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# Effect of Conjugation on the Oscillator Strength of the Ruthenium(III)−Cyanamide Chromophore

**Christopher E. B. Evans, Dean Ducharme, Mark L. Naklicki, and Robert J. Crutchley***

Ottawa-Carleton Chemistry Institute, Carleton University, 1125 Colonel By Drive,
Ottawa, Canada K1S 5B6

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The complexes, $[(NH_3)_5Ru(L)][ClO_4]_2$, where $L^-$ = cyanamide, phenylcyanamide, 4-cyanamidobiphenyl, 1-cyanamidonaphthalene, 2-cyanamidonaphthalene, 2-cyanamidophenanthrene, and 1-cyanamidopyrene anions, were synthesized and characterized by cyclic voltammetry and electronic absorption spectroscopy. The Ru(III/II) couple was shown to shift positively with increasing conjugation of the group attached to the cyanamide moiety and indicated withdrawal of cyanamide electron density onto the conjugated group. Extended Hueckel calculations of the free anion ligands permitted estimates of transition dipole moment lengths, $R$, for the $b_1^* \leftarrow b_1$ transition of the cyanamide complexes. Only an approximate positive correlation was shown between oscillator strength and $R^2$.

## Introduction

In earlier studies, following Mulliken,[1] we developed a qualitative expression for the oscillator strength of the Ru(III)−cyanamide anion LMCT chromophore[2,3] based on the magnitude of $\pi$ overlap, $S\pi$, between donor and acceptor wave functions

$$f \approx (1.085 \times 10^{-5}) G\bar{\nu}(S\pi^2)R^2 \qquad (1)$$

where $G$ is the degeneracy of the electronic transition, $\bar{\nu}$ is the energy in $cm^{-1}$ at band maximum, and $R$ is the transition dipole moment length in angstroms. Both inner sphere and outer sphere perturbations of the Ru(III)−cyanamide bond resulted in changes in the magnitude of the LMCT oscillator strength in a manner that could only be rationalized by variations in the magnitude of $S\pi$. For the Ru−cyanamide $b_1^* \leftarrow b_1$ LMCT chromophore, $S\pi$ can be expressed by

$$S\pi = C(N)\, \langle d\pi | p\pi \rangle = C(N) S_1 \qquad (2)$$

where $C$(N) is the electron density coefficient of the terminal cyanamide nitrogen that contributes to the $\pi_{nb}$ MO of the cyanamide group and $S_1$ is the optimum $\pi$ overlap that can occur between anion nitrogen 2p and ruthenium(III) 4d orbitals at a given separation.

For organic charge transfer complexes, the overlap between donor and acceptor wave functions is very small, and one might predict, on the basis of eq 1, that the charge transfer oscillator strength should be small as well. However, the oscillator strengths determined for organic charge transfer complexes can be large and theoretical treatments, using perturbation theory where the overlap integral is assumed to be zero, derive an expression for oscillator strength which relies largely on transition dipole moment length and the mixing coefficient $\alpha$ of donor and acceptor wave functions[4]

$$f \approx (1.085 \times 10^{-5}) G\bar{\nu}(\alpha^2 R^2) \qquad (3)$$

In this study, a series of complexes have been synthesized in which the Ru(III)−cyanamide bond is perturbed by varying the conjugation of the group attached to the cyanamide moiety. Because of the $\pi$ interaction between the cyanamide and conjugated groups, the transition dipole moment length of the ligand to metal charge transfer LMCT transition should increase with conjugation. The effect this has on LMCT oscillator strength and the electronic interactions between the cyanamide moiety and Ru(III) ion are examined by electronic absorption spectroscopy and cyclic voltammetry.

## Experimental Section

**Novel Cyanamide Ligands.** All chemicals and solvents were reagent grade or better and were used as received. Cyanamide, 4-aminobiphenyl, 1-aminonaphthalene, 2-aminonaphthalene, and 1-aminopyrene were purchased from Aldrich. 2-Aminophenanthrene was prepared from 2-acetylphenanthrene (Aldrich) by following a literature synthesis.[5] The amine derivatives were converted to cyanamide derivatives via the thiourea derivative.[6] Phenylcyanamide has been previously prepared and characterized.[2]

**4-Cyanamidobiphenyl·$^1/_2$H$_2$O (4-bpcydH).** A white microcrystalline product was crystallized from acetone/water. Yield: 29%. Mp: 141 °C Anal. Calcd for $C_{13}N_{11}N_2O_{0.5}$: C, 76.92; H, 5.63; N, 13.80. Found: C, 76.20; H, 5.49; N, 13.50. $\nu$(NCN) = 2221 $cm^{-1}$. $^{13}$C-NMR: 141.0 139.0, 136.6, 129.7, 129.0, 127.9, 127.3 116.4, 112.0 ppm.

**1-Cyanamidonaphthalene (1-nacydH).** White needles were crystallized from acetone/water. Yield: 58%. Mp: 141 °C. Anal. Calcd for $C_{11}H_8N_2$: C, 78.57; H, 4.76; N, 16.67. Found: C, 78.05; H, 4.93; N, 16.62. $\nu$(NCN) = 2232 $cm^{-1}$. $^{13}$C-NMR: 135.2, 135.2, 129.4, 127.5, 127.1, 126.7, 124.5, 124.4, 121.2, 112.6, 112.3 ppm.

**2-Cyanamidonaphthalene·$^1/_2$H$_2$O (2-nacydH).** White crystalline flakes were crystallized from acetone/water. Yield: 83%. Mp: 112 °C. Anal. Calcd for $C_{11}H_9N_2O_{0.5}$: C, 74.56; H, 5.12; N, 15.81. Found: C, 74.72; H, 5.16; N, 16.08. $\nu$(NCN) = 2232 $cm^{-1}$. $^{13}$C-

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NMR: 137.3, 135.1, 130.9, 130.8, 128.6, 127.9, 127.6, 125.4, 117.0, 112.1, 111.3 ppm.

**2-Cyanamidophenanthrene·$^1/_2$$H_2O$ (2-phcydH).** A white microcrystalline product was crystallized from acetone/water. Yield: 23%. Mp: 166 °C dec. Anal. Calcd for $C_{15}H_{11}N_2O_{0.5}$: C, 79.28; H, 4.88; N, 12.33. Found: C, 79.29; H, 4.49; N, 12.04. $\nu$(NCN) = 2231 cm$^{-1}$. $^{13}$C-NMR: 137.8, 133.1, 131.1, 130.1, 128.9, 128.3, 127.4, 126.6, 126.4, 125.6, 122.7, 116.0, 112.5, 112.3 ppm.

**1-Cyanamidopyrene (1-pycydH).** Yellow crystalline flakes were recrystallized from acetone/water. Yield: 40%. Mp: dec > 190 °C. Anal. Calcd for $C_{17}H_{10}N_2$: C, 84.28; H, 4.16; N, 11.56. Found: C, 83.40; H, 4.07; N, 11.48. $\nu$(NCN) = 2241 cm$^{-1}$. $^{13}$C-NMR: 132.3, 131.2, 130.6, 127.3, 127.2, 126.6, 126.0, 125.7, 125.1, 124.7, 123.9, 120.1, 118.4, 113.8, 112.8 ppm.

**Ruthenium Complexes.** The complex $[(NH_3)_5Ru(pcyd)][BPh_4]_2$ has been synthesized and characterized.[2] $[(NH_3)_5Ru(OH_2)][PF_6]_2$ was prepared according to literature procedures.[7] The general method for the synthesis of these complexes has already been published.[2] Significant modifications of this method are given for the synthesis of $[(NH_3)_5Ru(2\text{-nacyd})][ClO_4]_2$ and $[(NH_3)_5Ru(1\text{-pycyd})][ClO_4]_2$. For the 1-pycyd and 2-phcyd complexes, purification by ion exchange chromatography was not necessary because of the low solubility of the complexes' perchlorate salts in aqueous solution.

**$[(NH_3)_5Ru(2\text{-nacyd})][ClO_4]_2$·$^1/_2$acetone.** A solution of 2-cyanamidonaphthalene (0.43 g) in acetone (50 mL) was degassed, saturated with argon, and then transferred under argon to a vessel containing $[(NH_3)_5Ru(OH_2)][PF_6]_2$ (1.0 g). The red-orange solution rapidly turned brown and then a light green. After 30 min of stirring, the solution was poured into a 250 mL beaker and stirred for 2.5 h. The air oxidation of the complex resulted in a deep green solution. The acetone was evaporated, the residue dissolved in acetonitrile, and the solution filtered. Tetraethylammonium chloride (1.0 g) was then added to the filtrate, precipitating the complex. The crude chloride salt was collected and purified by ion exchange chromatography using Sephadex C-25 and eluting with 1.0 M NaCl solution. The green-blue product band was collected and the complex precipitated out of solution by the addition of excess ammonium perchlorate. Recrystallization by ether diffusion into an acetone solution of the complex yielded a green microcrystalline product (0.37 g, 31%). Anal. Calcd for $C_{12.5}H_{25}N_7O_{8.5}Cl_2Ru$: C, 25.83; H, 4.33; N, 16.87. Found: C, 25.71; H, 4.42; N, 16.30. $\nu$(NCN) = 2124 cm$^{-1}$.

**$[(NH_3)_5Ru(1\text{-nacyd})][ClO_4]_2$.** The complex was prepared by using the general procedure described above. The green microcrystalline product was obtained with a yield of 16% Anal. Calcd for $C_{11}H_{22}O_8Cl_2Ru$: C, 23.92; H, 4.02; N, 17.75. Found: C, 24.03; H, 3.85; N, 17.27. $\nu$(NCN) = 2113 cm$^{-1}$.

**$[(NH_3)_5Ru(cyd)][ClO_4]_2$·$^1/_{12}$acetone.** The complex was prepared by using the general procedure described above. The orange microcrystalline product was obtained with a yield of 9%. Anal. Calcd for $C_{1.25}H_{16.5}N_7O_{8.08}Cl_2Ru$: C, 3.48; H, 3.86; N, 22.75. Found: C, 3.50; H, 3.82; N, 22.75. $\nu$(NCN) = 2153 cm$^{-1}$. Repeated attempts to remove the residual acetone of recrystallization by vacuum-drying were unsuccessful.

**$[(NH_3)_5Ru(4\text{-bpcyd})][ClO_4]_2$.** The complex was prepared by using the general procedure described above. The blue microcrystalline product was obtained with a yield of 10%. Anal. Calcd for $C_{13}H_{24}N_7O_8Cl_2Ru$: C, 27.00; H, 4.18; N, 16.96. Found: C, 27.02; H, 4.08; N, 16.42. $\nu$(NCN) = 2111 cm$^{-1}$.

**$[(NH_3)_5Ru(1\text{-pycyd})][ClO_4]_2$·$^2/_3$acetone.** A degassed acetone solution containing 1-cyanamidopyrene (0.10 g) was transferred under argon to a vessel containing $[(NH_3)_5Ru(OH_2)][PF_6]_2$ (0.20 g), and the mixture was allowed to stir for 30 min. The solution was then poured into a beaker and stirred for 1.5 h. Air oxidation resulted in a deep red-purple solution. The product was precipitated from solution as an iodide salt by the addition of tetrabutylammonium iodide, collected, and washed with acetone. The iodide salt was then dissolved in water (50 mL) and the complex precipitated from solution by the addition of ammonium perchlorate (5 g). The perchlorate salt was collected and washed with ice-cold water. The purple microcrystalline complex was recrystallized by the diffusion of ether into an acetone solution of the complex. Yield: 0.075 g (28%). Anal. Calcd for $C_{19}H_{28}N_7O_{8.66}Cl_2Ru$: C, 34.31; H, 4.24; N, 14.74. Found: C, 34.32; H, 4.21; N, 14.45. $\nu$(NCN) = 2124 cm$^{-1}$.

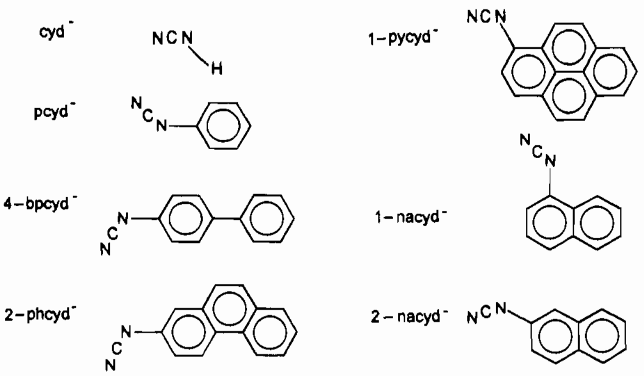


**Figure 1.** Glossary of cyanamide ligands showing the most stable planar configurations as determined by extended Hueckel calculations.

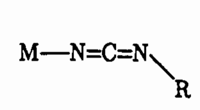
**$[(NH_3)_5Ru(2\text{-phcyd})][ClO_4]_2$·$^1/_2$acetone.** The complex was prepared by using the general procedure described above. The green microcrystalline product was obtained with a yield of 14%. Anal. Calcd for $C_{15.5}H_{27}N_7O_{8.5}Cl_2Ru$: C, 30.06; H, 4.39; N, 15.83. Found: C, 30.26; H, 3.98; N, 15.98. $\nu$(NCN) = 2112 cm$^{-1}$.

It is common for crystals of these pentaammineruthenium complexes to possess a solvent of recrystallization,[2,8] and in all cases where acetone is added to the molecular formula, its presence has been confirmed by the observation of $\nu$(C═O) at approximately 1700 cm$^{-1}$. In addition, the cyclic voltammetry of these complexes shows no evidence of redox-active impurities.

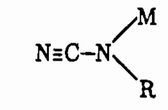
**Calculations.** Extended Hueckel calculations on the anionic cyanamide ligands in the planar configurations shown in Figure 1 were performed by using Quantum Chemistry Exchange Program No. QCMP 011, Forticon 8 for personal computers. The oscillator strengths of the $b_1^* \leftarrow b_1$ LMCT bands were determined by fitting the band profiles to a set of Gaussian bands with PeakFit v3.0 software from Jandel Scientific. For each band, the oscillator strength $f = 4.61 \times 10^{-9}(\sum_n \epsilon_{\max_n} \nu_{(1/2)n})$, where for the $n$th Gaussian band, $\epsilon_{\max}$ is the maximum extinction coefficient in M$^{-1}$ cm$^{-1}$ and $\nu_{(1/2)}$ is the bandwidth at one-half $\epsilon_{\max}$ in cm$^{-1}$.[9]

## Results and Discussion

Crystal structures of mononuclear phenylcyanamide complexes of transition metal ions have all shown coordination of the cyanamide group by the terminal nitrile nitrogen, **A**. The



**A**



**B**

Ru(III)−cyanamide bond is expected to be linear in order to maximize its $\pi$ interaction with the cyanamide anion moiety. The IR spectra of these complexes typically show $\nu$(NCN) ranging from 2100 to 2180 cm$^{-1}$, which seems to depend on the electronegativity of the ligand and metal ion.[2,10,11] Coordination to the amine nitrogen, **B**, will be sterically hindered by any bulky organic group attached to the cyanamide moiety. This steric hinderance will be significantly reduced for the cyd$^-$ ligand and the possibility of linkage isomerism cannot be completely discounted in the absence of neutron diffraction studies. However, for $[(NH_3)_5Ru(cyd)]^{2+}$, $\nu$(NCN) = 2153

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**Table 1.** Electronic Absorption Data[a] for the Pentaammineruthenium(III) Complexes of Cyanamide Ligands L

| L | $\pi^* \leftarrow \pi$ | LMCT $b_1^* \leftarrow b_2$ | LMCT $b_1^* \leftarrow b_1$ |
|---|---|---|---|
| cyd | | 220 (3.55)[b] | 450 (3.59) |
| pcyd | | 365 (3.44) | 743 (3.80) |
| 4-bpcyd | 200 (4.55), 287 (4.29) | 403 (3.44) | 795 (3.84) |
| 1-nacyd | 213 (4.54), 325 (3.84) | 493 (3.55) | 831 (3.76) |
| 2-nacyd | 212 (4.48), 248 (4.64) | 486 (3.35) | 797 (3.89) |
| 2-phcyd | 311 (4.09) | 447 (3.57) | 794 (4.00) |
| 1-pycyd | 240 (4.65), 284 (4.36)<br>386 (4.33) | 597 (4.03) | 1081 (3.99) |

[a] Data in nm with log $\epsilon_{max}$ ($M^{-1}$ $cm^{-1}$) in parentheses; acetonitrile solution. [b] Shoulder.

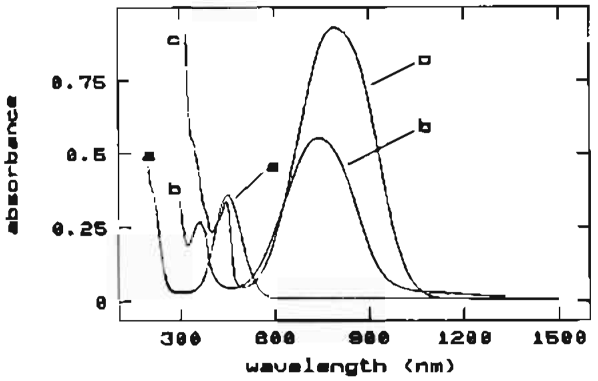


**Figure 2.** Electronic absorption spectra of the complexes $[(NH_3)_5Ru(cyd)][ClO_4]_2$ (a), $[(NH_3)_5Ru(pcyd)][BPh_4]_2$ (b), and $[(NH_3)_5Ru(1\text{-}phcyd)][ClO_4]_2$ (c). All complexes are $9.32 \times 10^{-5}$ M in acetonitrile solution.

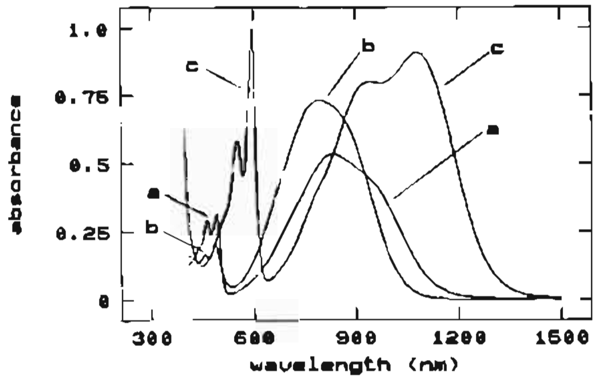


**Figure 3.** Electronic absorption spectra of the complexes $[(NH_3)_5Ru(1\text{-}nacyd)][ClO_4]_2$ (a), $[(NH_3)_5Ru(2\text{-}nacyd)][ClO_4]_2$ (b), and $[(NH_3)_5Ru(1\text{-}pycyd)][ClO_4]_2$ (c). All complexes are $9.32 \times 10^{-5}$ M in acetonitrile solution.

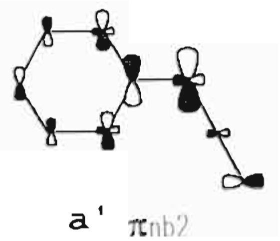
**Table 2.** Cyclic Voltammetry Data[a] for the Pentaammineruthenium(III) Complexes of Cyanamide Ligands L

| L | Ru(III/II) | L(0/1−)[b] | $\Delta E$[c] | $E_{op}$[d] |
|---|---|---|---|---|
| cyd | −0.182 | 1.799 | 1.941 | 2.76 |
| pcyd | 0.064 | 1.318 | 1.214 | 1.67 |
| 4-bpcyd | 0.082 | 1.303 | 1.181 | 1.56 |
| 1-nacyd | 0.081 | 1.182 | 1.061 | 1.49 |
| 2-nacyd | 0.086 | 1.199 | 1.073 | 1.55 |
| 2-phcyd | 0.094 | 1.243 | 1.109 | 1.56 |
| 1-pycyd | 0.104 | 0.987[e] | 0.883 | 1.15 |

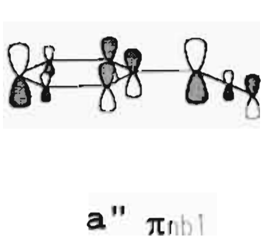
[a] All the data are in volts and the redox couples are versus NHE, with scan rate = 100 mV/s. [b] Irreversible with the maximum of the anodic current indicated. [c] $\Delta E$ = L(0/1−) − Ru(III/II). For complexes in which L(0/1−) was irreversible, the L(0/1−) couple was estimated to be 40 mV negative of the anodic peak. [d] The $b_1^* \leftarrow b_1$ band maximum in volts from Table 1. [e] Reversible couple.

$cm^{-1}$, and this is more consistent with coordination by the terminal nitrogen as in **A**. If coordination occurred as in **B**, $\nu$(NCN) would be expected to have a value similar to that of free $NCNH_2$ at 2260 $cm^{-1}$. In the discussion to follow, the correlation between LMCT energies and redox potentials for Ru(III) cyanamide complexes gives additional support to a common mode of coordination of the cyanamide moiety to Ru(III) for all cyanamide ligands.

UV−vis−near-IR electronic absorption data for the complexes are compiled in Table 1. Visible−near-IR absorption spectra that illustrate the LMCT transitions of the complexes are shown in Figures 2 and 3. A spectroscopic analysis of the ((2,3-dichlorophenyl)cyanamido)pentaammineruthenium(III) dication[6a] assuming $C_{2v}$ microsymmetry showed that two LMCT transitions can be expected from the Ru(III)−cyanamide chromophore. These two LMCT transitions arise from two nondegenerate pairs of nonbonding electrons that are delocalized in the cyanamide moiety. An extended Hueckel calculation of the phenylcyanamide anion in $C_s$ symmetry, where the $x$ and $y$ axes are in the plane of the phenyl ring, illustrates the extensive delocalization of the nonbonding molecular orbitals where the size of the lobes approximates the atom's contribution to the molecular orbital



a′ $\pi_{nb2}$



a″ $\pi_{nb1}$

The calculations show that a′ $\pi_{nb2}$ is more stable by 0.49 eV than a″ $\pi_{nb1}$, in contrast to the previous qualitative rationale.[6a] The HOMO, a″ $\pi_{nb1}$ will interact preferentially with the partially filled $d\pi$ orbital of Ru(III) and result in bonding $b_1$ and antibonding $b_1^*$ molecular orbitals. The lower energy LMCT band $b_1^* \leftarrow b_1$ is an allowed transition, while the higher energy LMCT band $b_1^* \leftarrow b_2$ is formally forbidden. Most pentaammineruthenium(III) cyanamide complexes[2] show relative intensities of these LMCT transitions similar to those seen for the complexes $[(NH_3)_5Ru(pcyd)]^{2+}$ and $[(NH_3)_5Ru(2\text{-}phcyd)]^{2+}$ (Figure 2b,c, respectively). The intensity of the $b_1^* \leftarrow b_2$ LMCT band probably arises from a lowering of symmetry and a mixing of charge transfer states. This effect is most dramatically seen in Figure 3 where $[(NH_3)_5Ru(1\text{-}pycyd)]^{2+}$ and $[(NH_3)_5Ru(1\text{-}nacyd)]^{2+}$ (Figure 3c,a, respectively) show a significant enhancement of $b_1^* \leftarrow b_2$ band intensity. While the mixing of charge transfer states is expected to increase the intensity of the $b_1^* \leftarrow b_2$ transition, it will have just the opposite effect on the $b_1^* \leftarrow b_1$ transition. This has obvious consequences to the discussion of $b_1^* \leftarrow b_1$ oscillator strength to follow.

Another feature that is seen in the spectrum of $[(NH_3)_5Ru(1\text{-}pycyd)]^{2+}$ (Figure 3c) is the splitting in both LMCT bands. These LMCT transitions are singly degenerate, and the splitting is suggested to be vibronic in origin. The difference between the frequencies of vibrational progression observed for $b_1^* \leftarrow b_2$ (≈1350 $cm^{-1}$) and $b_1^* \leftarrow b_1$ (≈1540 $cm^{-1}$) transitions is not unexpected, since they arise from different excited electronic states. The vibration responsible for the vibronic progression is unknown, since no excited state Raman or IR spectrum is available. The closest ground state vibration is the rocking mode of the ammine ligands at 1300 $cm^{-1}$.

The cyclic voltammetry of pentaammineruthenium(III) phenylcyanamide complexes in acetonitrile solution has been described in detail,[2,6a] and similar behavior is observed for the complexes of this study (Table 2). The Ru(III/II) couple has equivalent anodic and cathodic peak currents and demonstrates quasi-reversible behavior between scanning rates of 50 and 500 mV/s, with the potential separation between anodic and cathodic peaks increasing from 60 to 80 mV, respectively. In the case of substituted (phenylcyanamido)pentaammineruthenium(III) complexes, the cyanamide ligand reduction couple L(0/1−) is usually irreversible with only the anodic peak appearing in the voltammogram.[2] For the complexes of this study (Table 2), only the L(0/1−) couple of $[(NH_3)_5Ru(1\text{-pycyd})]^{2+}$ has a cathodic peak and gives quasi-reversible behavior.

The Ru(III/II) and L(0/1−) couples of pentaammineruthenium(III) complexes of substituted phenylcyanamide derivatives were observed to shift positively with an increasing number of electron-withdrawing substituents on the phenyl group.[2] This trend was rationalized to be due to the stabilization of cyanamide ligand electrons, which reduces the ligand's effectiveness in stabilizing the ruthenium 3+ oxidation state. In contrast, for the complexes of this study (Table 2), the Ru(III/II) couple shifts positively as the L(0/1−) couple shifts negatively. The trend in Ru(III/II) couples is consistent with the cyanamide group becoming a poorer $\sigma$- and $\pi$-donor with increasing conjugation of the group attached to the cyanamide moiety. Not suprisingly, the change in the Ru(III/II) couple is greatest between $[(NH_3)_5Ru(cyd)]^{2+}$ and $[(NH_3)_5Ru(pcyd)]^{2+}$ complexes and underlines the significant coupling between cyanamide and phenyl groups, which withdraws electron density from the cyanamide moiety. The trend in L(0/1−) couples seems counterintuitive when compared to the trend in Ru(III/II) couples but arises because of the stabilization of the radical oxidation product L(0) by increased conjugation. This is illustrated by the oxidations of benzene and pyrene, which occur at 2.30 and 1.16 V vs SCE, respectively.[12]

The optical energy $E_{op}$ of a LMCT charge transfer band maximum can be related[13,14] to the difference in electrochemical potentials, $\Delta E$, by the expression

$$E_{op} = [L(0/1-) - \{Ru(III/II) + D\}] + \chi = \Delta E + D + \chi \qquad (4)$$

where $D$ compensates for the experimental impossibility of measuring the Ru(III/II) couple of pentaammineruthenium(III) bound to the oxidized ligand and $\chi$ takes into account the change in inner and outer coordination sphere configurations. A plot of $E_{op}$ vs $\Delta E$ can only be linear if $D$ and $\chi$ are constant, and this will only occur for the ruthenium(III) complexes of this study, in particular $[(NH_3)_5Ru(cyd)]^{2+}$, if their properties are essentially the same with the only variable being the nature of the cyanamide ligand coordinated to Ru(III). Figure 4 shows the linear relationship between $E_{op}$ and $\Delta E$ from data obtained for the complexes of this study (Table 2) and additional data for the (substituted phenylcyanamido)pentaammineruthenium(III) complexes in ref 2. A linear least squares fit of the data points gave a slope of 1.35 with correlation coefficient $R$ = 0.977. The slope is larger than that required by eq 4 but more data points at the extremes of the range are necessary before any significance can be attached to the slope.

The main purpose of this study was to explore the effect conjugation of the group attached to the cyanamide moiety has on the oscillator strength of the $b_1^* \leftarrow b_1$ LMCT transition. This effect is qualitatively illustrated by Figure 3, where a progressive increase in the oscillator strength of the low-energy LMCT band is observed for the complexes $[(NH_3)_5Ru(L)]^{2+}$ where L = cyd⁻, pcyd⁻, and phcyd⁻. For pentaammineruthenium(III) complexes of substituted phenylcyanamide ligands, plots of $b_1^* \leftarrow b_1$ oscillator strength versus the energy of the LMCT band show a negative linear correlation.[2] It was suggested that as the energy gap between cyanamide and Ru(III) orbitals decreased, the effective $\pi$ overlap increased and that this resulted in enhanced oscillator strength according to eq 1. Figure 5 shows a plot of $b_1^* \leftarrow b_1$ oscillator strength versus the energy of this transition for the complexes of this study. A negative correlation is seen, but a significant variation in oscillator strength occurs with little change in LMCT band energy. In an attempt to obtain a more meaningful description of oscillator strength dependence, extended Hueckel calculations were performed on the cyanamide ligands.

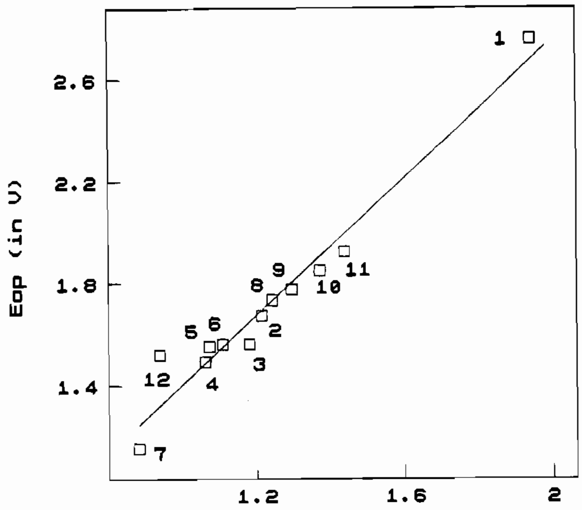


**Figure 4.** Plot of low-energy LMCT optical energy at $\lambda_{max}$, $E_{op}$, versus the difference in potential between Ru(III/II) and L(0/1−) redox couples, $\Delta E$. The data point numbering scheme is found in Table 3. Data points 8−12 are pentaammineruthenium(III) (2-chlorophenyl)-, (2,3-dichlorophenyl)-, (2,4,6-trichlorophenyl-), (pentachlorophenyl)-, and (3,4,5-trimethoxyphenyl)cyanamide complexes, respectively, and are found in ref 2. The equation for the line is $y = 1.35x + 4.65 \times 10^{-2}$, with correlation coefficient = 0.976. For data points 7 and 10−12, the L(0/1−) couple was reversible. For all the other data points, the L(0/1−) couple was approximated to be 40 mV negative of the anodic peak position.

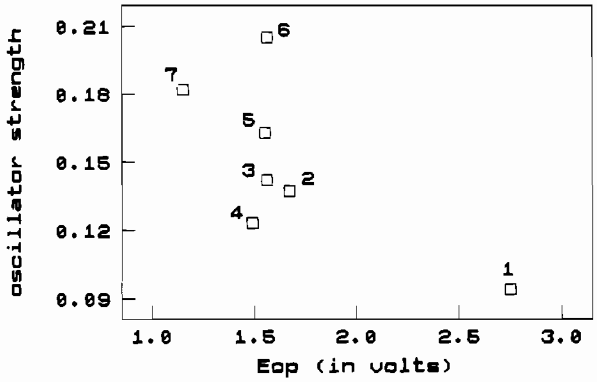


**Figure 5.** Plot of oscillator strength versus optical energy of the $b_1^* \leftarrow b_1$ LMCT transition. Data are from Tables 2 and 3. The number scheme is found in Table 3.

A number of simplifications are necessary in order to make the extended Hueckel treatment of these systems tractable. Because the pentaammineruthenium(III) moiety is unchanging for the series of complexes studied, its effect was considered constant and only the free anionic cyanamide ligands were treated. A large number of coordinated cyanamide ligand conformations are possible, and they are expected to contribute

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in varying degrees to the total oscillator strength of the $b_1^* \leftarrow b_1$ transition. Crystal structures of free[15] and coordinated phenylcyanamide ligands[2,8,10,11,16] have nearly all shown coplanarity of the cyanamide and phenyl ring groups. The single exception has been the sterically hindered 1,4-dicyanamido-2,3,5,6-tetramethylbenzene dianion, in which the cyanamide groups are out of the phenyl ring plane in anti configuration.[17] The planar conformation of the cyanamide ligand results in optimal $\pi$ coupling between cyanamide and the conjugated ring systems and is expected to be the major contributor to the total oscillator strength. Where rotation of the cyanamide group makes the ligand nonplanar, the $\pi$ nonbonding electrons involved in the $b_1^* \leftarrow b_1$ transition will be localized on the cyanamide group and the contribution to the oscillator strength made by these conformations can be approximated to be constant for all the cyanamide ligands. Therefore, any differences in the oscillator strength of the $b_1^* \leftarrow b_1$ LMCT transitions of the complexes of this study probably originate with the planar conformations seen in Figure 1, which were shown by extended Hueckel calculations to be the most stable.

The transition dipole moment length was approximated[18] to be the distance traveled by the electron from the cyanamide ligand $\pi$ HOMO to the Ru(III) $\pi$d orbital. A common Ru–NCN bond length of 2.0 Å and a common bond angle of 180° were assumed for all cyanamide ligands, and these were based on the experimentally determined Ru–NCN bond length of 1.980 (12) Å and bond angle of 171.4 (10)° found for $[(NH_3)_5Ru(2,3\text{-}Cl_2pcyd)]^{2+}$, where 2,3-$Cl_2$pcyd is the (2,3-dichlorophenyl)cyanamide anion.[2] The approximate transition dipole moment length for a one-electron transition between a filled ligand MO and a partially filled metal orbital is given by the expression[19]

$$R = \sum_n C_n^{\,2} r_n \qquad (5)$$

where the electron density coefficients $C_n$ are derived from the extended Hueckel determination of the cyanamide ligand HOMO and $r_n$ are the distances between the atoms of the HOMO and ruthenium(III). From the extended Hueckel calculations, values for $C$(N), the electron density coefficient of the terminal cyanamide nitrogen, and $R$ were determined for the cyanamide ligands and compiled, together with the respective oscillator strengths of the $b_1^* \leftarrow b_1$ transition, in Table 3.

Examination of the data in Table 3 shows that only $R$ roughly correlates with the oscillator strength of the $b_1^* \leftarrow b_1$ transition. Figure 6 shows the expected positive correlation between oscillator strength and $R^2$ as predicted by eq 1. This correlation can be improved further by recognizing that data points 4 and 7 correspond to the complexes $[(NH_3)_5Ru(1\text{-nacyd})]^{2+}$ and $[(NH_3Ru(1\text{-pycyd})]^{2+}$, respectively. As mentioned earlier for these complexes, the oscillator strength of the $b_1^* \leftarrow b_1$ transition would have been larger except for the mixing of charge transfer states, which increases the intensity of the $b_1^* \leftarrow b_2$ transition at the expense of the $b_1^* \leftarrow b_1$ transition. In addition, a range of $R^2$ is given for data point 3, $[(NH_3)_5Ru(4\text{-bpcyd})]^{2+}$, because steric repulsion of the ortho protons of 4-cyanamidobiphenyl will twist the phenyl rings out of plane. This will largely restrict delocalization of the cyanamide $\pi$ nonbonding electrons to just one phenyl ring. When these adjustments are made, the correlation between $f$ and $R^2$ is significantly improved.

**Table 3.** Extended Hueckel Estimates of Dipole Moment Length, $R$, and $b_1^* \leftarrow b_1$ LMCT Oscillator Strengths for the Pentaammineruthenium(III) Complexes of Cyanamide Ligands L

| no. | L | $C(N)^a$ | $R^b$ | $R^2C(N)^2$ | $f^c$ |
|---|---|---|---|---|---|
| 1 | cyd | 0.649 | 3.45 | 5.01 | 0.094 |
| 2 | pcyd | 0.291 | 5.56 | 2.62 | 0.137 |
| 3 | 1-bpcyd | 0.212 | 7.11 | 2.27 | 0.142 |
| 4 | 1-nacyd | 0.194 | 6.51 | 1.59 | 0.123 |
| 5 | 2-nacyd | 0.195 | 6.18 | 1.45 | 0.163 |
| 6 | 2-phcyd | 0.229 | 6.88 | 2.50 | 0.205 |
| 7 | 1-pycyd | $0.136^d$ | $8.11^d$ | $1.22^d$ | 0.182 |

[a] HOMO electron density coefficient of the terminal cyanamide nitrogen, derived from extended Hueckel calculations of the planar configurations shown in Figure 1. [b] Approximate dipole moment length in angstroms, calculated from $\sum_n C_n^{\,2} r_n$; see the text for details. [c] Oscillator strength of the $b_1^* \leftarrow b_1$ LMCT band calculated from the sum of fitted $n$ Gaussian bands, $f = 4.61 \times 10^{-9}(\sum_n \epsilon_{\max_n} \bar{\nu}_{(1/2)n})$. See ref 9. [d] Calculated from the third HOMO.

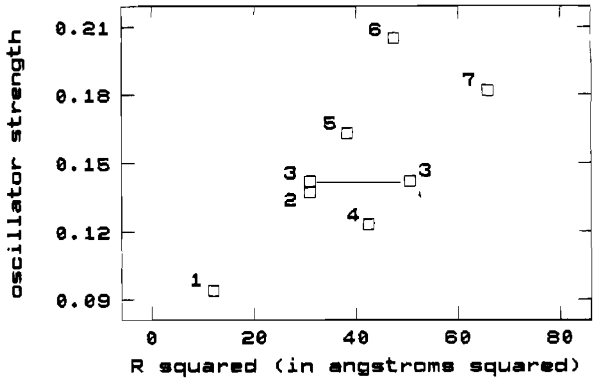

**Figure 6.** Plot of oscillator strength versus approximate transition dipole moment length of the $b_1^* \leftarrow b_1$ LMCT transition. The number scheme is found in Table 3.

The participation of the $\pi$ overlap integral $S\pi$ in determining the magnitude of the oscillator strength (eqs 1 and 2) is not at all evident from the trend in $C$(N) or $C(N)^2R^2$ in Table 3. On the other hand, eqs 1 and 2 have been used successfully in correlations of MLCT oscillator strengths for Cu(I)[20] and Ru(II)[21] diimine complexes. It is possible that the value of $S\pi$ for the complexes of this study is constant. However, the Ru(III/II) couples in Table 2 suggest a significant variation in the nature of the Ru–cyanamide bond, and we prefer to believe that more sophisticated theoretical calculations would reveal the relative importance of overlap and transition dipole moment length to the magnitude of $b_1^* \leftarrow b_1$ LMCT oscillator strength. These studies are in progress.

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**Supplementary Material Available:** Cyanamide ligand input data files for extended Hueckel calculations (4 pages). Ordering information is given on any current masthead page.

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