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Pentaammineruthenium(III) Phenylcyanamide Complexes: Crystal Structure Determination and the Dependence of $b_1^* \leftarrow b_1$ LMCT Oscillator Strength on the Nature of the Phenylcyanamide Ligand

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Seventeen pentaammineruthenium(III) complexes of phenylcyanamide anion ligands have been prepared and characterized by UV–vis spectroscopy and cyclic voltammetry. The complex $[(NH_3)_5Ru(2,3\text{-}Cl_2pcyd)][SO_4]\cdot C_2H_5OH$ was characterized by X-ray diffraction. The anionic cyanamide group of the ligand (2,3-dichlorophenyl)cyanamide is shown to be nearly coplanar with the phenyl group due to strong π coupling and coordinated to ruthenium(III) via the nitrile nitrogen. A significant degree of π bonding between the cyanamide group and ruthenium(III) is indicated by the nearly linear bond angle (171.4 (10)°) and short bond length (1.980 (12) Å). Crystal data are space group $P2_1/n$ with a = 6.267 (4) Å, b = 7.5227 (7) Å, c = 40.0978 (21) Å, β = 90.04 (1)°, V = 1968.74 (24) Å^3, and Z = 4. The structure was refined by using 1763 Cu Kα reflections with $I > 2.5\sigma(I)$ to an R factor of 0.068. A linear correlation was found between the $b_1^* \leftarrow b_1$ ligand to metal charge-transfer energy and the difference between ligand, L(0/–), and metal Ru(III/II), reduction couples, indicating the complexes have similar properties with the only variable being the nature of the cyanamide–ruthenium interaction. The oscillator strength of the $b_1^* \leftarrow b_1$ transition was found to decrease with increasing energy of the transition for the series of complexes studied. Using Mulliken's derivation of oscillator strength dependence on donor and acceptor overlap, we suggest that the trend in oscillator strength can be largely rationalized in terms of the π basicity of the phenylcyanamide ligand.

Introduction

Theoretical treatments of charge-transfer complexes have generally considered the extremes of weak and strong coupling cases. In the weak coupling case, a close relationship exists between thermal electron-transfer processes and electron transfer resulting from absorption or emission of light. The theoretical basis of the Hush model[3] relies on the above relationship, and the model has been shown to be successful in describing the electronic properties of weakly coupled mixed-valence complexes.[4] Recently, this relationship has been exploited to determine the possible role of partial dielectric saturation of the solvent on the "inverted region" of electron-transfer reactions.[5] In the strong coupling case, the Hush model is no longer successful because the overlap between donor and acceptor wave functions plays an important role in determining the magnitude of the charge-transfer transition moment and cannot be ignored. A number of models have been developed to deal with the strong coupling case in mixed-valence complexes.[6] The model developed by Ondrechen[6c] appears to be the more general and, importantly, includes the electronic properties of the bridging ligand. In this treatment, the expression for calculating absorption line strength, in the strong coupling limit, includes the square of the overlap integral, the Boltzmann-weighted Franck–Condon factors, and the dipole moment operator. A simpler form of this expression was originally developed by Mulliken,[7,8] who related the dependence of charge-transfer band oscillator strength on the overlap between donor and acceptor orbitals. In this study, we will use Mulliken's treatment to rationalize the dependence of the $b_1^* \leftarrow b_1$ ligand to metal charge transfer (LMCT) oscillator strength on the π-bonding overlap integral between Ru(III) and the anionic cyanamide group in pentaammineruthenium(III) complexes of anionic phenylcyanamide ligands (pcyd$^-$).

We are studying mixed-valence complexes in which metal ions are bridged by a 1,4-bis(cyanoamino)benzene dianion derivative. The importance of the bridging ligand as an electron-transfer moderator can be determined by varying the nature of the substituents on the benzene ring. Hunig et al.[9,10] have prepared a novel series of molecular metals by reacting cations with radical monoanion 1,4-bis(cyanoamino)benzene derivatives. The general electronic properties of both the above systems can be evaluated by determining the dependence of the complex energetics and ruthenium(III)/cyanamide π overlap on the nature of phenyl group substitution.

In a previous study,[11] a spectroscopic analysis detailed the origins of LMCT bands seen in the absorption spectra of pentaammineruthenium(III) complexes of neutral and anionic (2,3-dichlorophenyl)cyanamide ligands. This analysis assumed that the cyanamide group coordinates to ruthenium(III) via the terminal nitrogen and is coplanar with the phenyl ring. In addition, a comparison of the Ru(III/II) redox couples for pentaammineruthenium complexes of σ and π donor ligands suggested that anionic (2,3-dichlorophenyl)cyanamide (2,3-Cl$_2$pcyd$^-$) stabilized ruthenium(III) to approximately the same degree as Br$^-$ or Cl$^-$. It was suggested that, by varying the nature of the substituents on the phenyl group, the basicity of the cyanamide group could be "tuned" and the effect monitored by both redox chemistry and LMCT spectra.

In this study, we present the first crystal structure, to our knowledge, of a transition-metal complex that illustrates the coordination geometry of an anionic phenylcyanamide ligand. Seventeen pentaammineruthenium(III) complexes of phenylcyanamide ligands have been prepared to fully explore the dependence of the complexes' redox chemistry and LMCT band energies and oscillator strength on the nature of the phenylcyanamide ligand.

Experimental Section

Equipment. The equipment used to perform nonaqueous cyclic voltammetry and UV–vis and infrared spectroscopy have been described in a previous paper.[11] ^{13}C NMR spectra were determined by using a Varian XL200 NMR spectrometer at ambient temperature.

Materials. All solvents and solid chemicals were reagent grade or better. All aniline derivatives were purchased from Aldrich Chemical Co. and were used without further purification. Pentachloroaniline was synthesized from pentachloronitrobenzene.[12] $[(NH_3)_5Ru(H_2O)][PF_6]_2$[13] and $[(NH_3)_5RuCl][Cl]_2$[14] were prepared by literature methods. Ele-

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mental analyses were performed by Canadian Microanalytical Services Ltd.

Preparation of Neutral Monomer Phenylcyanamide Ligands (Hpcyd) and Dimer Phenylcyanamides ((Hpcyd)$_2$). The general preparation, involving desulfurization of a thiourea derivative, is given in ref 11. These ligands are sensitive to dimerization,[15] and careful control of reaction conditions is necessary to ensure product purity. In fact, we were only able to prepare dimers of (2,4,6-trichloro-, (2,3,5,6-tetrachloro-, and (pentachlorophenyl)cyanamides because of their greater sensitivity to polymerization. Addition of a weak base to an acetone/water solution of a dimer ligand creates an equilibrium between the dimer and its anion monomer.[15] When thallium acetate (caution: thallium is toxic) is added to the basic solution of the dimer ligand, the thallium salt of the phenylcyanamide anion is precipitated from solution, usually as long white needles, in close to quantitative yields.[15] Tables of elemental analyses of monomer and dimer phenylcyanamides, ^{13}C NMR and IR data, and melting points have been placed in the supplementary material.

Preparation of Pentaammineruthenium(III) Complexes of Anionic Phenylcyanamide Ligands. The general methods for the preparation of these complexes are given in ref 11. Complexes of the chloro-substituted phenylcyanamides could all be successfully prepared by reacting the thallium salt of the anionic ligand with $[(NH_3)_5RuCl][PF_6]_2$. Complexes of the methyl- and methoxy-substituted phenylcyanamides were prepared by reacting the neutral ligands with $[(NH_3)_5Ru(H_2O)][PF_6]_2$, followed by air oxidation, as shown below.

Preparation of $[(NH_3)_5Ru(3,4,5\text{-}(MeO)_3pcyd)][ClO_4]_2$. A 40-mL aliquot of acetone was transferred under argon gas to a reaction flask containing freshly prepared $[(NH_3)_5Ru(OH_2)][PF_6]_2$ (1.25 g) and (3,4,5-trimethoxyphenyl)cyanamide (1.0 g). The greenish yellow solution was stirred for 1 h and then evaporated to dryness. The pale green solid was dissolved in 40 mL of acetonitrile, and then a solution of 1.3 g of tetramethylammonium chloride in 20 mL of acetonitrile was added. This resulted in precipitation of the blue product (1.0 g), which was filtered out and washed with acetonitrile. The product was then purified by cation-exchange chromatography on Sephadex C25-120 and eluted with 1 M NaCl solution. Column dimensions were 22-cm height by 2.2-cm diameter. Elution of the blue product band was preceded by yellow and purple bands. The product was forced out of the eluent solution by addition of $NaClO_4$, filtered out, and washed with ice-cold water. The product was recrystallized by ether diffusion into an acetone solution of the product. Yield: 0.6 g (40%). Anal. Calcd for $C_{10}H_{26}N_7O_{11}Cl_2Ru$: C, 20.28; H, 4.42; N, 16.55. Found: C, 20.61; H, 4.43; N, 16.63.

All the complexes, except the unsubstituted phenylcyanamide, were isolated from aqueous solution as perchlorate salts and had satisfactory elemental analyses (see supplementary material). In later preparations, some of the complexes detonated upon being scraped from a glass filter frit. We urge caution when perchlorates are used and have determined, by isolating the tetraphenylborate salt of $[(NH_3)_5Ru(pcyd)]^{2+}$, that tetraphenylborate anion is a suitable substitute counterion for these complexes. In a few of the complexes, after vacuum drying for 12 h, water or acetone solvent of crystallization was present in the solid. The presence of acetone could be discerned in these complexes by a characteristic sharp IR absorption at approximately 1700 cm^{-1}, since no complex IR absorptions are nearby to interfere. Attempts to drive off these solvents by heating under vacuum decomposed the complexes. A complex, isolated as a crystalline solid, was judged sufficiently pure for elemental analysis when ion-exchange chromatography showed only one band present and its cyclic voltammetry was clean. All of the methoxy- and chloro-substituted phenylcyanamide complexes appeared to be stable in the solid state over a 6-month period. However, the methyl-substituted phenylcyanamides are unstable over the same time period, as determined by a decrease in LMCT absorption intensity. In particular, for $[(NH_3)_5Ru(2,4,6\text{-}Me_3pcyd)][ClO_4]_2$, a noticeable loss in LMCT intensity occurred only 1 day after initial preparation. Acetonitrile solutions of the complexes showed no significant drop in LMCT absorption intensity over a 1-h period.

Table I. Crystal Data for $[(NH_3)_5Ru(2,3\text{-}Cl_2pcyd)][SO_4]\cdot C_2H_5OH$

formula	$C_9H_{24}N_7O_5SCl_2Ru$
fw	514.37
cryst syst	monoclinic
space group	$P2_1/n$
a, b, c, Å	6.267 (4), 7.5227 (7), 40.0978 (21)
β, deg	90.04 (1)
V, Å^3	1968.74 (24)
Z	4
D_c, g/cm^3	1.807
cryst dimens, mm^3	0.07 × 0.12 × 0.2
radiation (λ, Å)	Cu Kα_1 (1.540 56)
μ, cm^{-1}	109.03
hkl ranges	$-7 \leq h \geq 7, 0 \leq k \geq 8, 0 \leq l \geq 44$
max 2θ	117.9
no. of reflcns measd	4531
no. of unique reflcns	2838
no. of reflcns with $I > 2.5\sigma(I)$	1763
transm range	0.132 866–0.361 339
R factor[a]	0.068
R_w factor[a]	0.081
goodness-of-fit ratio	2.509

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

Table II. Atomic Parameters and B_{iso}[a] for $[(NH_3)_5Ru(2,3\text{-}Cl_2pcyd)][SO_4]\cdot C_2H_5OH$

	x	y	z	B_{iso}[b]
Ru	0.79700 (16)	0.25438 (20)	0.07506 (3)	2.15 (5)
Cl(1)	−0.0632 (7)	0.3925 (8)	0.18844 (10)	4.7 (3)
Cl(2)	0.0070 (9)	0.3302 (8)	0.26474 (11)	5.7 (3)
S	0.2165 (5)	0.7549 (8)	0.04581 (9)	2.67 (16)
O(1)	0.2571 (20)	0.9124 (18)	0.0663 (3)	4.3 (7)
O(2)	0.2687 (20)	0.5873 (17)	0.0636 (3)	4.6 (7)
O(3)	−0.0020 (19)	0.7496 (22)	0.0370 (4)	8.1 (9)
O(4)	0.3461 (21)	0.7628 (21)	0.161 (3)	5.9 (7)
N(1)	0.9267 (21)	0.0550 (16)	0.1069 (3)	2.5 (6)
N(2)	0.6805 (21)	0.0445 (18)	0.0453 (3)	2.6 (6)
N(3)	1.0578 (16)	0.2467 (20)	0.0442 (3)	2.6 (6)
N(4)	0.6745 (22)	0.4424 (19)	0.0419 (3)	3.0 (7)
N(5)	0.9232 (21)	0.4637 (21)	0.1031 (3)	3.5 (8)
N(6)	0.5513 (17)	0.2576 (22)	0.1040 (3)	3.1 (6)
N(7)	0.2737 (18)	0.2776 (20)	0.1458 (3)	2.9 (6)
C(1)	0.1675 (24)	0.2920 (18)	0.2024 (4)	2.7 (7)
C(2)	0.195 (3)	0.263 (3)	0.2369 (4)	4.6 (10)
C(3)	0.375 (3)	0.1919 (24)	0.2495 (5)	4.7 (9)
C(4)	0.522 (3)	0.146 (3)	0.2265 (4)	4.2 (9)
C(5)	0.496 (3)	0.1683 (23)	0.1911 (4)	3.8 (8)
C(6)	0.3114 (21)	0.243 (3)	0.1800 (3)	2.7 (7)
C(7)	0.4232 (24)	0.257 (3)	0.1245 (4)	3.4 (8)
O(5)	0.5879 (18)	0.7663 (25)	0.1167 (3)	6.9 (8)
C(8)	0.307 (3)	0.757 (4)	0.1584 (5)	7.0 (13)
C(9)	0.526 (4)	0.713 (3)	0.1509 (6)	6.7 (14)

[a] Estimated standard deviations are in parentheses. [b] B_{iso} is the mean of the principal axes of the thermal ellipsoid, Å^2.

X-ray Diffraction Studies. Dark blue, prismatic crystals of $[(NH_3)_5Ru(2,3\text{-}Cl_2pcyd)][SO_4]\cdot C_2H_5OH$ were grown by ethanol diffusion at room temperature into an aqueous solution of the complex over a period of 2 weeks. Intensity data were collected on a Picker diffractometer, with profile analysis[16] in the $\theta/2\theta$ mode, using graphite-monochromatized Cu Kα radiation. Three reflections were monitored every 100 reflections measured and showed a 16% decrease during the data collection. Absorption corrections (μ_{Cu} = 109.03 cm^{-1}) were calculated by Gaussian integration even though the crystal used was quite small (Table I). Cell dimensions were derived by least squares from the optimized setting angles for 21 reflections in the 2θ range 100–110°. In spite of the fact that reflections with l odd were very weak, the structure solved readily by direct methods and D maps and was refined by full-matrix least squares. The final cycles were carried out with counting statistic weights and with refinement of all atoms anisotropically.[17] The final D map showed small peaks near the Ru atom, and no attempt was made to locate the hydrogen atoms. Crystal data are summarized in Table I, and the final atomic parameters are given in Table II. A listing of structure factors and a stereoview of the unit cell are found in the supplementary material.

Results

Monomer and dimer phenylcyanamide ligands were physically characterized by elemental analysis, IR and ^{13}C NMR spectroscopies, and melting points. The data have been tabulated and placed in the supplementary material. Monomer phenylcyanamide ligands generally have five- or seven-line ^{13}C NMR spectra, depending on the substituents' orientation on the phenyl ring. It

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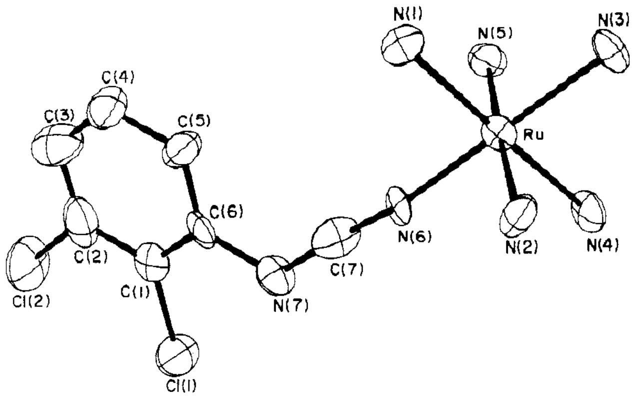

Figure 1. ORTEP drawing of the complex $[(NH_3)_5Ru(2,3\text{-}Cl_2pcyd)][SO_4]\cdot C_2H_5OH$. The sulfate ion and ethanol have not been included for the sake of clarity.

Table III. Selected Crystal Structure Data[a] for $[(NH_3)_5Ru(2,3\text{-}Cl_2pcyd)][SO_4]\cdot C_2H_5OH$

Bond Lengths, Å

Ru–N(1)	2.144 (12)	Ru–N(6)	1.980 (12)
Ru–N(2)	2.120 (12)	N(6)–C(7)	1.173 (20)
Ru–N(3)	2.105 (11)	N(7)–C(6)	1.417 (18)
Ru–N(4)	2.100 (13)	N(7)–C(7)	1.308 (20)
Ru–N(5)	2.102 (14)		

Bond Angles, deg

N(1)–Ru–N(2)	87.5 (5)	N(3)–Ru–N(4)	87.4 (5)
N(1)–Ru–N(3)	90.7 (5)	N(3)–Ru–N(5)	91.0 (5)
N(1)–Ru–N(4)	177.2 (5)	N(3)–Ru–N(6)	179.1 (6)
N(1)–Ru–N(5)	92.9 (5)	N(4)–Ru–N(5)	89.0 (6)
N(1)–Ru–N(6)	88.8 (5)	N(4)–Ru–N(6)	93.2 (5)
N(2)–Ru–N(3)	86.5 (5)	N(5)–Ru–N(6)	89.7 (6)
N(2)–Ru–N(4)	90.5 (5)	Ru–N(6)–C(7)	171.4 (10)
N(2)–Ru–N(5)	177.5 (5)	C(6)–N(7)–C(7)	118.9 (12)
N(2)–Ru–N(6)	92.8 (6)	N(6)–C(7)–N(7)	172.5 (22)

Distances to the Phenyl Ring Plane of Cyanamide Atoms, Å

N(7)	0.04 (3)	C(7)	0.23 (4)	N(6)	0.51 (4)

[a] Estimated standard deviations are in parentheses.

was possible to unambiguously assign the spectra because peak intensity is less for a substituted aromatic carbon and the range of possibilities was matched by the number of phenylcyanamide derivatives. ^{13}C NMR spectra of the (2,6-dichloro- and (2,4,6-trichlorophenyl)cyanamide dimers show the expected 10-line pattern, and only the cyanamide carbon was assigned.[15] As previously mentioned, the presence of an infrared absorption at approximately 1680 cm^{-1} in a spectrum of a monomer ligand can be taken as evidence for dimer impurity.[15]

Figure 1 shows an ORTEP drawing of $[(NH_3)_5Ru(2,3\text{-}Cl_2pcyd)]^{2+}$. Important bond lengths and bond angles are given in Table III. UV–vis electronic absorption data for all the complexes are compiled in Table IV. A representative spectrum has already been published.[11] Cyclic voltammetry data of the complexes are presented in Table V. The Ru(III/II) couple demonstrates quasi-reversible behavior between scanning rates of 50 and 500 mV/s, with the potential separation between anodic anc cathode peaks increasing from 60 to 80 mV, respectively. The phenylcyanamide reduction couple, L(0/–), is shifted anodically upon coordination[11] and demonstrates varying degrees of irreversibility depending on the nature of the phenylcyanamide ligand. For example, at 100 mV/s, the (pentachloro- and (2,4,6-trimethylphenyl)cyanamide complexes have ligand redox couples that exhibit reversible behavior, while the (2,3-dichloro- and (2-chlorophenyl)cyanamide complexes show only the ligand oxidation wave in their cyclic voltammograms. Since "dry" acetonitrile still contains approximately 1 mM H_2O, hydrolysis of coordinated nitrile to ruthenium(III) seems a possible explanation.[18,19] This reaction was not studied further.

Table IV. Electronic Spectroscopy Data[a] for Pentaammineruthenium(III) Complexes of Anionic Phenylcyanamide Ligands ($pcyd^-$)

		LMCT	
$pcyd^-$	$\pi^* \leftarrow \pi$	$b_1^* \leftarrow b_2$	$b_1^* \leftarrow b_1$
$2,4,6\text{-}Me_3pcyd$	209 (4.48), 251 (4.10), 281 (3.67)[b]	371 (3.43)	772 (3.81) [0.157]
$3,5\text{-}Me_2pcyd$	211 (4.45), 250 (4.10), 284 (3.57)[b]	369 (3.51)	768 (3.76) [0.134]
4-(Me)pcyd	203 (4.38), 249 (4.17), 275 (3.66)[b]	373 (3.47)	777 (3.85) [0.152]
$3,4,5\text{-}(OMe)_3\text{-}pcyd$	217 (4.53), 253 (4.13), 334 (3.50)	390 (3.43)	817 (3.89) [0.178]
$3,5\text{-}(OMe)_2\text{-}pcyd$	219 (4.51), 244 (4.05), 322 (3.43)	368 (3.44)	766 (3.84) [0.159]
pcyd[c]		365 (3.44)	743 (3.80) [0.135]
(2-Cl)pcyd	208 (4.43), 251 (4.17), 262 (3.73)[b]	361 (3.54)	716 (3.86) [0.155]
(3-Cl)pcyd	209 (4.41), 253 (4.18), 285 (3.69)[b]	362 (3.52)	712 (3.88) [0.160]
(4-Cl)pcyd	198 (4.44), 255 (4.25)	390 (3.55)	738 (3.89) [0.168]
$2,3\text{-}Cl_2pcyd$	217 (4.44), 259 (4.13), 285 (3.78)	365 (3.54)	699 (3.84) [0.147]
$2,4\text{-}Cl_2pcyd$	192 (4.38), 209 (4.44), 260 (4.24)	380 (3.55)	716 (3.86) [0.156]
$2,6\text{-}Cl_2pcyd$	215 (4.43), 256 (4.11), 284 (3.73)[b]	365 (3.48)	668 (3.80) [0.139]
$2,4,5\text{-}Cl_3pcyd$	195 (4.36), 217 (4.43), 265 (4.25)	377 (3.58)	692 (3.85) [0.148]
$2,4,6\text{-}Cl_3pcyd$	194 (4.30), 215 (4.40), 264 (4.16)	400 (3.52)	671 (3.78) [0.128]
$2,3,4,5\text{-}Cl_4\text{-}pcyd$	202 (4.38), 218 (4.46), 268 (4.16)	378 (3.58)	678 (3.73) [0.119]
$2,3,5,6\text{-}Cl_4\text{-}pcyd$	196 (4.37), 222 (4.48), 268 (4.02)	395 (3.52)	637 (3.70) [0.111]
Cl_5pcyd	206 (4.37), 225 (4.53), 273 (4.14)	406 (3.60)	645 (3.76) [0.126]

[a] The same batch was used for elemental analysis as to determine the UV–vis data. All data were recorded in acetonitrile solution and are in nm (log ϵ in parentheses and oscillator strength, calculated from eq 2, in brackets). [b] Shoulder. [c] Phenylcyanamide absorptions are obscured by the tetraphenylborate counteranion.

Table V. Electrochemical[a] and IR Data for Pentaammineruthenium(III) Phenylcyanamide Complexes

no.	$pcyd^-$ complex	*E* (Ru(III/II))	*E* (L(0/–))	ΔE^c	ν (N=C=N)[d]
1	$2,4,6\text{-}Me_3pcyd$	–0.280	0.840	1.120	2100
2	$3,5\text{-}Me_2pcyd$	–0.216	0.983[b]	1.159	2108
3	4-(Me)pcyd	–0.223	0.897	1.120	2117
4	$3,4,5\text{-}(OMe)_3pcyd$	–0.209	0.770[b]	0.939	2113
5	$3,5\text{-}(OMe)_2pcyd$	–0.179	1.048[b]	1.187	2115
6	pcyd	–0.201	1.053[b]	1.214	2112
7	(2-Cl)pcyd	–0.138	1.145[b]	1.243	2115
8	(3-Cl)pcyd	–0.147	1.201[b]	1.308	2111
9	(4-Cl)pcyd	–0.159	1.080	1.239	2109
10	$2,3\text{-}Cl_2pcyd$	–0.097	1.239[b]	1.296	2111
11	$2,4\text{-}Cl_2pcyd$	–0.111	1.180	1.291	2122
12	$2,6\text{-}Cl_2pcyd$	–0.131	1.234[b]	1.325	2121
13	$2,4,5\text{-}Cl_3pcyd$	–0.063	1.281	1.344	2111
14	$2,4,6\text{-}Cl_3pcyd$	–0.138	1.234	1.372	2149
15	$2,3,4,5\text{-}Cl_4pcyd$	–0.035	1.362	1.397	2132
16	$2,3,5,6\text{-}Cl_4pcyd$	–0.057	1.423[b]	1.440	2137
17	Cl_5pcyd	–0.036	1.403	1.439	2113

[a] In volts vs NHE, at 25 °C. Cyclic voltammetry experiments were performed in 0.1 M tetrabutylammonium hexafluorophosphate/acetonitrile solution, at a scan rate of 100 mV/s. [b] Irreversible, no cathodic peak present; the position of the anodic peak is indicated. [c] $\Delta E = E(L(0)/-)) - E(Ru(III/II))$, in V. When the L(0/–) couple shows no cathodic wave, the L(0/–) couple was approximated to be 40 mV cathodic of the anodic peak position. [d] Nujol mulls, in cm^{-1}. ν(N=C=N) absorptions are generally strong.

Discussion

Cyanamide ligands have a coordination configuration that depends primarily on the nature and oxidation state of the metal atom and whether the ligand is neutral or anionic. Neutral

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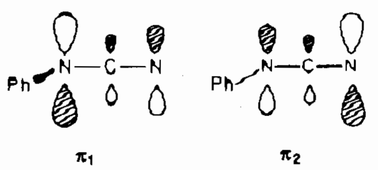
(18) Zanella, A. W.; Ford, P. C. *Inorg. Chem.* **1975**, *14*, 42.

(19) Dissociation of the oxidized ligand could also contribute but does not follow the expected trend in Ru–cyanamide bond strength.

Chart I



cyanamide ligands can bind "end-on" by the nitrile nitrogen[20] or "side-on" by the nitrile group[21,22] to the metal atom. To our knowledge,[23] a crystal structure of an anionic cyanamide ligand bound to a metal complex has not been performed. It is important to establish the coordination mode of these ligands to Ru(III) in order to validate the previous spectroscopic study of LMCT transitions,[11] which assumed coordination by the nitrile nitrogen and coplanarity of phenyl and cyanamide groups.

The ORTEP drawing of the complex $[(NH_3)_5Ru(2,3\text{-}Cl_2pcyd)]^{2+}$ (Figure 1) indicates that the coordination environment around Ru(III) is that of a distorted octahedron of nitrogen donor atoms, with the anionic cyanamide group coordinated end-on by the nitrile nitrogen. The average Ru–ammine bond length (2.11 Å) is approximately the same as that found in $[(NH_3)_5Ru(Cl)][Cl]_2$ (2.103 Å).[24] The bond between the anionic cyanamide group and Ru(III) is almost linear, having an angle of C(7)–N(6)–Ru = 171°, and is shorter, with Ru–N(6) = 1.98 Å, than the Ru–ammine bond lengths. This indicates a significant degree of π donation to Ru(III). The cyanamide group and phenyl ring are almost coplanar, the N(6) donor atom being only 0.5 Å out of the plane of the phenyl ring. This, in addition to the partial double-bond character of the N(7)–C(6) bond (1.42 Å),[25] is a result of the strong π interaction between cyanamide and phenyl groups. Other researchers have prepared molecular metals based on copper salts of radical-anion bis(cyanoamino)benzene derivatives. X-ray structures of these molecular metals have shown the radical-anion bis(cyanoamino)benzene molecule to be almost planar,[23,26] again illustrating the strong π interaction between cyanamide and phenyl groups.

The anionic cyanamide group is a resonance-stabilized π system, $Ph{-}N^-{-}C{\equiv}N \leftrightarrow Ph{-}N{=}C{=}N^-$, which when coordinated to Ru(III) ought to shift the resonance equilibrium toward the $Ph{-}N{=}C{=}N^-$ resonance structure. There are two pairs of nonbonding electrons of π symmetry that can delocalize into this three-atom π system and the resulting orthogonal π_1 and π_2 molecular orbitals may appear as in Chart I, where the atomic orbital size approximates[27] the magnitude of the electron density coefficient. π_1 is more stable than π_2 because only π_1 has the correct symmetry to delocalize into the phenyl ring as well as the nitrile group. These give rise to two ligand metal charge-transfer (LMCT) transitions in the visible region of the complex's electronic absorption spectrum. UV–vis electronic absorption data for all 17 complexes together with assignments[11] are given in Table IV. The lower energy LMCT band has been assigned to an allowed $b_1^* \leftarrow b_1$ ($d\pi^* \leftarrow \pi_2$) transition and is completely separated from any other absorption, allowing accurate calculation of the band's oscillator strength.

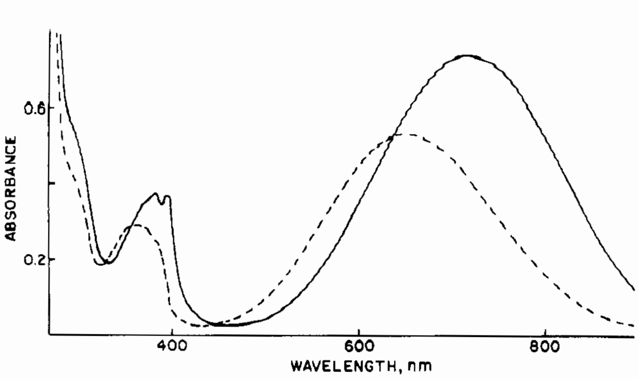


Figure 2. Visible electronic absorption spectra of $[(NH_3)_5Ru(2,4\text{-}Cl_2pcyd)][ClO_4]_2$ in acetonitrile (solid line) and water, pH = 5.8 (dashed line). The complex concentration is 1.03 × 10^{-4} M for both spectra.

The visible electronic absorption spectra of $[(NH_3)_5Ru(2,4\text{-}Cl_2pcyd)]^{2+}$, in acetonitrile and water, in Figure 2, reveal important features. The broad $b_1^* \leftarrow b_2$ LMCT transition, centered at 380 nm, in acetonitrile, has fine structure that is possibly vibronic in origin. Alternatively, these extra features could be underlying ligand field transitions. The dependence of charge-transfer energy on solvent polarity is a well-known phenomenon.[28] The shift to higher LMCT energies as solvent polarity is increased is consistent with ground-state stabilization of the complex's permanent dipole by the solvent. Importantly, both bands assigned to LMCT transitions are solvent sensitive. Figure 2 also reveals the dependence of electronic absorption oscillator strength on the nature of the solvent. The effect of solvent on oscillator strength has been long known[8] and can be partially accounted for by Lorentz–Lorenz forces.[29] For these complexes, preliminary studies have shown that the $b_1^* \leftarrow b_1$ oscillator strength solvent dependence can be understood by the strength of the hydrogen bond between donor solvent and ammine proton.[30]

By comparison of the lowest energy LMCT bands for the complexes in Table IV, a trend can be observed in increasing LMCT energies as the number of electron-withdrawing substituents on the phenyl ring increases. Clearly, while both ligand and metal orbitals are stabilized (see Table V) as electron-withdrawing substituents are added to the phenyl ring, the ligand orbital is stabilized to a greater extent.

Pentaammineruthenium(III) is a strong π acid, and its oxidation state is expected to be stabilized by π-donor ligands. By the placement of electron donor or withdrawing substituents on the phenyl ring, the σ and π basicity of the anionic cyanamide ligand can be "tuned". Importantly, the degree of π bonding is extremely sensitive to the electron density coefficient of the terminal nitrogen as represented by Chart I. Electron-withdrawing substituents on the phenyl ring would shift electron density away from the terminal nitrogen, reducing its contribution to the π-nonbonding molecular orbitals, and in turn result in the reduction of effective overlap with π-symmetry d orbitals on Ru(III). Changes in Ru(III) reduction should largely reflect variations in π bonding, since the LUMO of these complexes is of π symmetry.[11] The Ru(III/II) couples in Table V show the expected trend, moving cathodically from −0.036 V for $[(NH_3)_5Ru(Cl_5pcyd)]^{2+}$ to −0.280 V for $[(NH_3)_5Ru(2,4,6\text{-}Me_3pcyd)]^{2+}$. When coordinated to Ru(III), anionic (2,4,6-trimethylphenyl)cyanamide has a π basicity comparable to that of cytidine anion but still less than that of hydroxide.[11]

Correlations between electrochemical potentials and charge-transfer bands of charge-transfer complexes have been based on the hypothesis 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

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(23) Crystal structures of polymeric compounds, with stoichiometry $M(DCNQI)_2$, have shown end-on coordination of radical-anion dicyanamide ligands to alkali-metal, copper, and silver cations: Kato, R.; Kobayashi, H.; Kobayashi, A.; Mori, T.; Inokuchi, H. *Chem. Lett.* **1987**, 1579.

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(25) Kennard, O. *CRC Handbook of Chemistry and Physics*, 60th ed.; CRC Press, Inc.: Boca Raton, Fl, 1979; p F-216.

(26) Kobayashi, A.; Kato, R.; Kobayashi, H.; Mori, T.; Inokuchi, H. *Solid State Commun.* **1987**, *64*, 45.

(27) Electron densities of the cyanamide π nonbonding MO have been theoretically estimated for cyanamide, methylcyanamide, and dimethylcyanamide: Stafast, H.; Bock, H. *Chem. Ber.* **1974**, *107*, 1882. Drago, R. S.; Henneike, H. F. *J. Am. Chem. Soc.* **1968**, *90*, 5112.

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(29) Chako, N. Q. *J. Chem. Phys.* **1934**, *2*, 645.

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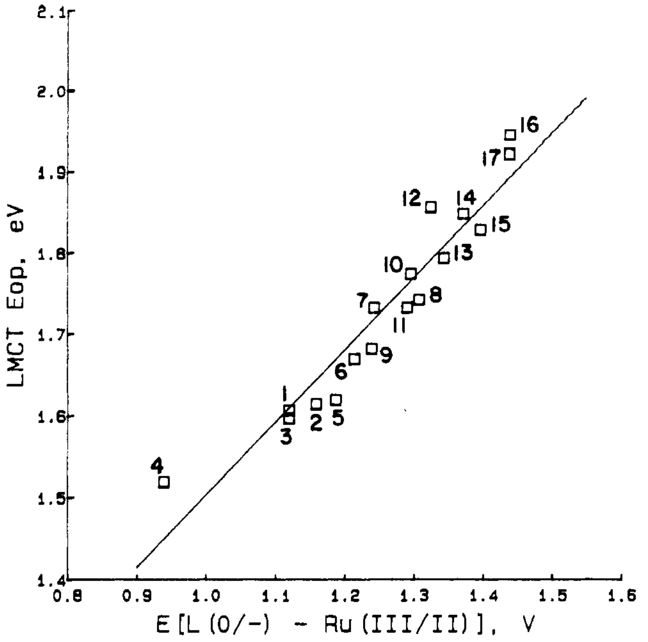

Figure 3. Correlation between the optical energy of the $b_1^* \leftarrow b_1$ LMCT transition (Table IV) and the difference between L(0/−) and Ru(III/II) reduction couples for pentaammineruthenium(III) complexes of anionic phenylcyanamide ligands (Table V). The equation for the line is $y = 0.89x + 0.61$, with $R = 0.95$.

the electrochemical reduction and oxidation potentials of the charge-transfer complex. For a series of similar charge-transfer complexes, this relationship will hold only if the differences in solvation energy are small, the entropy differences between the various redox components are small, and finally, the optical transition is of the (0″–0′) vibrational type. Since charge-transfer transitions typically involve bonding and antibonding molecular orbitals, the zeroth vibrational level of the excited state is associated with larger internuclear separations compared to the ground state. A Franck–Condon excitation will therefore populate excited vibrational levels, and so an additional correction, χ, is required to compensate for the change in inner and outer coordination sphere configurations. Other workers have attempted to evaluate the outer-sphere contribution to charge-transfer energies by varying the solvent.[31,32] In this study, only acetonitrile was used, and so solvent contributions to χ are assumed constant. We wish to establish that, within this set of phenylcyanamide complexes, properties are essentially the same, with the only variable being the interaction of the cyanamide group with Ru(III).

The optical energy of a LMCT charge-transfer band maximum, E_{opt}, can be related[28,32] to the difference in electrochemical potentials, ΔE, by the expression

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

The Ru(III/II) couple of pentaammineruthenium(III) bound to the oxidized ligand cannot be experimentally measured. This couple is expected to be more anodic than the experimentally measurable Ru(III/II) couple, and so the constant C is a positive value. The above expression predicts that a plot of LMCT optical energy, for a series of pentaammineruthenium(III) phenylcyanamide complexes, against ΔE should give a straight line relationship with unity slope, if C and χ are constant. Data from Table IV and V have been plotted to give the correlation shown in Figure 3. The slope is close to unity, being 0.89 with an R value of 0.95. It is perhaps surprising that the above equation is adequate, considering all the approximations. One is left with the conclusion that, within this set of similar complexes, C and χ do not vary to a significant extent.

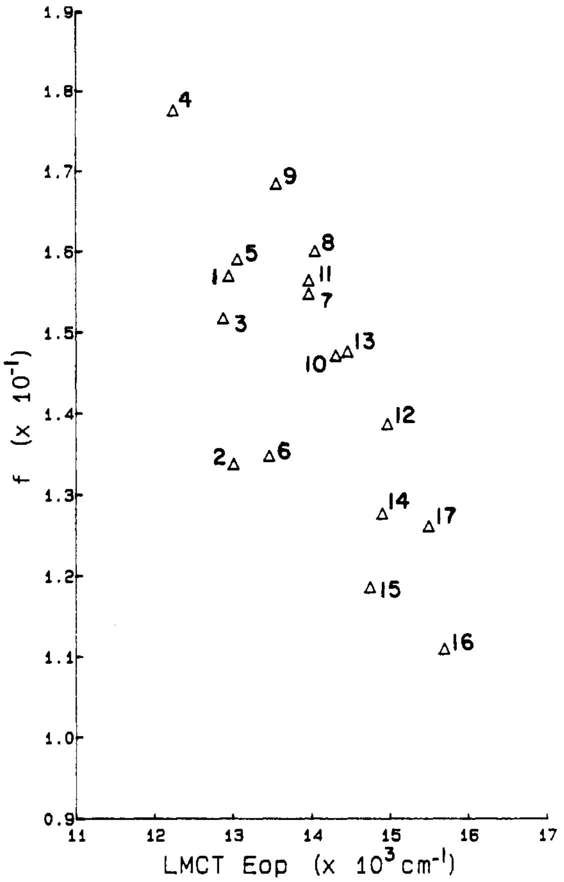

Figure 4. Distribution of $b_1^* \leftarrow b_1$ LMCT oscillator strengths relative to optical energy for pentaammineruthenium(III) complexes of anionic phenylcyanamide ligands.

The extinction coefficient of the $b_1^* \leftarrow b_1$ LMCT band in Table IV appears to decrease with increasing LMCT energy, as the cyanamide group becomes increasingly electronegative. Since there are no other transitions to interfere, the oscillator strength of this transition can be uniquely determined. Oscillator strength f can be calculated from experimental data,[28] assuming Gaussian band shape, by

$$f = (4.6 \times 10^{-6})\epsilon_{max}\bar{\nu}_{1/2} \qquad (2)$$

where ϵ_{max} is the extinction coefficient at maximum band wavelength in units of M^{-1} cm^{-1} and $\bar{\nu}_{1/2}$ is the bandwidth at half-ϵ_{max} in cm^{-1}. Oscillator strength values for the $b_1^* \leftarrow b_1$ LMCT transition have been compiled in Table IV and plotted against LMCT energy in Figure 4. The data points are not scattered, and there would appear to be a clear correlation. We are confident of the purity and stability of the complexes (see Experimental Section) and consider the variation in oscillator strengths within this set of similar complexes to be significant.

Oscillator strength can be calculated theoretically[28] by using the expression

$$f = (1.085 \times 10^{11})G\bar{\nu}M^2 \qquad (3)$$

where G refers to the degeneracy of the states concerned. For these complexes, the $b_1^* \leftarrow b_1$ transition is unidimensional and $G = 1$. $\bar{\nu}$ is the energy, in cm^{-1}, at ϵ_{max}, and M is the transition moment for dielectric dipole-allowed transitions. Equation 3 predicts that the oscillator strength should increase with increasing LMCT energy, which is the opposite to what is observed in Figure 4. The Ru–cyanamide bond length is predicted to increase as the cyanamide becomes a poorer σ and π donor. Since the dipole moment of ground and excited states increases with increasing bond length, the transition moment might be expected to increase with the number of electron-withdrawing substituents on phenylcyanamide. Again, this is the opposite to what is observed. This quandary can be resolved by recognizing that eq 3 leaves

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[31] Curtis, J. C.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 224.

[32] Dodsworth, E. S.; Lever, A. B. P. *Chem. Phys. Lett.* **1984**, *112*, 567; **1985**, *116*, 254 (erratum).

out an important factor. There must be some region of overlap between donor and acceptor for there to be an allowed transition between ground and excited charge-transfer states, and therefore, the transition moment should be expressable in terms of the overlap integral. Mulliken[7,8] recognized this and developed the expression, using the atomic orbital approximation, for interatomic charge transfer between two totally symmetric hydrogen wave functions

$$f = (1.085 \times 10^{-5})G\bar{\nu}S^2R^2(1 - S^4)^{-1} \tag{4}$$

or for moderate values of S

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

where G and $\bar{\nu}$ are the same as in eq 3, R is the transition dipole length, which can be approximated to be the separation between donor and acceptor wave functions, in angstroms, and S is the overlap integral.

As shown in Chart I, the π_2 MO is a three-atom π system. The contribution of the terminal nitrogen to the π_2 MO is determined by the magnitude of its electron density coefficient C_n. Therefore, the form of the π overlap integral associated with $b_1^* \leftarrow b_1$ transition is

$$S = C_n\langle d\pi|p\pi_2\rangle = C_nS_1 \tag{6}$$

where S_1 is the optimum π overlap that can occur between anion nitrogen 2p and ruthenium(III) 4d orbitals at a given separation. The trend in oscillator strength in Figure 4 can be now explained by an increase in π overlap as the basicity of the cyanamide group increases.

It should be recognized that to apply eq 5, derived from hydrogen atomic wave functions, to a many electron system is a gross simplification. For a many electron system, the transition moment is equal to the vector sum of all the changes in dipole moment experienced by the system. This would include both inner and outer coordination sphere electrons. We assume the outer coordination sphere effects for the complexes in acetonitrile are unimportant, since eq 1 appears to be obeyed. The variables to consider in the inner coordination sphere are the nature of the phenylcyanamide ligand and its interaction with Ru(III) and the magnitude of transition dipole length. The transition moment induced by the $b_1^* \leftarrow$ LMCT transition should result not only from the changes in dipole experienced by the electrons of the cyanamide group but also from those of the phenyl ring provided there is π coupling between the two systems. Recent electronic absorption studies of the metal to ligand charge-transfer (MLCT) bands of copper(I) diimine[33] and rhenium(I) *N*-methyl-4,4′-bipyridinium cation[34] complexes have shown that MLCT intensity increases when the acceptor orbital is extended out away from the metal center by conjugation, thereby increasing the transition dipole length. For the complexes in this study, this last factor is expected to be approximately constant (except for the variation induced by the nature of the phenyl ring substituents) if the substituted phenyl ring is coplanar with the cyanamide group,[35] as shown in Figure 1. This probably is not the case for $[(NH_3)_5Ru(2,4,6\text{-}Me_3pcyd)]^{2+}$.

The (2,4,6-trimethylphenyl)cyanamide anion ligand is the best π-donor ligand (compare Ru(III/II) couples in Table V) and yet has only moderate oscillator strength for the $b_1^* \leftarrow b_1$ LMCT band. A crystal structure[36] of the 1,4-bis(cyanoamino)-2,3,5,6-tetramethylbenzene dianion has shown that the terminal cyanamide nitrogens are 1.41 Å out of the plane of the phenyl ring with the result that the phenyl ring is decoupled from the nitrile group. This probably results from the weak π interaction between phenyl and cyanamide groups and the steric repulsion from *o*-methyl groups. We suggest that the same is true for $[(NH_3)_5Ru(2,4,6\text{-}Me_3pcyd)]^{2+}$ and likely accounts for the apparent reduction in LMCT oscillator strength.

The trend in oscillator strength (Figure 4) does follow the expected increase in π bonding for the methoxy- and chloro-substituted phenylcyanamide complexes and can be understood in terms of the degree of π overlap between cyanamide anion and Ru(III) and the transition moment dipole length.[37]

While the properties of the ruthenium dπ orbital are relatively constant, the coefficient of the bonding nitrogen of the π_2 orbital in Chart I and eq 6 is expected to be extremely sensitive to the nature of the substituents on the phenyl ring, decreasing as the number of electron-withdrawing substituents increases. This decrease in C_n also means that the π_2 MO's center of electron density has shifted away from the bonding nitrogen thereby increasing the transition dipole length. Increasing dipole length should increase the oscillator strength. However, the trend in oscillator strengths in Figure 4 indicates that the degree of π overlap is the dominate factor.

Numerical tables of two-center overlap integrals[38] have been compiled, by using Slater-type orbitals, that include all possible combinations of orbital parameters. From these tables and the $[(NH_3)_5Ru(2,3\text{-}Cl_2pcyd)]^{2+}$ Ru–N cyanamide bond length of 1.98 Å, we have determined an upper limit of 0.24 for the overlap integral between anionic nitrogen 2pπ and ruthenium(III) 4dπ orbitals. An estimate of the maximum oscillator strength for a given dipole length can then be calculated by using eq 5. Substituting $C_n = 1$, $S_1 = 0.25$, $R = 1.98$ Å, $\bar{\nu} = 14310$ cm^{-1}, and $G = 1$ into eqs 5 and 6 gives $f_{max} = 0.035$. For the $b_1^* \leftarrow b_1$ transition of $[(NH_3)_5Ru(2,3\text{-}Cl_2pcyd)]^{2+}$, $f = 0.147$, which is approximately four times greater than f_{max}. This discrepancy cannot be reasonably accounted for by a consideration of the three-atom π_2 system alone and may be partially explained by the extension of a transition dipole length due to the coupling of the phenyl ring into the cyanamide π system. Other researchers[33] have invoked a scale factor that was estimated from a least-squares fit of calculated and observed intensities.

For the ruthenium(III) phenylcyanamide complexes, the variations in Ru–N6 bond lengths and the influence of the phenyl ring (whether coupled or decoupled from the cyanamide group) require more quantitative theoretical calculations.[39]

Acknowledgment. R.J.C. acknowledges the Natural Sciences and Engineering Research Council of Canada for their financial support and a University Research Fellowship.

Supplementary Material Available: Listings of bond lengths, bond angles, anisotropic thermal parameters for non-hydrogen atoms, elemental analyses, IR and ^{13}C NMR data, and melting points of the monomer and dimer ligands, and elemental analyses of the complexes used in this study and a stereoreview of the unit cell (9 pages); a table of structure factors (14 pages). Ordering information is given on any current masthead page.

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(34) Chen, P.; Curry, M.; Meyer, T. J. *Inorg. Chem.* **1989**, *28*, 2271.

(35) A crystal structure[36] of 1,4-bis(cyanoamino)-2,3,5,6-tetrachlorobenzene dianion shows the cyanamide groups to be coplanar with the phenyl ring, which indicates that the steric repulsion of *o*-chloro substitution is not enough to overcome the strong π coupling between cyanamide and phenyl ring π systems.

(36) Aquino, M. A. S.; Lee, F. L.; Gabe, E. J.; Crutchley, R. J. To be published.

(37) We note that for chlorine-substituted phenylcyanamide ligands the overall trend in Figure 4 follows an inductive argument for the perturbation of the cyanamide group. However, for phenylcyanamide ligands with an equivalent number of chlorine substituents, a subtle dependence of oscillator strength on the position of phenyl ring substitution is observed. Resonance contributions may also be important in this case.

(38) Boudreaux, E. A.; Cusachs, L. C.; Dureau, L. D. *Numerical Tables of Two-Center Overlap Integrals*; W. A. Benjamin, Inc.: New York, 1970; p 191. The title of the table should read π and not δ overlaps.

(39) Work in progress.