**Synthesis and Study of Neutral Phenylcyanamide Complexes of
Ruthenium (II)**

by

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A Thesis submitted to the Faculty of Graduate Studies
in partial fulfillment of the requirements for the degree of
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Abstract

Complexes of the formula $[\text{Ru}(\text{terpy}^*)(\text{L}_2)\text{L}']$ were synthesized, where $\text{terpy}^* = 4,4'4''\text{-tri-}t\text{-butyl-terpyridine}$, $\text{L}_2 = 2\text{-pyrazinecarboxylato (2-pca)}$, $2\text{-pyridinecarboxylato (2-pic)}$, $\text{acetylacetonato (acac)}$ and $\text{L}' = \text{chloride}$, $3\text{-chlorophenylcyanamido (3-Clpcyd)}$, $2,3\text{-dichlorophenylcyanamido (2,3-Cl}_2\text{pcyd)}$, $2,4,6\text{-trichlorophenylcyanamido (2,4,6-Cl}_3\text{pcyd)}$, $2,3,4,5\text{-tetrachlorophenylcyanamido (2,3,4,5-Cl}_4\text{pcyd)}$ and $3,4,5\text{-trimethoxyphenylcyanamido (3,4,5-(OMe)}_3\text{pcyd)}$. The complexes were characterized and studied by spectroscopic methods (IR, UV-Visible, $^1\text{HNMR}$) and cyclic voltammetry.

Spectroelectrochemistry was used to generate the electronic absorption spectra of the Ru(III) complexes, $[\text{Ru}(\text{terpy}^*)(\text{L}_2)(\text{pcyd})]^+$ in DMF solution. In order to gain a greater understanding of the influence of spectator ligands on the nature of the Ru(II)-cyanamido

bond, spectral data associated with the Ru(III)-cyanamido LMCT chromophore of these complexes were compared to complexes of the formula $[\text{Ru}(\text{bpy})(\text{trpy})\text{L}]^{2+}$ and $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$. The data show greater covalency in the Ru(III)-cyanamido bond of the $[\text{Ru}(\text{terpy}^*)(\text{L}_2)(\text{pcyd})]^+$ complexes compared to the $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$ complexes but not greater than in the $[\text{Ru}(\text{bpy})(\text{trpy})\text{L}]^{2+}$ complexes. The cyclic voltammetry data of these three families were also compared to understand the effects of varying spectator ligands on the Ru(III)/(II) couples. The results show that bpy = 2,2' bipyridine stabilizes Ru(III)/(II) couple more followed by 2-pyrazinecarboxylato (2-pca), acetylacetonato (acac), 2-pyridinecarboxylato (2-pic) and then ammine being the least in stabilization of the Ru(III)/(II) couple.

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*****Dedication*****

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List of Abbreviations

acac	Acetylacetonato
bpy	2,2'Bipyridine
CDCl ₃	Deuterated chloroform
CH ₂ Cl ₂	Dichloromethane
CH ₃ CN	Acetonitrile
COSY	Correlated spectroscopy
CV	Cyclic voltammetry
DMF	<i>N,N'</i> - dimethylformamide
<i>f</i>	Oscillator strength
H _{LM}	Ru(III) Ligand-Metal Coupling Element
H _{ML}	Ru(III) Metal-ligand Coupling Element
H _{MM'}	Metal-Metal Coupling Element
¹ H-NMR	Proton nuclear magnetic resonance
HOMO	Highest occupied molecular orbital
IT	Intervalence transition
LMCT	Ligand-to-metal charge transfer
LUMO	Lowest unoccupied molecular orbital
MLCT	Metal-to-ligand charge transfer
N.H.E.	Normal hydrogen electrode
NIR	Near-infrared
OTTLE	Opitically transparent thin layer electrode
2pca	2-Pyrazine carboxylato

2pic	2-Pyridine carboxylato
pcyd ⁻	Phenylcyanamide anion
TBAH	Tetrabutylammonium hexafluorophosphate
terpy	2,2':6',2-Terpyridine
terpy*	4, 4', 4''-tri- <i>tert</i> -butyl-terpyridine
THF	Tetrahydrofuran

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1.0 INTRODUCTION

1.1 Non-linear optical materials and their application.

The information technology industry has grown drastically over the past years as the search for faster communication and information processing devices continue to drive today's society. This has lead to a new computing and communication revolution of photonics. Photonics is the technology of generating and harnessing radiant energy. This area of research has been involved in the design of rapid photonic switching devices, photonic circuits for processing information, optical fiber sensors and imaging devices.^{1,2} These devices could find application in areas such as environmental monitoring, nanoscale photonics, weather imaging, medical diagnosis and telecommunication.

Lately as the knowledge base of polymeric materials broadened, new functions of polymers have been investigated. New and improved polymeric/macromolecular materials have been found to show promising results in generating, processing and storing light signals.³ Extensive work has focused on the development of organic polymeric non-linear optical (NLO) materials because of their potential application in photonics.⁴ A greater understanding of conducting polymers and NLO chromophore is important if one is to come up with a high performance electro-optical device. Electro-optic activity of these devices is determined by the nature of the dipolar moiety, the extent of its noncentrosymmetric order in the solid state and the change in properties of the NLO material with the application of an electric field. Organic chromophores having D-spacer-A system, where D is the donor moiety, A is the acceptor moiety and the spacer is a π conjugated molecule that permits coupling between the donor and acceptor

moiety, have been well studied as a possible choice of dipolar moiety.⁵ However, these chromophores present disadvantages such as having high drive potential and strong π - π interactions which hinder noncentrosymmetric ordering,⁶ resulting in poor electro-optic activity of the material.

As an approach to overcome these obstacles, a new class of charge-transfer chromophores suitable for electro-optic applications has been introduced. These are mixed-valence complexes with conjugated organic bridging ligands, or more specifically ruthenium dinuclear complexes that incorporate dicyanamido bridging ligands. These complexes show well defined spectroscopic and redox properties and previous studies have shown how metal ion properties can be switched or “tuned” by varying the nature of the inner and outer coordination spheres. Also, studies have shown that there is a close energy match between the ruthenium $d\pi$ and the terminal nitrogen $p\pi$ orbitals of the cyanamide ligands,^{7,8} resulting in an extended conjugation system as shown in Figure 1.

Figure 1: Extended π conjugation in a mixed-valence complex, where L is a conjugated organic spacer.

The extended π conjugation allows for coupling between the metal ions and the π -HOMO of the bridging ligand. This results in high polarizability of the electrons involved in charge transfer which is a requirement to achieve low drive potentials compatible with semiconductor electronics (less than 6 V and preferably 1 V).⁶ In the past, a high degree of extended π conjugation has been achieved by synthesizing polythiophenes with alternating donor/acceptor repeat units.⁹⁻¹³ The higher the degree of extended π conjugation, the narrower the band gap. For example, the parent polythiophene has a band gap of 2 eV while the polythiophene with alternating donor/acceptor units (poly(diamino/dinitro) thiophene) has a band gap of 1.1 eV, (see Figure 2).

Figure 2: Polythiophenes and their respective band gaps.

The band gap is a bulk property and it can be related at molecular level to the energy difference between the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO). Depending on the size of the band gap in relation to the degree of extended π conjugation, materials can behave as conductors, semiconductors and insulators (see Figure 3). In a case where there is no conductivity due to a large band gap, doping of the material can result in reduction of these band gap hence conductivity is achieved. At the molecular level, the difference between the HOMO and LUMO can be affected by factors such as the nature of the bridging ligand, changing the nature of the spectator ligands and variation of the metal oxidation state. Optimization of orbital overlap between these two orbital can extend π conjugation resulting in conductivity hence low drive potentials. In addition to low drive potentials, the stability of these complexes will be an added advantage as NLO materials must show both thermal and photochemical stability. Thermal stability is important when looking at the high temperature (90 °C –140°C) at which poling is done. This also means that volatile ligands such as NH_3 and CO must be avoided. The solubility of mixed-valance complexes have been shown to be greatly improved by using multidentate ligands with organic substituents, for example 4'-*p*-tolyl-2,2':6',2''-terpyridine (ttrpy).⁶ It is important for the complex chromophore to exhibit appropriate solubility in spin casting solvents.

Figure 3: Band structures for insulators, semiconductors and conductors. (Picture from semiconductors website).

1.2 Donor-Acceptor system based on Ru-pcyd mononuclear systems.

Marcus-Hush theory and CNS theory can then be used to quantitatively model the mediation of the electronic interactions done by the spectator ligands or a bridging molecule.^{14,15} In order to understand the electronics involved in mixed valence systems, one has to first look at the mononuclear complexes which make up the target system, hence the purpose of this study. It has been shown that when Ru(III) is bound to π donating ligands such as phenylcyanamide (pcyd), there arises a low energy ligand to metal charge transfer (LMCT) band in the electronic spectrum^{7,16} shown in Figure 4 which arises from the Ru(III)-cyanamide chromophore.

Figure 4: Low energy ligand to metal charge transfer (LMCT) band 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/silver chloride wire reference electrode. Figure reproduced from reference 17.

The LMCT can be viewed as an electronic process by which a metal ion is reduced and the ligand is oxidized. For the Ru(III)-cyanamide LMCT chromophore, the LMCT energy, E_{LMCT} can therefore be related to the difference between the Ru(III)/(II) and cyanamide ligand (L(0/-1)) redox couples (ΔE).¹⁸ This relationship is shown in Figure 5.

Figure 5: State to state potential energy curves for a Ru(III) pcyd complex showing the relationship between ΔE and E_{LMCT} .

The expression for E_{LMCT} is given by Equation 1,

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

where C is the fudge factor which accounts for the impossibility of measuring $E(\text{Ru}^{(\text{III})/(\text{II})})$ after the oxidation of the ligand to $\text{L}(0)$, and χ represents the reorganization energies of the inner and outer coordination spheres during the LMCT event.

The integral of the molar absorptivity versus the energy of the charge transfer band can be used to experimentally derive the oscillator strength, f of the LMCT band. Oscillator strength can also be theoretical calculated from the transition dipole moment (M) of the LMCT¹⁹ by using the expression in Equation 2,

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

where G gives the degeneracy of the states. M is approximately given by Equation 3 below,

$$M \approx re \times S_{\text{ad}} \dots\dots\dots (3)$$

where r is the transition dipole moment length, e is the electronic charge. The overlap integral between the donor and acceptor wavefunctions (ψ) is given by S_{ad} .

Coupling elements can be derived by using Creutz, Newton and Sutin's (CNS) model.¹⁴ This model derives coupling elements from charge transfer band oscillator strengths. It assumes that the interaction between the donor and acceptor to be essentially ionic, that is the overlap between the metal and ligand orbital is zero. This model also assumes that the transition dipole moment lies along the bonding axis. The expression for ligand-to-metal coupling H_{LM} for a ligand-to-metal charge transfer (LMCT) band is given by Equation 4 in cm^{-1} ,

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

where r is the transition moment length given in Å, E_{LMCT} is the band energy at ϵ_{max} in cm^{-1} , f is the oscillator strength of the LMCT band. CNS have shown in studies of dinuclear pentaammine, tetraammine, triammine ruthenium (III) complexes that it is possible to determine metal-metal coupling elements from values of H_{LM} obtained from either mononuclear or dinuclear complex charge transfer data.

The Ru(III)-cyanamide LMCT chromophore is quite sensitive to the nature of the solvent,²⁰ and for Ru(III) ammine complexes, the energy and the oscillator strength of the LMCT band has been shown to vary drastically with a change in the donor number of the solvent. These changes have been related to ligand-to-metal coupling elements H_{LM} . By using these coupling elements, it was possible to predict metal-to-metal coupling in mixed-valence complexes. There was a good agreement between theory and experiment.

1.3 Donor-acceptor systems based on mixed-valence complexes.

A lot of research work has focused on the study of electron transfer both in the fields of biology and chemistry. In biology, electron transfer reactions have been extensively studied in proteins and in light harvesting systems.²¹ In chemistry, studies have been focused in electron transfer in dinuclear mixed-valence complexes such as Ru(II)-L-Ru(III), where L is the bridging ligand, have been long studied.²² According to Robin and Day, these complexes can be classified into three classes²³ as shown in Figure 6. The classification is based on the extent of delocalization of the odd electron between the two metal centers.²³ Class I complexes represent species in which the electron is completely valence trapped. In this class, there is no interaction between the two metal centers. Complexes which belong to this class, generally exhibit the properties of the isolated mononuclear complexes.

Class III complexes on the other hand, show properties which are unlike those of isolated complexes. The odd electron in Class III complexes is fully delocalized, and therefore equally shared by the two interacting metal centers. Class II complexes show intermediate behavior, that is there exist weak coupling between the metal centers and partial delocalization. Recent studies on mixed valence complexes have introduced a new class of complexes, Class II-III. Complexes of this class show localized electronic oxidation states but also show delocalized solvents effects.²⁴

Figure 6: Potential energy configuration diagrams for a symmetric Class I, Class II and Class III mixed valence complex.

1.4 Metal-metal coupling

Metal-metal coupling can occur through two major pathways: it can occur through direct overlap of the metal orbitals²⁵ or through superexchange pathways. The latter involves an exchange between two metal centers through the orbitals of the bridging ligand.²⁶ Superexchange pathways can further be divided into two processes where in one process we have coupling between metal centers enhanced through the ligand Highest Occupied π Molecular Orbital (π -HOMO), and in the other process, coupling is enhanced through the ligand Lowest Unoccupied π Molecular Orbital (π -LUMO). The former process is known as hole transfer (superexchange mechanism) and the latter is termed electron transfer (see Figure 7).

Figure 7: Electron transfer (A) and hole-transfer (B) superexchange mechanisms.

A mixed-valence complex can be produced in solution by the loss of an electron:

or the gain of an electron:

The sum of equation 5 and 5a gives the comproportionation equilibrium which defines K_C for Class II or Class III complexes. K_C gives the degree of metal-metal coupling in a mixed-valence complex.²⁶

Using cyclic voltammetry for the complex in solution, a measure of the free energy of comproportionation (ΔG_c) can be calculated (see Equation 7 and 8),

$$\Delta G_c = -nF\Delta E = -RT \ln Q = -RT \ln K_C \dots\dots\dots (8)$$

where ΔE is the difference between the redox couples of the two metal centers, F is the Faraday constant, n is the number of electrons involved in the half reaction, R is the gas constant, T is temperature in Kelvin and Q is the reaction quotient.

From equation 8, the comproportionation equilibrium constant K_c at 298 K is given by,

$$K_C = 10^{16.91 \Delta E} \dots\dots\dots (9)$$

where ΔE is in volts.

There are five factors which contribute to ΔG_c ,^{20,27} (see Equation 10).

$$\Delta G_c = \Delta G_s + \Delta G_e + \Delta G_i + \Delta G_{ex} + \Delta G_r \dots\dots\dots (10)$$

where ΔG_s is the statistical distribution of the comproportionation equilibrium, ΔG_e describes the electrostatic repulsion that exists between the two like charged metal centers, ΔG_i accounts for the inductive effects of competing coordination of the bridging ligand by metal centers, ΔG_{ex} is related to the stabilization of the reactions by antiferromagnetic exchange and ΔG_r describes the free energy of resonance exchange.

ΔG_r is the only factor of ΔG_c that actually represents metal-metal coupling and for Class III complexes, it plays a major role in determining ΔG_c (see Figure 8). In Figure 8, 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. Because of the mole ratios in equation 6, the free energy of resonance exchange per mole is given by $\Delta G_r' = \Delta G_r / 2$.

Figure 8: Superimposed potential energy surfaces showing metal to metal charge transfer band (MMCT) for a symmetric Class III complex (bold) and Class I (faint).

Amongst the many theoretical models that have been developed to calculate metal-metal coupling elements, the Hush model and the CNS model seem to be the most commonly used. The Hush model is appropriate for systems where there exists weak coupling between the donor and acceptor. The CNS model developed by Creutz, Newton and Sutin (CNS) is appropriate for systems where strong coupling exists.

Spectroelectrochemical oxidation of the [Ru(II)-Ru(II)] complex in solution can produce the mixed-valence species [Ru(III)-Ru(II)] and can be recognized spectroscopically by the appearance of metal-to-metal charge transfer (MMCT) band usually in the NIR region. For weakly coupled Class II complexes, metal-metal coupling elements H_{MM} can be calculated from the MMCT band energy and oscillator strength¹⁵ using Equation 11, (Hush Model)

$$H_{MM} = \frac{303(E_{MMCT} \times f)^{1/2}}{r} \dots\dots\dots (11)$$

Equation 11 is the same as Equation 4 except that charge transfer parameters are derived from an intervalence transition (MMCT). CNS model permits calculations of H_{MM} from metal-ligand coupling elements derived from LMCT or MLCT transitions,²⁰ as shown by Equation 12,

$$H_{MM'} = \frac{H_{ML} H_{M'L}}{2\Delta E_{ML}} + \frac{H_{LM} H_{LM'}}{\Delta E_{LM}} \dots\dots\dots (12)$$

where H_{LM} is coupling between the ligand and the metal and is calculated from Equation 4 using the LMCT band data from the electronic spectrum of [Ru(III)-Ru(II)] complex, H_{ML} is calculated using Equation 4 but in this case from the MLCT band observed in [Ru(II)-Ru(III)] complex. $H_{M'L}$ and $H_{LM'}$ cannot be determined experimentally, and 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 given by,

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

1.5 Project strategy

The target asymmetric mixed-valence chromophore can be divided into three stages; the donor moiety (a Ru(II) complex), acceptor moiety (a Ru(III) complex and the bridging ligand (a 1,4- dicyanamidobenzene dianion derivative). Figure 9 shows the complex summary. The final complex as shown in Figure 9 must have a neutral charge. If charged complexes are incorporated in the polymer matrix, poling would cause the complex to migrate to the pole of opposite charge. Figure 10 shows a process of poling in neutral complexes. Also neutral complexes prove to be important during synthetic handling when there are incorporated in polymer materials. Due to their neutral charge, there is lack of interferences between the polymer material and the complex. Interferences with the polymer material can result in decomposition hence the short lifetime of the polymer material. However, these neutral complexes tend to be insoluble in most solvents, solubility is therefore of major concern in the synthesis of these neutral complexes. Syntheses have to be adapted to overcome this problem.

Figure 9: Shows the target dinuclear mixed-valence complex summary.

Figure 10: Poling of a neutral complex (a) random orientation of polar domains prior to poling (b) introduction of electric field (poling) (c) electric field removed, dipole locked in a non random manner. Zigzag lines represent the polymer matrix.

Of the three parts that the target asymmetric mixed-valence chromophore must have, this project focuses on the donor moiety. The donor moiety must be soluble in most solvents: and must possess a stable oxidation state. The latter is important for long term stability of the chromophore in the polymer host. By using the Lever electrochemical parameterization table²⁸ as a guide in choosing ligands to modify Ru(III)/(II) couples, it will be possible to synthesize a series of neutral Ru(II) complexes with stable oxidation states.

Complexes of the formula $[\text{Ru}(\text{terpy}^*)(\text{L}_2)\text{L}']$ will be synthesized where $\text{terpy}^* = 4,4'4''$ -tri-*tert*-butyl-terpyridine, $\text{L}_2 = 2$ -pyrazinecarboxylato (2-pca), 2-pyridinecarboxylato (2-pic), acetylacetonato (acac) and $\text{L}' =$ chloride, 3-chlorophenylcyanamido (3-Clpcyd), 2,3-dichlorophenylcyanamido (2,3-Cl₂pcyd), 2,4,6-trichlorophenylcyanamido (2,4,6-Cl₃pcyd), 2,3,4,5-tetrachlorophenylcyanamido (2,3,4,5-Cl₄pcyd) and 3,4,5-trimethoxyphenylcyanamido (3,4,5-(OMe)₃pcyd). The phenylcyanamido anion ligands are depicted on Figure 11. The complexes will be characterized and studied by

spectroscopic methods (IR , UV- Visible, $^1\text{H-NMR}$) and cyclic voltammetry. The CNS model will then be used to calculate ligand to metal coupling elements.

Figure 11: The phenylcyanamido ligands (L) used in $[\text{Ru}(\text{terpy}^*)(\text{L}_2)\text{L}]$ complexes.

2.0 EXPERIMENTAL SECTION

2.1 Instrumentation and Techniques

Electronic spectra were recorded using a Cary 5 UV-Vis-NIR spectrophotometer with a quartz cell of 1 cm path length. A solvent baseline correction was run prior to all sample spectra. Infrared spectroscopy (KBr disk from oven dried KBr) were recorded on a BOMEM Michelson MB100-FT-IR spectrophotometer, the spectra were corrected for background air. ^1H -NMR and spectra were recorded at room temperature on a Bruker AMX-400 spectrometer in CDCl_3 and dimethyl- d_6 sulfoxide, all chemical shifts being relative to TMS. Sample size of 10 mg in 1.00 mL of CDCl_3 or dimethyl- d_6 sulphoxide in a Norell XR- 55 NMR tube was used for ^1H NMR.

Cyclic voltammetry studies were performed in 99.8% anhydrous *N,N*-dimethylformamide (Aldrich, HPLC grade) using a BAS CV-27W voltammetric analyzer and plotted on a BAS XY recorder. A three electrode arrangement consisting of a platinum disk electrode working electrode (BAS 1.6 mm diameter), a platinum wire auxiliary electrode, and a silver wire quasi-reference electrode was used. Cobaltocenium hexafluorophosphate ($E^\circ = -0.589\text{V}$ versus NHE)²⁹ was used as an internal reference. The electrochemical cell consisted of a double jacketed glass container with an internal volume of 15 mL. To control the temperature, a Haake D8-G reffridgerated bath and circulator was used to maintain the cell temperature at $25.0 \pm 0.1^\circ\text{C}$. Tetrabutylammonium hexafluorophosphate (0.1 M) was recrystallized³⁰ and used as the supporting electrolyte.

Solutions were degassed by bubbling in argon gas (ultra purity) for 7-10 minutes before scans. The background CV was performed at a scan rate of 0.1V/s. Sample size of about 10 mg was added to the cell and was magnetically stirred while argon was being bubbled through the solution. Electrodes were manually cleaned and polished with 1- μ m diamond polish prior to each individual scan. Scans were performed under argon gas.

An OTTLE (optically transparent thin layer electrode) cell was used to perform the spectroelectrochemistry.^{20,31} Cell arrangement is shown in Figure 12. The solvent and supporting electrolyte were the same as for CV. Elemental analysis were performed by Canadian Microanalytical Services Ltd., Delta, B.C., Canada.

Figure 12: Scheme of the OTTLE cell spacer (left) and the teflon superstructure (right).

a = Ag\AgCl wire, **b** = Platinum wire.

2.1 Solvents for Synthesis

Acetonitrile (Caledon Labs, reagent grade), *N,N*-dimethylformamide (Sigma reagent grade), anhydrous diethyl ether (Caledon Labs, ACS reagent), toluene (Caledon Labs, spectro grade), chloroform, hexanes, dichloromethane, anhydrous ethyl alcohol, and methanol (Caledon Labs, spectro grade) were used as received. Acetone (Caledon Labs, Laboratory grade) was distilled prior to use.

2.2.1 Solvents for Electrochemistry

N,N-Dimethylformamide, anhydrous 99.8% (Aldrich, HPLC grade) was used without drying. It was bubbled with argon after every use and stored in a glass bottle inside a polyethylene glove bag.

2.2.2 Solvents for NMR Spectroscopy

Chloroform-*d*₃ and dimethyl-*d*₆ sulfoxide (99.9 atom % D, CDN Isotopes) were used as received.

2.2 Reagents

All chemicals and solvents were reagent grade or better and were purchased from Aldrich. The phenylcyanamide ligands were prepared from established methods.⁷ Tetrabutylammonium hexafluorophosphate (TBAH), purchased from Aldrich was recrystallised twice from 1:1 ethanol:water. It was then vacuum dried at 110°C.

2.3 Synthetic work

2.4.1 Preparation of 4, 4', 4''-tri-*tert*-butyl-terpyridine (terpy*)

Terpy* was prepared according to literature method³² with modifications as outlined herein.

2 g palladium (10% on charcoal) in round bottom flask was degassed overnight using vacuum and heated at 180 °C in silicon oil bath. Freshly distilled 4-*tert*-butylpyridine (50 mL, 0.3338 mmol, F.W. 135.21 g/mol) was degassed 5 times before it was added to the palladium catalyst. The mixture was then degassed for 10 minutes and then refluxed under argon for 3 days. After cooling, THF (150 mL) was added and the mixture filtered to remove the catalyst. Using a rotary evaporator, the filtrate was then concentrated to about 100 mL. 60 g of neutral alumina was then added to the concentrated filtrate and the solvent evaporated to dryness using the rotary evaporator. A sublimation finger connected to a cooling system set at –30 °C was fitted into the round bottom flask containing the alumina mixture. Sublimation was done under vacuum and the mixture was heated with a silicon oil bath up to a temperature of 210 °C. The unreacted 4-*tert*-butylpyridine (3 to 6 mL) was removed first under vacuum pressure at 119 – 127 °C. 25 g of 4, 4'-di-*tert*-butyl-2, 2'-bipyridine (bpy*) was then removed by sublimation at 179 – 192 °C. Unsublimed residue which contains the desired product was separated from the alumina by dissolving the mixture in chloroform and filtering to remove the alumina. The filtrate was evaporated to dryness. To the solid, 120 mL of hexane was added and the mixture stirred overnight at room temperature. This mixture was then filtered and the filtrate evaporated to dryness to give pure white powder of terpy*. Yield: 23 g (51%). Melting point (m. p.)

239 – 241 °C. ^1H -NMR (400MHz, CDCl_3 - d): 8.74 (2H, dd), 8.63 (2H, dd), 8.48 (2H, s), 7.32 (2H, dd), 1.46 (9H, s), 1.42 (18H, s) ppm.

2.4.2 Preparation of $[\text{Ru}(\text{terpy}^*)\text{Cl}_3]\cdot 3\text{H}_2\text{O}$.

$[\text{Ru}(\text{terpy}^*)\text{Cl}_3]$ was prepared according to literature method³² with minor modifications as outlined herein.

Ruthenium trichloride (856 mg, 3.26 mmol, F.W. 263 g/mol) and terpy* (1.31 g, 3.27 mmol, F.W. 401g/mol) were dissolved in 180 mL of absolute ethanol. The mixture was heated and stirred at reflux for 3 hours and allowed to cool to room temperature. The solvent was evaporated to dryness to give brownish yellow residue which was dissolved in acetone and precipitated with water to give greenish brown solid. The solid was collected by filtration and washed 3 times with 20 mL portions of water followed by 10 mL of diethyl ether and vacuum dried overnight. Yield: 1.8 g (90%).

2.4.3 Preparation of [Ru(terpy*)(2pca)Cl]·¼CH₂Cl₂ (violet blue).

[Ru(terpy*)Cl₃] (0.274 g, 0.45 mmol, F.W. 609.023 g/mol) was added to a solution of 2pca (68.3 mg, 0.55 mmol, F.W. 124.10 g/mol) in absolute ethanol (40 mL). LiCl (200 mg, 4.72 mmol, F.W. 42.35 g/mol) and Et₃N (1 mL, 1 mmol, F.W. 101.19 g/mol) were added to the mixture. Upon addition of Et₃N, the colour of the mixture changed from green brown to deep green. The mixture was degassed for 5 minutes before being refluxed for 4 hours under argon. After 4 hours the solvent was rotary evaporated to dryness. CH₂Cl₂ (40 mL) was added and the mixture stirred under argon for 10 minutes, then the mixture was filtered through cellite. The filtrate was concentrated and hexane (80 mL) added to precipitate out the crude product. The crude product was collected by suction filtration and washed with hexane, water, and ether. Yield: 0.24 g (81%). ¹H-NMR (400MHz, CDCl₃-d): 10.13 (1H, d), 9.24 (1H, s), 8.92 (1H, d), 8.13 (2H, s), 8.07 (2H, d), 7.87 (2H, d), 7.29 (2H, dd), 7.26 (2H, s), 5.30 (CH₂Cl₂ of crystallization, s), 1.58 (9H, s), 1.40 (18H, s) ppm. Anal. Calcd for [Ru(terpy*)(2pca)Cl]·¼CH₂Cl₂ (C_{32.25}H_{38.5}N₅Cl_{1.5}O₂Ru): C, 56.76; H, 5.69; N, 10.26. Found: C, 56.57; H, 5.57; N, 10.01. The above method was used to prepare all the other [Ru(terpy*)(L₂)Cl] complexes where L₂ = 2pic and acac.

2.4.4 Preparation of [Ru(terpy*)(2pca)(3-Clpcyd)]·½CH₂Cl₂. (red brown)

[Ru(terpy*)(2pca)Cl] (0.452 g, 0.17 mmol, F.W. 661.217 g/mol) was dissolved in DMF (60 mL). Tl⁺[3-Clpcyd]⁻ (0.485 g, 0.34 mmol, F.W. 355.95 g/mol) was added and the mixture was refluxed overnight. The initial violet blue mixture changed to maroon with refluxing and white TlCl salt formed. After the overnight period, the mixture was left in the fridge to cool and TlCl salt collected at the bottom of the round bottom flask. Using cellite packed frit, TlCl was filtered out and the filtrate was rotary evaporated to dryness. The dry solid was dissolved in CH₂Cl₂ (30 mL) and hexane (60 mL) was added to precipitate out the crude product. The crude product was collected by suction filtration and washed with hexane and ether. Purification was achieved by column chromatography. The crude product was dissolved in a minimum volume of CH₃CN and passed down a column of 50 cm by 3 cm diameter. The column was packed with Silica gel slurry and CH₃CN was used as the eluent. The first violet blue band was assigned to starting material ([Ru(terpy*)(2pca)Cl]). The target band which was the second red brown band was eluted by (1:1) CH₃CN:CH₂Cl₂ from which the solvent was rotary evaporated. Recrystallisation was achieved by slow diffusion of ether into the saturated mixture of the complex in a minimum volume of CH₂Cl₂. Yield: 88 mg (16%). (IR KBr pellet): $\nu_{\text{NCN}} = 2167 \text{ cm}^{-1}$; ¹H-NMR (400MHz, CDCl₃-d): 9.65 (1H, dd), 9.30 (1H, d), 8.93 (1H, d), 8.14 (2H, s), 8.09 (2H, d), 7.82 (2H, d), 7.34 (2H, dd), 7.26 (2H, s), 6.81 (1H, t), 6.49 (1H, d), 6.27 (1H, d), 6.16 (1H, t), 5.30 (CH₂Cl₂ of crystallization, s), 1.59 (9H, s), 1.42 (18H, s) ppm. Anal. Calcd for [Ru(terpy*)(2pca)(3-Clpcyd)]·½CH₂Cl₂ (C_{39.5}H₄₃N₇Cl₂O₂Ru): C, 57.87; H, 5.29; N, 11.96. Found: C, 57.51; H, 5.23; N, 12.09.

2.4.5 [Ru(terpy*)(2pca)(2,3-Cl₂pcyd)]·³/₄CH₂Cl₂ (red brown) was prepared in the same manner as above. Yield: 102 mg (22%). (IR KBr pellet): $\nu_{\text{NCN}} = 2171 \text{ cm}^{-1}$; ¹H-NMR (400 MHz, CDCl₃-*d*): 9.65 (1H, s), 9.28 (1H, s), 8.93 (1H, s), 8.09 (2H, s), 8.06 (2H, d), 7.76 (2H, s), 7.33 (2H, dd), 7.26 (2H, s), 6.67 (1H, t), 6.46 (1H, d), 5.99 (1H, d), 5.30 (CH₂Cl₂ of crystallization, s), 1.59 (9H, s), 1.42 (18H, s) ppm. Anal. Calcd for [Ru(terpy*)(2pca)(2,3-Cl₂pcyd)]·³/₄CH₂Cl₂ (C_{39.75}H_{42.5}N₇Cl_{3.5}O₂Ru): C, 54.53; H, 4.89; N, 11.20. Found: C, 54.58; H, 4.92; N, 11.34.

2.4.6 Ru(terpy*)(2pca)(2,4,6-Cl₃pcyd)]·³/₁₀CH₂Cl₂ (red brown) was prepared in the same manner as above. Yield: 106 mg (24%). (IR KBr pellet): $\nu_{\text{NCN}} = 2173 \text{ cm}^{-1}$; ¹H-NMR (400 MHz, CDCl₃-*d*): 9.61 (1H, dd), 9.30 (1H, d), 8.93 (1H, d), 8.14 (2H, s), 8.09 (2H, d), 7.80 (2H, d), 7.34 (2H, dd), 7.26 (2H, s), 7.11 (1H, s), 6.12 (1H, s), 5.30 (CH₂Cl₂ of crystallization, s), 1.60 (9H, s), 1.43 (18H, s) ppm. Anal. Calcd for [Ru(terpy*)(2pca)(2,4,6-Cl₃pcyd)]·³/₁₀CH₂Cl₂ (C_{39.3}H_{40.6}N₇Cl_{3.6}O₂Ru): C, 54.15; H, 4.69; N, 11.25. Found: C, 53.90; H, 4.77; N, 11.10.

2.4.7 [Ru(terpy*)(2pca)(2,3,4,5-Cl₄pcyd)]·³/₄CH₂Cl₂ (red brown) was prepared in the same manner as above, however, the eluent used for column chromatography was CH₂Cl₂. Yield: 96 mg (16%). (IR KBr pellet): $\nu_{\text{NCN}} = 2178 \text{ cm}^{-1}$; ¹H-NMR (400 MHz, CDCl₃-*d*): 9.61 (1H, dd), 9.29 (1H, d), 8.92 (1H, d), 8.14 (2H, s), 8.09 (2H, d), 7.79 (2H, d), 7.35 (2H, dd), 7.26 (4H, s), 7.11 (1H, s), 6.11 (1H, s), 5.30 (CH₂Cl₂ of crystallization, s), 1.59 (9H, s), 1.42 (18H, s) ppm. Anal. Calcd for [Ru(terpy*)(2pca)(2,3,4,5-

$\text{Cl}_4\text{pcyd}]] \cdot \frac{1}{4}\text{CH}_2\text{Cl}_2$ ($\text{C}_{39.75}\text{H}_{40.5}\text{N}_7\text{Cl}_{5.5}\text{O}_2\text{Ru}$): C, 50.56; H, 4.32; N, 10.38. Found: C, 50.69; H, 4.48; N, 10.69.

2.4.8 $[\text{Ru}(\text{terpy}^*)(2\text{pic})(2,3\text{-Cl}_2\text{pcyd})] \cdot \frac{1}{4}\text{CH}_2\text{Cl}_2$ (purple) was prepared in the same manner as above. Yield: 240 mg (44%). (IR KBr pellet): $\nu_{\text{NCN}} = 2169 \text{ cm}^{-1}$; $^1\text{H-NMR}$ (400 MHz, $\text{CDCl}_3\text{-}d$): 9.66 (1H, dd), 9.29 (1H, qq), 8.28 (1H, q), 8.27 (1H, q), 8.07 (2H, s), 8.04 (2H, d), 8.01 (1H, d), 7.99 (4H, d), 7.80 (4H, m), 6.58 (2H, m), 6.09 (1H, dd), 5.30 (CH_2Cl_2 of crystallization, s), 1.58 (9H, s), 1.41 (18H, s) ppm. Anal. Calcd for $[\text{Ru}(\text{terpy}^*)(2\text{pic})(2,3\text{-Cl}_2\text{pcyd})] \cdot \frac{1}{4}\text{CH}_2\text{Cl}_2$ ($\text{C}_{40.25}\text{H}_{42.05}\text{N}_6\text{Cl}_{2.05}\text{O}_2\text{Ru}$): C, 58.10; H, 5.15; N, 10.10. Found: C, 58.37; H, 5.13; N, 10.19.

2.4.9 $[\text{Ru}(\text{terpy}^*)(\text{acac})(2,3\text{-Cl}_2\text{pcyd})] \cdot \frac{1}{2}\text{CH}_3\text{CN}$ (dark blue) was prepared in the same manner as above, except that the column was packed with grade I acidic alumina and (1:1) $\text{CH}_3\text{CN}:\text{CH}_2\text{Cl}_2$ was used as the eluent. Yield: 86 mg (15%). (IR KBr pellet): $\nu_{\text{NCN}} = 2170 \text{ cm}^{-1}$; $^1\text{H-NMR}$ (400 MHz, $\text{CDCl}_3\text{-}d$): 9.28 (1H, d), 8.06 (4H, d), 7.93 (2H, s), 7.69 (2H, dd), 7.26 (2H, s), 6.53 (2H, d), 5.91 (1H, s), 5.31 (1H, s), 2.18 (3H, s), 2.10 (CH_3CN of crystallization, s), 2.02 (3H, s), 1.58 (9H, s), 1.52 (18H, s) ppm. Anal. Calcd for $[\text{Ru}(\text{terpy}^*)(\text{acac})(2,3\text{-Cl}_2\text{pcyd})] \cdot \frac{1}{2}\text{CH}_3\text{CN}$ ($\text{C}_{40}\text{H}_{46.5}\text{N}_{5.5}\text{Cl}_2\text{O}_2\text{Ru}$): C, 59.44; H, 5.80; N, 9.53. Found: C, 59.36; H, 5.43; N, 9.91.

2.5.0 [Ru(terpy*)(2pca)(3,4,5-(OMe)₃pcyd)]·³/₄CH₂Cl₂. (brown) was prepared in the same manner as above. Yield: 86 mg (15%). (IR KBr pellet): $\nu_{\text{NCN}} = 2163 \text{ cm}^{-1}$; ¹H-NMR (400MHz, CDCl₃-*d*): 10.14 (1H, dd), 9.25 (1H, d), 8.92 (1H, d), 8.13 (2H, s), 8.07 (2H, d), 7.89 (2H, d), 7.29 (2H, dd), 7.26 (2H, d), 5.67 (2H, s), 5.30 (CH₂Cl₂ of crystallization, s), 3.66 (1H, s), 3.55 (4H, s), 1.59 (9H, s), 1.42 (18H, s) ppm. Anal. Calcd for [Ru(terpy*)(2pca)(3,4,5-OMe₃pcyd)]·³/₄CH₂Cl₂ (C_{42.75}H_{50.5}N₇Cl_{1.5}O₅Ru): C, 57.26; H, 5.68; N, 10.93. Found: C, 56.95; H, 5.68; N, 11.07.

2.5.1 Oscillator Strength Calculation

The LMCT bands generated in this study are non Gaussian, therefore, the use of Equation 13 below for calculating the oscillator strength gives an inexact value.

$$f = 4.61 \times 10^{-9} \varepsilon_{\max} \Delta \nu_{1/2} \dots\dots\dots(13)$$

In the above Equation, $\varepsilon_{\max}$ is the maximum extinction coefficient of the band in $M^{-1} \text{ cm}^1$ and $\Delta \nu_{1/2}$ is the bandwidth at half peak height in cm^{-1} . To get an exact value of the oscillator strength, the LMCT band envelope was fitted with multiple Gaussian bands using Jandel Scientific peakfitTM v3.0 software. Figure 13 shows the fitting procedure done on the low energy LMCT band of [Ru(terpy*)(2pca)3-Clpcyd] complex. The number of Gaussian bands does not necessarily represent electronic transitions or vibrational features of the complex.

The LMCT band oscillator strength (f) was then calculated by taking the sum of the contributions of the various fitted bands. Equation 13 then modifies to Equation 14 below where oscillator strength is now given by,

$$f = 4.61 \times 10^{-9} \sum_i \varepsilon_i \cdot \Delta \nu_i \dots\dots\dots(14)$$

where ε is the extinction coefficient at $\lambda_{\max}$ for each Gaussian peak and $\Delta \nu_{1/2}$ is the Gaussian band width at half peak height in cm^{-1} .

Figure 13: Electronic spectrum of [Ru(terpy*)(2pca)3-Clpcyd] showing the best fit of three Gaussian curves (dashed lines) used for the calculation of oscillator strength.

3.0 RESULTS

3.1 Synthesis.

The synthetic chemistry that led to the prepared complexes in this study are outlined in the flow chart in Scheme 1.

Scheme 1: Preparation of Neutral Ru(II) Cyanamide Complexes

The reaction between $[\text{Ru(terpy}^*\text{)Cl}_3]$ and L_2 in refluxing absolute ethanol in the presence of Et_3N and LiCl, yielded the starting material for all the complexes which were prepared in this study. Et_3N functioned as a reducing agent towards the $[\text{Ru(terpy}^*\text{)Cl}_3]$ and also as a deprotonating agent for the L_2 ligand. To prevent the dissociation of the Cl^- ligand from $[\text{Ru(terpy}^*\text{)(2pca)Cl}]$, LiCl was added.

The reaction mechanism for ligand substitution reactions for transition metal ion complexes depends on the structure of the complex, entering or leaving groups and reaction conditions. This makes it difficult to distinguish the mechanism type by which ligand substitution can occur. Ligand substitution reactions of Ru(II) complexes have been shown to occur by an associative mechanism³³ and also there are cases where a dissociative mechanism³⁴⁻³⁶ has been reported for Ru(II) complexes. However, having said all this, the mechanism for ligand substitution in complexes studied here is suggested to be by I_d (dissociative interchange). This mechanism is common for transition metals having large metal size, where steric effects are reduced. This reaction mechanism is shown below in Scheme 2.

Scheme 2: Ligand Substitution Reaction Mechanism Suggested to Being I_d Mechanism.

The first step involves formation of the solvent substituted complex which is held together by ion pairing. The reaction is rather favored to the left where the metal cation is stabilized by the anion leaving group. The reaction was carried out in refluxing DMF at 152 °C overnight so as to push it to the formation of the solvent substituted complex, hence it is the rate determining step. Substitution of the leaving group X by the pcyd occurs in step 2 where the reaction to reform the reagent complex is prevented by the precipitation of TlCl (metathesis) as shown in Scheme 3. In step 3 the solvent substituted complex rearranges itself to yield the neutral mononuclear complexes.

It is important to note that the suggested mechanism for ligand substitution of these Ru(II) complexes have not been tested experimental and is speculative.

While thallium is extremely toxic, it was used in these reactions as it is highly stable. Silver can play the same role as thallium, but it easily gets reduced by light. This can result in formation of oxidized forms of the complexes, which were not desired.

Scheme 3: Metathesis Reaction Resulting in Neutral Mononuclear Complexes.

All the reactions were carried out under argon to avoid oxidation. Since 2-pyridine carboxylato and 2-pyrazine carboxylato are asymmetric bidentate ligands, $[\text{Ru}(\text{terpy}^*)\text{L}_2\text{Cl}]$ can exist as two geometric isomers as shown in Scheme 4. The assignment of the isomeric forms *cis/trans* labels is made relative to the disposition of the anion donor groups, Cl^- and carboxylato. Studies made on these reactions have shown that when the reactions are carried out in absolute EtOH, the sole product that is formed is the *trans* product.^{37,39} However, when the reaction is carried out in a mixture of EtOH/H₂O, then both isomers are obtained.³⁸⁻⁴¹ This can be explained in terms of the polarity of the solvents. Highly polar solvents such as water will stabilize polar products and non polar solvents will stabilize non polar products.⁴² The *trans* isomer is less polar as compared to the *cis* isomer, hence its formation will be most favored in less polar solvents such as EtOH. In a mixture of EtOH/H₂O, the polarity is increased hence the *cis* isomers are also obtained. Therefore, the product observed in this reaction is assumed to be the *trans* isomer. $[\text{Ru}(\text{terpy}^*)\text{L}_2\text{Cl}]$ is isomerically pure as was shown by the appearance of one spot on a silica gel TLC plate, the mobile phase being CH_2Cl_2 . ¹H-NMR showed only one complex was present. Also cyclic voltammetry of the starting material confirmed formation of one isomer. Unfortunately crystals for structure determination could not be obtained and so an unambiguous assignment is not possible.

Scheme 4: Formation of Isomers of $[\text{Ru}(\text{terpy}^*)(2\text{pca})\text{Cl}]$

Purity of the complexes was achieved by column chromatography followed by slow diffusion of hexanes into saturated CH_2Cl_2 solution of the crude product. The complexes showed good solubility in organic solvents such as dichloromethane, chloroform, and DMF. However, the solubility of the complexes decreased with increasing number of chloro substituents on the phenyl ring.⁴³ This was observed in organic solvents such as acetone and acetonitrile. The first indication that the phenylcyanamide complexes had formed was the presence of the ν_{NCN} band in the range of ca. 2161- 2173 cm^{-1} in the IR spectrum of the complex. According to literature, thallium phenylcyanamide salts ν_{NCN} band is observed at lower frequencies⁷ than that of the deprotonated phenylcyanamide ligand coordinated to metal ion. In this study the thallium salts ν_{NCN} band was in the range of 2108-2127 cm^{-1} . The complexes were characterized by IR, uv-visible and near IR spectroscopy, cyclic voltammetry, ^1H -NMR spectroscopy, and elemental analysis.

3.2 Infrared Spectra

The infrared data for the free thallium salts of phenylcyanamide ligands have been reported elsewhere.^{7,16,44-46} Infrared data for the complexes synthesized is summarized in Table 1, showing only the phenylcyanamide stretch. Figure 14 shows the IR spectrum of the starting material, and Figure 15 shows that of [Ru(terpy*)(2pca)3-Clpcyd] which is representative of all the phenylcyanamide complexes. The phenylcyanamide stretch in the latter complex is found at 2167cm^{-1} . All the infrared spectra of the complexes showed a strong band at 2961cm^{-1} assigned to the $\nu(\text{C-H})$ of the *tert*-butyl groups on the terpy* ligand.⁴⁷ The coordinated C=O stretch of the acac and pyridine, and pyrazine carboxylato ligands is observed at a lower frequency than expected ($\text{ca. } 1620\text{cm}^{-1}$) as compared to the ketone C=O stretch which is observed at 1760 cm^{-1} .⁴⁷ This is because these ligands are negatively charged and the charge is delocalized due to resonance. This makes the C=O stretch weaker and hence, it is observed at lower energy. For 2pca and 2pic, the C=O stretch is observed at about 1645 and 1643 cm^{-1} respectively while that of acac is observed at 1608 cm^{-1} . The strong band in the region of 1480 cm^{-1} was assigned to the aromatic C=C stretch and the C-N stretch is observed in the region of 1343 cm^{-1} .

Table 1: Infrared Spectroscopy Data^a for the [Ru(terpy*)(L₂)pcyd] Complexes.

Complex	$\nu(\text{NCN}) \text{ cm}^{-1}$
[Ru(terpy*)(2pca)3-Clpcyd]· ¹ / ₂ CH ₂ Cl ₂	2167
[Ru(terpy*)(2pca)2,3-Cl ₂ pcyd]· ³ / ₄ CH ₂ Cl ₂	2171
[Ru(terpy*)(2pca)2,4,6-Cl ₃ pcyd]· ³ / ₁₀ CH ₂ Cl ₂	2173
[Ru(terpy*)(2pca)2,3,4,5-Cl ₄ pcyd]· ³ / ₄ CH ₂ Cl ₂	2178
[Ru(terpy*)(2pca)3,4,5-(OMe) ₃ pcyd]· ³ / ₄ CH ₂ Cl ₂	2163
[Ru(terpy*)(2pic)2,3-Cl ₂ pcyd]· ¹ / ₄ CH ₂ Cl ₂	2169
[Ru(terpy*)(acac)2,3-Cl ₂ pcyd]· ¹ / ₂ CH ₃ CN	2170

^aperformed as KBr pellets.

Figure 14: IR spectrum of starting material $[\text{Ru}(\text{terpy}^*)(2\text{pca})\text{Cl}] \cdot \frac{1}{4}\text{CH}_2\text{Cl}_2$ (KBr pellets)

Figure 15: IR spectrum of $[\text{Ru}(\text{terpy}^*)(2\text{pca})_3\text{-Clpcyd}] \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$ (KBr pellets)

3.3 ^1H -NMR Spectroscopy

The ^1H -NMR spectra of the starting material is shown in Figure 16 and that of [Ru(terpy*)(2pca)3-Clpcyd] complex is shown in Figure 17, which is representative of this family of complexes. All the resonance signals were unambiguously assigned (the assignments are listed in Section 2.4) on the basis of peak multiplicity, chemical shifts, splitting patterns, signal intensities, and by correlating with the spectrum of free ligands.^{32,44} Combining ^1H -NMR and ^1H -COSY (Correlated Spectroscopy) experiments, also helped to assign the resonance signals of the complexes.

Upon binding to Ru(II), protons on the ligands which are close to the metal centre show a downfield shift compared to the free ligand protons⁴⁸ see Figure 18 and 19. For all the complexes that were synthesized in this study, terpy* retained planarity when coordinated to Ru(II) metal ion, and this was shown by ^1H -NMR. The symmetry of the terpy* moiety with one set of signals for the central pyridine and one set of signals for the two equivalent terminal pyridines, simplified integrations and splitting patterns. The presence of the pcyd ligand in the complexes was confirmed by the resonance signals in the 6-7 ppm range, while the 2pca resonance signals were in the range of 8.8-10 ppm. For terpy*, the range was 7.1-8.3 ppm. Resonance signals for terpy* and 2pic protons, overlapped in the region of 7.2-8.3 ppm for [Ru(terpy*)(2pic)(2,3-Cl₂pcyd)] complex. This made it difficult to assign each resonance signal, however, integration corresponded to a total of twelve protons. For the acac complex, the acac ligand showed to be unsymmetrical,⁴⁹ with two methyl resonance signals and one methine resonance signal.

Figure 16: ^1H -NMR spectrum of starting material $[\text{Ru}(\text{terpy}^*)(2\text{pca})\text{Cl}] \cdot \frac{1}{4}\text{CH}_2\text{Cl}_2$ in CDCl_3 .

Figure 17: ^1H -NMR spectrum $[\text{Ru}(\text{terpy}^*)(2\text{pca})3\text{-Clpycd}] \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$ in CDCl_3 .

The information showing interaction of protons through space in the complexes was obtained from ^1H -COSY experiments. Figure 20 shows ^1H -COSY spectrum of $[\text{Ru}(\text{terpy}^*)(2\text{pca})2,4,6\text{-Cl}_3\text{pcyd}]$ complex. The protons on 2pca and those of terpy* show an interspace relationship.

Figure 20: ^1H -COSY spectrum (400MHz) of $[\text{Ru}(\text{terpy}^*)(2\text{pca})2,4,6\text{-Cl}_3\text{pcyd}]\cdot^{3/10}$ CH_2Cl_2 complex in CDCl_3 .

3.4 Electronic Absorption Spectra

The electronic absorption spectra of the starting material and $[\text{Ru}(\text{terpy}^*)(2\text{pca})3\text{-Clpcyd}] \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$ are shown in Figure 21 and 22 respectively. The spectra show a broad absorption in the visible region and many intense absorptions in the UV region. Complexes of the pcyd derivatives have similar spectra as that of the 3-Clpcyd complex (Figure 22). The electronic absorption spectral data of all the complexes recorded in DMF is given in Table 2. The assignment of the observed transitions was made based on similar ruthenium polypyridyl complexes.⁵⁰⁻⁵² The intense absorption bands in the UV region around (293-340 nm) are assigned as ($\pi \longrightarrow \pi^*$) transitions of terpy^* , 2pca, and 2pic. The absorption bands that are observed in the visible region, (400 nm to 800 nm) are as a result of metal-ligand charge-transfer (MLCT) transitions, that is the transition from Ru(II) d-orbitals to the π^* orbitals of terpy^* , 2pca, and 2pic ligand's $d\pi$ ($\text{Ru(II)} \longrightarrow \pi^*(\text{terpy}^*)$). Since terpy^* moiety has a more extended π system than both 2pca and 2pic, it is expected to give more stable π^* orbitals⁵² than 2pca and 2pic. This in turn results in the $d\pi(\text{Ru(II)}) \longrightarrow \pi^*(\text{terpy}^*)$ being at longer wavelength (ca. 331 nm) compared to that of 2pca and 2pic which are observed at ca. 328 and 321 nm respectively.

Figure 21: Electronic absorption spectrum of $[\text{Ru}(\text{terpy}^*)(2\text{pca})\text{Cl}]\cdot\frac{1}{4}\text{CH}_2\text{Cl}_2$ in DMF.

Figure 22: Electronic absorption spectrum of $[\text{Ru}(\text{terpy}^*)(2\text{pca})_3\text{-Clpcyd}]\cdot\frac{1}{2}\text{CH}_2\text{Cl}_2$ in DMF.

Table 2: Quantitative Electronic Spectral Data^a for the Starting Material and all Complexes in DMF.

COMPLEX	$\pi \longrightarrow \pi^*$	MLCT
Ru(terpy*)(2pca)Cl]	311(2.67), 323(3.63)	400(0.936), 460(0.821), 535(1.39)
[Ru(terpy*)(2pca)3-Clpcyd]	284(3.88), 308(3.34), 319(3.84)	400(0.966), 524(0.978)
[Ru(terpy*)(2pca)2,3-Cl ₂ pcyd]	283(3.79), 319(4.14), 394(1.04)	451(0.917), 521(1.09)
[Ru(terpy*)(2pca)2,4,6-Cl ₃ pcyd]	317(4.07), 321(4.16),373(1.06)	449(0.917), 523(1.02)
[Ru(terpy*)(2pca)2,3,4,5-Cl ₄ pcyd]	282(3.32),319(4.02), 365(1.04)	445(0.882), 517(0.965)
[Ru(terpy*)(acac)2,3-Cl ₂ pcyd]	292(5.71), 312(2.88), 323(2.92)	611(0.534)
[Ru(terpy*)(2pic)Cl]	293(1.05), 313(2.44)	323(3.18), 406(1.16), 552(0.940)
[Ru(terpy*)(2pic)2,3-Cl ₂ pcyd]	308(3.47), 312(3.41), 320(3.69), 389(1.22)	541(0.770)
[Ru(terpy*)(2pca)3,4,5-(OMe) ₃ pcyd]	308(2.88), 316(2.97), 3.22(3.36)	420(0.953), 531(0.977)

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

3.5 Spectroelectrochemistry

So as to be able to generate the expected two ligand-to-metal charge-transfer (LMCT) bands⁷ of the Ru(III)-cyanamide chromophore, spectroelectrochemistry was done on the complexes. This was executed by using an OTTLE cell²⁰ and all the experiments were done at room temperature. Oxidation was done by exposing the complex to electrical potential ranging from 0.0 V $\longrightarrow$ +1.40 V (ie versus the Ag/Ag⁺ pseudo-reference electrode). Upon oxidation, the MLCT band observed in all the complexes slowly decreases while a band in the near infrared region starts to grow. This low energy band is unambiguously assigned to a ligand to metal $\pi \longrightarrow d\pi^*$ (LMCT) charge transfer transition of Ru(III)-cyanamide chromophore.⁷ This chromophore has another transition at higher energy, however, spectral overlap with other transitions prevented an unambiguous assignment.

A representative spectrum for [Ru(terpy*)(2pca)pcyd] complexes is shown in Figure 23. The stability of the Ru(II) complexes was shown by the well defined isosbestic points. All the complexes except the [Ru(terpy*)(2pca)3,4,5-(OMe)₃pcyd] complex, showed very good reversibility (> 95%) in regenerating the Ru(II) spectra. The [Ru(terpy*)(2pca)3,4,5-(OMe)₃pcyd] complex also showed signs of decomposition and loss of the isosbestic point as the voltage was increased to potentials greater than 0.4 V, this is shown in Figure 24.

Figure 23: OTTLE cell electronic spectrum of $[\text{Ru}(\text{terpy}^*)(2\text{pca})_3\text{-Clpcyd}]^{0/1+}$ in DMF under increasing oxidation potentials (0.0 $\longrightarrow$ 0.8 V). 0.1 M TBAH; platinum wire working and counter electrodes; silver wire pseudo- reference electrode.

Figure 24: OTTLE cell electronic spectrum of $[\text{Ru}(\text{terpy}^*)(2\text{pca})3,4,5\text{-(OMe)}_3\text{pcyd}]^{0/1+}$ in DMF under increasing oxidation potentials (0.0 $\longrightarrow$ 0.4 V). 0.1 M TBAH; platinum wire working and counter electrodes; silver wire pseudo-reference electrode. Note that the oxidation is incomplete. Oxidation at more positive potentials resulted in loss of isosbestic point.

3.6 Electrochemistry

The electrochemical properties of the complexes in DMF have been studied by cyclic voltammetry (CV). Voltammetric data for the complexes including the starting material are presented in Table 3. Only the $E_{1/2}$ potentials are given in this Table. The $E_{1/2}$ potentials were determined from the average of the anodic and cathodic peak potentials ($E_{1/2} = (E_{pa} + E_{pc})/2$). A representative voltammogram of [Ru(terpy*)(2pca)L'] complexes is shown in Figure 25, and Figure 26 shows the cyclic voltammogram of the Ru(III)/(II) couple for [Ru(terpy*)(2pic)2,3-Cl₂pcyd]

The Ru(III)/(II) couple of all the complexes, except that of [Ru(terpy*)(2pca)3,4,5-(OMe)₃pcyd] complex, was quasi reversible with peak-peak separation of 64-70 mV at a scan rate of 100 mV/s. The Ru(III)/(II) couple was shown to be reversible even at increasing scan rates (50-500) mV/s. The scan rate dependence of [Ru(terpy*)(2pca)2,4,6-Cl₃pcyd] is shown in Figure 28. Ligand based reduction of terpy* is observed at negative potentials. The reduction corresponds to the formation of a radical anion as an electron is added to the π^* orbital of terpy*. Due to solvent limitations, the oxidation of the 2pca, 2pic, and acac could not be determined as these are expected to occur in the more positive potentials.

Figure 25: Cyclic voltammogram of $[\text{Ru}(\text{terpy}^*)(2\text{pic})2,3\text{-Cl}_2\text{pcyd}]$ in DMF with 0.1 M tetrabutylammonium hexafluorophosphate, using platinum counter and working electrode, silver wire pseudo-reference (cobaltocene internal reference) at scan rate of 100 mV/s.

Figure 26: Cyclic voltammogram of $[\text{Ru}(\text{terpy}^*)(2\text{pic})_2,3\text{-Cl}_2\text{pcyd}]$ in DMF with 0.1 M tetrabutylammonium hexafluorophosphate, using platinum counter and working electrode, silver wire pseudo-reference (cobaltocene internal reference) at scan rate of 100 mV/s. Showing only the Ru(III)/(II) couple which lies at 0.77 V vs NHE.

Figure 27: Cyclic voltammogram of $[\text{Ru}(\text{terpy}^*)(2\text{pic})2,3\text{-Cl}_2\text{pcyd}]$ in DMF with 0.1 M TBAH showing the scan rate dependence (50-500) mV/s of Ru(III)/(II) couple.

Table 3: Ru(III)/(II) Couples^a for the Starting Materials and all Complexes in DMF.

Complex	Ru(III/II)
[Ru(terpy*)(2pca)Cl]	0.78
[Ru(terpy*)(2pca)3-Clpcyd]	0.88
[Ru(terpy*)(2pca)2,3-Cl ₂ pcyd]	0.85
[Ru(terpy*)(2pca)2,4,6-Cl ₃ pcyd]	0.85
[Ru(terpy*)(2pca)2,3,4,5-Cl ₄ pcyd]	0.87
[Ru(terpy*)(2pca)3,4,5-(OMe) ₃ pcyd]	0.67
[Ru(terpy*)(2pic)Cl]	0.70
[Ru(terpy*)(2pic)2,3-Cl ₂ pcyd]	0.77
[Ru(terpy*)(acac)Cl]	0.76
[Ru(terpy*)(acac)2,3-Cl ₂ pcyd]	0.84

^a in Volts vs NHE at 25°C, scan rate 0.1 V/s; and 0.1 M TBAH electrolyte; using platinum counter and working electrode, silver wire pseudo-reference and cobaltocenium hexafluorophosphate ($E^\circ = -0.589\text{V}$ versus NHE)²⁹ used as internal reference.

4.0 DISCUSSION

Previous work by this group has examined certain aspects of outer and inner sphere perturbations to ligand-metal coupling in mononuclear complexes.^{7,8,16,17,43} Complexes incorporating ligands of the family of phenylcyanamide shown in Figure 11, allowed for the study of inner sphere perturbations. This was made possible by varying the substituents on the phenyl ring of the pcyd ligand. Greater perturbations on the inner sphere were observed on the mononuclear complexes as the monoanion bidentate ligand was varied from 2pca to 2pic to acac.

The emphasis of this chapter will be centered on a discussion of the electrochemistry, spectroelectrochemistry and electronic absorption results. The combination of these techniques with the CNS model of ligand-metal coupling provides an even deeper understanding of the nature of these complexes. Other techniques used in this study, such as ¹H-NMR spectroscopy and IR spectroscopy were most important for characterization purposes. However, before we discuss the results obtained by these techniques, it is important to look at the synthetic work and how the problem of solubility was solved which is the major concern for neutral complexes.

4.1 Synthesis of Complexes

Neutral coordination complexes as already mentioned in the introduction section, tend to be insoluble in most solvents. For example, the first complex that was made, [Ru(terpy)(2pca)3-Clpcyd], was insoluble in most of the solvents except DMF. This led to difficulties during purification by column chromatography. DMF, which was used as the mobile phase or eluent, interacted with the binding sites of alumina. This reduced the

number of active sites for the complex to bind to, hence poor separation was observed. Other methods of purification could not be used because of poor solubility.

This problem was solved by synthesizing terpy* which differs from terpy by the presence of *tert* butyl groups on the 4th position of each pyridine ring. Introduction of these groups greatly increased the solubility of the complexes. This was expected as it is known that branched groups have a tendency to increase the solubility of complexes by reducing lattice energy and by increasing Van Der Waals interaction between complex and solvent.⁴⁰ The complexes that were synthesized using terpy*, were purified by column chromatography, using dichloromethane (CH₂Cl₂) as the mobile phase. In this case, CH₂Cl₂ does not interfere with the complex's interaction with the stationary phase, and resulted in a good separation of bands. The complexes were soluble in most organic solvents such as dichloromethane, chloroform, ethanol and DMF. While the use of terpy* increased solubility, it had the unfortunate effect of causing the complex to form crystals poorly, preventing a crystal structure determination.

Three derivatives of the formula [Ru(terpy*)(L₂)2,3-Cl₂pcyd] were synthesized so as to be able to study the effects of the monoanion bidentate ligand on inner sphere perturbations. Of the three derivatives, the [Ru(terpy*)(2pic)2,3-Cl₂pcyd] complex proved to be easy to make as the yields were high compared to the other two, with [Ru(terpy*)(acac) 2,3-Cl₂pcyd] showing the poorest yield of all the three (see Scheme 2 and Section 2). This can be attributed to the fact that 2-pyridine carboxylato (2pic) is a better donor than 2-pyrazine carboxylato (2pca) and acetylacetonato (acac) ligands. Therefore it is able to compete effectively for the solvent coordinated site of the solvolysis complex which forms in step 1 (Scheme 2).

4.2 Characterization of Complexes

IR spectroscopy, ^1H -NMR spectroscopy and elemental analysis were performed upon the complexes to fully characterize them. Solvent of crystallization which was used to balance the elemental analysis was also observed in ^1H -NMR spectroscopy. The infrared spectroscopy data in Table 1, showed a slight shift to higher frequency of the ν_{NCN} band from a “free” phenylcyanamide ligand,⁵³ (Tl 2,3-Cl₂pcyd) of 2102 cm^{-1} to complexed ν_{NCN} band of ca. 2170 cm^{-1} . One can understand this shift in ν_{NCN} by looking at Scheme 5. The “free” phenylcyanamide anion ligand as shown in Scheme 5, is resonance stabilized with the ν_{NCN} for the carbodiimide form (A) ranging from 2100 cm^{-1} to 2150 cm^{-1} and the ν_{NCN} of the nitrile form (B) at ca 2250 cm^{-1} . The observed ν_{NCN} of the “free” phenylcyanamide anion ligand at 2102 cm^{-1} , has a value consistent with resonance form (A). Upon coordination of the anionic phenylcyanamide ligand to the metal cation, which occurs mostly through the terminal nitrogen or nitrile nitrogen of resonance form B,^{53,54} there is a shift in ν_{NCN} to higher energy as shown in Table 1. This suggests that resonance form (B) is making a significant contribution to the electronic structure of cyanamide anion group.

The trend of increasing ν_{NCN} with chlorine substitution on the phenyl ring is attributed to the fact that as the number of electron withdrawing substituents around the phenyl ring increases, the inductive effect of the phenyl ring on the cyanamide group caused a greater contribution of resonance form (B) to the cyanamide group. Electron donating substituents on the phenyl ring would favor resonance form (A).

Scheme 5: Representation of the Monoanion pcyd Ligand Showing the Two Resonance Forms (A) and (B).

4.3 Electrochemistry

As the nature and number of substituents on the phenyl ring varies from electron donor to electron withdrawing substituents, the donor properties of the phenylcyanamide ligand decreases. This is shown in Table 4 for $[\text{Ru}(\text{terpy}^*)(\text{L}_2)\text{L}]$, $[\text{Ru}(\text{bpy})(\text{trpy})\text{L}]^+$ and $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$ complexes where L = phenylcyanamido derivatives. The trend that is observed as one looks through each family of complexes, is that as the number of electron withdrawing substituents on the pcyd ligand increases, there is a shift towards more positive potentials of the Ru(III)/(II) couple. This is due to the electronic inductive effects of the chlorines on the pcyd ligand which then affect the metal. However, when

looking at the $[\text{Ru}(\text{terpy}^*)(\text{L}_2)\text{L}]$ family of complexes, the $[\text{Ru}(\text{terpy}^*)(2\text{pca})_3\text{-Clpcyd}]$ complex does not agree with the observed trend. To this no answer can be provided as to why it occurs especially because it was only observed in one family of complexes. Families of $[\text{Ru}(\text{bpy})(\text{trpy})\text{L}]^+$ and $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$ complexes having the same pcyd ligand, did not show this observation. To check for experimental errors, the cyclic voltammetry experiment was done more than twice on the same complex. However, results did not change, a new batch of the same complex was synthesized and cyclic voltammetry experiment repeated, but still no change was observed. Substituting the electron withdrawing groups on the pcyd with electron donating groups on the other hand, resulted in a shift towards more negative potentials of the Ru(III)/(II) couple. This was observed for the methoxy complex $[\text{Ru}(\text{terpy}^*)(2\text{pca})_3,4,5\text{-(OMe)}_3\text{pcyd}]$ which had its redox potentials of the Ru(III)/(II) couple at 0.67 V.

Table 4: Ru(III)/(II) Couples^a for [Ru(terpy*)(2pca)L]^b, [Ru(terpy*)(2pic)L]^b, [Ru(terpy*)(acac)L]^b, [Ru(bpy)(tpy)L]^c and [Ru(NH₃)₅L]^{2+c} Complexes.

	[Ru(terpy*)(2pca)L]	[Ru(terpy*)(2pic)L]	[Ru(terpy*)(acac)L]	[Ru(bpy)(tpy)L] ⁺	[Ru(NH ₃) ₅ L] ²⁺
L	Ru(III)/(II)	Ru(III)/(II)	Ru(III)/(II)	Ru(III)/(II)	Ru(III)/(II)
3-Clpcyd	0.88	-----	-----	0.93	0.12
2,3-Cl ₂ pcyd	0.85	0.77	0.84	-----	0.13
2,4-Cl ₂ pcyd	-----	-----	-----	1.00	0.15
2,4,6-Cl ₃ pcyd	0.85	-----	-----	1.03	0.13
2,4,5-Cl ₃ pcyd	-----	-----	-----	1.06	0.20
2,3,4,5-Cl ₄ pcyd	0.87	-----	-----	1.09	0.23
4-Me ₂ pcyd	-----	-----	-----	0.81	0.04
3,4,5-(OMe) ₃ pcyd	0.67	-----	-----	-----	-----

^a In volts vs. NHE at 25 °C and a scan rate of 0.1 V/s. ^b 0.1M TBAH in DMF, cobaltocenium hexafluorophosphate (E°= -0.589V versus NHE)²⁹ used as internal reference. ^c 0.1M TBAH in acetonitrile. ¹⁷ L = phenylcyanamido derivatives.

The change in potential for the Ru(III)/(II) couples as the chlorine substituents are increased on the pcyd ligand is small when compared to the effect of varying the monoanion bidentate ligand. This was studied by making complexes of the formula $[\text{Ru}(\text{terpy}^*)(\text{L}_2)\text{2,3-Cl}_2\text{pcyd}]$. Where $\text{L}_2 =$ 2-pyridinecarboxylato (2pic), 2-pyrazinecarboxylato (2pca) and acetylacetonato (acac). The results are compiled in Table 4. Pyridine and pyrazine are π acceptors while the carboxylate moiety is a σ and π donor. Thus both 2pic and 2pca are π acceptor and σ and π donor ligands. Acac on the other hand is a σ and π donor ligand. It was expected that when switching from 2pca to 2pic, the Ru(III)/(II) couple should shift to more negative potentials because pyridine is a better donor than pyrazine. A small negative shift of the Ru(III)/(II) couple (Table 4) was observed. The acac complex is expected to have the lowest potential of the Ru(III)/(II) couple compared to 2pca and 2pic, since the acac ligand is not a π acceptor. However, the above is not observed. The Ru(III)/(II) couple for the acac complex is less than that of the 2pca complex, but it is greater than that of the 2pic complex. This is because acac is a poor donor of electrons due to the electronegative oxygen donor atoms. The Ru(III)/(II) couples of $[\text{Ru}(\text{trpy})(\text{bpy})\text{L}]^+$ are at more positive potentials compare to 2pca and 2pic analogues, because neutral bipyridine (bpy) donates less net electron density to the Ru(II) than does the monoanion ligands 2pca and 2pic, Overall donor properties of the bidentate ligands in Table 4 are illustrated in Scheme 6.

Scheme 6: Ligand Series Showing the Relationship Between the Donor Properties of Ligands and the Ru(III)/(II) Reduction Couples.

Comparing $[\text{Ru}(\text{trpy})(\text{bpy})\text{L}]^+$ to $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$ (Table 4). The Ru(III)/(II) couples are observed at more negative potentials for the $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$ family. This is because NH_3 is a better donor than pyridine. σ donation by the NH_3 ligands is known to stabilize the Ru(III) oxidation state more than Ru(II) oxidation state.¹⁷

4.4 Electronic absorption spectra of the Ru(III) complexes.

Spectroelectrochemical oxidation of Ru(II) complexes gave the spectra of the fully oxidized Ru(III) complexes, except for the methoxy complex where signs of decomposition were observed. The Ru(III) spectra were dominated by an intense low energy band which is assigned to an LMCT transition⁷ of the Ru-cyanamide chromophore. This transition is between the high energy π –HOMO of the monoanion pcyd ligand and the metal πd orbital. Previous studies^{7,17,43,54} have shown that the anionic cyanamide group is a resonance stabilized π system (see Scheme 5). There are two pairs of nonbonding electrons of π symmetry which can delocalize into this three-atom π system resulting in orthogonal π_{nb1} and π_{nb2} molecular orbitals (see Figure 28). The π_{nb1} orbital is less stable than the π_{nb2} orbital, according to extended Hückel calculations.⁵⁴ In a spectroscopic analysis of Ru(III)-cyanamide complexes,^{7,54} it was shown that the Ru(III)–cyanamide chromophore will give rise to two LMCT transitions (see Figure 29). The $b_2 \longrightarrow b_1^*$ transition is expected to occur at higher energy and it is a formally forbidden transition, while the $b_1 \longrightarrow b_1^*$ transition is observed at lower energy and it is an allowed transition. The $b_2 \longrightarrow b_1^*$ LMCT band which is expected at higher energy could not be assigned, because in the region where this transition is expected to occur, there are other LMCT transitions such as the σ donation from the oxygen in the monoanion bidentate ligand to the metal.

Figure 28: Orthogonal π_{nb1} and π_{nb2} molecular orbitals of the anionic phenylecyanamide, obtained from extended Hückel calculations, π_{nb2} symmetry orbital being more stable.⁵⁴

Figure 29: Qualitative M.O. diagram for a mononuclear Ru(III) phenylcyanamide complex showing the LMCT transitions ($b_1 \rightarrow b_1^*$) and ($b_2 \rightarrow b_1^*$). Labeling is made assuming C_{2v} microsymmetry.⁵⁴

4.4.1 Oscillator Strength Calculation

The LMCT band that was assigned to ($b_1 \longrightarrow b_1^*$) transition, was used to determine the oscillator strength. As previously stated in Section 2.5.1, the LMCT bands of the complexes that were generated during the spectroelectrochemistry experiments are non-Gaussian. They had to be fitted by multiple Gaussian bands, and by using Equation 14 the oscillator strength of the phenylcyanamide complexes was calculated. Table 5 shows the calculated values of the oscillator strength (f) and other spectrochemical parameters obtained by modeling the LMCT band envelope with multiple Gaussian bands.

Table 5: Electronic Absorption Data for ($b_1 \longrightarrow b_1^*$) LMCT Transition of $[\text{Ru}(\text{terpy}^*)(\text{L}_2)\text{L}]^+$ Complexes.

COMPLEX	ϵ_{max}^a	$\nu_{max} (\text{cm}^{-1})$	f^b	H_{LM}
[Ru(terpy*)(2pca)3-Clpcyd]	9500	19000	0.105	2430
[Ru(terpy*)(2pca)2,3-Cl₂pcyd]	10600	19100	0.117	2580
[Ru(terpy*)(2pca)2,4,6-Cl₃pcyd]	9900	19200	0.105	2450
[Ru(terpy*)(2pca)2,3,4,5-Cl₄pcyd]	9400	19300	0.100	2390
[Ru(terpy*)(2pca)3,4,5-(OMe)₃pcyd]	9300	18700	0.104	2400
[Ru(terpy*)(2pic)2,3-Cl₂pcyd]	7300	18200	0.077	2040
[Ru(terpy*)(acac)2,3-Cl₂pcyd]	5000	17200	0.055	1680

^a ϵ_{max} has unit of $\text{L. mol}^{-1} \cdot \text{cm}^{-1}$, ^b Oscillator strength f , determined by using Equation 14 and ligand-metal coupling H_{LM} determined by using Equation 4.

The LMCT energies in Table 5 show a variation which is related to the donor ability of the pcyd ligand. As the donor ability of the pcyd is reduced the LMCT energies increases. The donor ability of the pcyd can be increased or reduced by introducing electron donating or withdrawing substituents, respectively, on the phenyl ring of the pcyd. The chlorine substituents on the pcyd ring reduces the donor ability of this ligand as already discussed in Section 4.3, this in turn stabilizes the π_{nb1} orbital (see Figure 28). The stabilization of this orbital results in an increase in energy gap between the π_{nb1} orbital (HOMO) of the pcyd ligand and the πd orbital (LUMO) of the metal, hence an increase in the LMCT energy (see Table 5).

Previous studies^{17,43,53,54} have shown that it is possible to correlate charge transfer band energies to the difference in redox couples between the centers involved in charge transfer events. The LMCT event entails the oxidation of the pcyd monoanion ligand and the reduction of the Ru(III) metal ion as discussed in the introduction (see Figure 5, Equation 1). This is equivalent to the difference between the L (0/-1) and Ru(III)/(II) reaction couples. If χ and 'C' are constant in Equation 1, then a plot of E_{LMCT} verses L(0/-1) - Ru(III)/(II) is expected to yield a straight line. For my complexes, the L(0/-1) couple could not be determined. Still, the plot of E_{LMCT} verses Ru(III)/(II) would be expected to give a straight line assuming that $E(L^{(0/-1)})$ is approximately constant. Figure 30 shows a plot of E_{LMCT} verses Ru(III)/(II).

Figure 30: LMCT energy verses Ru(III)/(II) couples.

Figure 30, however, does not show linear relationship and suggest that the assumption made about $E(L^{(0/-1)})$ being approximately constant is not true. There must be greater variation of the $(L^{(0/-1)})$ couple as the nature of the pcyd and L_2 ligand changes.

4.4.2 Metal-Ligand Coupling

Figure 31 shows a plot of oscillator strength, f (Table 6) versus LMCT energy for the $[Ru(terpy^*)(L_2)L]$ complexes. The general trend in oscillator strength with LMCT energy in Figure 32 is consistent with the predicted dependence of f on the energy of the transition (see Equation 2). However, a plot of oscillator strength, f or H_{LM} , which is proportional to $f^{1/2}$, versus LMCT energy in $[Ru(terpy^*)(L_2)L]$ complexes as well as $[Ru(trpy)(bpy)L]^{2+}$ and $[Ru(NH_3)_5L]^{2+}$ complexes, shows that when examined over a wide range of LMCT energies, a negative dependence of f (or H_{LM}) versus LMCT energy is observed (see Figure 32).

Figure 31: Oscillator strength (f) x 10 verses E_{LMCT} (eV) for all the complexes synthesized in this study of the formula $[Ru(terpy^*)(L_2)pcyd]^+$.

Table 6: LMCT Oscillator Strengths and Metal-Ligand Coupling Elements Derived from the ($b_1 \rightarrow b_1^*$) LMCT Transition of $[\text{Ru}(\text{terpy}^*)(2\text{pca})\text{L}]^{2+}$, $[\text{Ru}(\text{terpy}^*)(2\text{pic})\text{L}]^{2+}$, $[\text{Ru}(\text{terpy}^*)(\text{acac})\text{L}]^{2+}$, $[\text{Ru}(\text{bpy})(\text{trpy})\text{L}]^{2+}$ and $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$ Complexes.

L	$[\text{Ru}(\text{terpy}^*)(2\text{pca})\text{L}]$		$[\text{Ru}(\text{terpy}^*)(2\text{pic})\text{L}]$		$[\text{Ru}(\text{terpy}^*)(\text{acac})\text{L}]$		$[\text{Ru}(\text{bpy})(\text{trpy})\text{L}]^{2+}$		$[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$	
	f	H_{LM}	f	H_{LM}	f	H_{LM}	f	H_{LM}	f	H_{LM}
3-Clpcyd	0.105	2430	-----	-----	-----	-----	-----	-----	0.160	2580
2,3-Clapcyd	0.117	2580	0.077	2040	0.055	1680	-----	-----	0.146	2510
2,4-Clapcyd	-----	-----	-----	-----	-----	-----	-----	-----	0.156	2540
2,4,6-Cl3pcyd	0.105	2450	-----	-----	-----	-----	0.152	2050	0.128	2380
2,4,5-Cl3pcyd	-----	-----	-----	-----	-----	-----	-----	-----	0.148	2520
2,3,4,5-Cl4pcyd	0.100	2390	-----	-----	-----	-----	0.183	2270	0.119	2280
Cl3pcyd	-----	-----	-----	-----	-----	-----	0.154	2080	0.111	2270
4-Mepcyd	-----	-----	-----	-----	-----	-----	0.178	2260	0.126	2410
3,4,5-(OMe)3pcyd	0.104	2400	-----	-----	-----	-----	-----	-----	-----	-----

L = phenylcyanamido derivatives, and ^a in DMF solution, ^b in acetonitrile solutions.

Figure 32: Oscillator strength (f) x 10 verses E_{LMCT} (eV) for the various $[\text{Ru}(\text{bpy})(\text{trpy})\text{L}]^{2+}$, $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$ and $[\text{Ru}(\text{terpy}^*)(\text{L}_2)\text{pcyd}]^+$, values obtained from Table 6.

The equation derived by Mulliken⁵⁴ can be used to explain the observed trend in Figure 32 and is given by the expression below:

$$f = (1.885 \times 10^{-5}) G \times \bar{\nu} S^2 R^2 \dots\dots\dots(15)$$

where G is the same as in Equation 2 and $\bar{\nu}$ is the same as E_{LMCT} which is in Equation 2, R is the transition dipole length, which can be approximated to the separation between the donor and the acceptor wavefunctions (ψ) and it is given in Angstroms, and S is the overlap integral. Equation 15 brings up an important factor that is not included in Equation 2, which is the overlap integral. This explains that in order for an allowed transition to occur between the ground and excited charge transfer state, there must be some region of overlap between the donor and the acceptor. By using Equation 15, the oscillator strength of $b_1 \longrightarrow b_1^*$ band can be related to the magnitude of the Ru(III)-cyanamide π bond overlap as the nature of the phenylcyanamide varies. The trend in oscillator strength, f shown in Figure 32 can now be explained by an increase in π overlap as the donor properties of the phenylcyanamide increases.

5.0 CONCLUSION and FUTURE STUDIES

Synthesis and characterization of $[\text{Ru}(\text{terpy}^*)\text{L}_2\text{L}']$ family of complexes have been described herein. The solubility of these complexes was greatly improved by introducing *tert*-butyl groups on the 4th position of each pyridine group of terpy^* . Improved solubility of the complexes allowed for the necessary studies taken herein. Lack of suitable crystals for X-ray analysis prevented crystal structure determination. Three complexes of the formula $[\text{Ru}(\text{terpy}^*)(\text{L}_2)2,3\text{-Cl}_2\text{pcyd}]$ where $\text{L}_2 = 2\text{pca}$, 2pic and acac were synthesized and $[\text{Ru}(\text{terpy}^*)(2\text{pic})2,3\text{-Cl}_2\text{pcyd}]$ proved to be the easiest to make having the highest yield (Scheme 1), followed by $[\text{Ru}(\text{terpy}^*)(2\text{pca})2,3\text{-Cl}_2\text{pcyd}]$ then $[\text{Ru}(\text{terpy}^*)(\text{acac})2,3\text{-Cl}_2\text{pcyd}]$ with the lowest yield.

Cyclic voltammetry and spectroelectrochemistry made it possible to study the effects of the nature of the inner coordination sphere on the ruthenium(III)-cyanamide chromophore. Varying the donor properties of the phenylcyanamide have been shown to have an effect on the Ru(III)/(II) redox couples (Table 3 and 4). The most negative Ru(III)/(II) redox couple being that of the $[\text{Ru}(\text{terpy}^*)(2\text{pca})3,4,5\text{-(OMe)}_3\text{pcyd}]$ complex while the most positive couple was reported for $[\text{Ru}(\text{terpy}^*)(2\text{pca})3\text{-Clpcyd}]$ complex. Major effects on the Ru(III)/(II) redox couple were shown for complexes of the formula $[\text{Ru}(\text{terpy}^*)(\text{L}_2)2,3\text{-Cl}_2\text{pcyd}]$, where $[\text{Ru}(\text{terpy}^*)(2\text{pic})2,3\text{-Cl}_2\text{pcyd}]$ had the unexpected low Ru(III)/(II) couple compared to the $[\text{Ru}(\text{terpy}^*)(\text{acac})2,3\text{-Cl}_2\text{pcyd}]$. The sensitivity of the Ru(III)/(II) couple to changes made on the ligands around the metal was studied by comparing three families of complexes with the formula $[\text{Ru}(\text{terpy}^*)(2\text{pca})\text{L}]$, $[\text{Ru}(\text{trpy})(\text{bpy})\text{L}]^+$ and $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$ respectively, where $\text{L} =$ phenylcyanamide derivatives. The $[\text{Ru}(\text{trpy})(\text{bpy})\text{L}]^+$ complexes showed more positive potentials for the

Ru(III)/(II) couple followed by the $[\text{Ru}(\text{terpy}^*)(2\text{pca})\text{L}]$, then the $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$ complexes having the lowest positive potentials for the Ru(III)/(II) couple (Table 4). The NH_3 ligands are therefore better donors than bpy and 2pca. For synthesizing the mixed-valence dinuclear system, $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$ would appear to be a better donor moiety since its electrons can easily be polarized by the acceptor moiety (see introduction). However the fact that the complexes of this family have NH_3 ligands which are volatile makes them not suitable for making the mixed-valence dinuclear system for NLO materials since the complex will not be thermal stable.

Ligand-to-metal coupling (H_{LM}) calculated for the complexes synthesized herein showed an increase with a decrease in LMCT energy. This variation was qualitatively related to the magnitude of the Ru(III)/(II)-cyanamide π bond overlap by the use of Equation 15. Equation 14 could not be used to explain the variations that were observed (Figures 32). This shows the limitation of the CNS model which ignores the importance of the overlap integral.

More work will have to be done on the neutral mononuclear complexes to make a neutral mixed-valence complex which shows the desired properties of a donor-acceptor system that is suitable for NLO applications. At the moment, studies on the acceptor moiety (Ru(III) complex) are in progress. Growth of quality crystals for X-ray crystal structure determination is necessary to assign geometry unambiguously and to get a better understanding of the Ru(II)-cyanamide bond.

6.0 Appendix

6.1 Supporting Figures

Figure 33: ^1H -NMR spectrum of (terpy*) in CDCl_3 .

Figure 34: ^1H -NMR spectrum of (2pic) in CDCl_3 .

Figure 39: ¹H-NMR spectrum of [Ru(terpy*)(2pca)3,4,5-(OMe)₃pcyd]·³/₄CH₂Cl₂ in CDCl₃.

Figure 40: ¹H-NMR spectrum of [Ru(terpy*)(2pic)Cl]·¹/₄CH₂Cl₂ in CDCl₃.

Figure 41: ^1H -NMR spectrum of $[\text{Ru}(\text{terpy}^*)(2\text{pic})2,3\text{-Cl}_2\text{pcyd}]\cdot\frac{1}{4}\text{CH}_2\text{Cl}_2$ in CDCl_3 .

Figure 42: ^1H -NMR spectrum of $[\text{Ru}(\text{terpy}^*)(\text{acac})\text{Cl}]$ in CDCl_3 .

Figure 43: ^1H -NMR spectrum of $[\text{Ru}(\text{terpy}^*)(\text{acac})_2,3\text{-Cl}_2\text{pcyd}] \cdot \frac{1}{2}\text{CH}_3\text{CN}$ in CDCl_3 .

Figure 44: IR spectrum of $[\text{Ru}(\text{terpy}^*)(2\text{pca})2,3\text{-Cl}_2\text{pcyd}] \cdot \frac{3}{4}\text{CH}_2\text{Cl}_2$ (KBr pellets)

Figure 45: IR spectrum of $[\text{Ru}(\text{terpy}^*)(2\text{pca})2,4,6\text{-Cl}_3\text{pcyd}] \cdot \frac{3}{10}\text{CH}_2\text{Cl}_2$ (KBr pellets)

Figure 46: IR spectrum of $[\text{Ru}(\text{terpy}^*)(2\text{pca})2,3,4,5\text{-Cl}_4\text{pcyd}]\cdot\frac{3}{4}\text{CH}_2\text{Cl}_2$ (KBr pellets)

Figure 47: IR spectrum of $[\text{Ru}(\text{terpy}^*)(2\text{pca})3,4,5\text{-(OMe)}_3\text{pcyd}]\cdot\frac{3}{4}\text{CH}_2\text{Cl}_2$ (KBr pellets)

Figure 48: IR spectrum of $[\text{Ru}(\text{terpy}^*)(2\text{pic})\text{Cl}] \cdot \frac{3}{4}\text{CH}_2\text{Cl}_2$ (KBr pellets)

Figure 49: IR spectrum of $[\text{Ru}(\text{terpy}^*)(2\text{pic})2,3\text{-Cl}_2\text{pcyd}] \cdot \frac{1}{4}\text{CH}_2\text{Cl}_2$ (KBr pellets)

Figure 50: IR spectrum of $[\text{Ru}(\text{terpy}^*)(\text{acac})\text{Cl}]$. (KBr pellets)

Figure 51: IR spectrum of $[\text{Ru}(\text{terpy}^*)(\text{acac})_{2,3}\text{-Cl}_2\text{pcyd}] \cdot \frac{1}{2}\text{CH}_3\text{CN}$. (KBr pellets)

Figure 52: OTTLE cell electronic spectrum of $[\text{Ru}(\text{terpy}^*)(2\text{pca})\text{Cl}]^{0/1+}$ in DMF under increasing oxidation potentials (0.0 $\longrightarrow$ 0.8 V). 0.1 M TBAH; platinum wire working and counter electrodes; silver wire pseudo- reference electrode.

Figure 53: OTTLE cell electronic spectrum of $[\text{Ru}(\text{terpy}^*)(2\text{pca})2,3\text{-Cl}_2\text{pcyd}]^{0/1+}$ in DMF under increasing oxidation potentials (0.0 $\longrightarrow$ 0.8 V). 0.1 M TBAH; platinum wire working and counter electrodes; silver wire pseudo- reference electrode.

Figure 54: OTTLE cell electronic spectrum of $[\text{Ru}(\text{terpy}^*)(2\text{pca})2,4,6\text{-Cl}_3\text{pcyd}]^{0/1+}$ in DMF under increasing oxidation potentials (0.0 $\longrightarrow$ 0.8 V). 0.1 M TBAH; platinum wire working and counter electrodes; silver wire pseudo- reference electrode.

Figure 55: OTTLE cell electronic spectrum of $[\text{Ru}(\text{terpy}^*)(2\text{pca})2,3,4,5\text{-Cl}_4\text{pcyd}]^{0/1+}$ in DMF under increasing oxidation potentials (0.0 $\longrightarrow$ 0.8 V). 0.1 M TBAH; platinum wire working and counter electrodes; silver wire pseudo- reference electrode.

Figure 56: OTTLE cell electronic spectrum of $[\text{Ru}(\text{terpy}^*)(2\text{pic})\text{Cl}]^{0/1+}$ in DMF under increasing oxidation potentials (0.0 $\longrightarrow$ 0.8 V). 0.1 M TBAH; platinum wire working and counter electrodes; silver wire pseudo- reference electrode.

Figure 57: OTTLE cell electronic spectrum of $[\text{Ru}(\text{terpy}^*)(2\text{pic})2,3\text{-Cl}_2\text{pcyd}]^{0/1+}$ in DMF under increasing oxidation potentials (0.0 $\longrightarrow$ 0.8 V). 0.1 M TBAH; platinum wire working and counter electrodes; silver wire pseudo- reference electrode.

Figure 58: OTTLE cell electronic spectrum of $[\text{Ru}(\text{terpy}^*)(\text{acac})_2, 3\text{-Cl}_2\text{pcyd}]^{0/1+}$ in DMF under increasing oxidation potentials (0.0 $\longrightarrow$ 0.8 V). 0.1 M TBAH; platinum wire working and counter electrodes; silver wire pseudo- reference electrode.

Figure 59: Cyclic voltammogram of $[\text{Ru}(\text{terpy}^*)(2\text{pca})\text{Cl}]$ in DMF with 0.1 M tetrabutylammonium hexafluorophosphate, using platinum counter and working electrode, silver wire pseudo-reference (cobaltocene internal reference) at scan rate of 100 mV/s. Inset shows Ru(III)/(II) couple of the complex.

Figure 60: Cyclic voltammogram of $[\text{Ru}(\text{terpy}^*)(2\text{pca})_3\text{-Clpcyd}]$ in DMF with 0.1 M tetrabutylammonium hexafluorophosphate, using platinum counter and working electrode, silver wire pseudo-reference (cobaltocene internal reference) at scan rate of 100 mV/s.

Figure 61: Cyclic voltammogram of $[\text{Ru}(\text{terpy}^*)(2\text{pca})_2,3\text{-Cl}_2\text{pcyd}]$ in DMF with 0.1 M tetrabutylammonium hexafluorophosphate, using platinum counter and working electrode, silver wire pseudo-reference (cobaltocene internal reference) at scan rate of 100 mV/s. Inset shows Ru(III)/(II) couple of the complex.

Figure 62: Cyclic voltammogram of $[\text{Ru}(\text{terpy}^*)(2\text{pca})2,4,6\text{-Cl}_3\text{pcyd}]$ in DMF with 0.1 M tetrabutylammonium hexafluorophosphate, using platinum counter and working electrode, silver wire pseudo-reference (cobaltocene internal reference) at scan rate of 100 mV/s. Inset shows Ru(III)/(II) couple of the complex.

Figure 63: Cyclic voltammogram of $[\text{Ru}(\text{terpy}^*)(2\text{pca})_2,3,4,5\text{-Cl}_4\text{pcyd}]$ in DMF with 0.1 M tetrabutylammonium hexafluorophosphate, using platinum counter and working electrode, silver wire pseudo-reference (cobaltocene internal reference) at scan rate of 100 mV/s. Inset shows Ru(III)/(II) couple of the complex.

Figure 64: Cyclic voltammogram of $[\text{Ru}(\text{terpy}^*)(2\text{pca})_{3,4,5}\text{-(OMe)}_3\text{pcyd}]$ in DMF with 0.1 M tetrabutylammonium hexafluorophosphate, using platinum counter and working electrode, silver wire pseudo-reference (cobaltocene internal reference) at scan rate of 100 mV/s.

Figure 65: Cyclic voltammogram of $[\text{Ru}(\text{terpy}^*)(2\text{pic})\text{Cl}]$ in DMF with 0.1 M tetrabutylammonium hexafluorophosphate, using platinum counter and working electrode, silver wire pseudo-reference (cobaltocene internal reference) at scan rate of 100 mV/s. Inset shows Ru(III)/(II) couple of the complex.

Figure 66: Cyclic voltammogram of $[\text{Ru}(\text{terpy}^*)(\text{acac})\text{Cl}]$ in DMF with 0.1 M tetrabutylammonium hexafluorophosphate, using platinum counter and working electrode, silver wire pseudo-reference (cobaltocene internal reference) at scan rate of 100 mV/s. Inset shows Ru(III)/(II) couple of the complex.

Figure 67: Cyclic voltammogram of $[\text{Ru}(\text{terpy}^*)(\text{acac})_2, 3\text{-Cl}_2\text{pcyd}]$ in DMF with 0.1 M tetrabutylammonium hexafluorophosphate, using platinum counter and working electrode, silver wire pseudo-reference (cobaltocene internal reference) at scan rate of 100 mV/s.

7.0 References

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