

Synthesis, Characterization, Electrochemical and Spectroelectrochemical Properties of Ruthenium(II) Complexes Containing Phenylcyanamide Ligands and Effect of the Inner- Sphere on the Ru-NCN Chromophore

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ABSTRACT: *[Ru(terpy)(bpy)(L)]PF₆ complexes, where terpy is 2,2':6',2''-terpyridine, bpy is 2,2' - bipyridine and L is monoanions of 4 - bromophenylcyanamide (4 - Brpcyd), 4-methoxyphenylcyanamide (4 - MeOPcyd), 2, 4 - dibromophenylcyanamide (2,4 - Br₂pcyd), 2,4-dimethylphenylcyanamide (2,4 - Me₂pcyd), 2 - methylphenylcyanamide (2 - MePcyd), phenylcyanamide (Pcyd) and naphthylcyanamide (ncyd) have been prepared and characterized by elemental analysis, IR, ¹H-NMR and UV-vis spectroscopies and cyclic voltammetry. Spectroelectrochemistry was used to generate the electronic absorption spectra of the Ru(III) complexes, [Ru(terpy)(bpy)(L)]²⁺ in acetonitrile solution. The spectral data associated with the Ru(III)-cyanamido LMCT chromophore were compared to those derived from Ru(III) analogues in order to gain a greater understanding the effect of spectator ligands on the nature of the Ru(III)-Cyanamide bond. The data supports greater covalency in the Ru(III)-cyanamide bond of [Ru(terpy)(bpy)(L)]²⁺ complexes compared to their Ru(III) analogues.*

KEY WORDS: *Ruthenium (II) complex, Phenylcyanamide, Oscillator strength, Charge-transfer band.*

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 and optical properties. Such devices could find applications in a variety of areas

such as nanoscale electronics, biological probes, magnetic shields, and video displays [1-3].

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

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1021-9986/05/2/21

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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, the close energy and symmetrical matching between ruthenium $d\pi$ and terminal nitrogen $p\pi$ orbitals of cyanamide ligands ($N=C=N-R$) has been shown in number of publications [3-18]. 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 [3].

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 [3-22]. 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) [3,5]. Fig. 1 illustrates this qualitatively, while the expression for E_{LMCT} is given by:

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

where C is a fudge factor to account for the impossibility of measuring $E(Ru(III/II))$ after the ligand is oxidized to L(0), and χ represents the inner and outer-sphere reorganizational energies involved in the LMCT event [3,5,13].

The ligand-metal coupling element H_{LM} can be derived from the oscillator strength (f) of the LMCT band. Oscillator strength can be experimentally derived from the integral of the molar absorptivity versus energy of the charge transfer band, and it can be calculated theoretically from the transition dipole moment (M) of the LMCT by the expression [17, 23-24]:

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

where G is degeneracy of states, M can be 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 elements [24] from charge transfer band oscillator strengths assumes that the transition dipole moment lies along the bonding axis and that of 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 [23-24].

It has been shown in previous studies of mono and dinuclear ruthenium(III) and Co(III) complexes, that the Ru(III)-cyanamide LMCT chromophore is remarkably sensitive to the nature of the solvent [8,10,13,17,25-28]. 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 [3,23-24].

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 [Ru(terpy)(L)]⁺ (Fig.2) complexes were synthesized and characterized, where terpy is 2,2':6',2''-terpyridine, bpy is 2,2'-bipyridine, and L is the phenylcyanamide anion ligands as depicted in Fig. 3. Spectroelectrochemical oxidation to the Ru(III) complexes permitted an analysis of their LMCT spectral properties in comparison to their Ru(III) analogues [3,8,10,13].

EXPERIMENTAL

Materials

All of the chemicals and solvents used were reagent grade. Acetonitrile, diethylether, acetone and toluene were

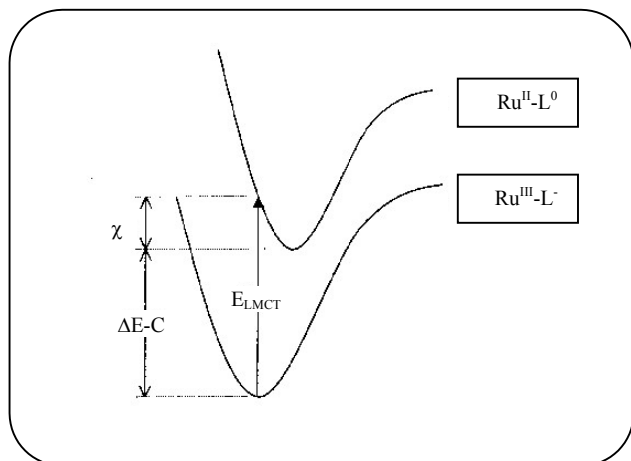


Fig. 1: State to state potential energy curves for a ruthenium(III)-phenylcyanamide complex illustrating the relationship between ΔE and E_{LMCT} .

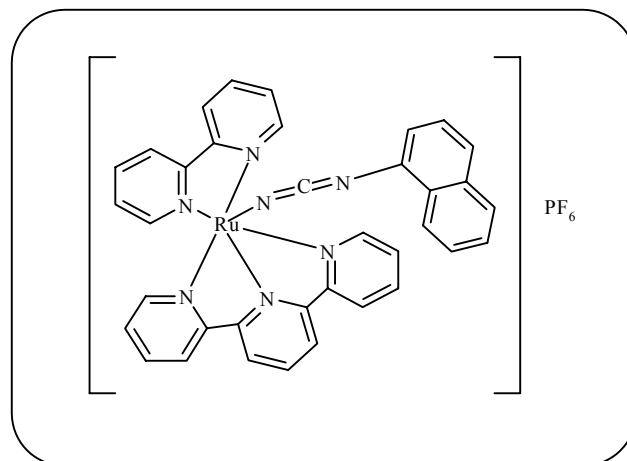


Fig. 2: $[Ru(terpy)(bpy)(ncyd)]PF_6$

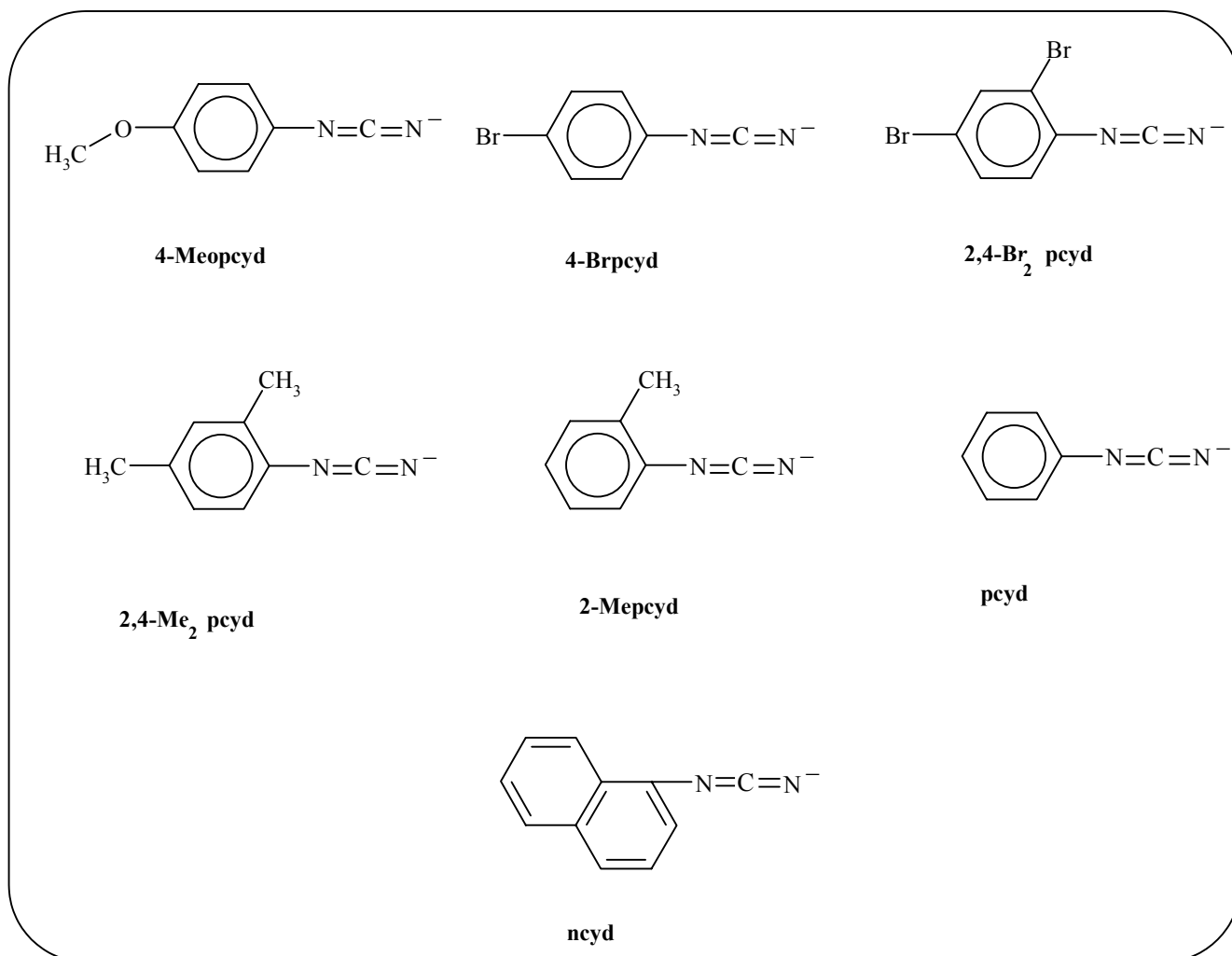


Fig. 3: The phenylcyanamide anion ligands (L) used in $[Ru(terpy)(bpy)(L)]^+$ complexes.

purchased from Merck. Thallium (I) acetate, ruthenium (III) chloride hydrate, tetrabutylammoniumhexafluorophosphate (TBAH), alumina (WA-1, 150 mesh), 2,2'-bipyridine, 2, 2': 6', 2''-terpyridine were purchased from Aldrich and used without further purification. Syntheses of $[\text{Ru}(\text{terpy})(\text{bpy})\text{Cl}]\text{PF}_6$ and the thallium salts of phenylcyanamide ligands have been previously described [5,29].

Measurements

UV-vis-NIR spectra were taken on a JASCO VSP-575 spectrophotometer. The spectra were measured in acetonitrile solution at room temperature. The IR spectra (KBr disks) were obtained on a Shimadzu 460 spectrophotometer. $^1\text{H-NMR}$ spectra were recorded on a Bruker DRX-500 MHz AVANCE spectrometer at ambient temperature in DMSO-d_6 . Elemental analyses were performed by Heraeus CHN-O-Rapid elemental analyzer. Cyclic voltammograms were recorded by using a Metrohm 694 apparatus. Three electrodes were utilized in this system, a platinum disk working electrode (RDE), a platinum wire auxiliary electrode and Ag/AgCl reference electrode. The platinum disk working electrode was manually cleaned with 1- μm diamond polish prior to each scan. The supporting electrolyte, tetrabutylammonium-hexafluorophosphate (TBAH), was recrystallized twice from ethanol-water (1/1) and vacuum-dried at 110 °C overnight. Acetonitrile was distilled over alumina and degassed under vacuum prior to use in cyclic voltammetry. The solutions were deoxygenated by bubbling with argon (Ar) for 15 min and blanketed with argon prior to each scan.

Spectroelectrochemistry was performed using an OTTLE (optically transparent thin-layer electrode) cell. Three electrodes were utilized in this cell, ITO (indium-tin oxide) coated glass for the working, counter electrodes and a Ag/AgCl reference electrode.

SYNTHESIS

General Methods

(2, 2' - bipyridine) (phenylcyanamide) (2, 2' : 6', 2''-terpyridine) ruthenium (II) hexafluorophosphate $[\text{Ru}(\text{terpy})(\text{bpy})(\text{pcyd})]\text{PF}_6$

A mixture of $[\text{Ru}(\text{terpy})(\text{bpy})\text{Cl}]\text{PF}_6$ (0.3 mmol, 201mg) and thallium(I) phenylcyanamide, pcydTl, (0.3 mmol, 96 mg) were dissolved in 100 ml acetonitrile in a 250 ml

round-bottom flask. The reaction mixture was stirred for 24 h at reflux temperature. The resulting reaction mixture was allowed to cool to room temperature and filtered to remove a white solid (TlCl). The filtrate was then transferred to a 500 ml round-bottom flask and the solvent was removed on a rotary evaporator.

The crude product was dissolved in 20 ml of 1:2 $\text{CH}_3\text{CN}/\text{toluene}$, filtered, and purified by chromatography on a 40 cm x 2 cm diameter column containing 120 g grade III alumina (weakly acidic, 150 mesh). One band containing starting material was eluted with 1:2 $\text{MeCN}/\text{toluene}$. A second band was eluted with 1:1 $\text{MeCN} / \text{toluene}$ and contained the target complex, $[\text{Ru}(\text{terpy})(\text{bpy})(\text{pcyd})]\text{PF}_6$, which crystallized from the solution upon evaporation of the MeCN . Recrystallization was achieved by the slow diffusion of diethylether into a saturated solution of the complex in MeCN at 0-2 °C. Yield 74%. Anal. Calcd for $\text{C}_{32}\text{H}_{24}\text{F}_6\text{N}_7\text{PRu}$: C, 51.07; H, 3.21; N, 13.03. Found: C, 50.95; H, 3.17; N, 13.10.

$[\text{Ru}(\text{terpy})(\text{bpy})(\text{ncyd})]\text{PF}_6$: Yield 72%. Anal. Calcd for $\text{C}_{36}\text{H}_{26}\text{F}_6\text{N}_7\text{PRu}$: C, 53.87; H, 3.26; N, 12.21. Found: C, 54.03; H, 3.30; N, 12.32.

$[\text{Ru}(\text{terpy})(\text{bpy})(2\text{-Mepcyd})]\text{PF}_6$: Yield 78%. Anal. Calcd for $\text{C}_{33}\text{H}_{26}\text{F}_6\text{N}_7\text{PRu}$: C, 51.70; H, 3.42; N, 12.79. Found: C, 51.52; H, 3.47; N, 12.86.

$[\text{Ru}(\text{terpy})(\text{bpy})(4\text{-MeOpcyd})]\text{PF}_6$: Yield 52%. Anal. Calcd for $\text{C}_{33}\text{H}_{26}\text{F}_6\text{N}_7\text{OPRu}$: C, 50.64; H, 3.35; N, 12.53. Found: C, 50.80; H, 3.38; N, 12.61.

$[\text{Ru}(\text{terpy})(\text{bpy})(2,4\text{-Me}_2\text{pcyd})]\text{PF}_6$: Yield 65%. Anal. Calcd for $\text{C}_{34}\text{H}_{28}\text{F}_6\text{N}_7\text{PRu}$: C, 52.31; H, 3.61; N, 12.56. Found: C, 52.03; H, 3.64; N, 12.40.

$[\text{Ru}(\text{terpy})(\text{bpy})(4\text{-Brpcyd})]\text{PF}_6$: Yield 80%. Anal. Calcd for $\text{C}_{32}\text{H}_{23}\text{BrF}_6\text{N}_7\text{PRu}$: C, 46.22; H, 2.79; N, 11.79. Found: C, 46.37; H, 2.82; N, 11.66.

$[\text{Ru}(\text{terpy})(\text{bpy})(2,4\text{-Br}_2\text{pcyd})]\text{PF}_6$: Yield 71%. Anal. Calcd for $\text{C}_{32}\text{H}_{22}\text{Br}_2\text{F}_6\text{N}_7\text{PRu}$: C, 42.22; H, 2.43; N, 10.77. Found: C, 42.40; H, 2.48; N, 10.71.

RESULTS AND DISCUSSION

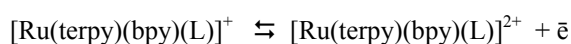
All complexes of this study were synthesized by metathesis reaction of $[\text{Ru}(\text{terpy})(\text{bpy})\text{Cl}]\text{PF}_6$ with the thallium salts of phenylcyanamide ligands in refluxing MeCN . Purification by column chromatography was required, but complexes were nevertheless isolated in good yields. Ru(II) complexes are air-stable and can be

readily recrystallized.

The infrared data for the free phenylcyanamide ligands (neutral and TI salt) have been reported elsewhere [3,5]. The sharp and intense band in the 2050-2200 cm^{-1} region for all seven complexes is assigned to $\nu(\text{N}=\text{C}=\text{N})$ of the coordinated cyanamide group. Although Ru(II) should be able to coordinate to either nitrogen of the phenylcyanamide ligands, $\nu(\text{N}=\text{C}=\text{N})$ indicates bonding to only the nitrile nitrogen (Table 2) [3,5-7,26-28]. This is also indicated by the $^1\text{H-NMR}$ of the complexes, which do not show the presence of any structural isomers. It seems reasonable to suggest that the nitrile nitrogen linkage isomer is more stable due to decrease in steric hindrance.

The $^1\text{H-NMR}$ spectrum of $[\text{Ru}(\text{terpy})(\text{bpy})(2,4\text{-Br}_2\text{pcyd})]\text{PF}_6$ in DMSO-d_6 (Fig. 4B) is typical of all $[\text{Ru}(\text{terpy})(\text{bpy})(\text{L})]\text{PF}_6$ complexes of studied. The bipyridine and terpyridine resonances occur between 7-10 ppm and have the same splitting pattern found in the starting material, $[\text{Ru}(\text{terpy})(\text{bpy})\text{Cl}]\text{PF}_6$ [29]. The uncomplexed cyanamide ligand 2,4- Br_2pcyd is shown in Fig. 4A, and the shifts in the pcyd peaks upon coordination with Ru(II) in Fig. 4B. The $^1\text{H-NMR}$ spectral data for all Ru(II) complexes are compiled in (Table 1).

Cyclic voltammetry data for the $[\text{Ru}(\text{terpy})(\text{bpy})(\text{L})]\text{PF}_6$ complexes are given in (Table 3) and a representative voltammogram of $[\text{Ru}(\text{terpy})(\text{bpy})(4\text{-Brpcyd})]\text{PF}_6$ appears in (Fig. 5). The Ru(III/II) couples are quasi-reversible and generally possess invariant anodic to cathodic peak separations of 75 mV at scan rates from 100 to 500 mV/s in acetonitrile.



The phenylcyanamide derivatives reduction $\text{L}(0/-)$ couples show quasi-reversible to irreversible behavior [3,8,10,13,17, 28].



The three quasi-reversible reduction couples at negative potential are assigned to the sequential reductions of bpy and terpy ligands as shown in following reaction [30-31].

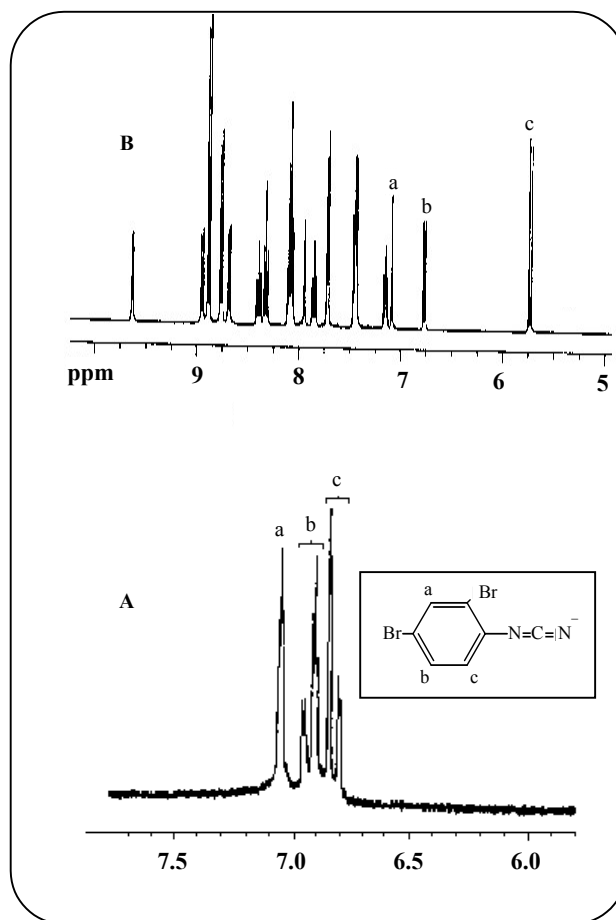
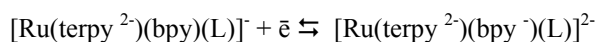
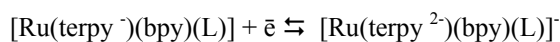
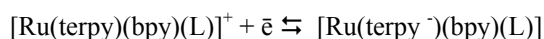


Fig. 4 :The $^1\text{H-NMR}$ spectrum of A) 2,4- Br_2pcyd anion and B) $[\text{Ru}(\text{terpy})(\text{bpy})(2,4\text{-Br}_2\text{pcyd})]\text{PF}_6$ in DMSO-d_6 .

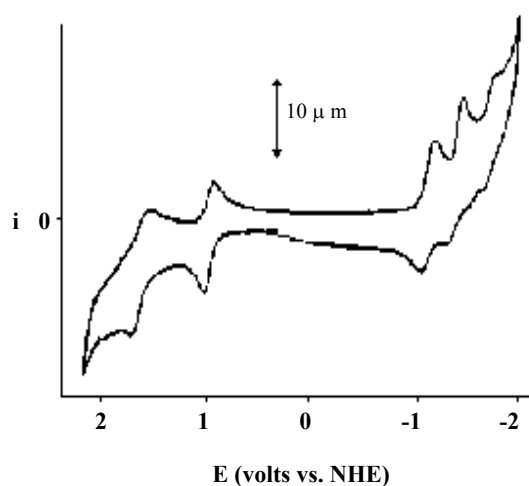


Fig. 5: Voltammogram of $[\text{Ru}(\text{terpy})(\text{bpy})(4\text{-Brpcyd})]\text{PF}_6$ in acetonitrile at a scan rate of 100mV/s ; 0.1 M TBAH.

Table 1: ¹H-NMR Spectral Data for [Ru(terpy)(bpy)(L)]PF₆ Complexes^a.

L	Methyl protons	Phenyl protons	terpy and bpy protons
pcyd	–	6.26(t), 6.64(d), 6.91(t)	7.28(t), 7.75(m), 7.84(d), 7.90(t), 8.09(m) 8.21(t), 8.33(t), 8.40(d), 8.51(d), 8.73(d), 8.88(d), 9.43(t)
4-Brpcyd	–	5.86(d), 6.69(d)	7.36(t), 7.80(m), 7.95(d), 8.04(t), 8.11(m) 8.28(t), 8.38(t), 8.59(d), 8.62(d), 8.86(d), 8.93(d), 9.55(t)
2,4-Br ₂ pcyd	–	6.81(d), 6.88(t), 6.95(d)	7.52(t), 7.93(m), 8.06(d), 8.24(t), 8.33(m) 8.41(t), 8.54(t), 8.67(d), 8.76(d), 8.99(d), 9.05(d), 9.60(t)
2-Mepcyd	2.17(s)	6.63(t), 6.77(t), 6.89(d), 6.95(d)	7.14(t), 7.68(m), 7.74(d), 7.85(t), 8.01(m) 8.18(t), 8.27(t), 8.32(d), 8.43(d), 8.70(d), 8.97(d), 9.39(t)
2,4-Me ₂ pcyd	2.21(s), 2.30(s)	6.72(s), 6.83(d), 6.90(d)	7.12(t), 7.29(m), 7.53(d), 7.78(t), 8.03(m) 8.11(t), 8.21(t), 8.35(d), 8.42(d), 8.65(d), 8.90(d), 9.37(t)
4-MeOpcyd	3.86(s)	5.24(d), 6.11(d)	7.52(t), 7.93(m), 8.06(d), 8.24(t), 8.33(m) 8.41(t), 8.54(t), 8.67(d), 8.76(d), 8.99(d), 9.05(d), 9.60(t)
ncyd	–	6.66(d), 6.72(d), 6.79(d), 6.85(d), 6.929t), 7.01(s)	7.56(t), 7.61(m), 7.75(d), 7.97(t), 8.10(m) 8.23(t), 8.31(t), 8.55(d), 8.56(d), 8.72(d), 8.84(d), 9.41(t)

^a in DMSO-*d*₆; data in ppm vs TMS reference at 0.00 ppm. Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet. Integrations are consistent with assignments.

Table 2: Electronic^a and Infrared^b Absorption Data for [Ru(terpy)(bpy)(L)]PF₆ Complexes.

L	$\pi \longrightarrow \pi^*$	MLCT	LMCT	$\nu(\text{NCN})$
pcyd	231(4.54), 269(4.62), 288(4.80), 317(3.71)	495(3.65)	1154(3.92)	2064
4-Brpcyd	240(3.14), 281(4.99), 289(5.14), 317(3.64)	489(3.28)	1156(3.84)	2177
2,4-Br ₂ pcyd	237(3.86), 284(5.01), 286(5.19), 315(3.77)	482(3.98)	1147(3.85)	2130
2-Mepcyd	232(4.18), 268(4.53), 283(4.35), 315(3.82)	497(3.83)	1163(3.41)	2190
2,4-Me ₂ pcyd	231(3.97), 265(4.17), 280(4.52), 319(3.00)	511(3.60)	1165(3.73)	2058
4-MeOpcyd	232(3.83), 262(4.97), 284(4.19), 320(3.42)	526(3.71)	1174(3.73)	2051
ncyd	230(4.27), 265(4.44), 282(3.90), 314(3.08)	503(3.35)	1160(3.68)	2056

^a λ in nm (log ϵ); in acetonitrile solution. ^bIR data (KBr) in cm⁻¹; strong absorptions.

Table 3: Electrochemical ^a Data for [Ru(terpy)(bpy)(L)]PF₆ Complexes

L	Ru (I I I / I I)	bpy and terpy reduction couples	L _{ox}
pcyd	991	-1111, -1384, -1576	1231
4-Brpcyd	1024	-1114, -1358, -1603	1648
2,4-Br ₂ pcyd	1037	-1119, -1381, -1569	1656
2-Mepcyd	989	-1106, -1361, -1590	11195
2,4-Me ₂ pcyd	947	-1110, -1374, -1597	1171
4-MeOpcyd	925	-1119, -1381, -1569	1217
ncyd	994	-1109, -1392, -1570	1249

^a Data in mV vs NHE(0.1 M TBAH acetonitrile solution) at a scan rate of 100 mV/s.^b Anodic wave only.**Table 4: Electrochemical and Electronic Calculating Parameters Data for [Ru(terpy)(bpy)(L)]PF₆ Complexes.**

L	$\Delta E^a = L(0/-)-Ru(I I I / I I)$	E_{LMCT}^b	f^c	H_{LM}^d
pcyd	240	1.074	0.142	1911.7
4-Brpcyd	624	0.813	0.148	1949.9
2,4-Br ₂ pcyd	619	0.816	0.152	1990.4
2-Mepcyd	228	1.100	0.144	1917.6
2,4-Me ₂ pcyd	248	1.080	0.137	1868.8
4-MeOpcyd	246	1.082	0.129	1806.5
ncyd	255	1.073	0.139	1886.5

^a data in mV^b optical energy in eV^c oscillator strength calculated from equation 5^d ligand-metal coupling calculated from equation 4

Electronic spectral data for these complexes in acetonitrile solution are given in (Table 2) and representative spectrum of $[\text{Ru}(\text{terpy})(\text{bpy})(4\text{-Brpcyd})]\text{PF}_6$ is shown in Fig. 6. The absorption bands seen in the UV region (230-320 nm) are assigned to ligand-centered transitions ($\pi \rightarrow \pi^*$) of the bpy and terpy ligands [23].

The broad absorption band at approximately 480-520 nm that appears in the complexes' spectra is assigned to a metal-to-ligand charge transfer (MLCT) transition. Spectroscopic assignments were made by comparison to literature [3,23]. The slight shift 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 [23, 32-33].

Spectroelectrochemistry was performed on these complexes in order to generate the Ru(III) spectra [25] and in turn to allow study of the spectral data associated with the Ru(III) - NCN LMCT chromophore.

A representative visible spectrum showing the electrochemical generation of the $[\text{Ru}(\text{terpy})(\text{bpy})(4\text{-Brpcyd})]\text{PF}_6$ in acetonitrile solution is given in (Fig. 7) and the low energy LMCT band data are collected in (Table 4).

The coordination sphere about the Ru(III) in these complexes has C_{4v} microsymmetry, i.e., similar to previous study on the $[\text{Ru}(\text{NH}_3)_5(\text{L})]^{2+}$, the low energy LMCT band at the NIR region is assigned to the $b_1 \rightarrow b_1^*$ transition [3,5,9,23]. Reversibility was evaluated by the maintainance of isobestic points in the absorption spectrum for both forward oxidation and reverse reduction processes, which were determined to be one electron processes by coulometry [3,13,25].

In previous studies, a linear correlation has been found between electrochemical potentials and charge-transfer bands [13,34]. This is an ionic model in which the electron involved in charge-transfer is located in the ground state on a ligand orbital and in the excited state on a metal orbital. The LMCT event involves the oxidation of the phenylcyanamide ligand and reduction of the Ru(III) ion. This is equivalent to the difference between the $\text{L}(0/-)$ and $\text{Ru}(\text{III}/\text{II})$ reduction couples which can be found by cyclic voltammetry. The expression dealing specifically with LMCT band is:

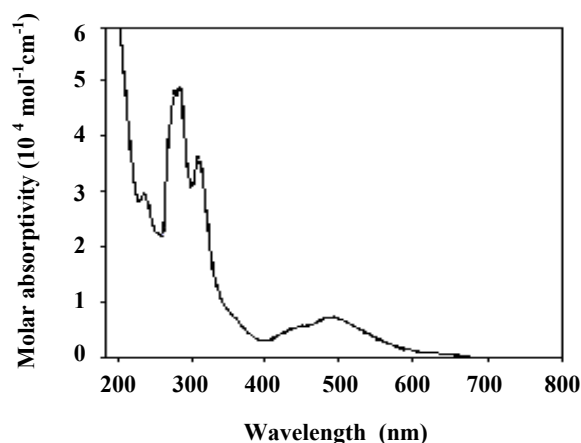


Fig.6: Electronic spectrum of $[\text{Ru}(\text{terpy})(\text{bpy})(4\text{-Brpcyd})]\text{PF}_6$ (6×10^{-5} M in acetonitrile).

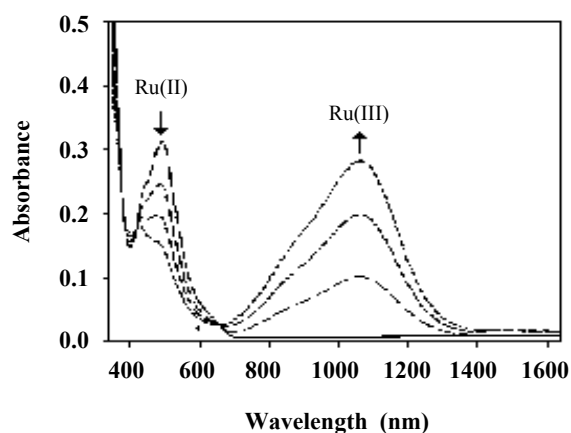


Fig.7: OTTLE cell electronic spectra of $[\text{Ru}(\text{terpy})(\text{bpy})(4\text{-Brpcyd})]\text{PF}_6$ in acetonitrile.

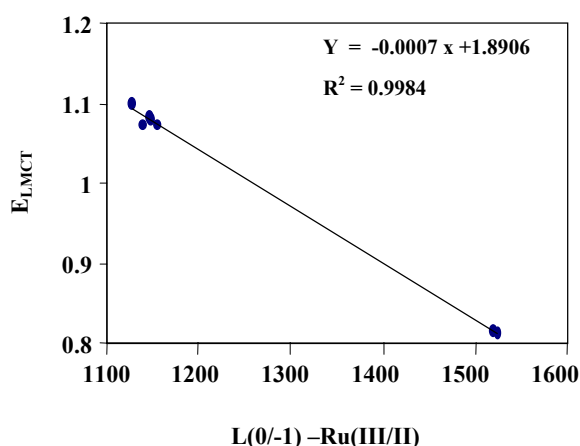


Fig.8: The plot of $\Delta E_{\text{red}} = \text{L}(0/-) - \text{Ru}(\text{III}/\text{II})$ versus E_{LMCT} for $[\text{Ru}(\text{terpy})(\text{bpy})(\text{L})]^+$ complexes.

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

Where C is a constant which takes into account the fact that it is impossible to experimentally measure the oxidation of Ru(II) when the oxidized ligands is bounded. C should remain constant for a similar group of complexes in a common solvent. The χ term is used to account for the outer- and inner-sphere reorganizations that occur upon an electronic transition [3,13,34]. Plot of $\Delta E_{red} = L(0/-) - Ru(III/II)$ versus E_{LMCT} for [Ru(terpy)(bpy)(L)]⁺ complexes is shown in Fig 8. In contrast to [Ru(NH₃)₅(L)]²⁺ analogous complexes, the plot of data points for ΔE_{red} versus E_{LMCT} gives a negative slope with correlation coefficient, R = 0.998. This behavior is contrary to a simple ionic model for the bonding between Ru(III) and the cyanamide anion ligand and can be explained if covalency of Ru(III)-NCN π bond is invoked. As the energy difference between donor and acceptor π orbitals becomes smaller, the amount of orbital mixing increase, and this results in an increase in the interaction energy. The extra stabilization of the ground state and corequisite destabilization of the excited state cause an increase in E_{op} beyond that predicted to the simple ionic model [3, 13,23,34].

Decreasing the energy difference between ligand and metal orbitals would be expected to increase the amount of ligand-metal coupling. This result is also reflected in the H_{LM} values. Because the LMCT bands are non-gaussian, the following equation used for computing oscillator strength [17,23-24,34] as:

$$f = 4.61 \times 10^{-9} \epsilon_{max} \Delta\nu_{1/2} \quad (5)$$

where ϵ_{max} is the maximum extinction coefficient in $M^{-1}cm^{-1}$ and $\Delta\nu_{1/2}$ 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 *Peak Fit* software and multiple gaussian peaks.

In this treatment, the number of gaussian bands does not reflect electronic transitions or vibrational features. Table 4 shows the H_{LM} values for the Ru(III) complexes calculated by equation (4). Note that H_{LM} for these complexes is considerably smaller than that for the [Ru(NH₃)₅(L)]²⁺ complexes. This would seem to indicate that Ru(III)-NCN $d\pi - p\pi$ bonding is weaker in the [Ru(terpy)(bpy)(L)]²⁺ complexes [3,5,9].

CONCLUSION

Seven novel phenylcyanamide Ru(II) complexes have been synthesized and characterized. Although Ru(II) should be able to coordinate to either nitrogen of the phenylcyanamide ligand, the IR spectra indicate bonding to only the nitrile (end) nitrogen. This also indicated by the ¹H-NMR of the complexes, which do not show the presence of any structural isomers. Cyclic voltammetry data show the Ru(III/II) couples are quasi-reversible and the pcyd L(0/-) couples are significantly less reversible having much larger peak-to-peak separation and greater sensitivity to scan rate. The cyclic voltammetry data for [Ru(terpy)(bpy)(L)]⁺ and [Ru(NH₃)₅(L)]²⁺ complexes show that switching from NH₃ to bpy and terpy ligands has a small effect ($\sim +0.2V$) on the pcyd ligand reduction couples. This is because the pyridine moieties cause Ru(III) to be more electropositive, which in turn draws electron density away from the pcyd anion ligand, making it more difficult to oxidize. The two strong absorptions appearing at UV region are assigned to $\pi \rightarrow \pi^*$ transition of bpy and terpy ligands. The slight shift in MLCT energy is due to the substituents on the pcyd ligand vary from \bar{e} -withdrawing to \bar{e} -donating is an indication of the donor ability of the pcyd ligand and its influence on ruthenium (II) ion stability. The complexes showed good reversibility upon oxidation as evidence by spectroelectrochemical studies. Plots of E_{LMCT} versus L(0/-)-Ru(III/II) for both the [Ru(terpy)(bpy)(L)]⁺ and [Ru(NH₃)₅(L)]²⁺ complexes are nearly linear. Although C value by equation (1) 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 equal since the inner coordination sphere of [Ru(NH₃)₅(L)]²⁺ is quite different from [Ru(terpy)(bpy)(L)]⁺. χ consist of net total of both, inner and outersphere reorganization energies so coincidentally, it may be possible that the difference between the outer and innersphere reorganizational energies of two families cancels each other. Decreasing the energy difference between ligand and metal orbitals would be expected to increase the amount of ligand-metal coupling. The CNS theory would predicted to be a linear relationship here, but instead the slope appears to taper off in the case of the [Ru(terpy)(bpy)(L)]⁺ complexes. This result also is reflected in the H_{LM} values since they were calculated from the oscillator strength.

H_{LM} for the $[Ru(terpy)(bpy)(L)]^+$ complexes is considerably smaller than that for the $[Ru(NH_3)_5(L)]^{2+}$ complexes. This would seem to indicate that Ru-cyanamide $d\pi-p\pi$ bonding is weaker in the $[Ru(terpy)(bpy)(L)]^+$ complexes. It may be that the Ru(III) $d\pi$ orbitals have shrunk as a result of stabilization by the pyridine moieties (π acceptors) which causes a decrease in π overlap with the cyanamide ligand.

Acknowledgment

The authors are grateful to the U.S.B. Research Council for supporting this work.

Received : 7th June 2004 ; Accepted : 7th December 2004

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