] spectra is shown in Figure 19 while the spectra resulting from the stepwise oxidation of $[\text{Ru}(\text{bpy})(\text{trpy})(\text{apc})]^+$ is shown in Figure 20. For $[\text{Ru}(\text{bpy})(\text{trpy})(\text{apc})]^+$, oxidation of Ru(II) is expected to result in the loss of the MLCT transition in the visible and the appearance of two new absorption bands due to the Ru(III)-cyanamide LMCT chromophore.³⁹ Only the band at 1179 nm in the spectrum of $[\text{Ru}(\text{bpy})(\text{trpy})(\text{apc})]^{2+}$ (Table 9 and Figure 20) can be unambiguously assigned to this LMCT chromophore, as the band at 448 nm is derived from ILCT and possibly LMCT transitions.

For $[\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-adpc})]^{2+}$, oxidation to the mixed-valence complex results in the appearance of three new spectral features at $\lambda_{\text{max}} = 652, 812$ and 1920 nm (Figure 19A). The band at 812 nm is assigned to the Ru(III)-cyanamide chromophore as it appears to gain absorptivity with the formation of the [III,III] complex (Figure 19B). However, the band at 652 nm decreases in intensity with the formation of [III,III]. This is tentatively

Table 9. Electronic spectral data^a for apc⁻, adpc²⁻ and their Ru(II) and Ru(III) complexes.

Compounds	Absorptions
Tl[apc]	325 ^b (4500), 490 (40300)
Tl ₂ [adpc]	340 (6700), 500 (54400), 523 (51500)
[Ru(trpy)(bpy)(apc)] ⁺	293 (43200), 318 (38000), 469 (35000)
[Ru(trpy)(bpy)(apc)] ²⁺	289 (45300), 311 (41600), 448 (10600), 1179 (3960)
[{Ru(trpy)(bpy)} ₂ (μ-adpc)] ²⁺	293 (81900), 317 (72100), 490 (69100)
[{Ru(trpy)(bpy)} ₂ (μ-adpc)] ³⁺	292 (86900), 314 (76700), 471 (41300), 652 (13900), 812 (12700), 1920 (10000)
[{Ru(trpy)(bpy)} ₂ (μ-adpc)] ⁴⁺	312 (73400), 456 (41900), 856 (12000)

^a in nm; molar extinction coefficient (Lmol⁻¹cm⁻¹) appears in parentheses; in DMF.

^b shoulder.

Figure 19. OTTLE cell vis-NIR spectra of $[Ru(bpy)(trpy)]_2(\mu\text{-adpc})^{2+}$ under increasing anodic potential in DMF at 25°C. **A** 0-0.75 V, and **B** 0.80-1.05 V (versus Ag | AgCl).

Figure 20. Spectroelectrochemical oxidation of $[\text{Ru}(\text{bpy})(\text{trpy})(\text{apc})]^+$ in DMF.

assigned to a Ru(II)→adpc MLCT transition as *ab initio* studies of adpc²⁻ (see discussion) show a low energy LUMO of π symmetry in the ligand. The intense absorption centered at 1920 nm (Figure 19A) is absent in the spectrum of the [II,II] and [III,III] complexes (Figure 19A and B) and is therefore assigned to a metal-to-metal charge transfer (MMCT). When the MMCT band is plotted against an energy axis, (Figure 21), the band shape is non-gaussian with a pronounced high-energy tail, which is characteristic of MMCT band properties of a Class III complex.⁴⁷ This result together with the very large comproportionation constant observed for [{Ru(bpy)(trpy)}₂(μ -adpc)]³⁺ designates this complex as a Class III system despite metal ions that are separated by 19.5 Å.⁴⁸ Recall in Figure 5 that for a Class III complex, the metal-metal coupling element H_{MM} is given by the MMCT band energy band energy as:^{20,21}

$$H_{MM'} = \frac{E_{MMCT}}{2} \quad (14)$$

Thus, for [{Ru(bpy)(trpy)}₂(μ -adpc)]³⁺ in DMF, $H_{MM'} = 2600 \text{ cm}^{-1}$. This is considerably smaller than what might have been predicted based on the magnitude of the comproportionation constant but is not unprecedented in the literature.⁴⁹

Class III complex properties should also be solvent independent so the MMCT properties of [{Ru(bpy)(trpy)}₂(μ -adpc)]³⁺ were also studied in nitromethane, acetonitrile and in DMF (Table 10). Both the energy and bandwidth of the MMCT band change very little with solvent. The oscillator strength however, was found to be significantly greater in DMF compared to the other solvents. This may simply be due to the greater instability of the [III,II] complex in acetonitrile and nitromethane as opposed to any solvent effects on the probability of the electron transfer event.

Figure 21. Metal-metal charge transfer band of $[\{ \text{Ru}(\text{bpy})(\text{trpy}) \}_2(\mu\text{-adpc})]^{3+}$ in DMF.

The [III,III] spectrum in DMF (Figure 19B) shows the growth of the LMCT bands since there are now two Ru(III)-cyanamide chromophores per complex. Unfortunately, the [III,III] complex is unstable, with only 90% of the [II,II] spectrum recovered by reducing [III,III] complex even when the temperature was lowered to 0 °C. The reversibility from the [III,III] complex in nitromethane or acetonitrile was noticeably poorer.

Table 10. Electrochemical and MMCT band spectral data for [$\{\text{Ru}(\text{trpy})(\text{bpy})\}_2(\mu\text{-adpc})\}^{3+}$ in various solvents.

	Solvent		
	Acetonitrile	DMF	Nitromethane
$\lambda_{\text{max}}^{\text{a}}$:	1800 (6900) [0.0935]	1920 (10000) [0.167]	1830 (8400) [0.119]
$\Delta\nu_{1/2}^{\text{b}}$:	2710 cm^{-1}	2870 cm^{-1}	2640 cm^{-1}
H_{MM}^{b} :	2780 cm^{-1}	2600 cm^{-1}	2730 cm^{-1}
ΔE^{c} :	0.775 V	~0.7 V	~0.8 V
K_{c} :	1.3×10^{13}	$10^{12} - 10^{13}$	$10^{13} - 10^{14}$

^a wavelength of maximum absorbance (in nm) with the extinction coefficient ($\text{M}^{-1}\text{cm}^{-1}$) in parentheses. The oscillator strength is shown in square brackets.

^b calculated from equation 14.

^c the oxidation limits of DMF and nitromethane made precise determinations of the 2nd Ru (III/II) oxidation couples difficult.

4.1 Discussion

Despite a metal-metal separation of 19.5 Angströms, the dinuclear mixed valence complex $[\{\text{Ru}(\text{trpy})(\text{bpy})\}_2(\mu\text{-adpc})]^{3+}$ was found to have Class III properties. This is extraordinary in that the only comparable Class III complex is $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-bqd})]^{5+}$, where bqd =

which has a metal-metal separation of 10 Å.⁵⁰ The comproportionation constant of $K_c = 1.3 \times 10^{13}$ for $[\{\text{Ru}(\text{trpy})(\text{bpy})\}_2(\mu\text{-adpc})]^{3+}$ is second only to $[\{\text{Ru}(\text{NH}_3)_4\}_2(\mu\text{-bptz})]^{5+}$, where bptz is 3,6-bis(2-pyridyl)tetrazine, with $K_c = 10^{15}$, but bearing a metal to metal separation of only 6.8 Å. Clearly the adpc^{2-} bridging ligand is an excellent superexchange pathway for metal-metal coupling but why should this be so?

Superexchange in dinuclear mixed valence complexes can occur via 2 separate pathways as illustrated in Figure 22. One pathway includes the LUMO²⁰ of the bridging ligand (termed electron transfer) and is the usual case for π -accepting ligands such as pyridines and pyrazines. The other pathway utilizes the HOMO⁵ of the bridging ligand (termed hole transfer), as seen with ligands bearing the cyanamide moiety (a π -donor) such as dicyd^{2-} .

Figure 22. Superexchange pathways in a dinuclear mixed valence ruthenium complex bridged by a ligand, L.

Due to energy and symmetry matching requirements between the ligand and the metals for superexchange to occur, it is only likely that one pathway will be suitable. This means that for equation 11, $H_{MM'} = \frac{H_{ML}H_{ML'}}{2\Delta E_{ML}} + \frac{H_{LM}H_{LM'}}{\Delta E_{LM}}$, often only one of the products on the right side of the equation needs to be considered. For example, in the case of

$[\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-dicyd})]^{3+}$, metal-metal coupling is believed to occur through hole transfer superexchange via the HOMO of the bridging dicyd ligand² and thus equation 11 can be simplified to $H_{MM'} = \frac{H_{LM}H_{LM'}}{\Delta E_{LM}}$. This however may not be the case with $[\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-adpc})]^{3+}$ since the bridging ligand contains both π -donors (cyanamide groups) and a π -accepting azo moiety.

Figure 23 shows a comparison between the HOMO and LUMO energies calculated⁵¹ for the ligands adpc^{2-} and dicyd^{2-} . It can be easily seen that in the case of the dicyd^{2-} ligand only the HOMO has the correct symmetry for π interaction with ruthenium d orbitals. The HOMO and LUMO π orbitals of the adpc^{2-} ligand, however, are both of suitable symmetry for π -bonding with ruthenium. Looking at the energy gap between the HOMO and LUMO of dicyd^{2-} shows it to be quite large at 2.59 eV, so it is unlikely that both orbitals would be close enough in energy to Ru(II) and Ru(III) $d\pi$ orbitals to allow for superexchange. On the other hand, the LUMO-HOMO band gap for adpc^{2-} is only 1.07 eV so both orbitals may be of suitable energy for superexchange pathways. This means that it should be possible for both the π -HOMO and π -LUMO of adpc^{2-} to simultaneously interact with both ruthenium(II) donor and ruthenium(III) acceptor $d\pi$ orbitals to provide increased metal-metal coupling (Figure 24).

A calculation of H_{MM} from equation 11 should be in agreement with that of equation 14 (which assumes a Class III complex) provided the theory holds. This would

Figure 23. *Ab initio* calculation of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of adpc^{2-} (A) and dicyd^{2-} (B). See ref. 34.

give further support for the Class III assignment of $[\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-adpc})]^{3+}$. The reduced energies ΔE_{ML} and ΔE_{LM} can be readily calculated from the spectral data in Table 9. Unfortunately, since the transition dipole moment lengths, r , of the MLCT and LMCT bands cannot easily be measured, then H_{ML} and H_{LM} cannot be determined for equation 11 and so a theoretical measure of H_{MM} is not possible at this time. It can be said, however, that the hole transfer superexchange pathway is expected to contribute more to H_{MM} than electron transfer in $[\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-adpc})]^{3+}$ because ΔE_{LM} is considerably smaller than ΔE_{ML} at 9000 cm^{-1} and 12200 cm^{-1} respectively.

Figure 24. Proposed superexchange pathways utilized by $[\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-adpc})]^{3+}$.

Electron transfer (upper pathway) uses the LUMO of the bridging ligand (L). Hole transfer occurs via the HOMO of the bridging ligand.

5. Conclusions and Future Studies

Cyclic voltammetry and spectroelectrochemistry showed the effects of the nature of the inner coordination sphere on the ruthenium(III)-cyanamide chromophore. The bathochromic shift seen in the ligand-to-metal charge transfer band on going from an inner coordination sphere of $\text{Ru}(\text{NH}_3)_5\text{L}$ to $\text{Ru}(\text{bpy})(\text{trpy})\text{L}$ was mirrored by an approximately 0.8 volt stabilization of the Ru(III) valence orbitals seen in cyclic voltammetry. A plot of LMCT band energy verses ΔE for both sets of complexes showed a common y-intercept, suggesting that the inner and outersphere reorganizational energies for the $[\text{Ru}(\text{bpy})(\text{trpy})\text{L}]^{2+}$ and $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$ LMCT chromophores were equivalent. As this seemed unlikely it was suggested that the difference in inner and outersphere energies between the two sets of complexes canceled out. Calculations of the ligand-metal coupling element H_{LM} for both sets of complexes showed stronger coupling for the $\text{Ru}(\text{NH}_3)_5$ complexes. As this was inconsistent with previous studies, it was suggested that the error lay in the assumption that the dipole moment length, r was equal to 5.56 Å for both sets of complexes. Greater covalency in the Ru-cyanamide bond of the $\text{Ru}(\text{bpy})(\text{trpy})\text{L}$ complexes would result in a smaller r and an increase in the actual value of H_{LM} . These studies provided some of the groundwork needed for the examination of dinuclear complexes.

The dinuclear complex $[\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-adpc})]^{3+}$ was found to be a Class III complex with a comproportionation constant, $K_c = 1.3 \times 10^{13}$ and a metal-metal coupling constant, H_{MM} , of 2600 cm^{-1} . It was shown that by alternating donor and acceptor groups within a bridging ligand it is possible to dramatically enhanced metal-metal coupling

within a dinuclear, mixed-valence complex. The alternation of donor and acceptor groups reduces the energy gap between the π HOMO and LUMO of adpc^{2-} and, as these orbitals can interact simultaneously with ruthenium ion $d\pi$ donor and acceptor orbitals, superexchange via both hole and electron transfer mechanisms is possible. The magnitude of coupling seen for $[\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-adpc})]^{3+}$, despite a separation of 19.5 Å between ruthenium ions suggests that the properties of the adpc^{2-} bridging ligand approach that of a truly conducting molecular wire.

It would be of significant merit to make use of the azo group in the adpc ligand. Azobenzenes are well known to undergo a photoinduced *trans-cis* (E to Z) isomerization and it may be possible to take advantage of this feature with the intent of controlling metal-metal coupling in $[\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-adpc})]^{3+}$. Initial attempts at photoisomerization of the complex in DMF were apparently unsuccessful. This may have been due to our inability to isolate the correct wavelength for irradiation, or it could be that isomerization back to the E isomer was too fast to allow for detection of the Z conformation. More tests will be required. While the Z conformation of $[\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-adpc})]^{3+}$ is expected to have about the same value for H_{MM} as the E isomer, since there is no change to the conjugation along the bridging ligand, it may be possible to couple the isomerization with an event that *will* effect H_{MM} .

Rotaxanes⁵² are a peculiar class of compounds in which two discrete molecules are joined together without the use of molecular bonds. This is accomplished by trapping a ring-shaped molecule around a linear molecule. Bulky groups at each end of the linear

molecule hold the ring in place by steric forces. The ring can be associated with the linear molecule by means of self-assembly. For example, a water-soluble ring with a hydrophobic interior will thread itself onto a linear lipophilic molecule when both are dissolved in aqueous solvent-provided this is energetically favorable.⁵² This act reduces the interaction of the non-polar ring interior with the polar solvent.

This has recently been accomplished⁵³ with the dinuclear complex $[\{\text{Fe}(\text{CN})_5\}_2(\mu\text{-azopyridine})]^{6-}$:

They formed rotaxanes using α -cyclodextrin, which is a ring shaped molecule formed from six α -(1 $\rightarrow$ 4)-linked D-(+)-glucopyranose units. It would be interesting to form a rotaxane by the inclusion of $[\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-adpc})]^{3+}$ within a cyclodextrin ring and examine its effect on metal-metal coupling in conjunction with E-Z isomerization of the azo group. It is suggested here that this molecule would appear as in Figure 25A when in the E configuration and that upon isomerization of the azo ligand, the cyclodextrin ring would shift position (Figure 25B) in order to alleviate steric hindrance brought about by the Z configuration. The new position of the cyclodextrin ring should perturb the Ru-*pcyd* orbital enough to affect the metal-ligand coupling and hence metal-metal coupling. Thus the E-Z isomerization of this rotaxane could act as a switch for metal-metal coupling.

Figure 25. A rotaxane formed by the association of a cyclodextrin ring (shaded cylinder) with $[\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-adpc})]^{2+}$. A: *trans* configuration, B: *cis* configuration. Note the shift in the position of the cyclodextrin ring upon isomerization.

Preliminary studies in deuterated 0.1M sodium hydroxide solution strongly suggest that an association does form between α -cyclodextrin and the free ligand H_2adpc . This was indicated by UV-VIS studies as well as by 1H NMR. The next step would be to form a rotaxane with the full $[\{Ru(trpy)(bpy)\}_2(\mu-adpc)]^{2+}$ complex.

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Appendix A. Crystallography data for [Ru(bpy)(trpy)(2,4-Cl₂pcyd)][PF₆] $\cdot$ DMF.

Table A1. Crystal data and structure refinements for [Ru(bpy)(trpy)(2,4-Cl₂pcyd)][PF₆].DMF.

Identification code	rc008
Empirical formula	C35 H29 Cl2 P6 N8 O P Ru
Formula weight	894.60
Temperature	238(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 11.681(4) Å alpha = 68.00(2) deg. b = 12.240(5) Å beta = 70.05(3) deg. c = 15.017(5) Å gamma = 78.55(2) deg.
Volume	1865(1) Å ³
Z, Calculated density	2, 1.593 Mg/m ³
Absorption coefficient	0.678 mm ⁻¹
F(000)	900
Crystal size	0.10 x 0.08 x 0.05 mm
Theta range for data collection	1.86 to 26.37 deg.
Limiting indices	-13<=h<=14, -13<=k<=15, 0<=l<=14
Reflections collected / unique	9530 / 4848 [R(int) = 0.0636]
Completeness to theta = 26.37	63.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.928077 and 0.407972
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4848 / 51 / 450
Goodness-of-fit on F ²	1.100
Final R indices [I>2sigma(I)]	R1 = 0.0722, WR2 = 0.2122
R indices (all data)	R1 = 0.0955, WR2 = 0.2397
Largest diff. peak and hole	0.889 and -0.862 e.Å ⁻³

Table A2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ru}(\text{bpy})(\text{trpy})(2,4\text{-Cl}_2\text{pcyd})][\text{PF}_6]\cdot\text{DMF}$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Ru	7409 (1)	6358 (1)	5826 (1)	29 (1)
P	7504 (3)	2367 (2)	11384 (3)	56 (1)
Cl (1)	9354 (4)	184 (3)	5946 (5)	132 (2)
Cl (2)	5776 (11)	-1462 (8)	9283 (8)	315 (7)
F (1)	7952 (7)	3667 (6)	10866 (7)	94 (3)
F (2)	7058 (8)	2521 (7)	12467 (6)	95 (3)
F (3)	7062 (6)	1068 (6)	11906 (7)	83 (3)
F (4)	7962 (8)	2214 (8)	10294 (7)	105 (3)
F (5)	8811 (6)	1854 (6)	11570 (6)	87 (3)
F (6)	6180 (6)	2889 (6)	11246 (7)	87 (3)
N (1)	5811 (6)	6205 (6)	5582 (8)	25 (3)
N (2)	6406 (6)	5663 (7)	7217 (7)	38 (3)
N (3)	8584 (6)	6344 (6)	6609 (8)	36 (2)
N (4)	6926 (6)	8113 (6)	5581 (7)	38 (2)
N (5)	8437 (5)	7083 (6)	4343 (7)	35 (2)
N (6)	8024 (5)	4612 (6)	5900 (6)	31 (2)
N (7)	8464 (6)	2551 (6)	6046 (7)	47 (3)
C (1)	5537 (8)	6613 (8)	4711 (11)	35 (4)
C (2)	4394 (8)	6521 (8)	4649 (9)	39 (3)
C (3)	3508 (8)	6010 (9)	5516 (12)	52 (4)
C (4)	3767 (7)	5583 (8)	6435 (10)	40 (4)
C (5)	4942 (8)	5713 (8)	6447 (10)	34 (3)
C (6)	5285 (8)	5311 (8)	7362 (11)	34 (4)
C (7)	4699 (10)	4582 (9)	8324 (11)	46 (4)
C (8)	5183 (11)	4269 (10)	9120 (11)	56 (4)
C (9)	6321 (10)	4639 (9)	8966 (10)	51 (4)
C (10)	6912 (8)	5324 (8)	7994 (10)	40 (3)
C (11)	8129 (9)	5788 (8)	7657 (10)	39 (3)
C (12)	8791 (10)	5725 (10)	8297 (11)	55 (3)
C (13)	9882 (9)	6240 (11)	7924 (13)	60 (4)
C (14)	10319 (9)	6790 (11)	6908 (13)	64 (5)
C (15)	9654 (7)	6821 (8)	6266 (9)	45 (3)
C (16)	6091 (8)	8590 (8)	6265 (9)	45 (3)
C (17)	5826 (11)	9800 (11)	6014 (12)	66 (4)
C (18)	6390 (12)	10534 (10)	5088 (13)	76 (5)
C (19)	7226 (9)	10069 (8)	4400 (10)	54 (3)
C (20)	7483 (7)	8855 (7)	4634 (9)	34 (3)
C (21)	8319 (7)	8293 (7)	3939 (9)	41 (3)
C (22)	8976 (8)	8876 (9)	2921 (9)	47 (3)
C (23)	9712 (9)	8242 (10)	2311 (10)	55 (3)
C (24)	9806 (8)	7037 (10)	2720 (10)	51 (3)
C (25)	9166 (7)	6473 (7)	3717 (9)	37 (3)
C (26)	8169 (7)	3629 (8)	6025 (7)	30 (3)
C (27)	8196 (8)	480 (7)	6844 (9)	95 (6)
C (28)	7576 (12)	-471 (5)	7583 (11)	127 (9)
C (29)	6582 (12)	-286 (10)	8361 (9)	158 (12)
C (30)	6207 (9)	851 (12)	8398 (7)	147 (9)
C (31)	6827 (7)	1803 (8)	7659 (8)	104 (5)
C (32)	7822 (7)	1617 (5)	6882 (7)	59 (3)

Table A2 continued

O	3261 (10)	2794 (11)	7762 (10)	120 (4)
N(8)	1964 (9)	1800 (9)	9255 (9)	70 (3)
C(33)	2903 (12)	1843 (14)	8382 (13)	88 (4)
C(34)	1456 (16)	2870 (16)	9425 (15)	123 (6)
C(35)	1562 (15)	658 (14)	9950 (14)	111 (5)

Table A3. Bond lengths (in Angströms) and angles (in degrees) for [Ru(bpy)(trpy)(2,4-Cl₂pcyd)][PF₆]-DMF.

Ru-N(2)	1.962(9)
Ru-N(4)	2.035(6)
Ru-N(5)	2.076(8)
Ru-N(1)	2.076(8)
Ru-N(3)	2.084(8)
Ru-N(6)	2.088(7)
P-F(3)	1.588(7)
P-F(1)	1.593(7)
P-F(2)	1.601(8)
P-F(6)	1.603(7)
P-F(5)	1.607(7)
P-F(4)	1.610(9)
Cl(1)-C(27)	1.645(11)
Cl(2)-C(29)	1.741(8)
N(1)-C(1)	1.339(13)
N(1)-C(5)	1.355(13)
N(2)-C(10)	1.377(14)
N(2)-C(6)	1.381(12)
N(3)-C(15)	1.339(11)
N(3)-C(11)	1.413(13)
N(4)-C(16)	1.373(11)
N(4)-C(20)	1.381(13)
N(5)-C(21)	1.372(11)
N(5)-C(25)	1.377(11)
N(6)-C(26)	1.132(10)
N(7)-C(26)	1.288(10)
N(7)-C(32)	1.437(10)
C(1)-C(2)	1.400(13)
C(2)-C(3)	1.373(16)
C(3)-C(4)	1.396(15)
C(4)-C(5)	1.420(12)
C(5)-C(6)	1.443(15)
C(6)-C(7)	1.397(16)
C(7)-C(8)	1.389(17)
C(8)-C(9)	1.405(16)
C(9)-C(10)	1.391(16)
C(10)-C(11)	1.488(14)
C(11)-C(12)	1.397(15)
C(12)-C(13)	1.380(15)
C(13)-C(14)	1.370(17)
C(14)-C(15)	1.416(16)
C(16)-C(17)	1.383(14)
C(17)-C(18)	1.359(18)
C(18)-C(19)	1.370(16)
C(19)-C(20)	1.388(11)
C(20)-C(21)	1.446(14)
C(21)-C(22)	1.427(15)
C(22)-C(23)	1.382(14)
C(23)-C(24)	1.367(15)
C(24)-C(25)	1.395(15)
C(27)-C(28)	1.3900
C(27)-C(32)	1.3900
C(28)-C(29)	1.3900
C(29)-C(30)	1.3900
C(30)-C(31)	1.3900
C(31)-C(32)	1.3900

O-C(33)	1.230(17)
N(8)-C(33)	1.383(17)
N(8)-C(34)	1.405(18)
N(8)-C(35)	1.448(18)
N(2)-Ru-N(4)	101.5(3)
N(2)-Ru-N(5)	178.5(3)
N(4)-Ru-N(5)	78.7(3)
N(2)-Ru-N(1)	79.7(4)
N(4)-Ru-N(1)	89.4(3)
N(5)-Ru-N(1)	98.8(3)
N(2)-Ru-N(3)	79.4(3)
N(4)-Ru-N(3)	91.4(3)
N(5)-Ru-N(3)	102.1(3)
N(1)-Ru-N(3)	158.8(4)
N(2)-Ru-N(6)	85.2(3)
N(4)-Ru-N(6)	173.3(3)
N(5)-Ru-N(6)	94.6(3)
N(1)-Ru-N(6)	91.2(2)
N(3)-Ru-N(6)	90.5(3)
F(3)-P-F(1)	179.5(5)
F(3)-P-F(2)	88.8(5)
F(1)-P-F(2)	90.9(5)
F(3)-P-F(6)	90.6(4)
F(1)-P-F(6)	89.8(4)
F(2)-P-F(6)	89.6(5)
F(3)-P-F(5)	89.5(4)
F(1)-P-F(5)	90.1(4)
F(2)-P-F(5)	87.8(5)
F(6)-P-F(5)	177.3(5)
F(3)-P-F(4)	91.4(5)
F(1)-P-F(4)	88.9(5)
F(2)-P-F(4)	179.6(5)
F(6)-P-F(4)	90.8(5)
F(5)-P-F(4)	91.8(5)
C(1)-N(1)-C(5)	119.3(9)
C(1)-N(1)-Ru	127.8(6)
C(5)-N(1)-Ru	112.6(8)
C(10)-N(2)-C(6)	121.1(10)
C(10)-N(2)-Ru	120.1(7)
C(6)-N(2)-Ru	117.5(8)
C(15)-N(3)-C(11)	117.1(9)
C(15)-N(3)-Ru	129.6(9)
C(11)-N(3)-Ru	113.3(6)
C(16)-N(4)-C(20)	119.3(8)
C(16)-N(4)-Ru	125.4(7)
C(20)-N(4)-Ru	115.4(5)
C(21)-N(5)-C(25)	117.3(9)
C(21)-N(5)-Ru	116.0(6)
C(25)-N(5)-Ru	126.6(6)
C(26)-N(6)-Ru	169.0(6)
C(26)-N(7)-C(32)	119.6(8)
N(1)-C(1)-C(2)	122.7(10)
C(3)-C(2)-C(1)	118.8(11)
C(2)-C(3)-C(4)	119.7(9)
C(3)-C(4)-C(5)	118.7(10)
N(1)-C(5)-C(4)	120.8(12)
N(1)-C(5)-C(6)	116.7(9)
C(4)-C(5)-C(6)	122.5(11)
N(2)-C(6)-C(7)	117.3(13)

Table A3 Continued

N(2)-C(6)-C(5)	112.5(9)
C(7)-C(6)-C(5)	130.0(11)
C(8)-C(7)-C(6)	121.9(12)
C(7)-C(8)-C(9)	120.3(13)
C(10)-C(9)-C(8)	116.8(13)
N(2)-C(10)-C(9)	122.5(10)
N(2)-C(10)-C(11)	111.6(10)
C(9)-C(10)-C(11)	125.9(12)
C(12)-C(11)-N(3)	120.7(11)
C(12)-C(11)-C(10)	124.8(12)
N(3)-C(11)-C(10)	114.5(9)
C(13)-C(12)-C(11)	120.9(14)
C(14)-C(13)-C(12)	118.4(13)
C(13)-C(14)-C(15)	120.1(11)
N(3)-C(15)-C(14)	122.8(12)
N(4)-C(16)-C(17)	120.4(11)
C(18)-C(17)-C(16)	120.5(10)
C(17)-C(18)-C(19)	119.7(10)
C(18)-C(19)-C(20)	120.5(12)
N(4)-C(20)-C(19)	119.6(9)
N(4)-C(20)-C(21)	116.5(7)
C(19)-C(20)-C(21)	123.9(10)
N(5)-C(21)-C(22)	120.3(9)
N(5)-C(21)-C(20)	113.4(9)
C(22)-C(21)-C(20)	126.2(8)
C(23)-C(22)-C(21)	121.1(10)
C(24)-C(23)-C(22)	117.9(11)
C(23)-C(24)-C(25)	120.7(9)
N(5)-C(25)-C(24)	122.6(8)
N(6)-C(26)-N(7)	171.5(10)
C(28)-C(27)-C(32)	120.0
C(28)-C(27)-Cl(1)	116.8(6)
C(32)-C(27)-Cl(1)	123.2(6)
C(29)-C(28)-C(27)	120.0
C(28)-C(29)-C(30)	120.0
C(28)-C(29)-Cl(2)	120.8(10)
C(30)-C(29)-Cl(2)	119.2(10)
C(31)-C(30)-C(29)	120.0
C(30)-C(31)-C(32)	120.0
C(31)-C(32)-C(27)	120.0
C(31)-C(32)-N(7)	124.0(6)
C(27)-C(32)-N(7)	115.8(6)
C(33)-N(8)-C(34)	118.1(13)
C(33)-N(8)-C(35)	118.6(12)
C(34)-N(8)-C(35)	123.3(13)
O-C(33)-N(8)	120.9(14)

Table A4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ru}(\text{bpy})(\text{trpy})(2,4\text{-Cl}_2\text{pcyd})][\text{PF}_6] \cdot \text{DMF}$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + \dots + 2h k a^* b^* U_{12}]$.

	U11	U22	U33	U23	U13	U12
Ru	30 (1)	25 (1)	32 (1)	-9 (1)	-14 (1)	5 (1)
P	66 (2)	46 (2)	51 (3)	-7 (2)	-27 (2)	6 (1)
Cl (1)	138 (4)	71 (2)	224 (6)	-87 (3)	-78 (4)	30 (2)
Cl (2)	447 (14)	221 (8)	255 (11)	140 (8)	-187 (10)	-267 (10)
F (1)	116 (6)	55 (4)	104 (8)	15 (5)	-60 (5)	-21 (4)
F (2)	156 (8)	83 (5)	45 (8)	-21 (5)	-37 (5)	4 (5)
F (3)	96 (5)	47 (4)	103 (8)	-2 (4)	-49 (5)	-4 (3)
F (4)	140 (7)	100 (6)	64 (8)	-31 (6)	-25 (5)	9 (5)
F (5)	67 (4)	76 (5)	98 (8)	-3 (5)	-36 (4)	9 (3)
F (6)	74 (4)	80 (5)	98 (8)	-10 (5)	-45 (4)	8 (3)
N (1)	36 (4)	18 (3)	16 (9)	0 (5)	-14 (4)	7 (3)
N (2)	41 (4)	38 (4)	35 (9)	-18 (5)	-12 (4)	6 (3)
N (3)	37 (4)	36 (4)	40 (8)	-16 (4)	-20 (4)	10 (3)
N (4)	41 (4)	26 (4)	47 (8)	-9 (5)	-22 (4)	5 (3)
N (5)	29 (3)	34 (4)	41 (8)	-12 (4)	-12 (3)	-3 (3)
N (6)	31 (3)	32 (4)	23 (7)	-1 (4)	-9 (3)	-3 (3)
N (7)	44 (4)	28 (4)	63 (8)	-14 (5)	-13 (4)	2 (3)
C (1)	44 (5)	22 (4)	33 (13)	0 (7)	-20 (6)	6 (3)
C (2)	48 (5)	36 (5)	40 (10)	-11 (6)	-31 (5)	11 (4)
C (3)	41 (5)	55 (6)	83 (14)	-44 (8)	-33 (7)	12 (4)
C (4)	30 (4)	35 (5)	49 (12)	-16 (6)	-7 (5)	1 (3)
C (5)	47 (5)	26 (4)	34 (12)	-8 (6)	-26 (6)	6 (4)
C (6)	40 (4)	34 (5)	23 (13)	-13 (7)	0 (5)	-2 (4)
C (7)	59 (6)	44 (6)	31 (13)	-1 (7)	-14 (7)	-14 (5)
C (8)	73 (7)	46 (6)	24 (14)	13 (8)	-11 (7)	-9 (5)
C (9)	65 (6)	51 (6)	24 (12)	3 (7)	-17 (6)	1 (5)
C (10)	46 (5)	37 (5)	31 (11)	-10 (6)	-10 (5)	3 (4)
C (11)	57 (5)	35 (5)	32 (9)	-12 (5)	-31 (5)	14 (4)
C (12)	72 (6)	60 (6)	46 (10)	-23 (7)	-41 (6)	19 (5)
C (13)	47 (6)	82 (8)	59 (14)	-27 (9)	-19 (7)	-9 (5)
C (14)	39 (5)	79 (8)	101 (16)	-58 (10)	-28 (7)	7 (5)
C (15)	37 (4)	50 (5)	54 (10)	-33 (6)	-10 (5)	8 (4)
C (16)	52 (5)	46 (5)	46 (10)	-27 (6)	-19 (5)	7 (4)
C (17)	70 (7)	61 (7)	93 (15)	-52 (9)	-44 (8)	27 (6)
C (18)	89 (9)	37 (6)	106 (16)	-34 (9)	-36 (9)	14 (6)
C (19)	70 (6)	27 (5)	63 (11)	-11 (6)	-28 (6)	4 (4)
C (20)	43 (4)	29 (4)	34 (10)	-2 (6)	-29 (5)	3 (4)
C (21)	42 (4)	21 (4)	58 (11)	2 (6)	-32 (5)	2 (3)
C (22)	53 (5)	41 (5)	36 (11)	-3 (7)	-12 (6)	-1 (4)
C (23)	50 (5)	60 (7)	39 (11)	-4 (7)	-9 (5)	-3 (5)
C (24)	41 (5)	76 (8)	45 (11)	-34 (8)	-15 (5)	10 (5)
C (25)	38 (4)	30 (4)	38 (10)	-5 (6)	-15 (5)	2 (3)
C (26)	30 (4)	39 (5)	18 (9)	-6 (5)	-8 (4)	1 (3)
C (27)	110 (10)	40 (6)	175 (18)	-31 (9)	-107 (11)	10 (6)
C (28)	190 (19)	55 (8)	180 (20)	15 (12)	-140 (17)	-54 (10)
C (29)	190 (20)	107 (15)	150 (30)	88 (16)	-107 (19)	-100 (16)
C (30)	124 (13)	162 (17)	104 (17)	51 (14)	-43 (10)	-73 (13)
C (31)	75 (8)	141 (13)	57 (13)	38 (9)	-30 (7)	-44 (8)
C (32)	61 (5)	27 (4)	95 (11)	5 (6)	-55 (5)	-8 (4)

Table A5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ru}(\text{bpy})(\text{trpy})(2,4\text{-Cl}_2\text{pcyd})][\text{PF}_6] \cdot \text{DMF}$.

	x	y	z	U(eq)
H(1A)	6138	6976	4118	42
H(2A)	4235	6805	4024	47
H(3A)	2730	5949	5491	62
H(4A)	3176	5215	7033	48
H(7A)	3956	4294	8435	56
H(8A)	4748	3809	9765	67
H(9A)	6666	4434	9494	61
H(12A)	8488	5327	8990	66
H(13A)	10316	6215	8357	72
H(14A)	11060	7148	6637	77
H(15A)	9978	7191	5570	54
H(16A)	5698	8091	6908	54
H(17A)	5250	10118	6486	79
H(18A)	6208	11356	4921	91
H(19A)	7629	10576	3765	65
H(22A)	8907	9707	2660	57
H(23A)	10135	8627	1638	66
H(24A)	10307	6584	2324	62
H(25A)	9236	5642	3972	45
H(28A)	7830	-1240	7558	152
H(30A)	5535	976	8924	177
H(31A)	6574	2572	7685	125
H(33A)	3273	1136	8262	105
H(34A)	1900	3516	8892	185
H(34B)	1511	2837	10065	185
H(34C)	605	2997	9437	185
H(35A)	2044	42	9689	166
H(35B)	706	633	10029	166
H(35C)	1664	535	10596	166

Appendix B. Crystallography data for $[\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-adpc})][\text{PF}_6]_2 \cdot 2(\text{ether}) \cdot 2\text{DMF}$.

Table B1. Crystal data and structure refinement for $[\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-adpc})][\text{PF}_6]_2 \cdot 2(\text{ether}) \cdot 2\text{DMF}$.

Identification code	rc011
Empirical formula	C76 H72 F12 N18 O2 P2 Ru2
Formula weight	1761.60
Temperature	203(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 12.480(2) Å alpha = 79.792(3) deg. b = 13.090(3) Å beta = 68.027(3) deg. c = 14.147(3) Å gamma = 64.447(3) deg.
Volume	1933.3(6) Å ³
Z, Calculated density	1, 1.513 Mg/m ³
Absorption coefficient	0.520 mm ⁻¹
F(000)	896
Crystal size	0.30 x 0.15 x 0.04 mm
Theta range for data collection	1.72 to 28.83 deg.
Limiting indices	-15 ≤ h ≤ 16, -17 ≤ k ≤ 17, 0 ≤ l ≤ 18
Reflections collected / unique	8763 / 8763 [R(int) = 0.0000]
Completeness to theta = 28.83	86.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.928078 and 0.690280
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	8763 / 0 / 506
Goodness-of-fit on F ²	1.044
Final R indices [I > 2sigma(I)]	R1 = 0.0421, wR2 = 0.0682
R indices (all data)	R1 = 0.0717, wR2 = 0.0719
Largest diff. peak and hole	0.461 and -0.485 e.Å ⁻³

Table B2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-adpc})][\text{PF}_6]_2 \cdot 2(\text{ether}) \cdot 2\text{DMF}$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Ru	6736 (1)	-6495 (1)	-2999 (1)	27 (1)
P (1)	5438 (1)	-12 (1)	-7212 (1)	44 (1)
F (1)	5260 (2)	-1056 (2)	-7445 (2)	100 (1)
F (2)	5088 (2)	653 (2)	-8166 (2)	97 (1)
F (3)	5621 (2)	1017 (2)	-6970 (2)	84 (1)
F (4)	5787 (2)	-698 (2)	-6256 (2)	90 (1)
F (5)	3990 (2)	523 (2)	-6516 (2)	73 (1)
F (6)	6882 (2)	-534 (2)	-7904 (2)	74 (1)
N (1)	8630 (2)	-7377 (2)	-3305 (2)	32 (1)
N (2)	6770 (2)	-7809 (2)	-1939 (2)	31 (1)
N (3)	6762 (2)	-7205 (2)	-4203 (2)	28 (1)
N (4)	6741 (2)	-5266 (2)	-4022 (2)	28 (1)
N (5)	6708 (2)	-5320 (2)	-2183 (2)	32 (1)
N (6)	4809 (2)	-5718 (2)	-2491 (2)	32 (1)
N (7)	2576 (2)	-4660 (2)	-1584 (2)	35 (1)
N (8)	592 (2)	-223 (2)	-235 (2)	37 (1)
N (9)	7449 (3)	-2528 (3)	155 (3)	68 (1)
O (1)	10207 (3)	-7055 (2)	-6468 (2)	76 (1)
C (1)	9533 (3)	-7109 (3)	-4022 (3)	43 (1)
C (2)	10801 (3)	-7691 (3)	-4125 (3)	56 (1)
C (3)	11142 (3)	-8570 (3)	-3464 (3)	60 (1)
C (4)	10234 (3)	-8875 (3)	-2740 (3)	52 (1)
C (5)	8975 (3)	-8284 (2)	-2667 (2)	36 (1)
C (6)	7942 (3)	-8561 (2)	-1946 (2)	34 (1)
C (7)	8083 (3)	-9515 (3)	-1304 (3)	50 (1)
C (8)	7047 (4)	-9695 (3)	-653 (3)	56 (1)
C (9)	5877 (3)	-8925 (3)	-639 (3)	49 (1)
C (10)	5779 (3)	-8008 (2)	-1303 (2)	38 (1)
C (11)	6785 (3)	-8228 (2)	-4257 (2)	34 (1)
C (12)	6840 (3)	-8617 (3)	-5124 (3)	42 (1)
C (13)	6912 (3)	-7944 (3)	-5990 (2)	43 (1)
C (14)	6889 (3)	-6882 (2)	-5961 (2)	36 (1)
C (15)	6807 (2)	-6525 (2)	-5067 (2)	28 (1)
C (16)	6715 (2)	-5396 (2)	-4940 (2)	27 (1)
C (17)	6551 (3)	-4483 (2)	-5621 (2)	36 (1)
C (18)	6408 (3)	-3459 (3)	-5341 (2)	38 (1)
C (19)	6424 (3)	-3341 (2)	-4400 (2)	35 (1)
C (20)	6586 (2)	-4265 (2)	-3738 (2)	28 (1)
C (21)	6590 (3)	-4301 (2)	-2688 (2)	31 (1)
C (22)	6492 (3)	-3395 (3)	-2238 (3)	43 (1)
C (23)	6534 (3)	-3505 (3)	-1263 (3)	55 (1)
C (24)	6676 (3)	-4536 (3)	-762 (3)	57 (1)
C (25)	6748 (3)	-5407 (3)	-1233 (3)	48 (1)
C (26)	3761 (3)	-5173 (2)	-2044 (2)	29 (1)
C (27)	2121 (3)	-3572 (2)	-1230 (2)	31 (1)
C (28)	819 (3)	-3038 (2)	-702 (2)	39 (1)
C (29)	297 (3)	-1959 (2)	-349 (2)	37 (1)
C (30)	1046 (3)	-1360 (2)	-522 (2)	33 (1)
C (31)	2329 (3)	-1883 (2)	-1022 (2)	39 (1)

Table B2 continued

C (32)	2867 (3)	-2975 (2)	-1369 (2)	36 (1)
C (33)	10455 (5)	-8066 (4)	-6900 (4)	88 (2)
C (34)	10484 (5)	-8986 (4)	-6097 (4)	102 (2)
C (35)	10116 (4)	-6121 (4)	-7154 (3)	80 (1)
C (36)	10023 (4)	-5161 (3)	-6642 (3)	80 (1)
C (37)	7766 (3)	-2827 (3)	834 (3)	51 (1)
C (38)	8204 (4)	-3220 (3)	1703 (3)	77 (1)

Table B3. Bond lengths (in Angströms) and angles (in degrees) for [$\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-adpc})][\text{PF}_6]_2 \cdot 2(\text{ether}) \cdot 2\text{DMF}$].

Ru-N(4)	1.964(2)
Ru-N(1)	2.041(2)
Ru-N(6)	2.046(2)
Ru-N(3)	2.065(2)
Ru-N(5)	2.062(2)
Ru-N(2)	2.069(2)
P(1)-F(3)	1.571(2)
P(1)-F(2)	1.571(2)
P(1)-F(4)	1.581(2)
P(1)-F(1)	1.582(2)
P(1)-F(6)	1.589(2)
P(1)-F(5)	1.596(2)
N(1)-C(1)	1.336(4)
N(1)-C(5)	1.371(3)
N(2)-C(10)	1.330(4)
N(2)-C(6)	1.364(3)
N(3)-C(11)	1.342(3)
N(3)-C(15)	1.377(3)
N(4)-C(20)	1.351(3)
N(4)-C(16)	1.355(3)
N(5)-C(25)	1.346(4)
N(5)-C(21)	1.372(3)
N(6)-C(26)	1.164(3)
N(7)-C(26)	1.281(4)
N(7)-C(27)	1.394(3)
N(8)-N(8)#1	1.274(4)
N(8)-C(30)	1.420(3)
N(9)-C(37)	1.118(4)
O(1)-C(35)	1.412(4)
O(1)-C(33)	1.419(4)
C(1)-C(2)	1.390(4)
C(2)-C(3)	1.369(5)
C(3)-C(4)	1.366(5)
C(4)-C(5)	1.391(4)
C(5)-C(6)	1.456(4)
C(6)-C(7)	1.395(4)
C(7)-C(8)	1.368(5)
C(8)-C(9)	1.365(4)
C(9)-C(10)	1.377(4)
C(11)-C(12)	1.378(4)
C(12)-C(13)	1.374(4)
C(13)-C(14)	1.386(4)
C(14)-C(15)	1.378(4)
C(15)-C(16)	1.471(4)
C(16)-C(17)	1.387(4)
C(17)-C(18)	1.384(4)
C(18)-C(19)	1.375(4)
C(19)-C(20)	1.382(4)
C(20)-C(21)	1.480(4)
C(21)-C(22)	1.383(4)
C(22)-C(23)	1.379(4)
C(23)-C(24)	1.380(4)
C(24)-C(25)	1.373(4)
C(27)-C(28)	1.408(4)
C(27)-C(32)	1.398(4)
C(28)-C(29)	1.372(4)

C(29) - C(30)	1.393 (4)
C(30) - C(31)	1.382 (4)
C(31) - C(32)	1.381 (4)
C(33) - C(34)	1.500 (6)
C(35) - C(36)	1.500 (5)
C(37) - C(38)	1.453 (5)
N(4) - Ru - N(1)	99.87 (9)
N(4) - Ru - N(6)	87.69 (9)
N(1) - Ru - N(6)	171.85 (10)
N(4) - Ru - N(3)	79.75 (9)
N(1) - Ru - N(3)	92.27 (9)
N(6) - Ru - N(3)	92.06 (9)
N(4) - Ru - N(5)	79.50 (10)
N(1) - Ru - N(5)	91.37 (9)
N(6) - Ru - N(5)	87.00 (9)
N(3) - Ru - N(5)	159.25 (9)
N(4) - Ru - N(2)	178.77 (11)
N(1) - Ru - N(2)	78.98 (9)
N(6) - Ru - N(2)	93.48 (9)
N(3) - Ru - N(2)	99.81 (9)
N(5) - Ru - N(2)	100.94 (9)
F(3) - P(1) - F(2)	89.92 (14)
F(3) - P(1) - F(4)	91.03 (13)
F(2) - P(1) - F(4)	179.05 (14)
F(3) - P(1) - F(1)	179.40 (15)
F(2) - P(1) - F(1)	90.67 (14)
F(4) - P(1) - F(1)	88.38 (14)
F(3) - P(1) - F(6)	89.84 (12)
F(2) - P(1) - F(6)	89.80 (13)
F(4) - P(1) - F(6)	90.20 (12)
F(1) - P(1) - F(6)	90.09 (12)
F(3) - P(1) - F(5)	89.62 (12)
F(2) - P(1) - F(5)	90.07 (13)
F(4) - P(1) - F(5)	89.94 (12)
F(1) - P(1) - F(5)	90.45 (12)
F(6) - P(1) - F(5)	179.45 (12)
C(1) - N(1) - C(5)	118.5 (3)
C(1) - N(1) - Ru	125.8 (2)
C(5) - N(1) - Ru	115.59 (19)
C(10) - N(2) - C(6)	118.3 (2)
C(10) - N(2) - Ru	126.47 (19)
C(6) - N(2) - Ru	115.14 (19)
C(11) - N(3) - C(15)	117.6 (2)
C(11) - N(3) - Ru	129.00 (19)
C(15) - N(3) - Ru	113.39 (18)
C(20) - N(4) - C(16)	121.9 (2)
C(20) - N(4) - Ru	118.83 (19)
C(16) - N(4) - Ru	118.60 (18)
C(25) - N(5) - C(21)	117.1 (3)
C(25) - N(5) - Ru	129.2 (2)
C(21) - N(5) - Ru	113.65 (18)
C(26) - N(6) - Ru	164.4 (2)
C(26) - N(7) - C(27)	118.7 (2)
N(8) #1 - N(8) - C(30)	114.0 (3)
C(35) - O(1) - C(33)	114.3 (3)
N(1) - C(1) - C(2)	122.5 (3)
C(3) - C(2) - C(1)	119.0 (3)
C(4) - C(3) - C(2)	119.3 (3)
C(3) - C(4) - C(5)	120.3 (3)

Table B3 continued

N(1)-C(5)-C(4)	120.4 (3)
N(1)-C(5)-C(6)	115.0 (2)
C(4)-C(5)-C(6)	124.6 (3)
N(2)-C(6)-C(7)	120.2 (3)
N(2)-C(6)-C(5)	114.9 (2)
C(7)-C(6)-C(5)	125.0 (3)
C(8)-C(7)-C(6)	120.3 (3)
C(9)-C(8)-C(7)	119.0 (3)
C(8)-C(9)-C(10)	119.0 (3)
N(2)-C(10)-C(9)	123.2 (3)
N(3)-C(11)-C(12)	123.3 (3)
C(13)-C(12)-C(11)	118.8 (3)
C(12)-C(13)-C(14)	119.4 (3)
C(15)-C(14)-C(13)	119.4 (3)
N(3)-C(15)-C(14)	121.6 (3)
N(3)-C(15)-C(16)	114.7 (2)
C(14)-C(15)-C(16)	123.7 (3)
N(4)-C(16)-C(17)	119.3 (3)
N(4)-C(16)-C(15)	113.2 (2)
C(17)-C(16)-C(15)	127.5 (3)
C(18)-C(17)-C(16)	119.2 (3)
C(19)-C(18)-C(17)	120.7 (3)
C(18)-C(19)-C(20)	118.7 (3)
N(4)-C(20)-C(19)	120.3 (3)
N(4)-C(20)-C(21)	112.8 (2)
C(19)-C(20)-C(21)	126.9 (3)
N(5)-C(21)-C(22)	121.7 (3)
N(5)-C(21)-C(20)	114.7 (2)
C(22)-C(21)-C(20)	123.7 (3)
C(21)-C(22)-C(23)	120.1 (3)
C(24)-C(23)-C(22)	118.1 (3)
C(23)-C(24)-C(25)	119.7 (3)
N(5)-C(25)-C(24)	123.3 (3)
N(6)-C(26)-N(7)	173.1 (3)
N(7)-C(27)-C(28)	117.7 (3)
N(7)-C(27)-C(32)	124.5 (3)
C(28)-C(27)-C(32)	117.9 (3)
C(29)-C(28)-C(27)	121.1 (3)
C(28)-C(29)-C(30)	120.4 (3)
C(31)-C(30)-C(29)	119.1 (3)
C(31)-C(30)-N(8)	116.0 (2)
C(29)-C(30)-N(8)	124.9 (3)
C(32)-C(31)-C(30)	121.0 (3)
C(31)-C(32)-C(27)	120.5 (3)
O(1)-C(33)-C(34)	109.7 (4)
O(1)-C(35)-C(36)	108.6 (4)
N(9)-C(37)-C(38)	178.9 (4)

Table B4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\{\text{Ru}(\text{bpy})(\text{tpy})\}_2(\mu\text{-adpc})][\text{PF}_6]_2 \cdot 2(\text{ether}) \cdot 2\text{DMF}$.
The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2h k a^* b^* U_{12}]$.

	U11	U22	U33	U23	U13	U12
Ru	29 (1)	24 (1)	26 (1)	1 (1)	-12 (1)	-8 (1)
P (1)	49 (1)	38 (1)	51 (1)	4 (1)	-19 (1)	-21 (1)
F (1)	97 (2)	87 (2)	130 (2)	-35 (2)	-10 (2)	-59 (2)
F (2)	108 (2)	114 (2)	60 (2)	21 (1)	-42 (2)	-33 (2)
F (3)	90 (2)	74 (2)	98 (2)	-30 (1)	-10 (2)	-51 (1)
F (4)	78 (2)	97 (2)	77 (2)	37 (1)	-37 (1)	-25 (1)
F (5)	45 (1)	70 (1)	85 (2)	4 (1)	-11 (1)	-18 (1)
F (6)	57 (1)	60 (1)	84 (2)	-6 (1)	0 (1)	-23 (1)
N (1)	31 (1)	34 (1)	30 (2)	-3 (1)	-10 (1)	-11 (1)
N (2)	38 (2)	27 (1)	25 (2)	1 (1)	-13 (1)	-10 (1)
N (3)	28 (1)	27 (1)	30 (2)	1 (1)	-12 (1)	-9 (1)
N (4)	27 (1)	26 (1)	28 (2)	1 (1)	-10 (1)	-8 (1)
N (5)	36 (1)	30 (1)	28 (2)	2 (1)	-14 (1)	-10 (1)
N (6)	35 (2)	26 (1)	32 (2)	0 (1)	-13 (1)	-8 (1)
N (7)	30 (1)	26 (1)	44 (2)	-4 (1)	-9 (1)	-7 (1)
N (8)	34 (1)	30 (2)	40 (2)	-5 (1)	-9 (1)	-9 (1)
N (9)	69 (2)	75 (2)	72 (3)	1 (2)	-28 (2)	-35 (2)
O (1)	89 (2)	59 (2)	77 (2)	-11 (2)	-34 (2)	-16 (2)
C (1)	38 (2)	47 (2)	45 (2)	-4 (2)	-13 (2)	-17 (2)
C (2)	35 (2)	71 (3)	63 (3)	-9 (2)	-9 (2)	-25 (2)
C (3)	33 (2)	66 (3)	73 (3)	-17 (2)	-23 (2)	-4 (2)
C (4)	43 (2)	51 (2)	59 (3)	1 (2)	-31 (2)	-6 (2)
C (5)	38 (2)	34 (2)	35 (2)	-7 (1)	-20 (2)	-5 (1)
C (6)	42 (2)	29 (2)	31 (2)	-2 (1)	-19 (2)	-7 (1)
C (7)	63 (2)	35 (2)	54 (3)	15 (2)	-38 (2)	-11 (2)
C (8)	78 (3)	36 (2)	55 (3)	20 (2)	-34 (2)	-23 (2)
C (9)	64 (2)	43 (2)	46 (2)	11 (2)	-22 (2)	-28 (2)
C (10)	46 (2)	32 (2)	36 (2)	3 (1)	-16 (2)	-15 (2)
C (11)	38 (2)	25 (2)	39 (2)	1 (1)	-13 (2)	-13 (1)
C (12)	53 (2)	36 (2)	42 (2)	-7 (2)	-14 (2)	-22 (2)
C (13)	53 (2)	46 (2)	35 (2)	-9 (2)	-16 (2)	-21 (2)
C (14)	44 (2)	39 (2)	28 (2)	3 (1)	-15 (2)	-18 (2)
C (15)	28 (2)	32 (2)	25 (2)	0 (1)	-10 (1)	-12 (1)
C (16)	23 (1)	31 (2)	25 (2)	-1 (1)	-7 (1)	-10 (1)
C (17)	40 (2)	40 (2)	27 (2)	5 (1)	-13 (2)	-17 (2)
C (18)	45 (2)	32 (2)	32 (2)	10 (1)	-15 (2)	-14 (2)
C (19)	40 (2)	27 (2)	40 (2)	3 (1)	-13 (2)	-15 (1)
C (20)	26 (2)	29 (2)	30 (2)	-4 (1)	-10 (1)	-11 (1)
C (21)	31 (2)	30 (2)	32 (2)	-6 (1)	-11 (1)	-9 (1)
C (22)	49 (2)	34 (2)	46 (2)	-6 (2)	-19 (2)	-13 (2)
C (23)	72 (3)	44 (2)	53 (3)	-13 (2)	-28 (2)	-16 (2)
C (24)	86 (3)	58 (3)	35 (2)	-8 (2)	-33 (2)	-22 (2)
C (25)	65 (2)	42 (2)	40 (2)	3 (2)	-27 (2)	-18 (2)
C (26)	42 (2)	24 (2)	25 (2)	3 (1)	-18 (2)	-13 (1)
C (27)	32 (2)	26 (2)	28 (2)	-1 (1)	-9 (1)	-6 (1)
C (28)	32 (2)	31 (2)	52 (2)	2 (2)	-13 (2)	-13 (1)
C (29)	25 (2)	34 (2)	42 (2)	-2 (2)	-6 (2)	-6 (1)
C (30)	33 (2)	28 (2)	36 (2)	1 (1)	-13 (2)	-10 (1)
C (31)	39 (2)	38 (2)	43 (2)	-2 (2)	-10 (2)	-20 (2)
C (32)	29 (2)	34 (2)	39 (2)	-7 (2)	-6 (2)	-8 (1)

Table B4 continued.

C(33)	102(4)	75(3)	91(4)	-33(3)	-29(3)	-31(3)
C(34)	127(4)	59(3)	126(5)	-20(3)	-59(4)	-20(3)
C(35)	72(3)	88(3)	81(4)	14(3)	-27(3)	-40(3)
C(36)	67(3)	69(3)	110(4)	-1(3)	-33(3)	-30(2)
C(37)	52(2)	45(2)	57(3)	-1(2)	-11(2)	-27(2)
C(38)	117(4)	62(3)	69(3)	18(2)	-47(3)	-45(3)

Table B5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\{\text{Ru}(\text{bpy})(\text{trpy})\}_2(\mu\text{-adpc})][\text{PF}_6]_2 \cdot 2(\text{ether}) \cdot 2\text{DMF}$.

	x	y	z	U(eq)
H(1A)	9303	-6502	-4475	52
H(2A)	11415	-7485	-4641	68
H(3A)	11991	-8961	-3507	72
H(4A)	10461	-9485	-2291	62
H(7A)	8894	-10037	-1318	60
H(8A)	7139	-10339	-221	67
H(9A)	5150	-9019	-184	59
H(10A)	4971	-7497	-1306	45
H(11A)	6762	-8702	-3673	41
H(12A)	6828	-9330	-5124	51
H(13A)	6975	-8201	-6596	52
H(14A)	6931	-6409	-6545	43
H(17A)	6536	-4559	-6264	43
H(18A)	6300	-2838	-5799	45
H(19A)	6326	-2644	-4210	42
H(22A)	6397	-2702	-2598	51
H(23A)	6468	-2895	-949	66
H(24A)	6723	-4642	-102	69
H(25A)	6829	-6098	-874	58
H(28A)	300	-3427	-589	47
H(29A)	-572	-1621	12	45
H(31A)	2842	-1490	-1128	47
H(32A)	3743	-3319	-1701	43
H(33A)	11268	-8297	-7455	106
H(33B)	9798	-7935	-7182	106
H(34A)	10609	-9664	-6386	154
H(34B)	9692	-8742	-5535	154
H(34C)	11170	-9148	-5850	154
H(35A)	9368	-5893	-7349	95
H(35B)	10861	-6327	-7772	95
H(36A)	9902	-4497	-7089	120
H(36B)	10794	-5373	-6498	120
H(36C)	9314	-4993	-6010	120
H(38A)	7635	-2708	2265	115
H(38B)	9044	-3239	1516	115
H(38C)	8226	-3974	1908	115