ion pairing[22b] within the low-dielectric solvent CD_2Cl_2. We are presently attempting a more extensive study of these three electron-exchange reactions in order to address these issues.

Conclusions

The redox and reaction chemistry revealed from this study complement that reported previously for other organometallic porphyrins, particularly the iron complexes. The nature of the reactions in Scheme I is similar to that reported by Kadish for various M(Por)R and $M(Por)R_2$ species; however, the details of the reactions in Scheme I are unique to Ru. First, the $[Ru(OEP)(C_6H_5)_n]^{+/0/-}$ complexes exhibit electron-transfer reactions easily studied by ^1H NMR spectroscopy. While electron exchange is likely to occur with other organometallic porphyrin complexes, the measurable differences in k_{ex} resulting from the subtle structural variations make the present systems particularly attractive. Second, $[Ru(OEP)(C_6H_5)]^+$, unlike the $[Fe(Por)(C_6H_5)]^+$ species,[7] does not N-arylate. Kadish has shown[7] that by varying the chemical nature (presumably, electron-withdrawing ability) of the Ar group, the propensity of the $[M(Por)(Ar)]^+$ to N-arylate is controllable. Presumably, $[Ru(OEP)(C_6H_5)]^+$ possesses a central Ru (Ru^{IV}, using the electron count formalism employed herein) that possesses enough electron density to support the C_6H_5 ligand.[3] We hope that, by preparing the analogous Ru(OEP)(Ar) species[5c] with Ar = $C_6H_4CH_3$, C_6F_5, or $C_6H_2F_3$, we can modulate the reactivity of the $[Ru(OEP)(AR)]^+$ species. Third, the $M(Por)(C_6H_5)_2$ species has not been reported for M = Fe, so direct comparison is not possible. However, the salient characteristics of $Ru(OEP)(C_6H_5)_2$ are the N-arylation of the cation, the porphyrin-localized first reduction, and the decomposition of the dianion linking the $Ru(OEP)(C_6H_5)_n$ redox schemes. Again, variation of the Ar group will provide additional information about the properties and reactivity of $[M(Por)(R)_n]^{+/0/-/2-}$ complexes. Combined with the extensive information gathered by others on related metals, our results with $Ru(Por)(R)_n$ complexes may permit a comprehensive and coherent picture of the properties of organometallic porphyrin complexes.

Acknowledgment. We thank the Purdue Research Foundation for financial support and Drs. Claude R. Jones and Scott Woehler for their assistance with NMR experiments. We thank Lance Safford for his assistance with the fast-scan cyclic voltammetry experiments. Professor Ian P. Rothwell provided C_6D_5Li and many useful comments. NMR experiments were performed on instruments funded by NIH Grant RR01077 and NSF Grant BBS-8714258.

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A Pentaammineruthenium Mixed-Valence Complex with 1,4-Dicyanamido-2,3,5,6-tetrachlorobenzene Dianion as Bridging Ligand: Symmetry-Attenuated Electronic Coupling between Redox Sites

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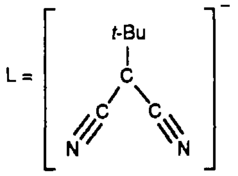
The dinuclear complex $[(NH_3)_5RuLRu(NH_3)_5][Cl]_4$, where L^{2-} = 1,4-dicyanamido-2,3,5,6-tetrachlorobenzene dianion, has been prepared. UV-vis-near-IR spectroscopy and electrochemical data strongly indicate that its mixed-valence derivative is a weakly coupled case, with H_{ab} estimated to be 185 cm^{-1}. It is suggested that coupling between the metal centers via the low-energy LMCT system is symmetry forbidden, while coupling via the high-energy LMCT system is energetically unfavorable.

Introduction

In coordination chemistry, mixed-valence complexes have been used to study the factors that control the extent of donor and acceptor interaction and the rates of thermal electron transfer.[1] Of primary importance to the degree of electronic coupling between donor and acceptor is the nature of the bridging ligand. For example, in the mixed-valence "Creutz–Taube" ion[2]

electronic coupling is believed to occur via ruthenium dπ and pyrazine pπ^* orbital mixing (a resonance-exchange mechanism) and is sufficiently strong to delocalize charge in the ground state, resulting in a partial oxidation state of 2.5 for each ruthenium.[3] Replacement of the bridging pyrazine with saturated 1,4-dithiane eliminates the π^* pathway for resonance exchange. This results in a trapped valence ground state in which Ru(II) is weakly coupled to Ru(III).[4] An alternative resonance-exchange mechanism for electronic coupling is that which occurs via the mixing of ruthenium dπ and the bridging ligand's highest occupied molecular orbital (HOMO). This mechanism (also called superexchange or hole transport) accounts for the delocalized mixed-valence state observed in $[(NH_3)_5Ru{-}L{-}Ru(NH_3)_5]^{4+}$,[5] where



There are only a few examples of mixed-valence complexes in which metal–metal coupling occurs via a superexchange mechanism,[5,6] and because of this, not much is known concerning the dependence of the superexchange mechanism for electronic coupling on the nature of the bridging ligand.

In this study, we have prepared a dinuclear pentaammineruthenium mixed-valence complex, using the bridging ligand 1,4-dicyanamido-2,3,5,6-tetrachlorobenzene dianion (L^{2-}). It has already been demonstrated[7,8] that anionic phenylcyanamide ligands are both σ and π donating and that the cyanamide group is coplanar with the phenyl ring even when coordinated to Ru(III), suggesting a significant degree of π coupling. Coupling between

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0020-1669/90/1329-3641$02.50/0

π-symmetry donor and acceptor ruthenium orbitals bridged by an easily oxidized aromatic π-donor ligand should occur via a superexchange mechanism. A discussion of the factors that influence the extent of electronic coupling in this complex and in particular the relative symmetry of the acceptor wave function and the bridging ligand's HOMO is presented.

Experimental Section

Physical Measurements. UV-vis spectra were taken on a Perkin-Elmer Lambda 4b spectrophotometer. The near-IR region was monitored by using a Cary 14 spectrophotometer. Equipment used to perform cyclic voltammetry measurements has been previously described.[7] Nonaqueous cyclic voltammetry was performed in dry acetonitrile[9] (0.1 M tetrabutylammonium hexafluorophosphate, TBAH) at 25 °C, with a three-electrode system consisting of platinum-disk working (BAS 1.6-mm diameter) and wire counter electrodes and a silver wire quasi-reference electrode. Ferrocene ($E°$ = 400 mV vs NHE)[10] was used as an internal reference. Aqueous cyclic voltammetry was performed in distilled water (0.1 M NaCl) at 25 °C, with a three-electrode system consisting of glassy-carbon working (BAS 5-mm diameter), platinum-wire counter, and saturated calomel reference electrodes. Elemental analysis was performed by Canadian Microanalytical Services Ltd.

Materials. All chemicals and solvents were reagent grade or better. Tetraphenylarsonium chloride monohydrate (Strem) was used as received. Tetrabutylammonium hexafluorophosphate (Aldrich) was recrystallized twice from ethanol/water and vacuum dried at 118 °C. $[(NH_3)_5RuCl][Cl]_2$,[11] $[(NH_3)_5Ru(OH_2)][PF_6]_2$,[12] $[(NH_3)_5Ru(2,3,5,6\text{-}Cl_4pcyd][ClO_4]_2$[7,8] (2,3,5,6-$Cl_4$pcyd = 2,3,5,6-tetrachlorophenylcyanamide anion), 2,3,5,6-tetrachloro-1,4-phenylenediamine[13] were prepared by literature methods.

Preparation of the Tetraphenylarsonium Salt of the 1,4-Dicyanamido-2,3,5,6-tetrachlorobenzene Dianion, $[AsPh_4]_2[L]$. Benzoyl chloride (26 g, 0.18 mol) in 200 mL of acetone was added dropwise to a magnetically stirred, refluxing solution of ammonium thiocyanate (14 g, 0.18 mol) in 200 mL of acetone. After the addition of the benzoyl chloride was complete, the reaction mixture was allowed to reflux for 5 min to ensure complete formation of the benzoyl isothiocyanate reactant. 2,3,5,6-Tetrachloro-1,4-phenylenediamine (9.2 g, 0.03 mol) in 100 mL of acetone was then added dropwise to the refluxing reaction mixture, precipitating the thiourea derivative. After the addition was complete, the reaction mixture was refluxed for 15 min and filtered hot, and the pale yellow thiourea derivative was washed with acetone, water, and then acetone and allowed to air dry. The thiourea derivative (6.2 g, 0.018 mol) was dissolved in 50 mL of 2 M NaOH by boiling for 10 min. The solution was cooled to 65 °C, and a solution of lead(II) acetate trihydrate (7.7 g, 0.021 mol) in 30 mL of water was slowly added with constant stirring. Immediately, black lead sulfide and white polymeric lead hydroxide coprecipitated. The reaction mixture was stirred at a temperature no greater than 70 °C until complete conversion to lead sulfide (approximately 5 min; excess heating will polymerize the ligand), and then filtered; the filtrate was cooled in an ice bath. Glacial acetic acid (6.1 g) was added to neutralize the filtrate and precipitate the neutral ligand, LH_2. The white product was filtered out and washed copiously with water until the smell of acetic acid was no longer noticeable. Under argon and with degassed solutions, crude LH_2 (3.2 g, 0.01 mol) was deprotonated by dissolving it in 100 mL of 2 M NaOH and precipitated from solution as $[AsPh_4]_2[L]$ by the addition of a solution of 9.4 g (0.023 mol) of $AsPH_4Cl\cdot H_2O$ in 100 mL of 2 M NaOH. The yellow product was filtered out, washed three times with 10 mL of water, and then vacuum dried. The product may be recrystallized from warm dimethyl sulfoxide. Yield: 7.0 g (66%). $[AsPh_4]_2[L]$ should be stored under argon but can be handled exposed to air for short periods of time without oxidation to the blue radical anion.

Preparation of $[\{(NH_3)_5Ru\}_2L][Cl]_4$. $[AsPh_4]_2[L]$ (0.53 g) and $[(NH_3)_5Ru(OH_2)][PF_6]_2$ (0.60 g) were placed in a 100-mL round-bottom flask fitted with a septum, and the flask was vacuum degassed and then placed under argon. Vacuum-degassed acetone (80 mL) was then transferred under argon to the reactant flask, and the mixture was stirred under argon for 2 h. The solution was then filtered to remove the $[AsPh_4][PF_6]$ precipitate and exposed to air to oxidized the complex to ruthenium(III). Addition of 3.2 g of tetrabutylammonium bromide in 25 mL of acetone to the filtrate precipitated the bromide salt of the complex. The crude product was filtered out and vacuum dried, yielding 0.39 g. The crude bromide salt was dissolved in a minimum amount of 0.3 M aqueous NaCl and loaded onto a 2.5 × 30 cm Sephadex C25-120 cation-exchange resin column. Elution with 0.3 M NaCl separated a faint yellow band that was not identified. Elution with 1.0 M NaCl separated a dark blue band that we tentatively identify as the mononuclear complex of L^{2-}. The desired dinuclear complex was obtained by elution with 2.0 M NaCl. The green-blue eluent was collected, concentrated to approximately 100 mL, and then stored at 4 °C for 16 h. This resulted in precipitation of the chloride salt, which was filtered out and washed with ice cold water. The product was recrystallized by acetone diffusion into an aqueous solution of the complex and vacuum dried. Yield: 20 mg (5%). Anal. Calcd for $C_8H_{30}N_{14}Cl_8Ru_2$: C, 11.89; H, 3.74; N, 24.26; Cl, 35.09. Found: C, 12.35; H, 3.85; N, 24.45; Cl, 34.55. The analysis suggests that a fractional amount of acetone has crystallized with the complex. This was confirmed by infrared spectroscopy. Unfortunately, vacuum drying at elevated temperatures to drive off this solvent of crystallization resulted in the decomposition of the complex.

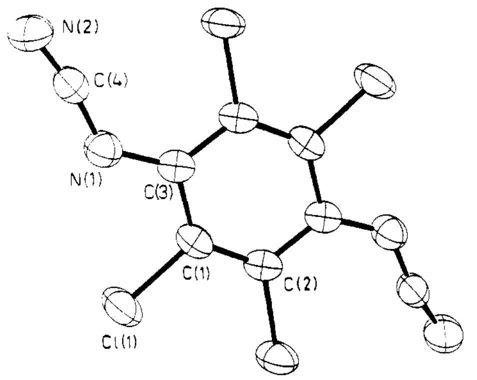

Figure 1. ORTEP diagram of 1,4-dicyanamido-2,3,5,6-tetrachlorobenzene dianion bridging ligand. The $[AsPh_4]^+$ counterions have been excluded for simplicity.

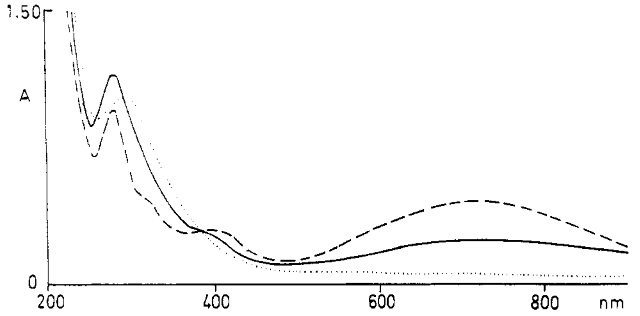

Figure 2. UV-vis spectra of $[2,L^{2-},2]$ (···), $[2,L^{2-},3]$ (—), and $[3,L^{2-},3]$ (- - -) in D_2O. All spectra are 8.3×10^{-5} M in metal complex.

Results and Discussion

A crystal structure determination of the tetraphenylarsonium salt of the bridging ligand L^{2-} has been performed,[14] and an ORTEP diagram of the ligand is shown in Figure 1. The cyanamide groups are in a trans configuration and are almost in the plane of the benzene ring; the terminal nitrogens (N(2)) being only 0.290 Å out of the plane. In addition, a bond length of 1.360 Å between the cyanamides' amine nitrogen and aromatic carbon (C(3)-N(1)) suggests a great deal of double-bond character and a strong π interaction between the cyanamide groups and the benzene ring. Although we were unable to perform crystallographic study of the dinuclear complex, we expect the ligand's conformation to be retained when coordinated to ruthenium(III), since a crystal structure of the monomer complex, $[(NH_3)_5Ru(2,3\text{-}Cl_2pycd)]^{2+}$, shows the phenyl ring to be nearly coplanar with the coordinated cyanamide group.[8] Electronic coupling between π-donor Ru(II) and π-acceptor Ru(III) bridged by L^{2-} would be expected to occur via a superexchange mechanism.

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Table I. Electronic Spectral Data[a] for $[(NH_3)_5RuLRu(NH_3)_5]^{2+,3+,4+\,b}$ and $[(NH_3)_5Ru(2,3,5,6\text{-}Cl_4pcyd]^{2+}$ (I)[c]

		LMCT		
complex	$\pi-\pi^*$	$b_1^* \leftarrow b_2$	$b_1^* \leftarrow b_1$	IT
$[2,L^{2-},2]$	212 (4.49), 297 (4.28)			
$[2,L^{2-},3]$[d]	218 (4.52), 284 (4.34)	402[e]	735 (3.64)	1220 (2.76)
$[3,L^{2-},3]$	225 (4.45), 278 (4.23), 325[e]	402 (3.67)	713 (3.93)	
I	222 (4.51), 265 (4.04), 306[e]	374 (3.43)	585 (3.63)	

[a] Data in nm (log ϵ). [b] In D_2O. [c] In H_2O. [d] A correction for the comproportionation equilibrium has not been made. [e] Shoulder.

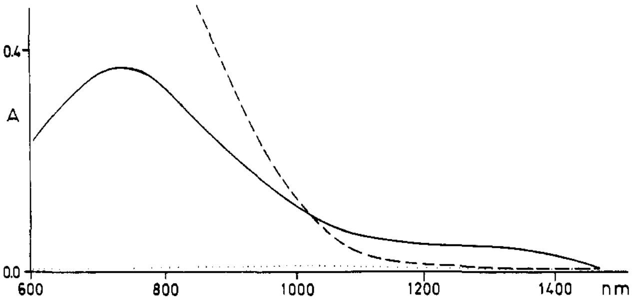

Figure 3. Near-IR spectra of $[2,L^{2-},2]$ (···), $[2,L^{2-},3]$ (—), and $[3,L^{2-},3]$ (- - -) in D_2O. All spectra are 8.3×10^{-5} M in metal complex.

The dinuclear complex, $[\{(NH_3)_5Ru\}_2L][Cl]_4$ ($[3,L^{2-},3]$), was prepared in low yields by the reaction of $[Ru(NH_3)_5(OH_2)]^{2+}$ with L^{2-} in acetone, under argon, followed by air oxidation. It is probable that the coordination of L^{2-} to one pentaammineruthenium(III) has a deactivating effect on the uncoordinated cyanamide group and may account for the low yield of the dinuclear complex. Reducing $[3,L^{2-},3]$, under argon, with Zn/Hg for approximately 2 h results in the formation of the pale yellow $[2,L^{2-},2]$ species. Upon exposure to air, the complex oxidizes to the green $[2,L^{2-},3]$ species and finally back to the fully oxidized $[3,L^{2-},3]$ complex. The UV–vis spectra of these complexes are given in Figure 2. The assignments of the major bands (Table I) are based on those of the analogous mononuclear complexes.[7,8] Importantly, the low-energy LMCT band of the mononuclear complex, $[(NH_3)_5Ru(2,3,5,6\text{-}Cl_4pcyd]^{2+}$, in Table I, has approximately half the absorptivity of that of the binuclear $[3,L^{2-},3]$ complex. A subtle difference is observed in the near-IR spectrum of $[2,L^{2-},3]$ (Figure 3). The LMCT band at 713 nm broadens, and a definite but weak low-energy shoulder appears. This shoulder is not seen in the $[2,L^{2-},2]$ and $[3,L^{2-},3]$ complexes, is independent of complex concentration (range 3.5×10^{-5} to 2.5×10^{-4} M), and is assigned to an intervalence transfer (IT) transition. No other features for the $[2,L^{2-},3]$ ion are observed up to 2000 nm. A second-derivative plot gave a band maximum at 1220 nm. The band is very broad and has an extinction coefficient of 570 M^{-1} cm^{-1}.[15] The low intensity and broad nature of this band are good indicators that we are dealing with a weakly coupled mixed-valence system, and this is clearly demonstrated by the cyclic voltammetry of the system.

Table II. Reduction Potentials[a] for $[(NH_3)_5Ru(2,3,5,6\text{-}Cl_4pcyd][ClO_4]_2$ (I),[b] $[(NH_3)_5RuLRu(NH_3)_5][Cl]_4$ (II),[b] and $[AsPh_4]_2[L]$ (III)[c]

species	Ru(III/II)	L(−/2−)	L(0/1−)
I	−0.008[e]		
II	−0.033[d]	0.892[e]	1.032[f]
III		−0.025[e]	0.570[e]

[a] Data in volts vs NHE. [b] Aqueous solution, 0.1 M NaCl, glassy-carbon working electrode, 25 °C, and 100 mV/s. [c] Acetonitrile solution, 0.1 M TBAH, platinum working electrode, 25 °C, and 100 mV/s. [d] Two overlapping Ru(III/II) couples. [e] Quasi-reversible. [f] Anodic peak only.

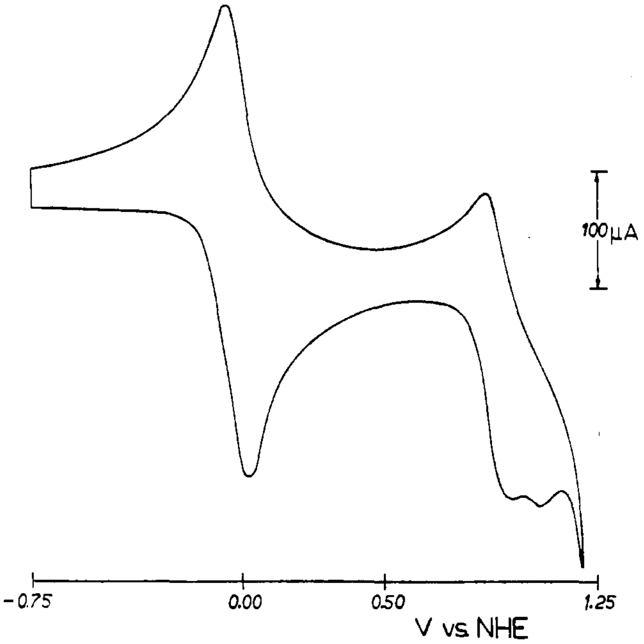

Figure 4. Cyclic voltammogram of a 1 mM $[(NH_3)_5RuLRu(NH_3)_5][Cl]_4$ aqueous solution (0.1 M NaCl, pH 7.1, 25 °C) at 100 mV/s.

The electrochemical data of the free ligand, L^{2-}, in acetonitrile, and complexes, in aqueous solution, are given in Table II. The cyclic voltammogram of L^{2-} shows two reversible redox couples (Table II) corresponding to the following reaction scheme:

$$L^{2-} \underset{L(-/2-)}{\overset{-e^-}{\rightleftharpoons}} L^- \underset{L(0/-)}{\overset{-e^-}{\rightleftharpoons}} L$$

where L is *N,N'*-dicyano-2,3,5,6-tetrachloroquinonediimine, and L^-, its radical anion. Coordination to two pentaamineruthenium(III) moieties shifts the first ligand reduction couple anodically by 917 mV. This stabilization is due largely to the π-acid properties of pentaammineruthenium(III).[7,8] The cyclic voltammogram (Figure 4) of a 10^{-3} M aqueous solution of $[3,L^{2-},3]$ shows a reduction couple centered at −0.033 V vs NHE with an anomolously large peak to peak separation of 92 mV and peak currents approximately twice as large as that for the reduction of the radical-anion bridging ligand at 0.892 V vs NHE. Under the same conditions, the monomer complex, $[(NH_3)_5(2,3,5,6\text{-}Cl_4pcyd]^{2+}$, has a ruthenium(III/II) couple at −0.008 V vs NHE with a 60-mV separation between anodic and cathodic waves. We have prepared the dinuclear complexes of the tetramethyl and unsubstituted bridging ligands.[14] The position of the wave corresponding to the reduction of the radical-anion bridging ligand shifts with the nature of the phenyl ring substitution in a way that is consistent with the corresponding wave of the free-radical-anion ligand.[16] In addition, the two reduction waves of the complexed dianion ligands are completely free of solvent cutoff potential and the ratio of Ru(III/II) reduction to ligand reduction peak currents is very close to two. Similar peak shapes, with large oxidation peak to reduction peak separations, have been observed in other weakly coupled systems, involving dipyridyl-bridged bis(pentaammineruthenium) dinuclear complexes.[17,18] Here the peak to peak separations ranged from 78 mV for the 4,4'-dipyridylmethane-bridged species to 127 mV for the complex bridged by 4,4'-dipyridylamine. In all of the cases, two successive one-electron processes are predicted; however, their proximity results in only a single wave being resolved. The comproportionation constant

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(15) Similar features have been seen in mixed-valence complexes containing dicyanobenzene bridges: Richardson, D. E.; Taube, H. *J. Am. Chem. Soc.* **1983**, *105*, 40.

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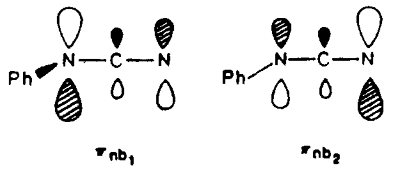
(K_c) of each dipyridyl-bridged species was determined by a redox titration of the IT band,[18] and K_c was found to be ≤26. This measurement was not feasible in our case due to the instability of the complex to oxidation and the proximity of the IT band to the LMCT band; however, K_c is predicted to be of magnitude similar to those above and is characteristic of a weakly coupled system.

It is possible to estimate the resonance integral, H_{ab}, for the [2,L^{2-},3] complex by using the expression, derived by Hush[1,19]

$$H_{ab} = \frac{2.05 \times 10^{-2}}{r}[(\epsilon_{max}\Delta\bar{\nu}_{1/2})\bar{\nu}_{max}]^{1/2}$$

where ϵ_{max} is the extinction coefficient at IT band maximum, in M^{-1} cm^{-1}, $\bar{\nu}_{max}$ is the IT band energy at ϵ_{max}, in cm^{-1}, $\Delta\bar{\nu}_{1/2}$ is the bandwidth at $\epsilon_{max}/2$, in cm^{-1}, and r is the separation between redox sites in angstroms. An upper limit of the degree of electronic coupling between metal centers was estimated to be 185 cm^{-1}, assuming a value of r = 15.8 Å and using the data in Table I and Figure 3.

The foregoing results are surprising since the delocalized nature of the π-nonbonding electrons on the bridging ligand should be favorable for strong electronic coupling between the metal centers. If π coupling between the cyanamide groups and the phenyl ring is continuous, then a discontinuity must be associated with the nature of the π interaction of the cyanamide group with Ru(III). This interaction and the origin of the LMCT transitions have been presented elsewhere.[7] In brief, the cyanamide anion group can be represented by the resonance structures $Ph{-}N{=}C{=}N^- \leftrightarrow Ph{-}N^-{-}C{\equiv}N$. When the ligand is bonded to Ru(III), it is expected that the resonance form $Ph{-}N{=}C{=}N^-$ will be preferentially stabilized. The two nonbonding electron pairs on the cyanamide group can delocalize into the cyanamide three-atom π system, and their qualitative molecular orbitals can be represented by



where the size of the atomic orbital approximates its contribution to the molecular orbital.[20] The two π_{nb} MOs are orthogonal to each other and not equivalent in energy because only the π_{nb_1} MO has the correct symmetry to interact with the phenyl π system. Ru(III) has a partially filled π-symmetry 4d orbital that will preferentially interact with the less stable π_{nb_2} MO. This results in an allowed $b_1^* \leftarrow b_1$ ($\pi_{nb_2} \rightarrow d\pi$) low-energy LMCT transition seen at 735 nm in the spectrum of the mixed-valence complex. The high-energy LMCT transition at 402 nm in the same spectrum is assigned to a formally forbidden $b_1^* \leftarrow b_2$ ($\pi_{nb_1} \rightarrow d\pi$). It follows from the above that *the Ru(III) π-acceptor orbital is orthogonal to the phenyl ring π system.* If symmetry arguments were absolute, there would be no coupling at all between donor and acceptor in the mixed-valence complex. However, small distortions from planarity will relax this rule and allow for some degree of coupling. We conclude that coupling between metal centers via the low-energy LMCT system is symmetry forbidden, while coupling via the high-energy LMCT system is energetically unfavorable.

The importance of matching symmetry of donor and acceptor wave functions to electronic coupling has a firm theoretical basis in Mulliken's charge-transfer theory[21] and in recent theories of intramolecular electron transfer.[22,23] Where a bridging ligand exists between donor and acceptor, the symmetry of the ligand orbitals used in electronic coupling must coincide with that of donor and acceptor for there to be strong coupling.

A new class of molecular metals has been synthesized having the stoichiometry $Cu(DCNQI)_2$, where DCNQI is the radical anion of a *N,N'*-dicyanoquinonediimine derivative.[24] In one study, significant transverse conductivity was measured in the direction of the Cu–DCNQI–Cu bridges and it was suggested that the copper ions are significantly coupled to the DCNQI π system.[25]

The radical anion of DCNQI is simply the one-electron oxidation product of a 1,4-dicyanamidobenzene dianion bridging ligand of the type used in this study. We are currently investigating the coordination chemistry of mononuclear and dinuclear copper complexes of phenylcyanamide anion ligands in order to model the copper site in $Cu(DCNQI)_2$ molecular metals.

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