modes and the latter through strong coupling to carbonyl modes (particularly in the D_4 clusters)—and only ν_{M_2H}(asym) is likely to be a "pure" mode.

It is to be hoped that the principles we have used in this study may enable the spectra of other clusters with multiple hydride ligands to be interpreted satisfactorily.

Experimental Section

$[H_4Ru_4(CO)_{12}]$ and $[D_4Ru_4(CO)_{12}]$ were prepared by the literature method.[3] Samples of $[H_4Os_4(CO)_{12}]$ and $[D_4Os_4(CO)_{12}]$ were kindly provided by Dr. B. F. G. Johnson, University of Cambridge. Infrared spectra of samples in KBr disks were measured on a Digilab FTS-20 FT-IR spectrophotometer; an RIIC low-temperature cell with liquid N_2 as coolant was used for the low-temperature (ca. 100 K) spectra. The Raman spectra were recorded on a Model 1401 Spex Raman spectrophotometer, equipped with a Spectra Physics Model 165 Kr ion laser (exciting line 647.1 nm) with incident power of ca. 250 mW.

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Investigation of the Redox States of $[Ru(bpy)_2CN]_2CN^+$: Evidence for Valence Delocalization of the Singly Oxidized Complex

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A spectroelectrochemical study of both the oxidized and reduced forms of $[Ru(bpy)_2CN]_2CN^+$ is reported. Th UV–vis spectra of the parent and reduced species indicate that the complex consists of two identical chromophores, which are nearly identical with the $Ru(bpy)_2(CN)_2$ chromophore, even though one ruthenium is bound to the carbon of the bridging CN while the other is nitrogen bound. Only the shift in the bridging CN stretching frequency with reduction offers any distinction between the two metal centers. The one-electron oxidation product of the bimetallic species is assigned as valence delocalized on the basis of the following observations: (1) only two CN stretches are observed in the oxidized form, (2) the shift to higher energy of the terminal CN stretches for the bimetallic species is half of that observed upon oxidation of the monometallic complex, (3) the sharpness and solvent independence of the near-IR band is not consistent with Hush predictions for the IVT band, and (4) the separation of the oxidation waves implies a comproportionation constant for the bimetallic species of 1.38×10^{10} (assuming no difference in metal centers) comparable in magnitude to other delocalized systems.

Introduction

Recently, there has been a great deal of interest in the synthesis of new coordination compounds in which a photosensitizer center is bound to a reactive center that acts as an electron donor, electron acceptor, or energy acceptor.[1] The presence of both moieties in the same complex alleviates the need for long photosensitizer lifetimes as well as high concentrations of the reactive moiety. These multimetallic coordination compounds are also being suggested as possible multielectron donors or acceptors, a necessary requirement for artificial photosynthesis.[1,2] Another application is the design of supramolecular photochemical devices using these coordination compounds as building blocks.[2] Central to the design of all of these schemes is the requirement of efficient electron or energy transfer between the two centers. Since there is usually no direct overlap between two metal centers, the transfer pathway is mediated by the bridging ligand. Several methods for evaluating the degree of communication between the centers exist in the literature.[3-17] With the synthesis and subsequent investigations of the Creutz–Taube ion, a great deal of controversy has arisen concerning strongly interacting systems approaching a delocalized limit in terms of the valence shell.[3-17] Theoretical treatments of these systems have contributed much to the basic understanding of electron-transfer theory.[4,11-13,15,18-30] The complex $[Ru(bpy)_2CN]_2CN^+$, thus, has multifold aspects of interest. It not only meets the requirements of a photosensitizer strongly absorbing in the visible region and possessing a long-lived emission (τ = 90 ns)[14] but also possesses additional coordination sites (CN) so that supramolecular species can be made. Indeed, such systems based on a $[Ru(bpy)_2CN]_2CN^+$ building block have already been reported.[2] In addition, the mixed-valence species offers the op-

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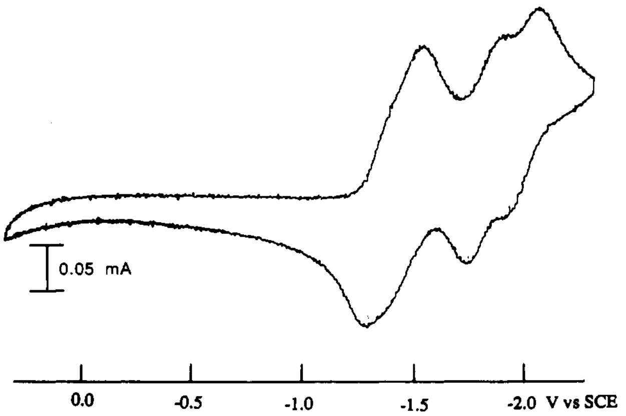

Figure 1. Cyclic voltammogram of $\{[Ru(bpy)_2(CN)]_2(CN)\}\{PF_6\}$ in 0.1 M TBAH/DMF at Pt and at a 200 mV/s scan rate.

portunity to investigate the extent of interaction for a nonsymmetrically bridged system. This study focuses on the assignment of the redox orbitals for this complex and the effect of the nonsymmetrical bridge with respect to optical and redox properties of the complex. In addition, the degree of delocalization for the mixed-valence species will be investigated and interpreted in terms of the unsymmetrical nature of the complex.

Experimental Section

Chemicals. Anhydrous, 99+% *N,N*-dimethylformamide (DMF) and acetonitrile purchased from Aldrich were used as supplied from the manufacturer. The sample of $\{[Ru(bpy)_2CN]_2CN\}\{PF_6\}$ was used as received from Dr. Franco Scandola. *cis*-$Ru(bpy)_2(CN)_2$ was synthesized according to the method of Demas et al.[18] Tetrabutylammonium hexafluorophosphate (TBAH) was purchased from Aldrich, recrystallized twice from ethanol, and dried under vacuum.

Electrochemistry. A solution of the sample (5 mM for FTIR and resonance Raman; 0.5 mM for UV/vis) and TBAH (100 mM) was prepared in a Vacuum Atmospheres Co. drybox under nitrogen atmosphere. The solution was loaded into an electrochemical H-cell with Pt-mesh working and counter electrodes and a saturated calomel reference electrode (SCE). Voltammetry was carried out with a Princeton Applied Research (PAR) Model 173 potentiostat/175 universal programmer system connected to a Nicolet 3091 digital oscilloscope, while the extent of reduction was monitored with an in-line PAR Model 379 digital coulometer. The data were downloaded to an AT&T 6300 computer for analysis.

Resonance Raman Spectra. The sealed H-cell was placed in the sample compartment of a Jarrell-Ash double 1-m Raman spectrometer equipped with a cooled RCA c31034A photomultiplier tube, and the reductions were carried out in situ. A Spectra Physics Model 171 Ar^+ ion laser was used either to serve as a stand alone source or to pump a Spectra Physics Model 375 dye laser with Coumarin 540 dye (Exciton). The spectra were collected and stored on computer for analyses. All frequencies were determined relative to the solvent peak at 865 cm^{-1} (DMF) and are expected to be accurate to ~ 2 cm^{-1}.

FTIR Spectra. A Mattson Polaris FTIR spectrometer equipped with an NEC Powermate 2 computer, KBr beamsplitter, and MCT detector was used to obtain the spectra. The FTIR spectra were acquired by using a specular reflectance cell.[31] The spectra were acquired by reflecting off of the polished platinum working electrode, which was flush against the cell window (<6 μm). A potential was applied to the working electrode, and the extent of reduction/oxidation was monitored by changes in the spectrum.

Electronic Spectra. The sample reductions were carried out in the drybox, and the redox products were transferred to a 1 mm path length cell, which was sealed and placed in a Cary 2300 spectrometer.

Nature of the Reduced Species

Electrochemistry. The cyclic voltammogram of $[Ru(bpy)_2(CN)]_2(CN)^+$ in DMF between +0.35 and −2.30 V vs SCE is shown in Figure 1. Two pairs of redox couples can be seen. For the first pair, the two redox processes are almost superimposed with approximate $E_{1/2}$'s of −1.40 and −1.48 V. The second pair shows a slightly greater separation with $E_{1/2}$ values of −1.84 and −2.00 V. The separation between the anodic and cathodic peaks for each couple ($\sim$60 mV) as well as the regeneration of the CV upon bulk electrolysis passed any of the redox couples maintains that all four redox processes are completely reversible. Sine the two ruthenium centers are identical with the expection that one is bound to the nitrogen at the CN bridge while the other is bound to the carbon, it is reasonable that the first redox electron enters a bpy orbital on the carbon-bound side, since the bridge will be acting as a weaker σ base and a better π acid with respect to the nitrogen-bound side. However, it should be noted that the small separation of redox waves for the complex suggests that the energy difference between the redox sites is relatively small and due in large part to electrostatic effects.

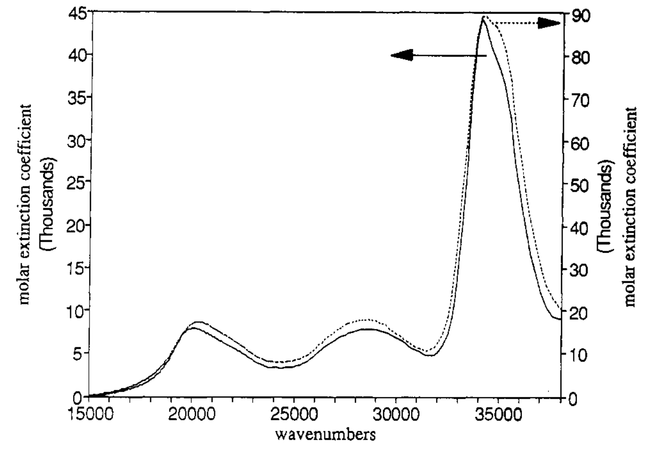

Figure 2. Electronic spectra of $[Ru(bpy)_2(CN)]_2(CN)^+$ (dotted) and $Ru(bpy)_2(CN)_2$ (solid) in DMF. Arrows indicate the appropriate extinction coefficient axis for each.

Electronic Spectra. The near degeneracy of bpy LUMO's suggested by the electrochemistry is also reflected by the UV–vis spectra of $[Ru(bpy)_2(CN)]_2(CN)^+$ and $Ru(bpy)_2(CN)_2$. As shown in Figure 2, the two spectra exhibit similar features with almost a perfect overlap throughout the UV–vis region, the only difference being the approximate 2-fold intensity increase of the binuclear species. On the basis of the assignments of the mononuclear complex,[32] the peak at 35.0×10^3 cm^{-1} and its high-energy shoulder can be assigned as a $\pi \rightarrow \pi^*$ intraligand transition, while both the 20.0×10^3 and the 28.5×10^3 cm^{-1} peaks correspond to MLCT's. The relatively small effect of the binding site at the bridging CN is perhaps best demonstrated by the single peak in the visible portion of the spectrum. The peaks are at the same energy ($\pm$300 cm^{-1}) and exhibit the same structure (the high-energy shoulder has been assigned for the mononuclear species as vibronic) for both complexes, indicating that the two lowest states are nearly degenerate. Although it could be argued that the increase in the d-orbital energies of the N-bound Ru due a decreased interaction with the CN π^* is matched by the increase of the bpy π^* caused by an increased interaction with the dπ with no net change in the MLCT energy, the electrochemical data suggest that the changes in orbital energy must be small.

With each consecutive reduction of binuclear species, there is a monotonic decrease in the $\pi \rightarrow \pi^*$ intensity at 35.0×10^3 cm^{-1} indicative of biyridine-localized redox orbitals (Figures 2–4).[33-39]

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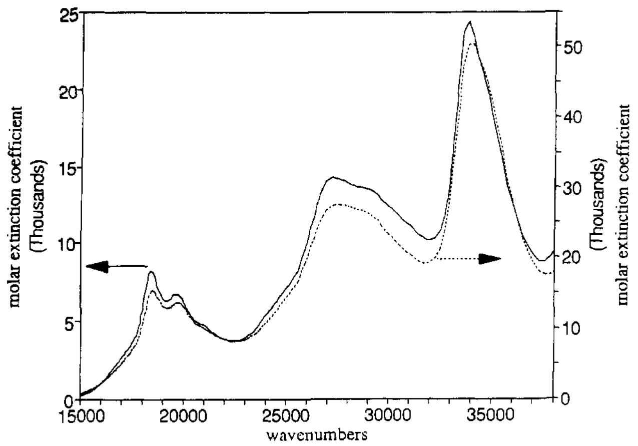

Figure 3. Electronic spectra of $[Ru(bpy)_2(CN)]_2(CN)^-$ (dotted) and $Ru(bpy)_2(CN)_2^-$ (solid) in DMF. Arrows indicate the appropriate extinction coefficient axis for each.

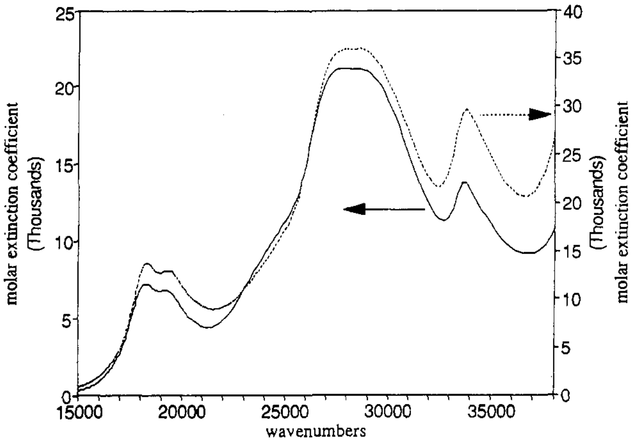

Figure 4. Electronic spectra of $[Ru(bpy)_2(CN)]_2(CN)^{3-}$ (dotted) and $Ru(bpy)_2(CN)_2^{2-}$ (solid) in DMF. Arrows indicate the appropriate extinction coefficient axis for each.

Concomitant with this intensity decrease is an increase in intensity around 28 × 10^3 cm^{-1}, consistent with the growth of $\pi^* \rightarrow \pi^*$ transitions involving a redox electron. A comparison of the binuclear two electron and the mononuclear one electron species as well as the binuclear four electron and the mononuclear two electron indicates a one-to-one correspondence for every peak in the spectra (Figures 3 and 4). Although the relative intensities deviate slightly, the energies of the transitions (and thus the states) match almost exactly. Thus, it appears that not only are the redox orbitals bpy localized but the behavior of the complex is consistent with two individual chromophores, both of which are similar to that of the mononuclear species.

Vibrational Spectra. The resonance Raman spectra for the binuclear redox series are identical with those obtained for the mononuclear complex[32] with the expected differences in intensities due to differing number of bipyridines. As in the previous study, a peak is observed at ~1591 cm^{-1} in the reduced bpy spectrum supportive of the 10-cm^{-1} shift with reduction of the bipyridines as reported therein. Since the spectral interpretation is identical with that given in the monometallic study, no further discussion will be given here.

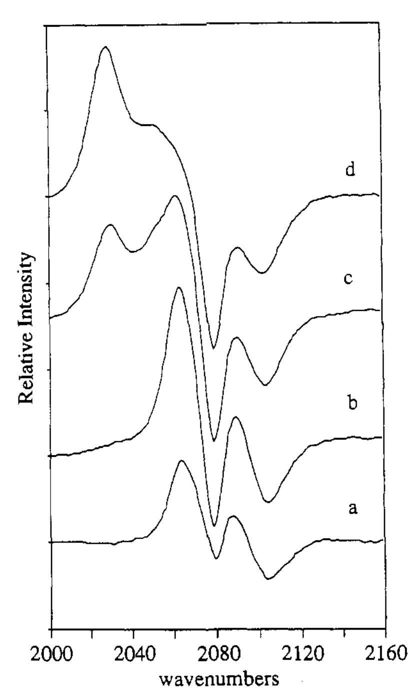

Figure 5. Difference FTIR spectra for 5.7 mM $[Ru(bpy)_2(CN)]_2(CN)^{1-n}$ in 0.1 M KI/DMF at (a) −1.4 V ($n \sim 1$), (b) −1.6 V ($n \sim 2$), (c) −1.8 V ($n \sim 3$), and (d) −2.1 V ($n \sim 4$). Negative absorbance corresponds to the unreduced complex whereas positive absorbance corresponds to the total absorbance of the resulting mixture of reduction products.

Table I. C≡N Stretching Frequencies (cm^{-1}) for $Ru(bpy)_2(CN)_2^n$ and $[Ru(bpy)(CN)]_2CN^{n+1}$ and Suggested Assignments[a]

	$Ru(bpy)_2(CN)_1^n$		$[Ru(bpy)(CN)]_2CN^{n+1}$		
n	A	S	T_C	T_N	B
+1	2095[b]	2117[b]	2096	2096	2108
0	2071/2069[b]	2081/2077[b]	2079	2079	2103
−1	2056	2066	2065[c]	2079[c]	2088[c]
−2	2029	2043	2065[c]	2065[c]	2088[c]
−3			2029[c]	2065[c]	2057[c]
−4			2029[c]	2029[c]	2057[c]

[a] A = antisymmetric; S = symmetric; T_C = terminal CN of C-bound ruthenium; T_N = terminal CN of N-bound ruthenium; B = bridging CN. [b] Solvent is CH_2Cl_2; all others in DMF. [c] Frequencies determined by using Lorentzian band-fit program.

The difference FTIR spectra of the redox series $[Ru(bpy)_2(CN)]_2(CN)^{(1-n)+}$ (Figure 5) show both the terminal and bridging cyanides shifting to lower energy with increasing n, the number of redox electrons. The small separation between the redox couples results in a mixture of products being present, resulting in composite spectra. However, a Lorentzian band-fit procedure has been used to resolve the resulting difference spectra, and the frequencies determined by this procedure are given in Table I. As previously reported,[14] the bridging cyanide is expected at higher energy, thus the 2103-cm^{-1} mode is assigned to the bridging CN, while both of the two terminal CN's are assigned to the more intense peak at 2079 cm^{-1}. This apparent degeneracy of the two terminal CN stretches is also indicative of the similarity of the two Ru^{II} centers. The first reduction of the binuclear complex results in a shift of the bridging CN to 2088 cm^{-1}, a shift of one of the terminal CN's to 2065 cm^{-1}, and no shift in the other terminal mode. Upon a second reduction, the previously unchanged terminal CN stretch shifts down to 2065 cm^{-1}, again making the terminal modes degenerate, since neither of the other two modes change. This same pattern is repeated as the third and fourth electron are added; i.e., the bridge and one terminal mode shift for the third, while the other terminal shifts with the fourth addition. Thus, the four-electron product consists of two peaks at 2057 and 2029 cm^{-1}. The trend in these shifts parallel those found for the mononuclear complex[32] in that the second shift in frequency (~30 cm^{-1}) is substantially greater than the first (~15 cm^{-1}). The fact that the bridging CN only shifts significantly with alternating reductions allows some speculation as to the assignment of the order of bpy reduction. Since the carbon-bound side of the bridge would be predicted to involve a greater degree of π communication, it is reasonable to propose that bpy reductions resulting in a shift of the bridging CN can be attributed to the bpy's coordinated to the ruthenium, that is bound to the bridging CN's carbon. Alternating reductions at the two centers is in keeping with electrostatic considerations (greatest charge separation between consecutive reductions). Although the first (and third) reduc-

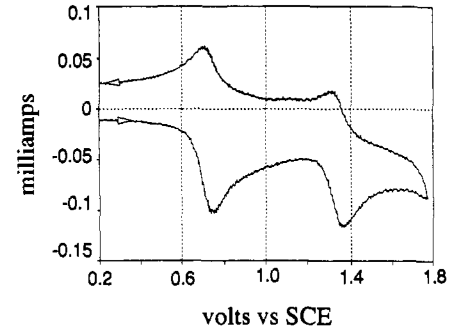

Figure 6. Cyclic voltammogram of $\{[Ru(bpy)_2(CN)]_2(CN)\}\{PF_6\}$ in CH_3CN and 0.1 M TBAH at platinum and at a 200 mV/s scan rate.

tion(s) can be reasonably assigned to the carbon-bound site, it is more difficult to assign this reduction to the cis- or trans-coordinated bpy.

Investigation of "Mixed-Valence" Species

Electrochemistry. One of the most interesting aspects of this binuclear complex is the unusually large separation of its two metal oxidations, which are found at +0.78 and +1.38 V vs SCE in acetonitrile (Figure 6). The large separation reflects a number of effects, which may include significant stabilization of the "II,III" species relative to the II,II and III,III species. The metal charges are in quotes, since in the case of a large degree of delocalization the species is better described as 2.5,2.5. However, another factor that may contribute to the large separation of the redox couples is the asymmetry of the CN bridge, since it can be argued that the nitrogen-bound ruthenium $d\pi$ orbitals would be the more easily oxidized as they lack the stabilization of the interaction with the CN π^* system.[14] Yet, since no differences in the metal centers of the II,II species are indicated spectroscopically, it may still be instructive to consider the comproportionation constant[3-5] $K_c = [\mathrm{III,II}]^2/[\mathrm{II,II}][\mathrm{III,III}]$ or $\log K_c = 16.9\,(E^\circ_1 - E^\circ_2)$ at 25 °C. The resulting value of 1.38×10^{10} for $[Ru(bpy)_2(CN)]_2CN^{2+}$ is comparable to those reported for dicyanogen,[6] oxide,[7,8] and *tert*-butylmalononitrile anion[9] bridged Ru complexes, all of which have been characterized as completely delocalized. The magnitude of K_c is dependent upon several factors in addition to the asymmetry of the CN bridge. When electron delocalization is not operative, an electrostatic interaction will favor the mixed-valence state.[4] When some degree of delocalization across the bridging ligand occurs, there are additional factors contributing to a larger K_c (greater mixed-valence stabilization). On one hand, the mixed-valence state is stabilized by back-bonding between the Ru(II) and the bridging ligand as charge is removed from the electron-rich Ru(II) center. This also results in a stabilization of the Ru(II) center due to an increased ligand field effect. Magnetic studies on several complexes[10] as well as the spectroscopic data presented thus far indicate that this stabilization is nonexistent for the isovalent states, as would be expected. The final and most controversial factor contributing to the magnitude of K_c, excluding superexchange pathways that have also been proposed by several authors,[11,12] is stabilization arising from delocalization of the charge across both metal centers and the bridging ligand. In the case where there is no direct overlap of the metal's d orbitals, electron delocalization can occur via an empty bridging ligand π^* orbital (LUMO), while hole delocalization can occur through a filled bridging ligand π orbital (HOMO).[9]

Spectroscopy. Assuming a simple Hush model for two symmetric potential wells representing the initial and final surfaces, the barrier to electron transfer can be approximated as a fourth of the intervalence charge-transfer (IVCT) energy. Indeed, when the binuclear complex is oxidized, a new strong transition grows in (Figure 7) at 7700 cm^{-1} ($\epsilon = 8500$). Using Hush[13] parameters, Bignozzi and co-workers[14] have calculated a 200-cm^{-1} electronic stabilization and a 7% delocalization. On the basis of their results, they concluded that the binuclear species was best described as a mixed-valence system with strong delocalization stabilization.

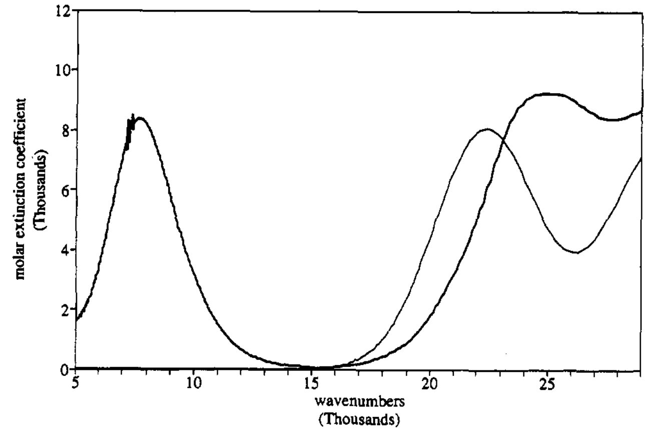

Figure 7. Electronic spectra of the oxidized species $[Ru(bpy)_2(CN)]_2(CN)^{2+}$ (bold) and $Ru(bpy)_2(CN)_2^+$ (solid) in CH_3CN and 0.1 M TBAH.

However, several studies have indicated that the Hush theory is not reliable for strongly coupled, mixed-valence systems[4] and is not applicable to completely delocalized systems.[6-9] This limitation of the Hush model is manifest in the inability of the electronic coupling parameter H_{AB} to correctly reflect the role of the bridging ligand, since it assumes a simple two-site one-electron premise. When applied to this system, the Hush relationship $\nu_{max} = (\mathrm{fwhm})^2/2310$ erroneously gives a fwhm of ~4200 cm^{-1} when experimentally it is 3300 cm^{-1}. Similar systems that have been characterized as completely delocalized have also noted a narrower band shape than predicted by Hush theory.[6-9] In addition, the near-IR band energy shows no solvent dependence as predicted for a mixed-valence IVCT. A likely explanation involves complete delocalization of the valence state across the bridging ligand so that the near-IR transition does not involve a charge transfer but rather a promotion of an electron from a filled Ru–CN–Ru orbital to the partially occupied Ru–CN–Ru orbital.

The visible spectra of the singly oxidized mono- and binuclear complexes are shown in Figure 7. Meyer et al.[40] have placed the bpy → Ru^{III} LMCT at 24 × 10^3 cm^{-1} in $[(bpy)_2Ru^{III}Cl]_2(pyrazine)$; thus, the band at 22 × 10^3 cm^{-1} is assigned to an LMCT from either the bpy or the CN. The broad band at 25 × 10^3 cm^{-1} in the spectrum of the bimetallic complex has been assigned as a Ru^{II} → bpy MLCT,[14] which would imply a 5 × 10^3 cm^{-1} blue shift from the II,II species and argue for a very strongly coupled system. Therefore, in a trapped-valence scenario, this band could be attributed to either or both types of transitions (MLCT and LMCT). It is more difficult to explain the visible spectrum in the delocalized limit, since the role of the cyanide is uncertain. Other delocalized systems have also involved small anionic bridges[6-9] with high-lying HOMO's, and it has been suggested that the hole is delocalized through the bridging π system. If the cyanide is substantially involved in the hole delocalization, then the loss of metal electron density during the oxidation will be offset somewhat by the cyanide π system. In addition, if the MO's are delocalized over both metals and the cyanide, the terms MLCT and LMCT lose some of their meaning and a simple description of the transitions becomes difficult. Certainly, the visible spectrum does not argue strongly for delocalization, but neither does it necessarily argue against it.

In order to better elucidate the nature of the $[Ru(bpy)_2(CN)]_2(CN)^{2+}$ valence state, the FTIR spectra of the parent and singly oxidized species were investigated. For a mixed-valence state, it would be predicted that three CN stretching frequencies would be observed: two terminals ($Ru^{III}—C{\equiv}N$ and $Ru^{II}—C{\equiv}N$) and a bridge ($Ru^{II}—C{\equiv}N—Ru^{III}$). It might be argued that the presence of a Ru^{III} center would have a dramatic effect on the $Ru^{II}—C{\equiv}N$ stretch, but it is highly unlikely that this effect could be nearly as dramatic as the removal of a full electron from

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(40) Johnson, E. C.; Callahan, R. W.; Eckberg, R. P.; Hatfield, W. E.; Meyer, T. J. *Inorg. Chem.* **1979**, *18*, 618.

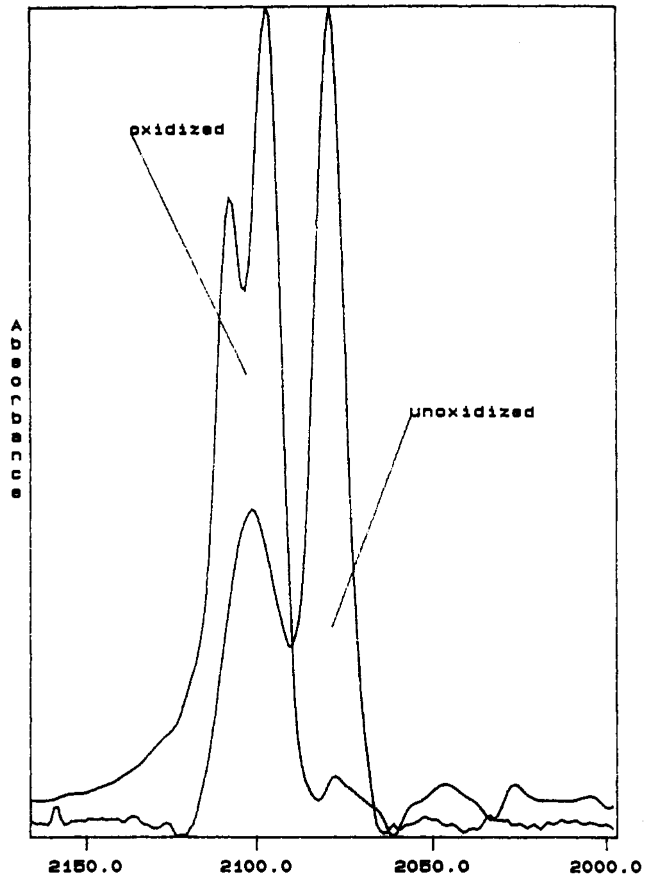

Figure 8. FTIR reflectance spectra of $[Ru(bpy)_2(CN)]_2(CN)^+$ and $[Ru(bpy)_2(CN)]_2(CN)^{2+}$ (oxidized) ratioed to 0.1 M KBr/DMF.

the bound metal. On the other hand, a delocalized valence state would predict the presence of only two C≡N frequencies: one bridging, $Ru^{2.5}$—C≡N—$RuN^{2.5}$, and only one terminal, $Ru^{2.5}$—C≡N, since it is unlikely that the two terminal cyanides would couple through the five bonds separating them, i.e., through the CN bridge and two metal centers. As shown in Figure 8, only two C≡N peaks are seen upon oxidation with no indication of the increased bandwidth for either peak that would be expected if the terminal CN's of a valence-trapped system were nearly degenerate. The terminal CN's both shift to higher energy by 17 cm^{-1} or half of the 33-cm^{-1} shift observed upon oxidation of the monomer, consistent with only partial oxidation of the metal. Upon reduction of a bipyridine, the bridging CN shifted to lower energy by 15 cm^{-1}, but upon metal oxidation, it shifts to higher energy by only 5 cm^{-1}. This small shift can be understood if we again assume that hole delocalization is operative in this CN-bridged system, since two interactions dictate the shift in the bridging CN frequency upon metal oxidation. First, a reduction of electron density at the metal centers will result in a decrease in the interaction between the filled d orbitals and the CN bridge's π^* orbitals and, consequently, shift of the bridge's frequency to higher energy. Counterbalancing this effect, however, would be the delocalization of the hole via the CN π orbital resulting in a decrease in the bridging CN's π-bonding character. The net result then would be a relatively small shift as is observed.

Table II. Frequencies ($\times 10^{-3}$ cm^{-1}) of Absorption (Room Temperature), Emission (77 K), and Stokes Shift in DMF

sample	absorption (^{1}MLCT)	emission (^{3}MLCT)	ΔE
$Ru(bpy)_2(CN)_2$	20.0	16.2	3.8
$[Ru(bpy)_2CN]_2CN^+$	20.3	15.4	4.9

The visible absorption maxima, emission maxima, and Stokes shifts for the mono- and bimetallic complexes are given in Table II. It will be noted that the Stokes shift for the binuclear complex is 1100 cm^{-1} greater than that of the monometallic species. Bignozzi and co-workers have assigned the emission of the bimetallic species as resulting from a N-bound Ru-bpy moiety, which is expected to lie lower than that from a C-bound Ru-bpy. This conclusion is based on the premise that the N-bound metal d orbitals are not as stabilized resulting in the lower energy MLCT state. Indeed, the trend in oxidation potentials (in acetonitrile) that they report on going from the mononuclear complex (NC–Ru–CN, $E_{1/2}$ = 0.86 V), to the binuclear complex (CN–Ru–CN, $E_{1/2}$ = 0.74 V), to the trinuclear complex (CN–Ru–NC, $E_{1/2}$ = 0.66 V) does support this conclusion. If their proposal is correct, then the monometallic species should have the highest MLCT energy, but in the visible spectra for the parent (unoxidized) complexes, which they report in acetonitrile, only one band is observed for each of the three complexes, not the multiple transitions expected with different metal centers, and the mononuclear complex is the lowest in energy. Indeed, as discussed above, our results indicate little difference between the coordinatively different centers for the binuclear complex. Bignozzi and co-workers have also reported the visible spectra for these complexes in D_2O, and for the trinuclear species there does appear to be a second band growing in at lower energy. Since this is absent in acetonitrile, it is probably best attributed to hydrogen (deuterium) bonding effects at the terminal CN's, so that in the case of the trinuclear complex, the CN's of the central $Ru(bpy)_2$ moiety are insulated from the solvent and do not experience any H-bonding effects. Thus, for non-hydrogen-bonding solvents such as DMF and acetonitrile, we are still left with the anomaly of the lowest energy singlet excited states for the species being near degenerate, while the emitting triplet states show a progressive red shift with increasing number of metal centers. Given the delocalized nature of the $Ru^{2.5}$–CN–$Ru^{2.5}$ species, it is possible that in the ^{3}MLCT state there is some degree of metal valence delocalization resulting in a red-shifted emission. In addition, conformational changes about the bridging cyanide can take place and lead to several stable conformers, thus lowering the energy of the emitting state.

Conclusion

The unsymmetrical nature of the –C≡N– bridge is manifest only in the shift of the C≡N stretches with reduction of the bipyridines, since the electronic spectrum of the parent monometallic and bimetallic species are identical except for extinction coefficients. The fact that only two CN stretches are observed for the singly oxidized species suggests that it is valence delocalized, i.e., 2.5,2.5 and not 2,3. Consistent with this conclusion is the large separation of oxidation potentials, which, in the absence of asymmetry due to the bridge, implies a comproportionation constant of 1.38×10^{10}. The spectra data are best explained in terms of the hole delocalized through the bridging CN π system.

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