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The Nature of the Redox Orbital in *cis*-Ru(bpy)$_2$(CN)$_2$

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FTIR, UV-vis, and resonance Raman (RR) spectra are reported for the redox series Ru(bpy)$_2$(CN)$_2^{n-}$ (bpy = 2,2′-bipyridine and n = 0–2). The UV-vis and RR spectra indicate that the redox orbital is bipyridine localized. The appearance of the symmetric C≡N stretch in the RR spectrum of the unreduced compound while the Ru → bipyridine metal to ligand charge transfer (MLCT) is probed is explained in terms of a shorter C≡N bond and a longer Ru—CN bond in the photoexcited state. Similarly, the decrease of the ν(C≡N) and the increase of the ν(Ru—CN) frequencies upon reduction indicate that the C≡N bond lengthens while the Ru—CN bond shortens in the reduced species. The resonance Raman data also indicate that the bipyridine modes, in both the free ligand and its metal complexes, may shift only ~10 cm^{-1} upon reduction, not the 50–60 cm^{-1} suggested in earlier studies. Finally, changes in the inter-ring separation and CCH bond angles in the excited- and redox-state geometries are considered on the basis of resonance enhancement and frequency shifts.

Introduction

Ruthenium 2,2′-bipyridine (bpy) complexes have stimulated much interest in the past two decades due to their possible use in photochemical energy storage and as potential photocatalysts.[1,2] Much of this interest has been in the area of redox chemistry, since many of the reduced complexes have been shown to model the excited-state complexes in as far as the redox orbital for these complexes is the same as the LUMO involved in the MLCT.[3] In fact, it has been shown that there is a linear correlation between the Ru → bpy MLCT energy and the redox potential energy difference ($E_{\mathrm{Ru(III)/Ru(II)}} - E_{\mathrm{bpy/bpy^-}}$) so that the MLCT energy can be estimated from the redox potentials and vice versa.[3,4] Studies involving Ru(bpy)$_3^{2+}$ have unequivocally shown that the ^{3}MLCT excited state is localized on a bipyridine ligand,[5–7] as are the redox orbitals of the series Ru(bpy)$_3^{1+/0/1-}$.[6,8]

The bis-substituted cyano complex Ru(bpy)$_2$(CN)$_2$ has recently received attention due to its excited-state properties, its unusual solvatochromatic behavior, and its ability to form multinuclear species via cyano bridges.[9] The solvent dependence of the MLCT energy enables the molecule to capture a large portion f the visible spectrum as a photocatalyst. In addition, binding of additional metal centers to the molecule has been shown to be possible while its solvatochromatic and excited-state properties are still retained. Thus, multielectron photocatalytic processes[9a,b] may be envisioned.

Previous studies of 4,4′- and 5,5′-substituted bipyridine complexes of ruthenium and their reduction products have indicated that the influence of electron-withdrawing substituents on the bipyridine ligands results in π back-bonding between the unreduced ligands and the metal.[10] Studies of Ru(biquinoline)$_3^{2-n}$ (n = 0–3) suggest the presence of two distinct types of redox orbitals: one involving the bpy portion of the biquinoline ligand and one involving the quinoline portion.[11] It is evident from both studies that modifications of the bpy ligand can result in a change in the nature of the redox orbital. However, to date, no spectroscopic studies have examined the effects of metal-bound, π-interacting ligands upon the nature of the bpy redox orbital in mixed-ligand complexes. This paper presents a detailed spectroscopic analysis of Ru(bpy)$_2$(CN)$_2$ and its one- and two-electron-reduction products in an attempt to elucidate the nature of the redox orbital and the degree of interaction between the cyanide and bipyridine ligands.

Table I. Frequencies (10^3 cm^{-1}) for the Electronic Spectra of Ru(bpy)$_2$(CN$_2$)$^{0/1-/2-}$ in DMF and 0.1 M TBAH (Molar Extinction Coefficients (×10^{-3}) in Parentheses)

Ru(bpy)$_2$(CN)$_2^{n-}$			
n = 0	n = 1	n = 2	assgnt
35.2 (sh)			bpy π–π^*
33.9 (48.0)	33.9 (26.0)		bpy π–π^*
28.5 (8.3)	28.5 (14.5)	28.5 (26.2)	CT
	27.0 (15.2)	27.0 (25.5)	bpy$^-$ π^*–π^*
	20.9 (sh)		bpy$^-$ [a]
20.0 (8.5)			MLCT[b]
	19.7 (7.1)	19.2 (7.5)	bpy$^-$ π^*–π^*
	18.4 (8.7)	18.2 (8.0)	bpy$^-$ π^*–π^*

[a] Reduced bpy transition, possibly vibronic in nature. [b] Charge transfer into redox orbital.

Experimental Section

Chemicals. Anhydrous, 99+% *N,N*-dimethylformamide (DMF) purchased from Aldrich and Acetonitrile-d_3 (d-AN; 99.7% isotopic purity) purchased from ICN were used as supplied from the manufacturer. *cis*-Ru(bpy)$_2$(CN)$_2$ was synthesized according to the method of Demas et al.[12] Tetrabutylammonium hexafluorophosphate (TBAH) was purchased from Aldrich, recrystallized twice from ethanol, and dried under vacuum.

Electrochemistry. A solution of Ru(bpy)$_2$(CN)$_2$ (1 mM for FTIR and RR spectra and 0.5 mM for UV-vis spectra) 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 referenced to a saturated calomel electrode (SCE). Voltammetry was carried out with a Princeton Applied Research (PAR) Model 173 potentiostat/175 universal programmer system, while the extent of reduction was monitored with an in-line PAR Model 379 digital coulometer.

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 as a stand alone source or as a pump for a Spectra Physics Model 375 dye laser with Coumarin 540 dye (Exciton). The spectra were collected and stored on computer for analysis. All frequencies were determined relative to the solvent peaks at 865 cm^{-1} (DMF) or 832 cm^{-1} (d-AN) and are expected to be accurate to ±2 cm^{-1}.

FTIR Spectra. The sample reductions were carried out in the drybox, and aliquots of the working solution were transferred to an O-ring-sealed, demountable Harrick liquid cell with ZnSe windows and a 1-mm path length. A Mattson Polaris FTIR spectrometer equipped with an NEC Powermate 2 computer, KBr beam splitter, and DTGS detector was used to obtain the spectra. The difference spectrum was obtained by first

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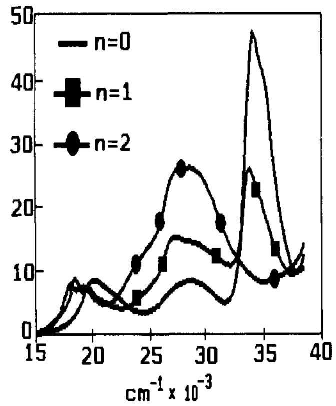

Figure 1. Electronic absorption spectrum of $Ru(bpy)_2(CN)^{n-}$ in ϵ is the extinction coefficient in dm^3 mol^{-1} cm^{-1}.

reducing the sample to $Ru(bpy)_2(CN)_2^{1-/2-}$ (RED) and recording its spectrum and then oxidizing the sample back to $Ru(bpy)_2(CN)_2$ by exposing it to air in the IR cell before obtaining the spectrum of the unreduced sample (OX). The FTIR OX-RED difference was determined with a subtraction factor of 1.00. Each of the OX and RED spectra consists of a minimum of 400 scans.

Electronic Spectra. The sample reductions were carried out in the drybox, the redox products were transferred to a 1 mm path length cell, which was sealed and placed in a Cary 2300 spectrometer. Correction for small amounts of subsequent sample reoxidation was accomplished with a spectral subtraction routine.

Results and Discussion

Electrochemistry. The cyclic voltammogram of $Ru(bpy)_2(CN)_2$ (bpy = 2,2′-bipyridine) in dimethylformamide (DMF) with 0.1 M TBAH indicates redox processes with $E_{1/2}$ values of −1.64 and −1.87 V vs SCE with peak to peak separations of ~69 mV. Cyclic voltammograms taken after bulk electrolysis for both the first and second reductions remain unchanged. Also, cyclic voltammograms taken after reoxidation of the reduced species remain unchanged, indicating that the reduction products are stable in bulk solution.

Electronic Spectra. The UV–vis spectra and data for $Ru(bpy)_2(CN)_2^{n-}$ (n = 0–2) are shown in Figure 1 and Table I. In the UV portion of the spectrum of the unreduced complex (n = 0), there is an intense band at 33.9 × 10^3 cm^{-1} with a shoulder at 35.2 × 10^3 cm^{-1} (band centers determined by a Gaussian band-fit routine). A peak near 34 × 10^3 cm^{-1} observed in other metal bpy complexes has been shown to be dependent on the number of bpy's and has been assigned as a bpy $\pi \rightarrow \pi^*$ transition.[13-16] The high-energy shoulder is present in various Fe, Ru, and Os bpy mixed-ligand complexes that do not contain a cyanide ligand, and on the basis of the observation that the separation between it and the main absorption is dependent upon both the metal and the substituted ligand, it has been ascribed to a $\pi \rightarrow \pi^*$ transition[17-19] and not a vibronic band. Both the 33.9 × 10^3 and the 35.2 × 10^3 cm^{-1} peak intensities decrease by one-half upon the first reduction of $Ru(bpy)_2(CN)_2$ and completely disappear upon the second reduction. This behavior of the $\pi \rightarrow \pi^*$ transition strongly indicates that the redox electron occupies a single ligand-localized π^* orbital.

In the remainder of the UV–vis spectrum of the parent complex, there are peaks at 20.0 × 10^3 and 28.5 × 10^3 cm^{-1}. The energies of both transitions are solvent dependent, shifting over a range exceeding 3000 cm^{-1}.[20] It is unlikely that the higher energy peak at 28.5 × 10^3 cm^{-1} is due to an intraligand bpy transition, since no corresponding peak exists in the spectrum of bipyridine or $Ru(bpy)_3^{2+}$. The solvent dependence of this peak suggests that it is charge transfer in nature, and it has been assigned to a MLCT involving a low-lying bpy π^* orbital.[17] A peak at 27.0 × 10^3 cm^{-1} appears upon reduction, which essentially doubles in intensity with further reduction. A similar peak that is present in the spectra of the MLCT excited state of $Ru(bpy)_3^{2+}$,[5,6] the redox series $Ru(bpy)_3^{1+/0/1-}$,[21] and Ru–bpy mixed-ligand complexes[22] has been accepted as a $\pi^* \rightarrow \pi^*$ transition involving the redox electron. The observation of both the 33.8 × 10^3 and the 28.5 × 10^3 cm^{-1} peaks in the electronic spectrum of $Ru(bpy)_2(CN)_2^-$ establishes the presence of two chromophores, one reduced and one unreduced bipyridine, and also suggests single bipyridine-localized redox orbitals.

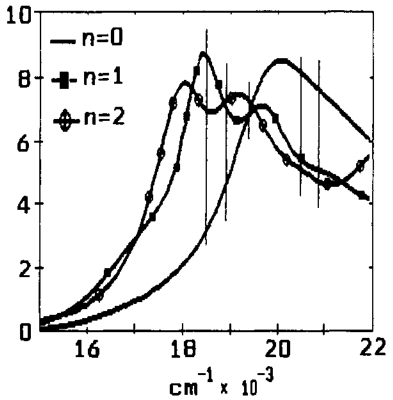

Figure 2. Visible region of the absorption spectrum of a 0.8 mM solution of $Ru(bpy)_2(CN)^{n-}$ in DMF. ϵ is the extinction coefficient in dm^3 mol^{-1} cm^{-1}. The vertical lines correspond to the exciting lines used in the resonance Raman studies.

An expanded view of the visible region of the spectrum is given in Figure 2. It is widely accepted that the low-energy transition in analogous Ru–bpy complexes results from a Ru → bpy MLCT.[1,2] Upon reduction, this MLCT into the unreduced bpy is expected to red-shift due to electrostatic repulsion between the redox electron and the filled d orbitals.[7,23] Simultaneously, at least one bpy^- $\pi^* \rightarrow \pi^*$ transition should appear in this region, presumably involving the redox orbital.[6] For the one-electron species, there are two distinct peaks in the visible region, 18.4 × 10^3 and 19.7 × 10^3 cm^{-1}, as well as a weak band near 21 × 10^3 cm^{-1}, and two peaks are observed in the visible region for the two-electron species at 18.2 × 10^3 and 19.2 × 10^3 cm^{-1}. Since the separation between the two distinct bands changes by 300 cm^{-1} upon reduction, it seems unlikely that the higher energy band is vibronic in nature. Furthremore, since no MLCT is expected in the visible region for the two-electron product, the two bands are assigned as bpy intraligand $\pi^* \rightarrow \pi^*$ transitions. Evidence for these assignments as well as the location of the MLCT in the one-electron product will be presented in the bipyridine vibrational discussion.

Vibrational Spectra. The resonance Raman spectrum and data for $Ru(bpy)_2(CN)_2$ recorded at 20.5 × 10^3 cm^{-1} (MLCT) are presented in Figure 3 and Table II. The separate bipyridine ligands do not couple vibrationally and so can be treated under a local C_{2v} symmetry, which yields 20 A_1 modes, including four C–H stretching vibrations, which occur around 3000 cm^{-1} and were not studied. The $Ru(N_2)_2(CN)_2$ skeleton (where N_2 represents the nitrogens on one bipyridine) has C_2 symmetry and contributes 11 totally symmetric modes. Therefore, excluding the ν(C–H) modes, there are 27 totally symmetric modes for the complex that might be expected to show RR activity through a Franck–Condon mechanism. It is interesting to note that all of the weak combination bands in the 1600–2000-cm^{-1} range can

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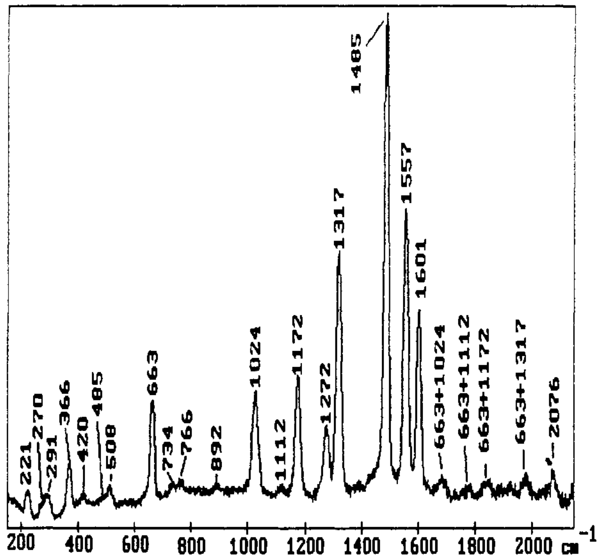

Figure 3. Resonance Raman spectrum of $Ru(bpy)_2(CN)_2$ recorded as a KBr pellet. The excitation was at 20.5 × 10^3 cm^{-1} (488 nm).

Table II. Resonance Raman Frequencies for Tris(bipyridine)ruthenium(II) Hexafluorophosphate and Bis(bipyridine)dicyanoruthenium(II) and Its Reduction Products at the Indicated Exciting Lines in 10^{-3} cm^{-1}

$Ru(bpy)_3^{2+}$	$Ru(bpy)_2(CN)_2^{n-}$						
	$n = 0$		$n = 1$			$n = 2$	
21.8[a]	20.5[a]	20.5	20.9	19.4	18.5	19.4	18.5
202	221	222					261
269	270						
282	291			314		314	322
343							
376	366	359	358	358	367	358	368
	415	406	407	402	402	400	405
480	485			487			
	508				527		534
			600				
672	663	660	658	656	658	658	659
730	734		716				681
768	766		741	745	744	745	742
891	892						
			1005	1003		1009	1012
1027	1024	1020	1020	1019	1016		
1041				1040	1040		1030
1067		1060	1056	1060			
1109	1112			1115	1122		
1173	1172	1171	1149	1162	1158	1152	1155
			1230	1215	1212	1220	1217
1254					1259		
1276	1272	1271	1280	1270	1276	1274	1280
1317	1317	1318		1317	1317		
			1354	1353	1353	1354	1351
1489	1485	1485	1477	1485	1485	1478	1477
			1500	1500	1502	1502	1500
					1542		
1558	1557	1558	1554	1559	1560	1568	1566
1604	1601	1604	1593	1594	1594	1594	1593
	2076	2074					

[a] Recorded as KBr pellets. All others are in DMF solutions.

be attributed to combinations with the fundamental at 663 cm^{-1}. The asymmetry of the MLCT band on the high-energy side could well be due to a series of vibronic side bands of this type.

Cyanide Modes. A comparison of the RR spectra of $Ru(bpy)_2(CN)_2$ and $Ru(bpy)_3(PF_6)_2$ indicates that all of the bpy modes match closely (Table II). There are, however, two additional modes (508 and 2076 cm^{-1}) that are not present in $Ru(bpy)_3^{2+}$ and cannot be attributed to overtone or combination bands. The IR spectrum of a KBr pellet of $Ru(bpy)_2(CN)_2$ contains peaks in this region at 2072 and 2055 cm^{-1}. On the basis of its appearance in the RR spectrum, the higher energy mode is assigned as the symmetric or in-phase C≡N stretch and the latter as the antisymmetric or out-of-phase mode. The 508-cm^{-1} peak is assigned as the symmetric Ru—CN stretch, ν(Ru—C), which has been reported to occur between 510 and 530 cm^{-1} for analogous complexes.[24] The weak enhancement of these cyanide modes in the RR spectrum maintains that both the Ru—C and the C≡N bond lengths change slightly upon excitation into the ^{1}MLCT state. These bond length changes can be understood in terms of electron density being removed from the metal during the MLCT, causing a subsequent change in the degree of excited-state back-bonding between the metal and the cyanide ligands. The implication is that the Ru—C bond lengthenes and the C≡N bond shortens in the ^{1}MLCT excited state as electron density is removed from the metal–carbon π bond and, consequently, from the C≡N π* orbital. The change in these bond lengths may be relevant to studies that employ the linear relationship between $\Delta E_{\text{optical}}$ (the energy of the MLCT) and ΔE_{redox} (the energy separation of the $Ru^{II/III}$ couple and the L/L^- couple).[3,4] The fact that $Ru(bpy)_2(CN)_2$ does not fall on this line has been attributed to its solvatochromatic behavior.[4b] The model used to explain this linear relationship assumes that the inner-sphere reorganization energies for the complexes are all about the same, since the same transition, Ru → bpy MLCT, is involved.[4b] If, however, the MLCT results in distortions of ligands other than those involved in the MLCT, these reorganization energies can differ and also lead to deviations from the linear relationship.

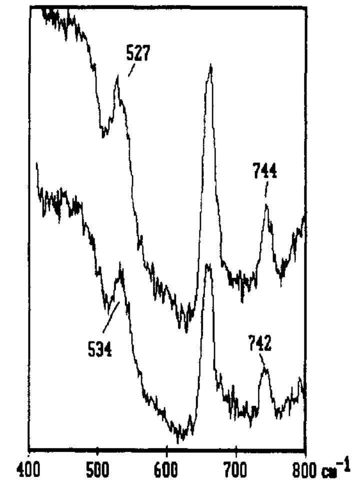

Figure 4. Resonance Raman spectra of the Ru–C stretching region of DMF solutions of (top) $Ru(bpy)_2(CN)^-$ and (bottom) $Ru(bpy)_2(CN)^{2-}$ with 1.85 × 10^3 cm^{-1} excitation.

Figure 4 shows the RR spectrum in the region of ν(Ru—C) of a DMF solution of $Ru(bpy)_2(CN)_2^{1-/2-}$. There is a broad scattering in this region due to glass that would obscure any weak peak in the region of the 508-cm^{-1} band observed in the KBr pellet spectrum for the unreduced complex. However, upon reduction, a peak is observed at 527 cm^{-1} that shifts to 534 cm^{-1} with further reduction. Thus, the Ru—C stretching frequency has shifted to higher energy as the bipyridine is reduced and indicates that the Ru—C bond length decreases as electrons are added to the redox orbital. The FTIR $Ru(bpy)_2(CN)_2$–$Ru(bpy)_2(CN)_2^{1-/2-}$ difference spectra for in the ν(C≡N) region are shown in Figure 5. In the parent species, there is a peak at 2082 cm^{-1} with a distinct shoulder at 2073 cm^{-1}. The higher energy mode is again assigned to the symmetric C≡N stretch, and the lower energy mode, to the antisymmetric C≡N stretch. Upon reduction, the symmetric mode shifts to 2065 cm^{-1} while the antisymmetric mode shifts to 2057 cm^{-1}. The apparent intensity reversal in the singly reduced spectrum is due to the overlap of the parent peak at 2073 cm^{-1} and the singly reduced peak at 2065 cm^{-1}, which results in a mutual decrease in intensities upon subtraction. The second

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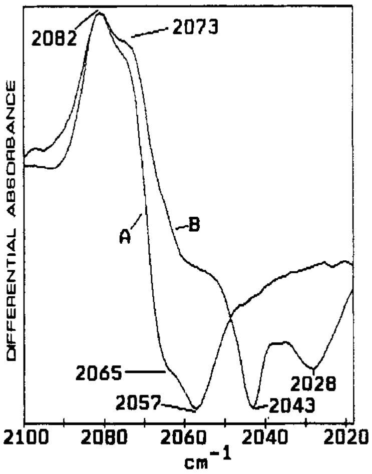

Figure 5. FTIR difference spectra of 5 mM solutions in DMF and 0.1 M TBAH recorded in a 0.5 mm path length ZnSe cell: (A) [Ru(bpy)$_2$(CN)$_2$] - [Ru(bpy)$_2$(CN)$_2$$^{1-}$]; (B) [Ru(bpy)$_2(CN)_2$] - [Ru(bpy)$_2(CN)_2$$^{1-}$].

reduction results in a further shift of both modes to lower wavenumber, implying a lengthening of the C≡N bond. Since the Ru—C bond shortens and the C≡N bond lengthens as the bipyridine ligand is reduced, it is evident that there is some degree of communication between the bipyridines and cyanides. It is reasonable to propose that the reduced bpy is a π base resulting in π-electron donation to Ru and a subsequent increase in the Ru—CN back-bonding. Indeed, the appearance of the Ru—C stretch in the resonance Raman spectrum when the complex is excited into a bipyridine-localized $\pi^* \rightarrow \pi^*$ transition argues for some d character in the redox orbital. The $\pi^* \rightarrow \pi^*$ transition then would have the effect of removing electron density from the metal, as in the MLCT. Alternatively, one can view the effect of the redox electron as an electrostatic destabilization of the filled ruthenium d orbitals that results in a better energy match with the CN π^* orbitals, thus enhancing the back-bonding. Either way, the back-bonding increases and results in a shift to higher energy of ν(Ru—C) and to lower energy of ν(C≡N). The structures of the Ru—C≡N portion of the complex then are different in the redox and photoexcited states.

Bipyridine Modes. Recent normal-coordinate calculations performed on the Ru–bpy moiety[27] indicate that 11 A_1 modes are expected between 1000 and 1650 cm^{-1}. The resonance Raman spectra for the parent and reduced species in the 900–1650-cm^{-1} region at various excitation frequencies are shown in Figure 6. In the case where the redox orbital is single ligand localized, the Raman spectrum of the $n = 1$ case should consist of vibrations due to the reduced and/or the unreduced ligand, depending on whether the $\pi^* \rightarrow \pi^*$ transition of the reduced ligand and/or the MLCT into the unreduced ligand is being probed. In the delocalized limit, only one set of bipyridine vibrations at frequencies intermediate between the two limits is expected.

The UV spectrum can be best understood in terms of a localized redox orbital, but only one pair of vibrations in the Raman spectrum is clearly supportive of localization. Consistent with previous assignments for the excited state[7,28] and for the redox series M(bpy)$_3$$^{2-n}$ (M = Ru,[8] Fe[23]), the peak at 1318 cm^{-1} (Figure 6a) is correlated with the mode at 1351 cm^{-1} (Figure 6f) in the reduced species. In the $n = 1$ spectrum recorded at 19.4 × 10^3 cm^{-1} in DMF (Figure 6c) and in d-AN nFigure 7(1)), both of these peaks are clearly present, indicating the presence of both bpy and bpy$^-$. The excitation-dependent behavior of this mode allows us to make the following assignment of the electronic spectrum in the visible region of the reduced species (Figure 2 and Table I). The bands at 18.4 × 10^3 and 20.9 × 10^3 cm^{-1} for the $n = 1$ species are assigned to bpy$^-$ transitions, since at these exciting lines, the 1351-cm^{-1} peak dominates its unreduced analogue in the resonance Raman spectrum. The 19.7 × 10^3 cm^{-1} band in the $n = 1$ species has contributions from both bpy and bpy$^-$, since the 1318- and 1351-cm^{-1} bands are of comparable intensities in the resonance Raman spectrum recorded at 19.4 × 10^3 cm^{-1}. Since the 19.7 × 10^3 cm^{-1} band is present in the $n = 2$ species, it is assigned to a $\pi^* \rightarrow \pi^*$ transition of bpy$^-$, but the MLCT in the $n = 1$ case is evidently buried under it. The behavior

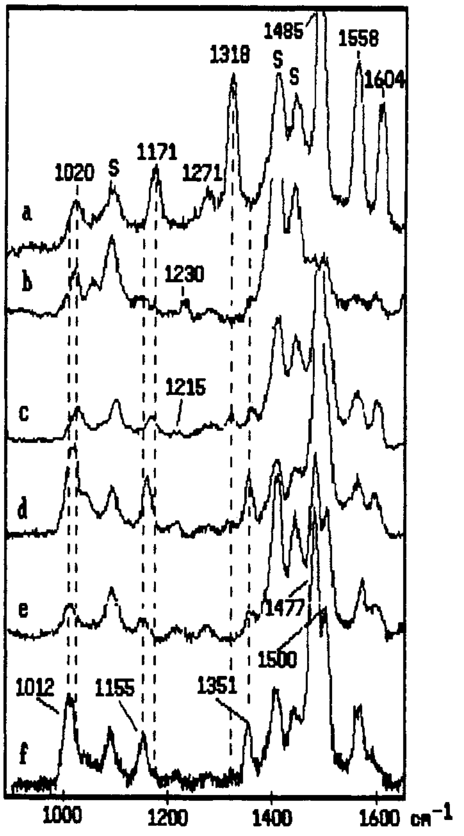

Figure 6. Resonance Raman spectra of the bipyridine modes of Ru(bpy)$_2$(CN)$^{n-}$ recorded in a DMF solution. The vertical dotted lines are to show the initial ($n = 0$) and final ($n = 2$) frequencies of the indicates modes. S = modes due to DMF. Labels are as follows: (a) $n = 0$, excitation 20.5 × 10^3 cm^{-1}; (b) $n = 1$, excitation 20.9 × 10^3 cm^{-1}; (c) $n = 1$, excitation 19.4 × 10^3 cm^{-1}; (d) $n = 1$, excitation 18.5 × 10^3 cm^{-1}; (e) $n = 2$, excitation 19.4 × 10^3 cm^{-1}; (f) $n = 2$, excitation 18.5 × 10^3 cm^{-1}.

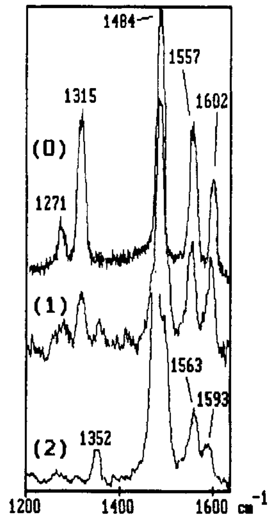

Figure 7. RR spectra of Ru(bpy)$_2$(CN)$^{n-}$ (n indicated in parentheses) recorded at 19.4 × 10^3 cm^{-1} in CD$_3$CN to remove solvent modes from the 1400-cm^{-1} region.

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of the 1171- and 1155-cm^{-1} pair supports this assignment to a lesser degree. With 19.4 × 10^3 cm^{-1} excitation, where the MLCT is assigned, the frequency of this mode is 1162 cm^{-1} (between the reduced and unreduced frequencies), but at 20.9 and 18.5 × 10^3 cm^{-1}, where there is little MLCT adsorption, the frequency is 1158 cm^{-1} (very close to the reduced frequency). It appears that, with an exciting line of 19.4 × 10^3 cm^{-1}, both the 1155- and 1171-cm^{-1} bands are enhanced but not resolved, resulting in a single peak at an intermediate frequency (1162 cm^{-1}). Similar conclusions can be drawn from the behavior of the 1020- and 1012-cm^{-1} pair.

The spectral range above 1400 cm^{-1} for the resonance Raman spectrum is the most difficult to interpret. As is typical in bipyridine complexes, three strong lines are observed in the $n = 0$ case (1485, 1558, and 1604 cm^{-1}). In the $n = 2$ case, however, four bands are observed in this region both in DMF (1478, 1502, 1568, and 1594 cm^{-1} in Figure 6e) and in d-AN (1478, 1498, 1563, and 1593 cm^{-1} in Figure 7(2)). In the $n = 1$ species, some combination of the two extremes is obtained, depending on the choice of excitation energy.

Woodruff et al.[5a] first proposed that peaks at 1605 and 1561 cm^{-1} in the resonance Raman spectrum of $Ru(bpy)_3^{2+}$ shift to 1548 and 1502 cm^{-1}, respectively, in $[Ru(bpy)_3^{2+}]^*$ (^{3}MLCT state), suggesting that each mode shifted approximately 50 cm^{-1}. This assignment is consistent with the fact that the highest energy band in the resonance Raman spectrum of the bpy^- anion was observed at 1554 cm^{-1} when 350.7-nm excitation was used.[5b] This interpretation, however, is not consistent with the RR spectrum of $[Ru(bpy)_2(CN)_2]^{n-}$ due to the existence of the peak at 1593 cm^{-1} in the two-electron-reduced species (no unreduced bpy). This band is also observed in the FTIR difference spectrum with the same intensity as that of the unreduced peak at 1603 cm^{-1}, and it disappears upon reoxidation, yielding the unreduced spectrum. Given the behavior of this band in the IR spectrum, it seems unlikely that it is due to an impurity. If it is, it would have to be one that is electroactive at the same potential and shows resonance enhancements comparable to those of $Ru(bpy)_2(CN)_2$, and it would have to represent a substantial portion of the sample (RR and FTIR intensities). None of the data collected, CV, UV–vis, RR, or FTIR, indicate any other evidence for an impurity. Moreover, the IR work of Konig and Lindner[25] indicates a weak IR band at 1597 cm^{-1} for bpy^-. Forster and Hester[7] report a weak peak at 1598 cm^{-1} in the RR spectrum of bpy^- when excitation occurs at 406.7 nm but do not include it in their correlation, simply stating that the two excited-state RR spectral studies[5,7] are subject to different resonance effects. Angel et al.[23] also observe a band at 1600 cm^{-1} in $Fe(bpy)_3^+$ when excitation occurs into a clearly resolved $\pi^* \rightarrow \pi^*$ transition of the reduced ligand. They also report the existence of a weak RR band at 1595 cm^{-1} for $Ru(bpy)_3^-$ where all of the bipyridines have been reduced.[8] Finally, there is no combination of Raman frequencies that can account for the 1593-cm^{-1} band. We, therefore, propose that upon reduction the bipyridine Raman mode above 1600 cm^{-1} only shifts by about 10 cm^{-1} upon reduction both in the free ligand and in the metal complexes and shows little to no resonance enhancement when $\pi^* \rightarrow \pi^*$ transitions are probed.

Therefore, one of the peaks above 1400 cm^{-1} in the spectrum of the reduced ligand is not present in the unreduced species. Since all of the Raman peaks are polarized and all of the A_1 fundamentals in this region have been accounted for, the only possibility is a combination or overtone band, but the peak at 1568 cm^{-1} cannot be reasonably assigned as such. However, the overtone of the 742-cm^{-1} fundamental (Figure 4) would lie at 1484 cm^{-1} in close proximity to the strongest band in the RR spectrum of the sample prior to reduction (1485 cm^{-1}). We propose that the 1475- and 1500-cm^{-1} modes form a Fermi resonance pair centered around 1485 cm^{-1}. The effect of this Fermi resonance is the repulsion of the energy levels and a mixing of the vibrational wave functions, resulting in an unusually strong overtone. Since the fundamental of this overtone has a frequency of ~765 cm^{-1} in the unreduced bipyridine (ref 5, 7 and Figure 3), its overtone would occur at ~1530 cm^{-1}, which is ~30 cm^{-1} from the closest peak, and therefore Fermi resonance would not be expected to be important. This would then imply that the 1557-cm^{-1} band shifts up to 1568 cm^{-1} upon reduction and the 1485-cm^{-1} band remains essentially unchanged except for the Fermi repulsion. It should be noted that these changes are much more consistent with the changes observed in the lower energy region, where much smaller shifts are reported. If our assignment is correct, the RR spectrum of the reduced species then indicates that the bpy modes shift only ~10 cm^{-1} or less upon reduction (excepting the 1318- and 1171-cm^{-1} modes), not the 50–60 cm^{-1} reported previously for $[Ru(bpy)_3^{2+}]^*$.[5] It must be understood that this proposed decrease in the shift of the Raman modes upon reduction does not argue against a full one-electron reduction of the bipyridine ligand, since we propose that the same changes occur upon reduction of free bipyridine.

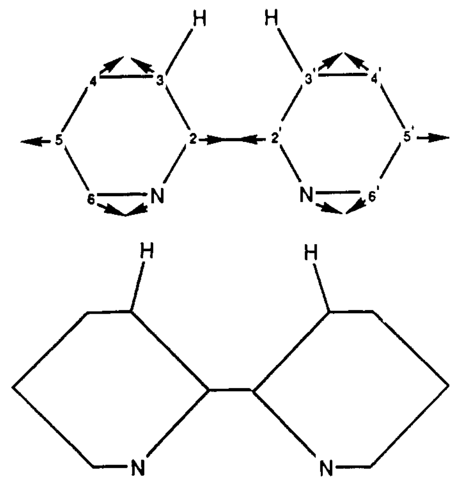

Figure 8. Top: Proposed nuclear displacements resulting from placing an electron into the LUMO of bipyridine. Bottom: Exaggerated view of the resulting distorted bipyridine that represents the proposed redox- and photoexcited-state structure. The 3,3′-hydrogens are shown to indicate the decrease in steric crowding that this model suggests.

If indeed the average shift of a bipyridine mode upon reduction is only about 10 cm^{-1}, then, of all the enhanced bpy modes, the 1171- and 1318-cm^{-1} peaks are affected the most. Kincaid and McClanahan[26] have reported that the 1175-cm^{-1} peak in the RR spectrum of $Ru(bpy)_3^{2+}$ shifts to 852 cm^{-1} upon perdeuteration and have assigned it to predominantly a δ(CCH) at the 3,3′-position (see Figure 8 for atom numbering), and recent normal-coordinate calculations indicate that the mode is 81% CCH bending.[27] A peak at 1320 cm^{-1} has been assigned as the C—C inter-ring stretch in $Ru(bpy)_3^{2+}$ [7,26] and in $Fe(bpy)_3^{2+}$,[23] and normal-coordinate calculations[27] have determined that the potential energy of this mode comprises 17% inter-ring stretch, 36% C(2)C(3)H bending, and 23% other CCH bending. Previous studies have correlated this peak in $Ru(bpy)_3^{2+}$ with the 1354-cm^{-1} peak in the excited-state RR spectra[7,28] and in the reduced species.[8] The substantial shift ($\Delta\nu = -20$ cm^{-1}) of a δ(CCH) upon addition of an electron to a π^* orbital and its strong resonance enhancement when excitation occurs into an MLCT excited state that involves a π^* system were unexpected. Also unexpected were both the magnitude and direction of the frequency shift of the inter-ring stretch ($\Delta\nu = +34$ cm^{-1}). These observations can be understood in terms of the structural changes that the bipyridine might be expected to undergo on being reduced or photoexcited. MNDO calculations of Ohsawa et al.[29] for *cis*-2,2′-bipyridine indicate that the LUMO has increased electron density in the inter-ring C–C bond, as well as the C(3)–C(4) and C(6)–N bonds of both rings and nodal planes between the other atoms. Consistent with these calculations, Caswell and Spiro[28] suggest that the dominant resonance structure of the photoexcited state of $Ru(bpy)_3^{2+}$ involves double bonds in the inter-ring bond, the C(3)–C(4) and C(6)–N bonds of both rings with single bonds between the other atoms. Figure 8a shows the type of nuclear displacements that would lengthen those bonds that decrease in bond order and shorten those that increase in bond order, and Figure 8b represents an exaggerated view of the resulting geometry. One of the effects of this change is an increase in the C(2)C(3)H bond angle, resulting in the 3,3′-H's moving apart even though the inter-ring bond is shortened. The shift of the 1318-cm^{-1} mode to higher energy and the enhancement of the δ(CCH) would then be expected. In addition, the shift of the mode at 1171 cm^{-1} with reduction can be understood if the mode contains substantial contribution from the 3,3′-H's, since the steric crowding of these H's would be reduced considerably as they move apart. Indeed, additional modes observed at 1215, 1230, and 1280 cm^{-1} might also be attributed to the other C–C–H deformations of the reduced bipyridine.

Conclusion

The appearance of two sets of A_1 vibrations for the singly reduced species in the RR spectrum and the stepwise reduction of the intensity of the $\pi \rightarrow \pi^*$ transition in the UV spectrum clearly support a single-bpy-localized model for the redox electron. Both the RR and FTIR spectra for the reduced species indicate that there is interaction between the bpy-localized redox orbital and an empty metal d orbital. This interaction results in stronger π back-bonding between the cyanides and the metal and a subsequent decrease in C≡N bond order for the cyanides. The enhancement of ν(Ru—CN) and ν(C≡N) when the MLCT of the unreduced species is probed has been interpreted as an elongation of the Ru—C bond and a compression of the C≡N bond as electron density is removed from the filled d orbitals and back-bonding decreases. Thus, the bond length changes in the Ru—C≡N portion of $Ru(bpy)_2(CN)_2$ are different upon reduction and excitation into the ^{1}MLCT state. Also, a decrease in the inter-ring separation and an increase in the separation between the 3- and 3′-hydrogens in the photoexcited and redox states are suggested to account for the observed resonance enhancement and the frequency shifts of CCH deformations and inter-ring stretch. The RR data also indicate that the average frequency shift of bipyridine modes upon reduction may be on the order of 10 cm^{-1}.

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Electron-Transfer Autocatalytic Formation, Intramolecular Charge Transfer, and Qualitatively Different Solvatochromism of σ and π Transition-Metal Carbonyl Complexes with Polynitrile Ligands[†]

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Mononuclear transition-metal carbonyl complexes (η^1-TCNE)$Cr(CO)_2(C_6Me_6)$ and (η^1-L)$Mn(CO)_2(\eta^5\text{-}C_5Me_nH_{5-n})$ with σ (end-on) coordinated ligands L = tetracyanoethene (TCNE), 2,5-dimethyl-7,8-dicyano-*p*-quinone diimine, 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) and the complexes (η^2-TCNE or $\eta^{\geq 2}$-TCNQ)$M(CO)_5$ (M = Cr, W) and (η^2-fumarodinitrile)$Mn(CO)_2(\eta^5\text{-}C_5Me_5)$ with a π (side-on) coordinated polycyano ligand have been studied by cyclic voltammetry (TCNE complexes) and electron absorption spectroscopy. Reduction potentials of the complexes were found above and below the values of free TCNE, indicating varying degrees of metal-to-ligand electron transfer in the ground state. This electron transfer is confirmed by vibrational spectroscopy and UV/vis/near-IR spectral response on C_5R_5 ligand modification. Solvent-induced dissociation into the simultaneously ESR detectable paramagnetic metal fragment and the anion radical of the ligand was observed in one instance. Intense charge-transfer (MLCT/LMCT) transitions of the complexes occur in the visible and near-infrared part of the spectrum. The π-coordinated complexes were found to exhibit a very different spectral response toward solvent variation than the σ-bonded derivatives.

Introduction

There is increasing recognition of the essential role of electron-transfer processes in organometallic chemistry and in areas (catalysis, organic synthesis) that make use of organometallics.[1–5] The tetracyanoethene (TCNE) molecule may safely be called the *E. coli* of electron-transfer chemistry in view of the numerous investigations using this highly π-electron-deficient system as a potential one-electron acceptor.[1,5,6] While even the reactions of TCNE with main-group organometallics,[2] e.g. organosilicon compounds, reveal an enormous variability,[6] the number of reviews[1,6,8] and recent solid-state studies of transition-metal complexes with π-accepting TCNE[9] and the related tetracyano-*p*-quinodimethane (TCNQ)[10] indicate that this seems to be a particularly fruitful area of organometallic chemistry.[6,11] Much effort has been devoted to the structural aspect of bonding; these acceptor ligands may coordinate in a σ fashion (via the nitrile N lone pair)[10c,12–14] or in a π type of arrangement (i.e. via the C=C olefinic bond in TCNE)[8,15] or stay "free" as in complexes with certain coordinatively saturated metallocenes.[9,16]

Besides the structural ambivalence, there is also frequent ambiguity concerning the oxidation states within these complexes.

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[†] Part 5 of a series on electron-transfer-catalyzed substitution in carbonyl complexes. Part 4: Reference 25.

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