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Tetrakis(pyridine)ruthenium Trans Complexes of Phenylcyanamide Ligands: Crystallography, Electronic Absorption Spectroscopy, and Cyclic Voltammetry

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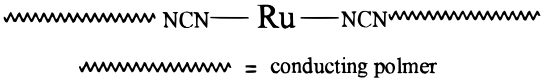
The complexes *trans*-[Ru(py)$_4$L$_2$] where py = pyridine and L = (2-chlorophenyl)-, (2,3-dichlorophenyl)-, (2,4,5-trichlorophenyl)-, (2,3,4,5-tetrachlorophenyl)- and (pentachlorophenyl)cyanamide were synthesized and characterized by electronic and ^{1}H NMR spectroscopies. A crystal structure of *trans*-[Ru(py)$_4$((2-chlorophenyl)cyanamide)$_2$] showed the expected trans coordination of the phenylcyanamide ligands. Crystal structure data: space group $C2/c$, with a, b, and c = 40.6441(3), 9.2003(1), and 22.6946(2) Å, respectively, $\beta = 116.387(1)°$, $V = 7602.2(1)$ Å^3, and $Z = 8$. The structure was refined by using 4943 independent reflections with $I > 2\sigma(I)$ to a final R factor of 0.060. Spectroelectrochemistry was used to generate the electronic absorption spectra of the Ru(III) complexes *trans*-[Ru(py)$_4$L$_2$]$^+$. Ru(III)−cyanamide coupling elements derived from charge transfer spectral data of the *trans*-[Ru(py)$_4$L$_2$]$^+$ complexes were significantly larger than those of the corresponding [Ru(NH$_3$)$_5$L]$^{2+}$ complexes.

Introduction

The creation of macromolecular electronic structures that fulfill specific functions, such as conduction and switching,[1] is spurred by the growing realization that the extent to which electronic components, based on bulk properties, can be miniaturized is finite and may have already been reached. In this regard, the study of conductive organic polymeric[2] and metallic coordination polymeric materials[3−5] holds great interest. Organic polymers, such as polyaniline[6] and polythiophene,[7] are of interest not only for their high conductivity (i.e., between 10 and 100 S cm^{-1} when doped) but also for their unique photonic[8] and optical[9] properties. Likewise, coordination polymers also hold promise as novel materials because of their magnetic,[10] nonlinear optical,[11] and conductive[4] properties. Development of such systems has been hampered by mediocre synthetic routes, which produce poorly defined, low molecular weight, insoluble, and often intractable products, and much work is currently directed toward developing strategies that will produce well-defined architectures.[2−12]

We are attempting to construct conductive organic polymer chains that are cross-linked by cyanamide anion groups to a coordination complex:



Conductivity within these linked systems will arise provided the polymer pπ orbitals and the metal dπ orbital are both symmetry and energy matched. Our extensive studies of mixed-valence dinuclear ruthenium complexes incorporating the 1,4-dicyanamidobenzene dianion bridging ligand have shown that the magnitude of metal−metal coupling can be dramatically perturbed by the nature of either the inner or the outer coordination sphere.[13] Indeed, this remarkable sensitivity of metal−metal coupling suggests polymer chains linked by ruthenium−cyanamide bonds can function as molecular switching devices.[14]

In this study, a series of *trans*-di(phenylcyanamido)tetrakis(pyridine)ruthenium(II) complexes were synthesized and one complex was characterized by crystallography to develop the synthetic and interpretive tools necessary to produce conductive cross-linked polymer systems. Spectroscopic and electrochemical comparisons between these complexes and the corresponding [Ru(NH$_3$)$_5$L]$^{2+}$ complexes[15] provide a conceptual basis for future research.

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Experimental Section

Chemicals were all of reagent grade or better and were used as received. The thallium salts (*caution!* thallium is extremely toxic) of (2-chlorophenyl)cyanamide (2-Cl-pcyd), (2,3-dichlorophenyl)cyanamide (2,3-Cl$_2$pcyd), (2,4,5-trichlorophenyl)cyanamide (2,4,5-Cl$_3$pcyd), (2,3,4,5-tetrachlorophenyl)cyanamide (2,3,4,5-Cl$_4$pcyd), and (pentachlorophenyl)cyanamide (Cl$_5$pcyd) were prepared according to established procedures.[15,16] The synthesis of *trans*-[Ru(py)$_4$Cl$_2$],[17,18] where py is pyridine, was accomplished by following literature methods.

The syntheses of the *trans*-bis(phenylcyanamido)ruthenium complexes are very similar. Only one example is given.

***trans*-[Ru(py)$_4$(2-Cl-pcyd)$_2$].** A 200 mg (0.5 mmol) sample of Ru(py)$_4$Cl$_2$ and 356 mg (1.0 mmol) of Tl(2-Cl-pcyd) were combined with 20 mL of reagent grade DMF. The solution was degassed, blanketed with Ar gas, and allowed to reflux for 3 h. The reaction mixture was cooled and filtered to remove TlCl, and the filtrate was added to 400 mL of water. The crude product precipitated as a yellow powder and was collected by filtration. Purification was effected by column chromatography using WA-1 acid alumina activity grade I (Chromatography grade, Sigma) and 10% acetonitrile in dichloromethane as the eluting solvent (acetonitrile was Anachemia Accusolve spectroscopy grade and dichloromethane was Anachemia reagent grade). Two bands appeared which were (in the order with which they eluted) a yellow (major) band and a green (minor) band. The yellow band was collected and the product isolated by evaporation of the solvent; however, the green band eluted very slowly and was not collected. The column load was approximately 100 mg, from which 50 mg of purified product was obtained. After vacuum-drying, the final yield based on ruthenium starting material was 36%. Anal. Calc for $C_{34}H_{28}Cl_2N_8Ru$: C, 56.67; H, 3.92; N, 15.55. Found: C, 56.22; H, 3.93; N, 15.61. ^{1}H NMR (CDCl$_3$ + 1% TMS): phenylcyanamide protons, 6.56, 6.92, and 7.22 ppm; bipyridine protons, 7.16, 7.69, and 8.48 ppm. ν(NCN) = 2153 cm^{-1}.

***trans*-[Ru(py)$_4$(2,3-Cl$_2$pcyd)$_2$]·$^2/_3$H$_2$O.** The yield of pure product was 33.2%. Anal. Calc for $C_{102}H_{82}N_{24}Cl_{12}O_2Ru_3$: C, 50.95; H, 3.44; N, 13.98. Found: C, 51.43; H, 3.53; N, 13.51. The presence of water was verified by NMR spectroscopy. ^{1}H NMR (CDCl$_3$ + 1% TMS): phenylcyanamide protons, 6.78 ppm; bipyridine protons, 7.18, 7.71, and 8.44 ppm. ν(NCN) = 2159 cm^{-1}.

***trans*-[Ru(py)$_4$(2,4,5-Cl$_3$pcyd)$_2$]·$^1/_4$ H$_2$O·$^1/_4$CH$_2$Cl$_2$.** The yield of purified product was 39.5%. Anal. Calc for $C_{137}H_{100}Cl_{26}N_{32}ORu_4$: C, 46.53; H, 2.85; N, 12.67. Found: C, 46.56; H, 2.85; N, 12.93. The presence and quantity of water and dichloromethane were confirmed by NMR spectroscopy. ^{1}H NMR (CDCl$_3$ + 1% TMS): phenylcyanamide protons, 6.92 and 7.26 ppm; bipyridine protons, 7.24, 7.75, and 8.41 ppm. ν(NCN) = 2169 cm^{-1}.

***trans*-[Ru(py)$_4$(2,3,4,5-Cl$_4$pcyd)$_2$].** The yield of purified complex was 26%. Anal. Calc (%) for $C_{34}H_{22}Cl_8N_8Ru$: C, 44.04; H, 2.39; N, 12.08. Found: C, 43.76; H, 2.34; N, 11.93. ^{1}H NMR (CDCl$_3$ + 1% TMS): phenylcyanamide proton, 6.97 ppm; bipyridine protons, 7.33, 7.81, and 8.45 ppm. ν(NCN) = 2165 cm^{-1}.

***trans*-[Ru(py)$_4$(Cl$_5$pcyd)$_2$].** The yield of purified complex was 42%. Anal. Calc for $C_{34}H_{20}Cl_{10}N_8Ru$: C, 40.99; H, 2.02; N, 11.25. Found: C, 40.44; H, 2.04; N, 11.15. ^{1}H NMR (CDCl$_3$ + 1% TMS): bipyridine protons, 7.18, 7.69, and 8.42 ppm. ν(NCN) = 2167 cm^{-1}.

***trans*-[Ru(py)$_4$(4-NO$_2$pcyd)$_2$]·$^1/_2$H$_2$O·$^1/_4$CH$_2$Cl$_2$.** The yield of purified product was 48%. Anal. Calc (%) for $C_{137}H_{118}Cl_2N_{40}O_{18}Ru_4$: C, 53.29; H, 3.85; N, 18.14. Found: C, 53.16; H, 3.93; N, 17.76. The presence and quantity of water and dichloromethane were confirmed by NMR spectroscopy. ^{1}H NMR (CDCl$_3$ + 1% TMS): phenylcyanamide protons, 6.71 and 8.00 ppm; bipyridine protons, 7.26, 7.78, and 8.37 ppm. ν(NCN) = 2154 cm^{-1}.

The properties of the Ru(III) oxidation state of the above complexes were studied by spectroelectrochemical techniques. Nevertheless, it is possible to isolate these complexes in their Ru(III) oxidation state as shown in the synthesis below.

***trans*-[Ru(py)$_4$(Cl$_5$pcyd)$_2$][PF$_6$].** A 100 mg (0.10 mmol) sample of *trans*-[Ru(py)$_4$(Cl$_5$pcyd)$_2$] and 168 mg (0.175 mmol) of [Fe(2,2′-bipyridine)$_3$][PF$_6$]$_3$[19] were combined in ∼20 mL of MeCN, and the mixture was stirred for 15 min. The solution was taken to dryness by gently heating on the hotplate, and the residue was then dissolved in 10 mL of 10% MeCN/CH$_2$Cl$_2$ (the same solvent mixture used for the column chromatography of the previous five complexes). The resulting solution was then passed through a column packed with activity grade 1 WA-1 acid alumina, and four bands were observed: minor yellow band (first to come off the column, likely unoxidized Ru$^{\text{II}}$ complex), major green band (Ru(III) complex), minor blue/green band, and major red immobile band (most likely [Fe(2,2′-bipyridine)$_3$][PF$_6$]$_2$). The major green band was collected and the solvent removed by evaporation using a rotary evaporator. The resulting residue was dried overnight under vacuum. Yield: 46% relative to *trans*-[Ru(py)$_4$(Cl$_5$pcyd)$_2$] starting material. Anal. Calc for $C_{34}H_{20}Cl_{10}F_6N_8PRu$: C, 35.79; H, 1.72; N, 9.82. Found: C, 35.56; H, 1.86; N, 9.83. ν(NCN) = 2108 cm^{-1}.

Physical Measurements. UV−vis−NIR spectra were taken on a Cary 5 spectrophotometer. The spectra were measured in acetonitrile (Accusolve, Anachemia) and dimethylformamide (DMF, reagent, Anachemia) at room temperature. ^{1}H NMR spectra were recorded using a Bruker AMX-400 NMR spectrometer at 300 K in deuterated chloroform (CDCl$_3$, 99.9% atom % D, CDN Isotopes) and were referenced to tetramethylsilane (TMS, Aldrich) at 0.00 ppm. The IR spectra (KBr disks) were collected by using both a Bomem Michelson 100 FTIR and a Perkin-Elmer 1600 series FTIR spectrophotometer. Cyclic voltammetry was performed by using a BAS CV-27 apparatus. The electrochemical cell consisted of a jacketed glass container with an inner volume of ∼20 mL. Cell temperature was maintained at 25.0 ± 0.1 °C by using a Haake D8-G refrigerated bath and circulator. The cell was fitted with a Teflon lid through which holes had been drilled to accommodate the electrodes (BAS, 1.6 mm platinum disk working, Pt wire counter, and Ag wire quasi-reference electrodes) and an argon gas bubbler. Cobaltocenium hexafluorophosphate, $E° = -664$ mV vs NHE in acetonitrile and $E° = -589$ mV vs NHE in DMF,[20] was used as an internal reference. The solvents used for electrochemistry were Anachemia Accusolve grade. Acetonitrile was dried and distilled over P$_2$O$_5$ (reagent, Anachemia), under vacuum, and at room temperature. Dimethylformamide was dried over activated 5 Å molecular sieves ($^1/_8$ in. pellets BDH). Nitromethane was dried over activated WA-1 acid alumina (Chromatography grade, Sigma) and distilled under vacuum at room temperature. Acetone was distilled under vacuum at room temperature. The supporting electrolyte, tetrabutylammonium hexafluorophosphate (TBAH), was purified by recrystallization from ethanol/water and vacuum-dried at 110 °C overnight. Electrolyte concentration was 0.1 M. Spectroelectrochemistry was performed using an optically transparent thin-layer electrochemical (OTTLE) cell of published design.[21,22] Elemental analyses were performed by Canadian Microanalytical Services Ltd.

Crystallography. Block-shaped crystals of [Ru(py)$_4$(2-Cl-pcyd)$_2$] were grown from a solution of water and acetone by slow evaporation of the acetone. The data were collected on a 1K Siemens Smart/CCD using Mo Kα radiation ($\lambda = 0.710\,73$ Å) at 296 K using an $\omega-2\theta$ scan technique and corrected for absorption using equivalent reflections.[23] The structure was solved by direct methods and refined with full-matrix least-squares procedures. Anisotropic refinement was performed on all non-hydrogen atoms. All hydrogen atoms were calculated. Scattering factors are contained in the SHELXTL 5.03 program library.

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Results and Discussion

The Ru(II) complexes were synthesized in high yields according to the metathesis reaction

$$\textit{trans}\text{-Ru(py)}_4\text{Cl}_2 + 2\text{TlL} \xrightarrow[\text{DMF}]{\Delta} \textit{trans}\text{-Ru(py)}_4\text{L}_2 + 2\text{TlCl}\downarrow$$

Purification by chromatography on alumina yielded yellow *trans*-[Ru(py)$_4$L$_2$] crystalline powder (except for the deep orange crystals of *trans*-[Ru(py)$_4$(4-NO$_2$pcyd)$_2$]). These complexes are slightly sensitive to oxidation, and this can be easily recognized by the appearance of the intense Ru(III)−NCN ligand-to-metal charge transfer band at ca. 1000 nm in their electronic absorption spectra. No effort was made to exclude air for NMR and electronic absorption spectrosopy studies and for crystal growth. The Ru(II) complexes were sufficiently soluble in DMF to permit quantitative characterization. However, the complexes' solubility in acetonitrile noticeably decreased as the number of chloro substituents on the phenyl group increased. The ^{1}H NMR spectra of the complexes were consistent with their formulation and showed no evidence of phenylcyanamide linkage isomerism. Recently, the ^{1}H and ^{13}C NMR spectroscopy of Ru(II) complexes containing 2,6-bis(1-methylbenzimidazol-2-yl)pyridine provided strong evidence for the initial formation of the amido coordination mode of the phenylcyanamide ligand which with time or heating converted to the more thermodynamically stable nitrile nitrogen coordination mode.[24] Numerous crystal structures of phenylcyanamide complexes[15b,25] have all shown nitrile nitrogen coordination, and it is suggested that the thermodynamic stability of nitrile nitrogen coordination is primarily due to reduced steric crowding about the metal ion.

The crystallographic data for *trans*-[Ru(py)$_4$(2-Cl-pcyd)$_2$]·acetone are summarized in Table 1, and Figure 1 shows an ORTEP drawing of the complex. Selected of bond lengths and angles are given in Table 2. In Figure 1, it is clear that both (2-chlorophenyl)cyanamide ligands are coordinated to Ru(II) through their nitrile nitrogens. It is also interesting to note that the arrangement of pyridine ligands about Ru(II) is one that minimizes steric crowding between pyridines. The gauche orientation of the phenylcyanamide ligands in Figure 1 should be energetically unfavorable and probably arises from crystal packing forces. The coordination geometry about Ru(II) is that of a distorted octahedron of nitrogen donor atoms in which the trans-cyanamide nitrogens have slightly shorter bonds to ruthenium than the pyridine nitrogens (Table 2). The Ru(II)−cyanamide bond lengths of 2.041(6) and 2.060(6) Å are larger than the average Ru(III)−cyanamide bond length of 1.97(2) Å that was derived from six Ru(III)−cyanamide structures[15b,25] and can be attributed to the effect of the ruthenium oxidation state.

Quantitative electronic spectra of the *trans*-[Ru(py)$_4$L$_2$] complexes were taken in DMF, and the data and spectroscopic assignments are summarized in Table 3. A representative spectrum of *trans*-[Ru(py)$_4$(2-Cl-pcyd)$_2$] can be seen in the Supporting Information. The orange color of *trans*-[Ru(py)$_4$(4-NO$_2$pcyd)$_2$] arises from a cyanamide-to-nitro group intraligand charge transfer transition centered at 470 nm. This transition is also present in the thallium salt of the (4-nitrophenyl)cyanamide anion.

Table 1. Crystal Data and Structure Refinement Details for *trans*-[Ru(py)$_4$(2-Cl-pcyd)$_2$]·acetone

empirical formula	C$_{37}$H$_{34}$Cl$_2$N$_8$ORu
fw	778.69
temp	296(2) K
wavelength	0.717 03 Å
crystal system	monoclinic
space group	*C*2/*c*
unit cell dimens	$a = 40.6441(3)$ Å $b = 9.2003(1)$ Å $c = 22.6946(2)$ Å $\alpha = 90°$ $\beta = 116.387(1)°$ $\gamma = 90°$
volume, *Z*	7602.2(1) Å^3, 8
density (calc)	1.361 Mg/m^3
abs coeff	0.593 mm^{-1}
F(000)	3184
crystal size	0.20 × 0.10 × 0.10 mm
θ range for data collection	1.12−22.50°
limiting indices	$-34 \le h \le 53$, $-12 \le k \le 12$, $-29 \le l \le 28$
no. of reflns collected	14 841
no of indepen reflns	4944 [*R*(int) = 0.0570]
abs corr	semiempirical from equivalents
max and min transmn	0.4745 and 0.4291
refinement method	full-matrix least-squares on F^2
data/restraints/params	4943/0/422
goodness-of-fit on F^2	1.019
R1^a	0.0600
*w*R2^b	0.0874

^{a} $\mathrm{R1} = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $\mathrm{wR2} = [\sum w(F_o^2 - F_c^2)/\sum wF_o^4]^{1/2}$.

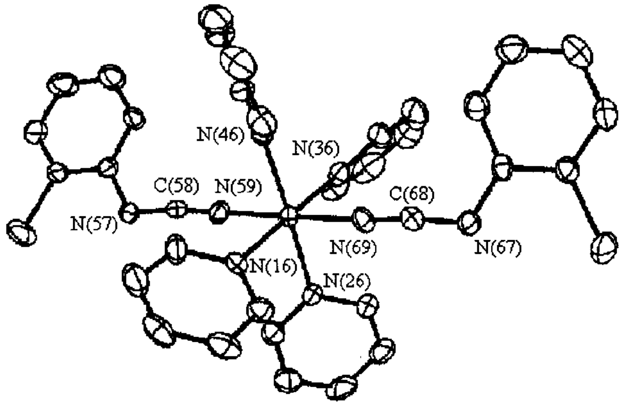

Figure 1. ORTEP drawing of *trans*-[Ru(py)$_4$(2-Cl-pcyd)$_2$] with thermal ellipsoids depicted at 30% probability. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths and Angles^a for *trans*-[Ru(py)$_4$(2-Cl-pcyd)$_2$] ·acetone

Bond Lengths, Å			
Ru−N69	2.041(6)	Ru−N46	2.095(6)
Ru−N59	2.060(6)	Ru−N16	2.099(5)
Ru−N36	2.093(5)	Ru−N26	2.099(5)
Bond Angles, deg			
N69−Ru−N59	179.9(2)	N26−Ru−N46	178.2(2)
N36−Ru−N16	178.5(2)	N36−Ru−N59	91.0(2)
N36−Ru−N46	90.6(2)	N36−Ru−N69	88.9(2)
N36−Ru−N26	89.8(2)		

^{a} Estimated errors in parentheses.

Cyclic voltammetry data for the complexes in DMF and acetonitrile solutions are given in the Supporting Information. The $E_{1/2}$ potentials were determined from the average of the anodic and cathodic peak potentials ($E_{1/2} = (E_{pa} + E_{pc})/2$), at a scan rate of 250 mV/s and calibrated against the [Co(η^5-cyclopentadienyl)$_2$]$^{+/0}$ couple.[20] The voltammograms of the

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Table 3. Electronic Absorption Spectral Data[a] for *trans*-[Ru(py)$_4$L$_2$] and *trans*-[Ru(py)$_4$L$_2$]$^+$ Complexes

phenylcyanamide L	*trans*-[Ru(py)$_4$L$_2$]		*trans*-[Ru(py)$_4$L$_2$]$^+$	
	$\pi \rightarrow \pi^*$	CT	$b_{3u} \rightarrow b_{2g}$	$b_{2u} \rightarrow b_{2g}$
2Cl-pcyd$^-$	295 (4.59)	381 (4.33)[b]	365 (3.78)[c]	1044 (4.29)[c]
2,3-Cl$_2$pcyd$^-$	302 (4.57)	374 (4.33)[b]	374 (3.70)[c]	1006 (4.24)[c]
2,4,5-Cl$_3$pcyd$^-$	308 (4.54)	360 (4.40)[b]	384 (3.70)[c]	1018 (4.27)[c]
2,3,4,5-Cl$_5$pcyd$^-$	322 (454)	350 (4.52)[b]	391 (3.81)[c]	994 (4.35)[c]
Cl$_5$pcyd$^-$	364 (4.61)[d]		399 (3.76)[c]	913 (4.25)[c]
4-NO$_2$pcyd$^-$	370 (4.50)[d]	470 (4.57)[e]	472 (3.96)[f]	982 (4.38)[c]

[a] All data in nm; log of ϵ in M^{-1} cm^{-1} in parentheses; DMF solution. [b] Metal-to-ligand charge transfer. [c] Ligand-to-metal charge transfer. [d] Pyridine $\pi \rightarrow \pi^*$ and MLCT transitions. [e] Intraligand charge transfer. [f] LMCT and intraligand charge transfer.

complexes showed equivalent anodic and cathodic currents for the Ru(III/II) couple. However, quasi-reversibility of this couple was indicated by anodic to cathodic peak separations varying from 70 to 150 mV, when scanned between 50 and 250 mV/s, respectively. Cyanamide ligand oxidation waves were irreversible, and only the anodic current peak positions are given. Both the Ru(III/II) couple and ligand oxidation waves shift to more positive potentials with an increase in the number of chloro substituents on the phenyl ring. This is consistent with the expected decrease in basicity of phenylcyanamide ligands. The Ru(III/II) couples of the *trans*-[Ru(py)$_4$L$_2$]$^+$ complexes are shifted positively[15,26] by some 400−500 mV compared to the Ru(III/II) couples of the corresponding [Ru(NH$_3$)$_5$L]$^{2+}$ complexes. It is tempting to conclude that this is largely a consequence of the poorer donor properties of pyridine compared to ammonia, but the π-acceptor properties of pyridine probably play a role as well in stabilizing the Ru(II) oxidation state.

Spectroelectrochemistry experiments were performed to obtain the electronic absorption spectra of the Ru(III) complexes *trans*-[Ru(py)$_4$L$_2$]$^+$. An example of this experiment showing the oxidation of *trans*-[Ru(py)$_4$(2-Cl-pcyd)$_2$] in DMF solution is given in the Supporting Information. The maintenance of isosbestic points and the restoration of both the Ru(III) and Ru(II) spectra during repeated potential cycles demonstrated good reversibility.

The oxidation of *trans*-[Ru(py)$_4$(2-Cl-pcyd)$_2$] results in the loss of the MLCT transition at 381 nm and the appearance of two new bands at 365 and 1044 nm that we assign to the Ru(III)−cyanamide LMCT chromophore. This spectrum is similar to those analyzed for [Ru(NH$_3$)$_5$(phenylcyanamide)]$^{2+}$ complexes,[15a,27] but in the present case, the spectroscopic analysis must take into account the higher symmetry of the *trans*-[Ru(py)$_4$L$_2$] complexes and the linear combinations of nondegenerate π_{nb} electrons. The qualitative molecular orbital scheme illustrating the π interactions between cyanamide groups and the Ru(III) dπ orbitals is shown in Figure 2. The microsymmetry of the Ru(III) coordination sphere was chosen to be D_{2h} to reflect the nondegenerate π_{nb} orbitals of the cyanamide group. This arises from the planar geometry of the phenylcyanamide ligand, which allows preferential mixing of one of the two cyanamide π_{nb} orbitals with the phenyl π system. In Figure 2, only the $b_{2u} \rightarrow b_{2g}$ transition is allowed and is assigned to the low-energy LMCT band at 1044 nm in the spectrum of *trans*-[Ru(py)$_4$(2-Cl-pcyd)$_2$]$^+$ (Supporting Information). This band possesses a shoulder at approximately 1000 cm^{-1} greater energy that we attribute to a vibrational feature rather than the forbidden $b_{2g} \rightarrow b_{2g}$ transition (Figure 2). The difference in energy between $b_{2g} \rightarrow b_{2g}$ and $b_{2u} \rightarrow b_{2g}$ transitions reflects π-bonding energy and should be on the order of 3000−4000 cm^{-1} on the basis of previous spectroscopic studies of Ru(III) phenylcyanamide[28] and halide complexes.[29] The high-energy LMCT band centered at 365 nm (Supporting Information) is assigned to the formally forbidden transition $b_{3u} \rightarrow b_{2g}$ and probably gains its intensity from a lower complex symmetry than D_{2h} or an intensity-stealing mechanism. The spectral data associated with the $b_{2u} \rightarrow b_{2g}$ LMCT band of the *trans*-[Ru(py)$_4$(2-Cl-pcyd)$_2$]$^+$ complexes have been compiled in Table 3.

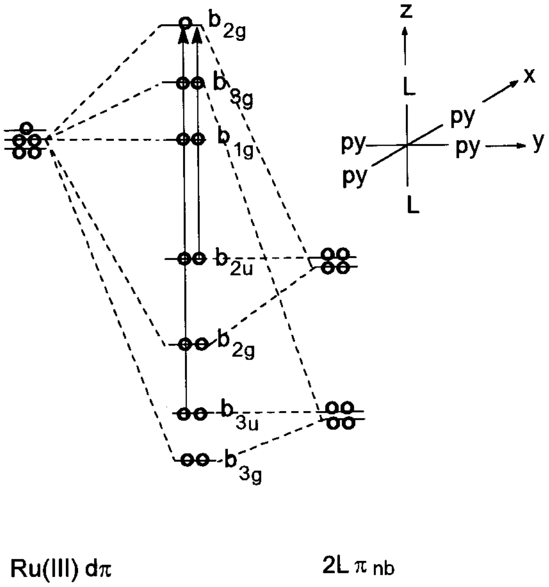

Figure 2. Qualitative molecular orbital scheme of π interactions in *trans*-[Ru(py)$_4$L$_2$]$^+$, where L is a phenylcyanamide anion ligand, showing the origins of the LMCT transitions. The microsymmetry of the complex was chosen to be D_{2h} to reflect the nondegeneracy of the cyanamide π_{nb} orbitals.

In previous studies, we calculated metal−metal coupling elements in dinuclear complexes from metal−ligand coupling elements H_{LM} that were derived in turn from bridging ligand-to-metal charge transfer spectral data.[13,30] The calculated metal−metal coupling was in excellent agreement with that determined experimentally. As a consequence, it has become clear that charge transfer spectral data can be used to evaluate molecular properties derived from frontier orbitals.

We hope to develop the spectroscopic tools to evaluate the electronic properties of Ru−cyanamide linkages when they are incorporated into a conducting polymer. Toward this end, a comparison of the metal−ligand coupling elements derived from the LMCT band properties of the *trans*-[Ru(py)$_4$L$_2$]$^+$ model

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(26) The Ru(III/II) couples reported in ref 15b were calibrated against a ferrocenium/ferrocene couple of 400 mV vs NHE instead of the more recent value of 665 mV vs NHE and should be corrected accordingly.

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Table 4. Ligand−Metal Coupling Elements[a] for $[Ru(NH_3)_5L]^{2+}$ and *trans*-$[Ru(py)_4(L)_2]^+$ Complexes Derived from $b_1 \rightarrow b_1$ and $b_{2u} \rightarrow b_{2g}$ LMCT Bands, Respectively

phenylcyanamide L	H_{LM}[b]	
	$[Ru(NH_3)_5L]^{2+}$ [c]	trans-$[Ru(py)L_2]^+$
2-Cl-pcyd$^-$	2540	2800
2,3-Cl_2pcyd$^-$	2510	2500
2,4,5-Cl_3pcyd$^-$	2530	2800
2,3,4,5-Cl_5pcyd$^-$	2290	3100
Cl_5pcyd$^-$	2410	3100
4-NO_2pcyd$^-$		3200

[a] All data in cm^{-1}. [b] Calculated by using eq 1. [c] Data from ref 15b.

complexes with those derived from the LMCT band properties of the corresponding $[Ru(NH_3)_5L]^{2+}$ complexes will test whether the results are consistent with predictions based upon the properties of the metal ion. Metal−ligand coupling elements were calculated by using the charge transfer spectral data derived from the low-energy $b_{2u} \rightarrow b_{2g}$ transition of the *trans*-$[Ru(py)_4L_2]^+$ complexes and comparing them with those derived from the low-energy $b_1 \rightarrow b_1$ transition of the $[Ru(NH_3)_5L]^{2+}$ complexes (Table 4). The equation used to calculate metal−ligand coupling elements is

$$H_{LM} = \frac{3.03 \times 10^2}{r}(E_{LMCT}f)^{1/2} \tag{1}$$

where f is the total oscillator strength of the low-energy LMCT, E_{LMCT} is the energy of the LMCT at the band maximum, and r is the transition dipole moment length which for phenylcyanamide ligands was estimated to be 5.56 Å.[27] As the LMCT bands are non-Gaussian, the total oscillator strengths were determined by using a previously discussed fitting procedure.[27] Equation 1 was originally derived by Hush,[31] who applied Mulliken's treatment[32] of charge transfer oscillator strength to the problem of resonance exchange in mixed-valence complexes. Creutz, Newton, and Sutin[33] showed that this expression can be applied to any charge transfer system, provided the transition dipole lies along the donor−acceptor axis and donor−acceptor overlap can be ignored.

In Table 4, H_{LM} values for the *trans*-$[Ru(py)_4L_2]^+$ complexes are larger than those for the $[Ru(NH_3)_5L]^{2+}$ complexes, and this is to be expected as Ru(III) in *trans*-$[Ru(py)_4L_2]^+$ is significantly more electropositive (as discussed above) and should form a stronger Ru(III)−cyanamide π bond. However, this interaction is shared between two cyanamide groups and so the H_{LM} per Ru(III)−cyanamide group (H_{LM}') is half the *trans*-$[Ru(py)_4L_2]^+$ H_{LM} in Table 4.[34] The value of H_{LM}' is important as it largely determines the efficiency of the NCN−Ru−NCN link to mediate donor−acceptor coupling according to the equation[33]

$$H_{ad} = \frac{(H_{LM}')^2}{\Delta E_{eff}} \tag{2}$$

where H_{ad} is the donor−acceptor resonance exchange integral (or donor−acceptor coupling element) and ΔE_{eff} is the reduced energy gap for superexchange. Equation 2 has successfully predicted the magnitude of metal−metal coupling from very weakly to strongly coupled mixed-valence complexes whereas the older Hush expression (eq 1 and spectral data from the intervalence band) is adequate only for the weakly coupled cases.[13]

An essential study to evaluate the electronic properties of the NCN−Ru−NCN bridge will be conducted after the synthesis of a mixed-valence system incorporating this bridge. Both the nature of the auxiliary ligands and the oxidation state of ruthenium can be changed to tune dπ orbital energies. Work is currently underway on these and related projects.

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Supporting Information Available: Listings of crystal data and structure refinement details, atomic parameters and U(eq) values, anisotropic thermal parameters, bond lengths, and bond angles, a fully labeled ORTEP diagram of the complex cation, an electronic spectrum showing the spectroelectrochemical oxidation of *trans*-$[Ru(py)_4(2\text{-Cl-pcyd})_2]$, and a table of cyclic voltammetry data. This material is available free of charge via the Internet at http://pubs.acs.org.

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