

Dependence of the Ru(III)–Cyanamide Chromophore on Inner-Sphere Coordination: Comparison of cis -[Ru(bpy)₂(pcyd)₂]⁺ and [Ru(NH₃)₅(pcyd)]²⁺ Complexes

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Six bis(bipyridine)ruthenium(II) complexes of chloro-substituted phenylcyanamide anion ligands cis -[Ru(bpy)₂(L)₂], where L = monoanions of phenylcyanamide (pcyd), (2-chlorophenyl)cyanamide (2-Cl-pcyd), (2,3-dichlorophenyl)cyanamide (2,3-Cl₂pcyd), (2,4,5-trichloro-phenyl)cyanamide (2,4,5-Cl₃pcyd), (2,3,4,5-tetrachlorophenyl)cyanamide (2,3,4,5-Cl₄pcyd) and (pentachlorophenyl)cyanamide (Cl₅pcyd), have been synthesized and characterized by elemental analysis, ¹H-NMR, IR, and UV–vis near-IR spectroscopies, and cyclic voltammetry. Oxidation of the complexes by controlled-potential electrolysis generated cis -[Ru(bpy)₂(L)₂]⁺. These Ru(III) complexes possess low-energy ligand to metal charge-transfer bands that are associated with the Ru(III)–NCN chromophore. A spectroscopic analysis of these LMCT transitions, which assumed C_{2v} microsymmetry about Ru(III), determined their electronic origins. Differences between the properties of [Ru(NH₃)₅L]²⁺ and [Ru(bpy)₂(L)₂]⁺ complexes suggest that for the latter the covalency of the Ru(III)–NCN π bond has significantly increased.

Introduction

The stabilization resulting from the formation of a transition metal coordination sphere is largely derived from σ interactions. The electrons involved in these interactions are stabilized to such an extent suggesting that significant mixing of ligand and metal orbitals has occurred. However, the same cannot be said about π interactions, which are considerably weaker because of the nondirectional overlap of π-symmetry orbital and the relatively long metal–ligand bond. The fact that there are two types of π interactions in which either the metal or ligand can act as donor or acceptor adds further complexity to the issue. Some researchers¹ have invoked perturbation theory, where the overlap between metal π-donor orbital and ligand π-acceptor orbital is considered equal to zero, to derive the extent of orbital mixing between Ru(II) π-donor and ligand π-acceptor complexes. Others have expressly considered the extent of overlap between ligand π-donor orbitals and metal π-acceptor orbitals to be important and necessary to explain variations in ligand to metal charge-transfer (LMCT) band oscillator strength in [Ru(NH₃)₅(L)]²⁺ complexes, where L = a phenylcyanamide anion ligand.^{2,3} It has also been shown that for dinuclear ruthenium(III) ammine complexes in which the metal ions are bridged by the 1,4-dicyanamidobenzene dianion, a continuous and energetically favorable π interaction permits strong antiferromagnetic superexchange at a separation of 13 Å between metal centers.⁴ From these results, it seems clear that more studies should be done to elucidate the circumstances under which π-orbital overlap must be considered or can be ignored.

The electronic properties of the Ru(III)–cyanamide LMCT chromophore have been probed by varying the nature of the cyanamide ligand² and by the outer-sphere perturbation of solvent molecules.³ It is well-known that the nature of the spectator

ligands can play an important role in adjusting the energy and size of metal orbitals and can therefore be used to significantly perturb the Ru(III)–cyanamide chromophore. Replacing ammine ligands with bipyridine ligands in a Ru(III) complex will stabilize the ruthenium d orbitals because of the poorer σ-donor properties of the bipyridine compared to the ammine ligand. To examine this perturbation, the complexes [Ru(bpy)₂(L)₂]⁺, where L = a phenylcyanamide anion ligand, have been prepared. The LMCT spectra and redox chemistry of these complexes have been compared to those for [Ru(NH₃)₅L]²⁺ and the differences related to the changing nature of the Ru(III)–cyanamide π interaction.

Experimental Section

Physical Measurements. UV–vis near-IR spectra were taken on a Cary 5 spectrophotometer. The spectra were measured in acetonitrile solution at room temperature. ¹H-NMR spectra were recorded on a Varian XL200 NMR spectrometer at ambient temperature in dimethyl-d₆ sulfoxide. The IR spectra (KBr disks) were obtained on a Perkin-Elmer 1600 series FTIR spectrophotometer. Cyclic voltammograms were recorded by using a BAS CV-27 apparatus. The electrochemical cell consisted of a double-jacketed glass container with an inner volume of approximately 15 mL. Cell temperature was set at 25 °C by means of a Haake D8-G refrigerated bath and circulator (accuracy ±0.02 °C). The cell was fitted with a Teflon plug through which holes had been drilled to permit insertion of electrodes and argon gas inlet and outlet tubes. Three electrodes were utilized in this system, a platinum disk working electrode (BAS, 1.6-mm diameter), a platinum wire auxiliary electrode, and a silver wire quasi-reference electrode. The platinum disk working electrode was manually cleaned with 1-μm diamond polish prior to each scan. Ferrocene (*E*^o = 665 mV vs NHE) was used as an internal reference.⁵ Caledon HPLC grade acetonitrile was distilled over activated alumina and Anachemia Accusolv grade dimethylformamide (DMF) was used as received. The supporting electrolyte, 0.1 M tetrabutylammonium hexafluorophosphate (TBAH), was recrystallized twice from ethanol and vacuum-dried at 110 °C overnight. Acetonitrile and dimethylformamide were distilled over alumina and degassed under vacuum prior to use in cyclic voltammetry and electrolysis. The solutions were deoxygenated by bubbling with argon for 15 min and blanketed with argon prior to each scan. Electrolysis was conducted with the following slight modifications to the CV cell: the inner cell volume was approximately 50 mL and Pt mesh (4-cm diameter × 12-cm height) was used as the working electrode. The auxiliary electrode was separated from the main solution by a fritted-glass compartment. Elemental analysis was performed by Canadian Microanalytical Services Ltd.

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Table 1. $^1\text{H-NMR}$ Spectral Data for Bis(bipyridine)ruthenium(II) Phenylcyanamide Complexes^a

complex	δ	
	phenylcyanamide	bipyridine
Ru(bpy) ₂ (pcyd) ₂	6.40 (t), 6.65 (d), 6.95 (t)	7.29 (t), 7.75 (d), 7.90 (m), 8.23 (t), 8.65 (d), 8.80 (d), 9.52 (d)
Ru(bpy) ₂ (2-Cl-pcyd) ₂	6.15 (d), 6.40 (t), 6.73 (t), 7.03 (d)	7.29 (t), 7.75 (d), 7.90 (m), 8.23 (t), 8.65 (d), 8.8 (d), 9.50 (d)
Ru(bpy) ₂ (2,3-Cl ₂ pcyd) ₂	6.28 (d), 6.70 (m)	6.30 (t), 7.75 (t), 7.95 (m), 8.25 (t), 8.70 (d), 8.83 (d), 9.48 (d)
Ru(bpy) ₂ (2,4,5-Cl ₃ pcyd) ₂	6.15 (s), 7.33 (s)	7.33 (t), 7.78 (d), 7.95 (m), 8.28 (t), 8.70 (d), 8.85 (d), 9.48 (d)
Ru(bpy) ₂ (2,4,5,6-Cl ₄ pcyd) ₂	6.17 (s)	7.34 (t), 7.78 (d), 7.96 (m), 8.29 (t), 8.72 (d), 8.85 (d), 9.45 (d)
Ru(bpy) ₂ (Cl ₅ pcyd) ₂		7.35 (t), 7.79 (d), 7.96 (m), 8.28 (t), 8.73 (d), 8.86 (d), 9.43 (d)

^a In dimethyl-*d*₆ sulfoxide; 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 Bis(bipyridine)ruthenium(II) Phenylcyanamide Complexes

complex	$\pi \rightarrow \pi^*$	MLCT	$\nu(\text{NCN})$
Ru(bpy) ₂ (pcyd) ₂	247 (4.49), 485 (4.82), 294 (4.75)	374 (4.04), 535 (3.90)	2168
Ru(bpy) ₂ (2-Cl-pcyd) ₂	246 (4.53), 284 (4.86), 294 (4.80)	371 (4.05), 531 (3.93)	2169
Ru(bpy) ₂ (2,3-Cl ₂ pcyd) ₂	245 (4.52), 296 (4.89), 325 (4.23)	365 (4.11), 518 (3.96)	2171
Ru(bpy) ₂ (2,4,5-Cl ₃ pcyd) ₂	246 (4.51), 295 (4.90)	343 (4.29), 511 (3.93)	2174
Ru(bpy) ₂ (2,3,4,5-Cl ₄ pcyd) ₂	218 (4.81), 295 (4.87)	333 (4.35), 507 (3.94)	2176
Ru(bpy) ₂ (Cl ₅ pcyd) ₂ ^c	300 (4.86)	347 (4.44), 521 (3.95)	2178

^a λ in nm (log ϵ); in acetonitrile solution. ^b IR data (KBr) in cm^{-1} ; strong absorptions. ^c Dimethylformamide solution.

Materials. All chemicals and solvents were reagent grade or better. All aniline derivatives were purchased from Aldrich Chemical Co. and were used without further purification. The thallium salts of phenylcyanamide derivatives pcyd, 2-Cl-pcyd, 2,3-Cl₂pcyd, 2,4,5-Cl₃pcyd, 2,3,4,5-Cl₄pcyd, and 2,3,4,5,6-Cl₅pcyd^{2,6,7} and Ru(bpy)₂Cl₂⁸ were prepared by literature methods.

Preparation of *cis*-Bis(phenylcyanamido)bis(2,2'-bipyridine)ruthenium(II) Complexes. General Methods. A mixture of deprotonated phenylcyanamide (Tl salt) (1×10^{-3} mol) and Ru(bpy)₂Cl₂ (5×10^{-4} mol) dissolved in 20 mL of DMF was stirred at reflux temperature for 3 h. The resulting reaction mixture was allowed to cool to room temperature and then left in a refrigerator overnight. A white solid (TlCl) was filtered off. Ether (500 mL) was added to the deep purple filtrate, and the solution was placed in the refrigerator overnight. The dark brown product which precipitated was filtered off and washed with ether. For further purification, the complexes were recrystallized by diffusing ether into a DMF solution, yielding deep purple needles.

Ru(bpy)₂(pcyd)₂: yield 60%. Anal. Calcd for C₃₂H₂₆N₈Ru: C, 63.06; H, 4.018; N, 17.31. Found: C, 62.41; H, 4.12; N, 17.22.

Ru(bpy)₂(2-Cl-pcyd)₂: yield 56%. Anal. Calcd for C₃₄H₂₄N₈Cl₂Ru: C, 56.98; H, 3.35; N, 15.64. Found: C, 56.81; H, 3.53; N, 15.92.

Ru(bpy)₂(2,3-Cl₂pcyd)₂: yield 72%. Anal. Calcd for C₃₄H₂₂N₈Cl₄Ru: C, 52.97; H, 2.80; N, 14.26. Found: C, 52.21; H, 2.97; N, 14.45.

Ru(bpy)₂(2,4,5-Cl₃pcyd)₂: yield 70%. Anal. Calcd for C₃₄H₂₀N₈Cl₆Ru: C, 47.77; H, 2.34; N, 13.11. Found: C, 48.10; H, 2.50; N, 13.35.

Ru(bpy)₂(2,3,4,5-Cl₄pcyd)₂: yield 65%. Anal. Calcd for C₃₄H₁₈N₈Cl₈Ru: C, 44.20; H, 1.95; N, 12.13. Found: C, 44.33; H, 2.25; N, 11.92.

Ru(bpy)₂(2,3,4,5,6-Cl₅pcyd)₂: yield 80%. Anal. Calcd for C₃₄H₁₆N₈Cl₁₀Ru: C, 41.12; H, 1.61; N, 11.29. Found: C, 40.70; H, 1.76; N, 11.32.

Electrooxidation of Bis(2,2'-bipyridine)ruthenium(II) Complexes of Phenylcyanamide Derivatives. Acetonitrile solutions were prepared containing 4×10^{-5} M Ru complex and 0.1 M electrolyte (TBAH). Under an argon atmosphere, a potential of approximately 1.0 V vs Ag⁺/Ag for the oxidation of Ru(II) to Ru(III) or -1.0 V vs Ag⁺/Ag for the reduction of Ru(III) to Ru(II) was applied to the Pt mesh cylinder working electrode. To increase the reaction rate, the solution was stirred throughout the experiment. The reaction was monitored by taking the UV-vis near-IR spectra of aliquots of the reaction mixture during the course of electrolysis.

Results and Discussion

The *cis*-bis(phenylcyanamido)bis(2,2'-bipyridine)ruthenium(II) complexes were prepared from the metathesis reaction of *cis*-[Ru(bpy)₂Cl₂] with an excess of the thallium salt of a phenylcyanamide anion derivative. The neutral complexes crystallize as deep purple needles, and their solubilities in organic solvents decrease with increasing number of chloro substituents

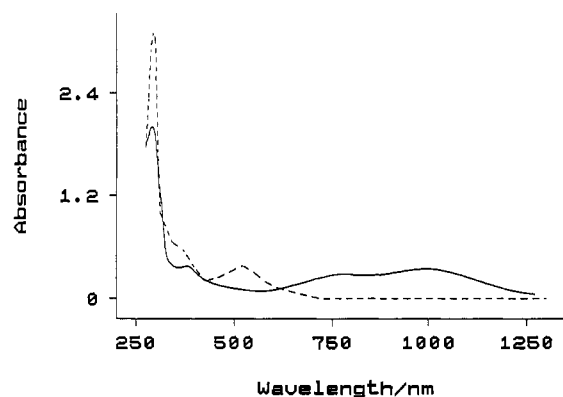


Figure 1. UV-vis spectra of (a) Ru(bpy)₂(2,3-Cl₂pcyd)₂ (---) and (b) [Ru(bpy)₂(2,3-Cl₂pcyd)₂]⁺ (—) in dimethylformamide (0.1 M TBAH).

on the phenyl ring. The elemental analyses of the complexes are consistent with their formulation, as are the following spectroscopic and electrochemical characterizations.

The $^1\text{H-NMR}$ spectral data for the Ru(II) complexes are compiled in Table 1. The integration of phenyl protons and comparison with those of bipyridine suggest that both phenylcyanamide anion ligands occupy magnetically equivalent coordination environments. The bipyridine ligands in a *cis* complex have two magnetically inequivalent pyridine moieties and should result in two ABCD pyridine proton patterns for a total of eight chemical shifts. Only seven are observed (Table 1), and that is because the chemical shifts of the 3,3'-protons are nearly equivalent.^{9,10}

Electronic spectral data for the Ru(II) complexes in acetonitrile and dimethylformamide are assembled in Table 2, and a representative spectrum of [Ru(bpy)₂(2,3-Cl₂pcyd)₂] is shown in Figure 1a. The absorption bands seen in the UV region are assigned to ligand-centered $\pi \rightarrow \pi^*$ transitions.^{6,7,11} The two bands centered at approximately 355 and 520 nm are assigned to metal to ligand charge transfer (MLCT) ($d\pi \rightarrow \pi^*$) by analogy to other Ru(II) bipyridine complexes.^{11,12}

The infrared data for the free phenylcyanamide ligands (Tl salt) have been reported elsewhere.^{2,6} These ligands have a sharp

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Table 3. Electrochemical^a Data for Bis(bipyridine)ruthenium(II) and Pentaammineruthenium(III)^b Phenylcyanamide Complexes

L	Ru(bpy) ₂ (L) ₂				[Ru(NH ₃) ₅ (L)] ²⁺			
	Ru(III/II)	L _{ox1} ^c	L _{ox2} ^c	η	Ru(III/II)	L _{ox1}	η	Δη
pcyd	0.595	1.355	1.545	-0.220	0.064	1.318 ^c	-0.285	-0.064
2-Cl-pcyd	0.705	1.385	1.535	-0.165	0.127	1.410 ^c	-0.225	-0.059
2,3-Cl ₂ pcyd	0.755	1.405	1.585	-0.140	0.163	1.504 ^c	-0.185	-0.044
2,4,5-Cl ₃ pcyd	0.815	1.475	1.765	-0.110	0.202	1.546	-0.145	-0.034
2,3,4,5-Cl ₄ pcyd	0.935	1.545	1.965	-0.050	0.230	1.627	-0.115	-0.064
Cl ₅ pcyd	0.965 ^d			-0.035	0.229	1.668	-0.125	-0.089

^a Data in V vs NHE (0.1 M TBAH acetonitrile solution). ^b Data from ref 2 and corrected for Fc⁺/Fc = 665 mV (vs NHE). ^c Anodic wave only. ^d Estimated value in acetonitrile. The value in DMF was determined and corrected for solvent shift by using Ru(bpy)₂(2,3,4,5-Cl₄pcyd)₂ as a calibrant.

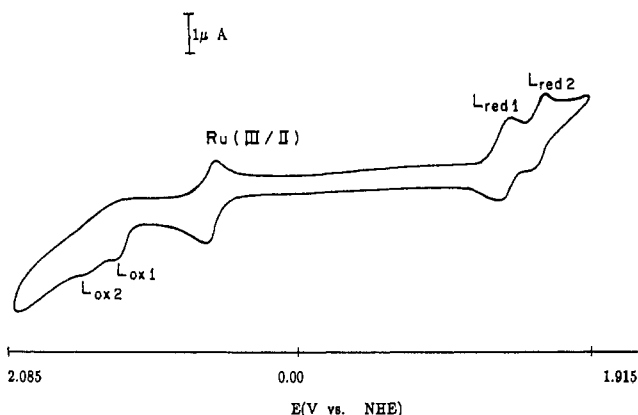
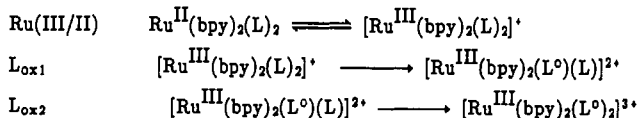


Figure 2. Cyclic voltammetry of Ru(bpy)₂(2,3-Cl₂pcyd)₂ 1.1 × 10⁻⁴ M in dry acetonitrile (0.1 M TBAH) at a scan rate of 100 mV/s.

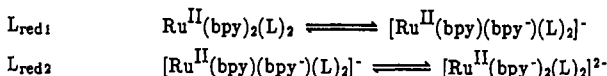
and intense absorption band located around 2100 cm⁻¹, which is assigned to ν(NCN). When a phenylcyanamide ligand coordinates to a transition metal ion, ν(NCN) is shifted to higher energies.^{2,13,14} The presence of only one sharp and intense absorption band for the cyanamide stretching frequency (Table 2) in all the complexes provides evidence that both cyanamide ligands are equivalent in the solid state. When the cyanamide ligands are inequivalent, multiple ν(NCN) bands are observed.¹³ A small positive shift in ν(NCN) is observed with increasing chloro substitution of the phenyl ring.

The electrochemical data for the six complexes are given in Table 3, and a representative voltammogram of [Ru(bpy)₂(2,3-Cl₂pcyd)₂] is shown in Figure 2. Cyclic voltammetry experiments were performed on acetonitrile solutions of the complexes with the exception of [Ru(bpy)₂(Cl₅pcyd)₂], which was sufficiently soluble in DMF. E_{1/2} values were calculated from the average of the anodic and cathodic peak potentials (E_{1/2} = (E_{pa} + E_{pc})/2) at a scan rate of 100 mV s⁻¹. The electrochemical reactions associated with the labeled cyclic voltammetry waves in Figure 2 are given in the following general scheme:

Oxidation processes



Reduction processes



The Ru(III/II) couple demonstrates quasi-reversible behavior between scanning rates of 50 and 250 mV/s, with the separation

between anodic and cathodic peaks increasing from 60 to 70 mV, respectively. The two irreversible oxidations at positive potentials (Figure 2) are assigned to the sequential oxidations of the coordinated phenylcyanamide anion ligands, which are shifted anodically because of their coordination to Ru(III).⁶ The two reversible reduction waves at negative potential are assigned to the sequential reductions of the two bipyridine ligands by analogy to [Ru(bpy)₃]²⁺.¹⁵

The electrochemical data for the analogous pentaammineruthenium(III) phenylcyanamide complexes have been added to Table 3 to permit comparison between the ruthenium complexes. The first ligand oxidation couple L_{ox1} is usually irreversible and appears to be insensitive to whether ammine or bipyridine ligands are coordinated to Ru(III). This is not true for the Ru(III/II) couples, which illustrate the stabilization of the Ru(II) oxidation state by π-acceptor bipyridine ligands. Lever¹⁶ has developed a ligand additivity relationship for the determination of the potential of Ru(III/II) couples. For each ligand, a single electrochemical value η can be assigned that reflects the ligands' contribution to the total potential of the Ru(III/II) couple. The ligand additivity relationship has been shown to hold true for a large number of complexes with disparate ligands. The η values for pcyd ligands have been calculated for each complex and are found in Table 3. The η value for a given pcyd ligand should remain independent of the other ligands about ruthenium. However, the η values for [Ru(NH₃)₅(L)]²⁺ complexes are significantly more negative (see Δη in Table 3) than those for the corresponding [Ru(bpy)₂(L)₂]⁺ complexes. Lever¹⁷ describes this behavior of the phenylcyanamide anion ligands as "noninnocent" in that the value of η depends on how electron rich the metal center is. No clear trend in Δη can be resolved in Table 3, and more data are necessary before anything definitive can be said concerning the origin of this effect. Nevertheless, we speculate that, for [Ru(bpy)₂(L)₂]⁺ complexes, an increase in covalency of the Ru(III)–cyanamide bond may lower the calculated value of η for these ligands. In the Ru(NH₃)₅(L)]²⁺ complexes, the covalency of the Ru(III)–cyanamide bond is less because of the larger energy difference between Ru(III) and cyanamide orbitals (see Table 3). The presence of π-acceptor bipyridines in the ruthenium coordination sphere may also play a synergistic role. Evidence of the greater covalency of the Ru(III)–NCN bond in [Ru(bpy)₂(L)₂]⁺ compared to [Ru(NH₃)₅(L)]²⁺ complexes can be found in an analysis of the complexes' visible absorption spectra.

Controlled-potential electrolysis of [Ru(bpy)₂(L)₂] in DMF was used to generate the absorption spectra of the [Ru(bpy)₂(L)₂]⁺ complexes.¹⁸ The UV–vis spectra of aliquots of the electrolysis solution were taken during the course of the experiment. Reversibility was evaluated by the maintainance of isosbestic points in the absorption spectrum for both forward oxidation and reverse reduction processes, which were determined to be one-electron processes by coulometry. Both [Ru(bpy)₂(pcyd)₂]⁺ and [Ru(bpy)₂(2-Cl-pcyd)₂]⁺ decomposed during the

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(18) In acetonitrile solution, [Ru(bpy)(L)₂]⁺ complexes rapidly decompose.

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Table 4. Electronic Spectral Data (LMCT Bands)^a for Bis(bipyridine)ruthenium(III)^b and Pentaammineruthenium(III)^c Complexes of Anionic Phenylcyanamide Ligands (L)

L	[Ru(bpy) ₂ (L) ₂] ⁺		[Ru(NH ₃) ₅ (L)] ²⁺
	a ₁ → a ₁ [*]	b ₁ → a ₁ [*]	b ₁ → b ₁ [*] ^e
pcyd ^d	811	1067	743 (3.80, 0.135)
2-Cl-pcyd ^d	800	1051	716 (3.86, 0.155)
2,3-Cl ₂ pcyd	793 (3.76, 0.132)	1023 (3.70, 0.052)	699 (3.84, 0.147)
2,4,5-Cl ₃ pcyd	803 (3.79, 0.144)	1035 (3.75, 0.056)	692 (3.85, 0.148)
2,3,4,5-Cl ₄ pcyd	789 (3.81, 0.138)	1013 (3.72, 0.056)	678 (3.78, 0.119)
Cl ₅ pcyd	764 (3.79, 0.128)	957 (3.67, 0.049)	645 (3.76, 0.126)

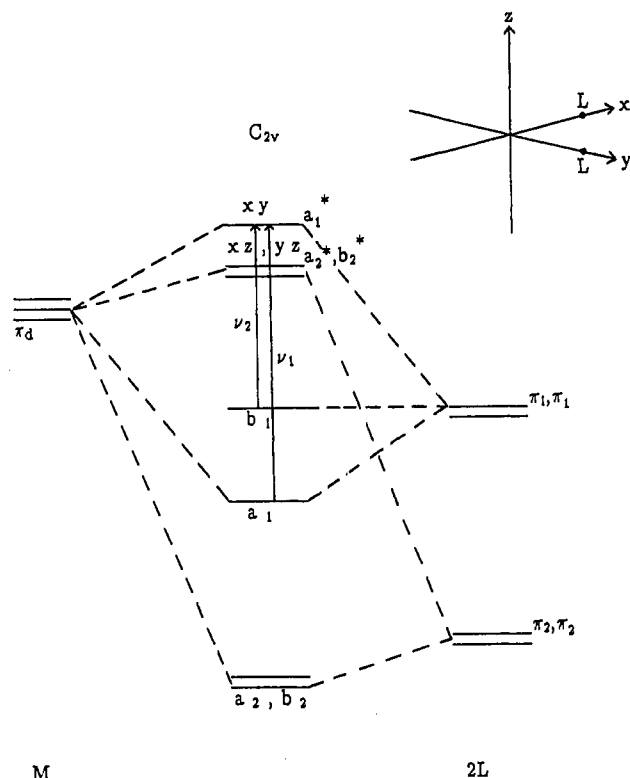
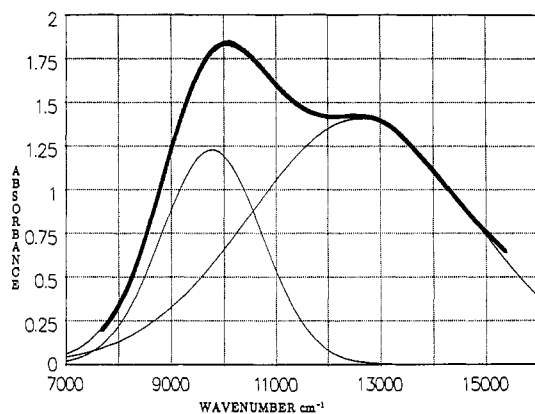
^a All data are in nm (log ε_{max}, f). The oscillator strength f was calculated by using the equation f = (4.61 × 10⁻⁹)ε_{max}(Δν), where Δν in cm⁻¹ is the bandwidth at half ε_{max}. ^b In DMF. ^c In acetonitrile; from ref 2. ^d Decomposes too rapidly for quantitative data. ^e Assignment is derived in ref 6.

oxidation step, and so only the position of the absorption bands could be determined with accuracy. The other oxidized complexes proved to be sufficiently stable (for periods no longer than 15 min) to allow the determination of accurate molar extinction coefficients. The visible absorption data for [Ru(bpy)₂(L)₂]⁺ together with analogous [Ru(NH₃)₅(L)]²⁺ complexes are compiled together with their assignments in Table 4. A representative spectrum of [Ru(bpy)₂(2,3-Cl₂pcyd)₂]⁺ is shown in Figure 1b.

In Figure 1b, the oxidation of [Ru(bpy)₂(2,3-Cl₂pcyd)₂]⁺ results in the disappearance of the MLCT transitions centered at 518 nm and the appearance of new bands at lower energy. These low-energy bands are assigned to ligand to metal charge-transfer (LMCT) π → dπ* transitions associated with the Ru(III)-cyanamide chromophore. The dependence of charge-transfer energy on solvent polarity is a well-known phenomenon.^{19,20} For the [Ru(bpy)₂(L)₂]⁺ complexes, changing the solvent from acetonitrile to dimethylformamide represents an increase in solvent polarity and causes the low-energy LMCT bands to shift to higher energy. This behavior is consistent with ground-state stabilization of the complexes' permanent dipoles by the solvent.

In an earlier study,⁶ it was shown that the cyanamide group possesses two nondegenerate π_{nb} pairs of electrons. For the complexes of this study, linear combinations of two sets of two π_{nb} molecular orbitals must be considered.²¹ If the coordination sphere about Ru(III) has C_{2v} microsymmetry, the interaction between cyanamide π_{nb} orbitals and Ru(III) is suggested to be represented by Figure 3. This MO scheme predicts two low-energy LMCT transitions, a₁ → a₁^{*} and b₁ → a₁^{*}, and a single high-energy transition, a₂, b₂ → a₁^{*}, and forms the basis of the assignments given in Table 4. The lower energy LMCT bands of [Ru(bpy)₂(2,3-Cl₂pcyd)₂]⁺ were resolved into their components by fitting the band envelope to a two-Gaussian-band model (Figure 4). This analysis gave good fits for all the complexes with the square of the correlation coefficients greater than 0.999.²² The spectral data derived from the analyses are found in Table 4.

The Gaussian band for the lowest energy LMCT transition b₁ → a₁^{*} has a smaller oscillator strength than that for the a₁ → a₁^{*} transition. This is expected since the b₁ → a₁^{*} LMCT transition is formally forbidden. In addition, the bandwidth for this transition is less than half that for the a₁ → a₁^{*} transition. A large contribution to bandwidth occurs when there is a large difference in internuclear separation between ground and excited states, as is seen in transitions between bonding and antibonding orbitals. The b₁ MO is formally nonbonding, and so transitions between it and a₁^{*} would be expected to have smaller bandwidths

**Figure 3.** Qualitative MO scheme resulting from the interaction between Ru(III) π_d and phenylcyanamide π_{nb} orbitals in C_{2v} microsymmetry.**Figure 4.** Assuming two transitions, the best Gaussian fit of the lower energy LMCT band envelope of Ru(bpy)₂(2,3-Cl₂pcyd)₂ (DMF solution spectrum).

compared to transitions between bonding a₁ and antibonding a^{*} π-MO's.

There have been a number of studies in which linear correlations have been found between electrochemical potentials and charge-transfer bands of charge-transfer complexes.^{6,23} The rationale has been that since donor and acceptor are oxidized and reduced, respectively, in the formation of a charge-transfer excited state, the energy difference between charge-transfer ground and excited states should be proportional to the difference between the electrochemical reduction and oxidation potentials of the charge-transfer complex. This description 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. For a series of similar charge-transfer complexes where the differences in solvation energy are small, the entropy differences between various redox components are small and the optical transitions

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(22) Jandel Scientific Peakfit software was used in this analysis. Despite the high correlation coefficients, the residuals of the fits did show systematic trends which are indicative of an inappropriate or incomplete model. Departures from ideal Gaussian band shape or the presence of additional bands is the likely source of this error.

(23) (a) Curtis, J. C.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 224. (b) Dodsworth, E. S.; Lever, A. B. P. *Chem. Phys. Lett.* **1984**, *22*, 224; **1985**, *116*, 254 (erratum).

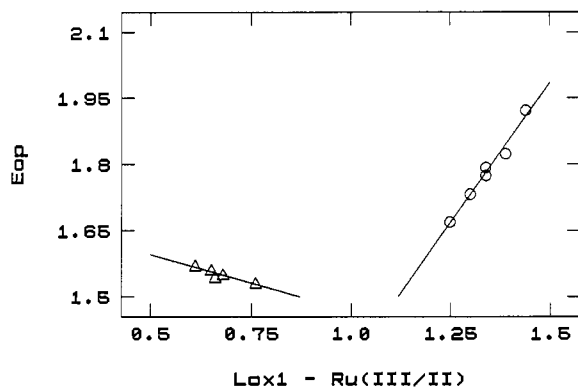


Figure 5. Correlation between the optical energy of the LMCT transitions ($b_1 \rightarrow b_1^*$ and $a_1 \rightarrow a_1^*$, respectively) and the difference between L_{ox1} and Ru(III/II) couples for both $Ru(NH_3)_5(L)_2^{2+}$ (O) and $[Ru(bpy)_2(L)_2]^+$ (Δ) complexes using the data in Tables 3 and 4.

are of the ($0''-0'$) vibrational type, the following expression is expected to hold

$$E_{op} = \Delta E + \chi = \{E(L_{ox1}) - [E(Ru(III/II)) + C]\} + \chi \quad (1)$$

where C is a constant which takes into account the fact that it is not possible to experimentally measure the oxidation of Ru(II) when the oxidized ligand is bound and χ takes into account the outer- and inner-sphere reorganizations that occur upon an electronic transition.^{23a} The above expression predicts that a plot of the difference in energy between metal reduction and ligand oxidation potentials ΔE_{red} versus optical energy of a LMCT band E_{op} should give a linear correlation, provided C and χ are constant. When the data points for ΔE_{red} vs E_{op} are plotted for both $[Ru(NH_3)_5(L)_2]^{2+}$ and $[Ru(bpy)_2(L)_2]^+$ complexes (Figure 5), linear distributions are seen but with important differences between the two sets of complexes. The most dramatic observation is the negative slope seen for the $[Ru(bpy)_2(L)_2]^+$ data points.²⁴ 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 the Ru(III)-NCN π bond is invoked. As the energy difference between donor and acceptor π orbitals becomes smaller, the amount of orbital mixing increases, 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 by the simple ionic model. A modified expression for E_{op} is given by

$$E_{op} = \Delta E + \chi + E_{cov} \quad (2)$$

which attempts to take into account the added energy E_{cov} that covalency contributes to the optical transition energy. If the interaction between donor and acceptor orbitals is entirely covalent, $\Delta E = 0$ and the optical energy will depend largely on E_{cov} . The above expression although simple in form is extremely difficult to solve experimentally because of the interdependence of each of the terms.

The matching of donor and acceptor orbital energies is a necessary prerequisite to a delocalized system and the ability of such a system to transmit electronic information. Future studies will continue to explore the electronic properties of an increasingly covalent ruthenium-cyanamide π bond.

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(24) Ideally, all the data should have been derived from one solvent system. However, $[Ru(bpy)_2(L)_2]^+$ complex instability and in one case insolubility required the substitution of DMF for acetonitrile. The resulting solvent correction term is expected not to vary significantly between the $[Ru(bpy)_2(L)_2]^+$ complexes and cannot be used to explain the negative slope seen in Figure 5.