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Spectroscopic Study of the Parent and Reduction Products of Some Substituted Bipyridine Complexes of Iron(II) and Osmium(II). 1. Substitution at the 5,5′ Positions

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The electronic absorption and resonance Raman spectra of the reduction products of some tris(5,5′-substituted bipyridine) complexes of iron and osmium provide "model" behavior for single-ligand localized redox orbitals. While the electron-withdrawing nature of the ethylcarboxy and phenyl substituents allows for the stable electrochemical addition of six electrons, the physical measurements are explicable within the framework developed for the tris bipyridine compounds, for which only the first three reduction products have been studied. Therefore, addition of more than one electron per ligand does not disrupt the localization mechanism for this set of iron and osmium complexes. Furthermore, the effects of π back-bonding to these ligands are explored by comparing the results for the different metals.

Introduction

To characterize the optically excited states of Ru(2,2′-bipyridine)$_3^{2+}$ and its analogues, attention has been focused on the electrochemically generated reduction products of these species. The absorption spectra of Ru(bpy)$_3^{2-n}$, n = 0, 1, 2, 3[2] and Fe(bpy)$_3^{2-n}$, n = 0, 1,[3] as well as the ESR studies of these complexes,[4,5] support a single-ligand localized description of the redox orbitals. Thus, the reduction products of the metal (M$^{\text{II}}$) tris(diimine) ligand ((L)$_3$) systems can be written as

$$[\text{M}^{\text{II}}(\text{L})_{3-n}(\text{L}^-)_n]^{2-n}, \qquad n = 0, 1, 2, 3$$

where n is the number of redox electrons and L$^-$ is the reduced ligand. This description of the reduced species, where n = 1, is very similar to the description of the long-lived excited state of Ru(bpy)$_3^{2+}$ as proposed in the excited-state resonance Raman (RR) studies of Woodruff and co-workers[6] and the photoselection results of Carlin and DeArmond.[7]

The RR studies of the reduction products of the d^6 metal tris(diimine) systems began with an investigation of the parent and first three reduction products of Ru(bpy)$_3^{2-n}$ (n 0, 1, 2, 3).[8] The vibrational spectrum of the singly reduced product displayed peaks characteristic of both the unreduced and triply reduced products. Since the triply reduced product represents the case where all three of the ligands have a full negative charge, the vibrational energies of that product are those of the reduced ligand. Because the singly reduced product exhibits a composite RR spectrum consisting of vibrational energies arising from both the unreduced (n = 0) and fully reduced (n = 3) products, it was concluded that there are separate unreduced and reduced chromophores present. Furthermore, vibrational spectra of both reduced and unreduced bpy was also found in a RR study of Fe(bpy)$_3^{1+}$.[3] Therefore, both the iron and ruthenium tris bpy systems exhibit RR behavior consistent with a localized description of the redox orbitals.

Elliot and Hershenhart generated more than three stable reduction products for some substituted bipyridine complexes of ruthenium.[9] In particular, the tris(5,5′-bis(ethoxycarbonyl)-2,2′-bipyridine)-substituted complex exhibits six stable reduction products in N,N-dimethylformamide (DMF) at room temperature. The stabilization of the redox orbitals of the substituted systems is a result of the conjugative and inductive effects of the substituent.[8] This stabilization is reflected in the $E_{1/2}$ values of the substituted complex relative to those of Ru(bpy)$_3^{2-n}$.[8] In order to establish the spatial extent of the fourth, fifth, and sixth redox electrons, the RR spectra of the ruthenium products have been studied.[9]

While the vibrational features associated with the reduced ligand are constant throughout the n = 1–3 redox series as in the unsubstituted tris bpy complex,[10] the vibrational energies of the unreduced ligands are shifted to lower energy upon reduction of the complex. Although this small frequency shift was unexpected, the localized nature of the redox electrons was indicated by the UV absorption[11,12] results. Therefore, an attempt was made to rationalize the observed frequency shifts within the framework of a localized description of the redox orbitals by invoking π back-bonding between the metal orbitals and the unreduced ligands. The absorption spectra of the n = 1 products of the tris(diimine) complexes show that the metal-to-ligand charge-transfer (MLCT) shifts to lower energy upon reduction. This shift has been attributed to Coulombic interaction between the redox and metal electrons.[3] The destabilization of the metal electrons relative to the LUMO of the unreduced ligands may be partially compensated by back-bonding with that orbital. This back-bonding would result in greater electron density on the *unreduced* ligands in the n = 1 products, but this electron density would not come directly from the redox electron. Thus, the remaining unreduced chromophores in the reduced products will attain some π^* character and the observed vibrations might be expected to shift to lower energy due to increased antibonding character. This rationalization is consistent with the a localized description of the redox orbitals and also satisfactorily explains the observed shifts

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(1) Consistent with the previous notation, the complexes will be referred to as follows: the initial symbol will be the atomic symbol of the central metal atom followed by a number designating the position of the substituent (e.g., 5 = 5,5′-) followed by a code for the substituent (COOEt = diester, Ph = diphenyl). Thus, the osmium 5,5′-diester complex will be written as Os5COOEt^{2-n} (where n is the number of redox electrons). M will be used to designate a nonspecific metal center (Fe, Ru, Os).

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of the unreduced ligand vibrations.

The RR study of the $n = 4, 5, 6$ products of the 5,5′-substituted ruthenium complexes indicated that the redox orbitals remain localized in these products. The presence of a singly reduced ligand(s) was evident in the RR of the $n = 4$ and $n = 5$ products.[11] The vibrational spectrum of the doubly reduced ligand (i.e., the RR spectrum of the $n = 6$ product) was found with the same relative intensities and frequencies in the $n = 4$ and $n = 5$ products when probing the appropriate electronic transition. To investigate further the possibility of back-bonding in these substituted 5,5′-substituent complexes, the RR and UV–vis spectra of the osmium and iron analogues have been obtained and are presented here.

Experimental Section

Acetonitrile and DMF were purified by previously described procedures.[3,12] The supporting electrolyte (tetrabutylammonium hexafluorophosphate—TBAH) was prepared by metathesis of the chloride salt (Kodak), recrystallized from absolute ethanol 3 times, and dried in a vacuum oven.

Synthesis. Ligands. The 5,5′-diester ligand was prepared by a previously published procedure.[9] The synthesis of 5,5′-diphenyl-2,2′-bipyridine has been described elsewhere.[11] (The distillation of the starting material used in that procedure (3-phenylpyridine) over NaOH pellets is helpful in reducing impurities.[9] The diester ligand was recrystallized twice from absolute ethanol and the diphenyl ligand twice from benzene prior to use.

Complexes. The iron diester complex was prepared by the procedure used by Elliot and Hershenhart in the synthesis of the iron 4,4′-diester complex.[9] Attempts to purify the iron complexes by column chromatography on Sephadex LH-20 in both acetone and acetonitrile were not successful. In particular, the iron 5,5′-complexes exhibited greater lability than the osmium or ruthenium analogues, as evidenced by their behavior on the LH-20 column. Overall, the best results were obained by simple rotary-evaporation/recrystallization of the iron complexes from a mixture of acetonitrile and *tert*-butyl alcohol. Although the synthesis of the iron 5,5′-diphenyl product appeared to be successful, all efforts to purify the product were unsuccessful with the presence of free ligand clearly indicated. As a result, this product was not studied.

The osmium complexes were prepared by adapting the method of Klassen et al.[13] used in the preparation of the osmium tris(biquinoline) product. Approximately 0.15 g of $(NH_4)_2OsCl_6$ and a slight excess of the appropriate ligand were refluxed in 15 mL of ethylene glycol for approximately 6 h. After the reflux was halted, the reaction mixture was allowed to cool to 80–90 °C and diluted with hot water. A solution of ammonium hexafluorophosphate was then added dropwise. The mixture was refrigerated overnight and the solid portion collected by filtration. Acetone was used to extract the complex from the solid. After filtration, absolute ethanol was added and the acetone was removed from the mixture by rotary evaporation. In those instances where a significant amount of complex appeared to remain in solution even after removal of the acetone, a solution of ammonium hexafluorophosphate was added and the mixture was again refrigerated overnight. The solid was collected and chromatographed on LH-20 in acetone. The eluent was added to absolute ethanol and the acetone was removed by rotary evaporation. Cyclic voltammetry and luminescence results for the osmium 5,5′-diester (a brown-purple solid) indicated highly purified products. The cyclic voltammetry of the diphenyl product (a brown solid) indicated a small amount of impurity (not ligand) which further recrystallization and chromatography did not remove. This impurity may be a result of minor decomposition of the complex in DMF (as observed for the iron 5,5′-complexes). The spectroscopic results indicate that this amount of impurity is not significant.

Procedure. The absorption spectra were obtained with 1-mm path length quartz cells equipped with ground-glass joints on a Cary 2300 UV–vis–near-IR spectrometer. The samples (approximately 0.2 mM in concentration) were prepared in a Vacuum Atmospheres Model HE 43-2 glovebox by a previously described[11] bulk electrolysis technique. The absorption spectra were redrawn to be linear in energy.

TABLE I: $E_{1/2}{}^{r/s\,a}$ Values of Substituted Iron, Ruthenium, and Osmium Complexes (V vs. SCE)

r/s	Fe5COOEt[b]	Ru5COOEt[c]	Os5COOEt
2/1	−0.73	−0.62	−0.57
1/0	−0.84	−0.71	−0.67
0/−1	−1.00	−0.87	−0.87
−1/−2	−1.41	−1.32	−1.28
−2/−3	−1.56	−1.52	−1.54
−3/−4	−1.80[(d)]	−1.76	−1.82

r/s	Ru5Ph	Os5Ph
2/1	−1.05	−1.01
1/0	−1.18	−1.14
0/−1	−1.38	−1.41
−1/−2	−1.86	−1.84
−2/−3	−2.04	−2.08
−3/−4	−2.22	

[a] Scan rate = 100 mV/s. [b] Values obtained in CH_3CN, all others in DMF. [c] See also ref 45. [d] Irreversible wave.

In the study of the iron complexes, immediate decomposition was observed upon addition of the 5,5′-diester complex to DMF. As a result, the iron complexes were studied in acetonitrile. Attempts to study the osmium complexes in acetonitrile were hampered by the low solubility of some of the redox products in that solvent. Thus, it was necessary to study the substituted iron and osmium complexes in different solvents. Results obtained in the study of the osmium 5,5′-diester complex in DMF indicated that there were no significant differences in either the absorption or RR spectra when compared to the available data obtained in acetonitrile.

The resonance Raman spectra were obtained with a sealed in-situ electrochemical cell that was placed in the sample compartment of a Jarrell-Ash Model 25-300 Raman monochromator. The samples were maintained at the appropriate electrolysis potential during data collection, and the extent of reduction was monitored by the current meter on the PAR Model 174 potentiostat used for the electrolysis. Cyclic voltammetry was used intermittently to monitor sample integrity. ($E_{1/2}$ values are listed in Table I.) The laser excitation energy was supplied by a Spectra Physics Model 171/09 Ar^+ laser either alone or pumping a Model 375 dye laser using rhodamine 590 or 640 and coumarin 540 laser dyes (Exciton). The data was transmitted to an MTU-130 computer for storage and treatment. Resonance Raman frequencies are reported relative to the 865-cm^{-1} peak of DMF or the 918-cm^{-1} peak of acetonitrile. These two reference peaks were checked for self-consistency by measuring the Raman peaks in a mixed DMF/acetonitrile solution.

Results

(*a*) *Absorption Spectra.* (*1*) *Effect of Variation of n* ($n = 0$, ... 6). The spectra of the $n = 0 ... 3$ redox series of $Fe5COOEt^{2-n}$ are presented in Figure 1 and those of $n = 3 ... 6$ in Figure 2. The intense absorption feature near 32 kK in the $n = 0 ... 2$ spectra remains relatively unshifted and shows the steady decrease in intensity that was observed for a similar band in the spectra of $Ru(bpy)_3{}^{2-n}$, $n = 0 ... 2$.[3] Therefore, it is assigned as an unreduced intraligand π–π^* transition (IL). The bands near 15 and 25 × 10^3 cm^{-1} show little variation in energy and a monotonic increase in intensity for $n = 1 ... 3$ followed by a steady decrease in intensity for $n = 4 ... 6$ and are assigned as intraligand transitions centered on a singly reduced ligand (IL^-). The feature near 20 × 10^3 cm^{-1} that first appears in the $n = 4$ spectrum and gains intensity for $n = 4 ... 6$ is assigned as a doubly reduced ligand transition (IL^{2-}). Only the metal-to-ligand charge-transfer (MLCT) bands show a strong energy dependence on n. In addition to the $n = 0$ spectra, these bands are usually detectable in the spectra of the $n = 1$ products, where they are generally red-shifted from and weaker than their $n = 0$ counterparts. Table II lists the absorption band

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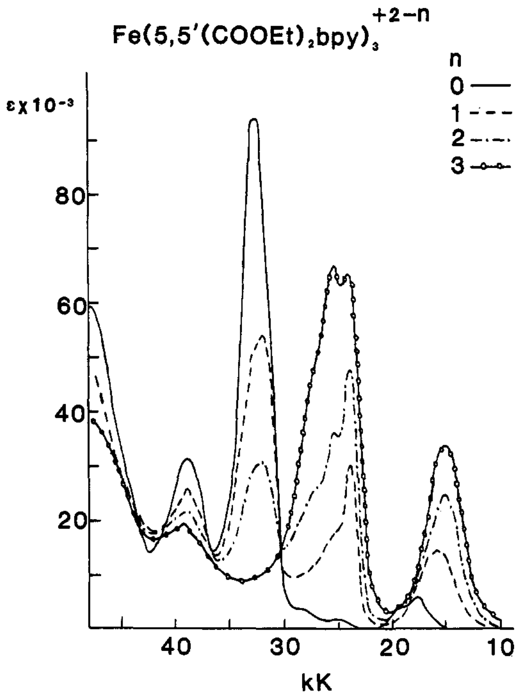

Figure 1. Absorption spectra of $Fe(5,5'(COOEt)_2bpy)_3^{2-n}$ in CH_3CN; $n = 0–3$. (1 kK = kiloKaiser = 10^3 cm^{-1}.)

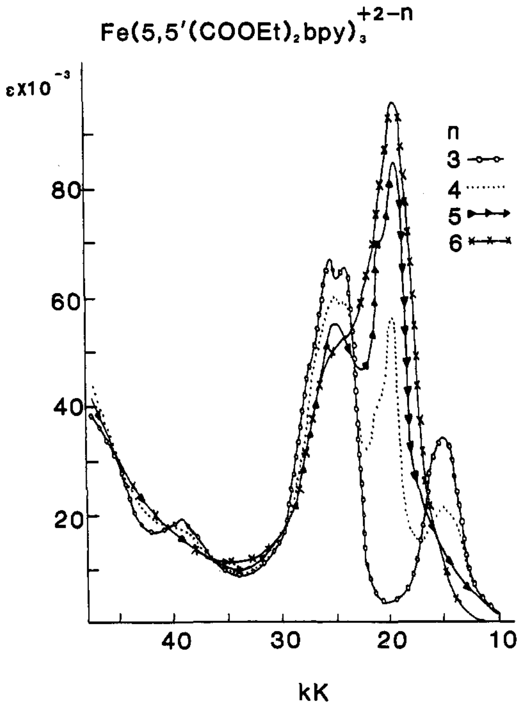

Figure 2. Absorption spectra of $Fe(5,5'(COOEt)_2bpy)_3^{2-n}$ in CH_3CN, $n = 3–6$.

energies, extinction coefficients, and assignments for the iron and osmium complexes.

(*2*) *Effect of Variation of M*. The absorption spectra of the $n = 1 \ldots 6$ redox series of both $Fe5COOEt^{2-n}$ and $Os5COOEt^{2-n}$ are very similar to the spectra of the $Ru5COOEt^{2-n}$ as obtained by Elliot and Hershenhart[9] and extended in this lab. The various IL, IL^-, and IL^{2-} absorption features characteristic of a particular 5,5′-ligand are largely unchanged in energy and relative (not absolute) intensity with variation of M. As expected, the MLCT bands do show a significant dependence on M. Thus, the $n = 0$ spectra for the three different metals differ.

(*b*) *RR Spectra* (*Effects of Variation of n and M*). The RR spectra obtained when probing the IL^- and IL^{2-} bands are unchanged by variation of n or M. As an example, the RR of the $n = 1$ product of the $M5COOEt^{2-n}$ complexes obtained with 15.5 × 10^3 cm^{-1} excitation is the same as the RR spectra of the $n = 2 \ldots 4$ products obtained at the same energy regardless of M. As such, the RR spectra can be categorized by the nature of the ligand transition being probed, and the unique vibrational patterns characteristic of the singly or doubly reduced ligands are easily identifiable. The RR spectra representative of the unreduced and singly and doubly reduced 5,5′-chromophores are presented in Figures 3 and 4.

TABLE II: Absorption Maxima, Approximate Extinction Coefficients, and Assignments for the Bands of the Redox Series of $M(5,5'(COOEt)_2bpy)_3^{2-n}$ (M = Fe, Os; n = 0–6)[a]

n	$Fe(5,5'(COOEt)_2bpy)_3^{2-n}$
0	[17.3 (6200), 18.9 (4000), 25.0 (2000), 28.1 (3900)] = MLCT [32.7 (94 000), 37.9 (27 000), 39.2 (31 000)] = IL
1	[15.2 (15 000), 16 (sh), 24.0 (30 000), 25.6 (17 000)] = IL^- [31.9 (54 000), 33 (sh), 39.1 (26 000)] = IL
2	[15.1 (25 000), 23.8 (47 000) 25.4 (36 000), 28 (sh)] = IL^- [32.0 (31 000)] = IL [39.1 (22 000)] = IL (+IL^-)
3	[15.1 (34 000), 24.0 (65 000), 25.4 (36 000), 28 (sh), 39.4 (19 000)] = IL^-
4	[19.8 (57 000), 21 (sh)] = IL^{-2} [15 (21 000), 39 (sh)] = IL^- [24.3 (59 000), 25.1 (60 000)] = IL^- (+IL^{2-})
5	[19.4 (85 000), 21 (sh)] = IL^{-2} [13 (sh)] = IL^- [25.1 (55 000)] = IL^- (+IL^{2-})
6	[19.6 (96 000), 25 (sh)] = IL^{2-}
n	$Os(5,5'(COOEt)_2bpy)_3^{2-n}$
0	[33.0 (120 000)] = IL [18.5 (12 000), 21.2 (9000), 26.6 (11 000)] = MLCT [13 (3000), 15 (3000)] = 3MLCT
1	[32.6 (83 000)] = IL [16.7 (19 000)] = IL^- [24.3 (27 000)] = IL^- + (MLCT) [20 (10 000)] = MLCT (+IL–)
2	[32.2 (52 000)] = IL [16.1 (29 000), 25.0 (41 000), 26.4 (43 000)] = IL^-
3	[15.5 (34 000), 25.8 (66 000), 28.0 (62 000)] = IL^-
4	[16.4 (26 000)] = IL^- [26.4 58 000), 28.1 (57 000)] = IL^- IL^{2-}) [19.7 (54 000), 21.1 (sh)] = IL^{2-}
5	[19.4 (75 000)] = IL^{2-} [24.9 (49 000), 27.7 (51 000)] = IL^{2-} (+IL^-)
6	[19.3 (83 000), 23 (sh), 28.1 (48 000)] = IL^{2-}

[a] Maxima reported in 10^3 cm^{-1} and extinction coefficients in M^{-1} cm^{-1}. IL indicates unreduced ligand transition; IL^-, singly reduced ligand transition; IL^{2-}, doubly reduced ligand transition. MLCT indicates metal to ligand charge transfer.

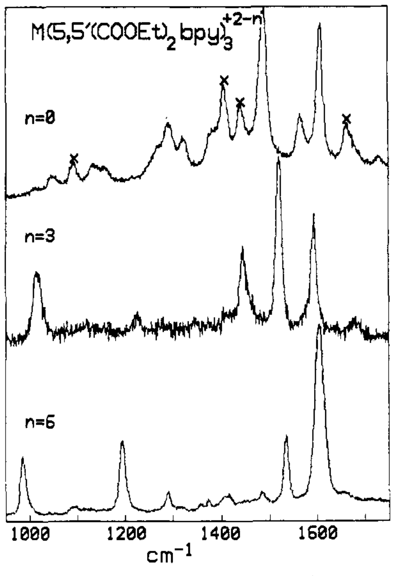

Figure 3. Resonance Raman spectra of the unreduced (n = 0, M = Os), singly reduced (n = 3, M = Fe), and doubly reduced (n = 6, M = Ru) chromophores in the 5,5′-diester complexes. X = solvent mode.

The RR spectra obtained when exciting into the MLCT bands show a slight but definite dependence on both n and M. Some of the frequencies associated with the unreduced chromophore shift as the metal is varied. The largest shift is in the RR spectra

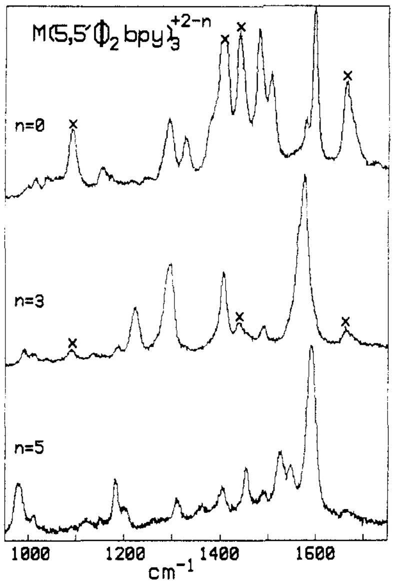

Figure 4. Resonance Raman spectra of the unreduced (n = 0, M = Ru), singly reduced (n = 3, M = Os), and doubly reduced (n = 5, M = Os) chromophores in the 5,5′-diphenyl complexes. X = solvent mode.

of the M5COOEt^{2+} complexes, where a peak at 1571 cm^{-1} in the M = Fe and Ru spectra is found at 1563 cm^{-1} in the M = Os spectrum. As stated, one purpose of this study is to examine the metal dependence of the degree of shift of MLCT RR peaks between the n = 0 and n = 1 RR spectra since back-bonding is suspected as a reason for the shift. The RR of the unreduced ligand is difficult to study in the n = 1 products as a result of the overlapping $\pi^* \rightarrow \pi^*$ transitions with strong enhancement of the singly reduced ligand vibrations. Some peaks showing enhancement from resonance with the MLCT transition in the RR of the n = 1 products are visible and are clearly shifted relative to their n = 0 counterparts, but any change in the extent of the shift as M is varied is not evident.

Discussion

(*a*) *Absorption Spectra.* The spectroscopic behavior of the 5,5′-complexes is exactly as expected for a localized *redox orbital* series. The variation of M and n does not have a significant effect on the energies of the intraligand absorption features observed in the reduced complexes. The presence of isosbestic points in the near-UV portion of the spectra indicates that the redox orbitals are isolated from each other such that the single-ligand chromophores follow Beer's law with the "concentration" of a particular chromophore changing by $^1/_3$ with the addition of each reduction electron. The small energy shifts observed in the maxima of a transition arising from one chromophore upon addition of a redox electron to a separate chromophore are consistent with the expected degree of electrostatic interaction between the redox electrons. Only the MLCT transitions are metal and charge dependent. The fact that the absorption spectra of the reduction products of the three different M5COOEt^{2-n} complexes are similar while the spectra of the unreduced products differ indicates the minimal amount of metal character in the redox orbitals.

(*b*) *RR Spectra.* The RR spectra, like the absorption spectra, clearly indicate both the single ring localization and the lack of significant metal character in the redox orbitals. The former property is indicated by the constancy of the vibrational energies associated with the reduced ligands as further redox electrons are added and the latter by the invariance of the RR data as M is varied. This localized behavior extends throughout the redox series: the singly reduced chromophores are isolated from the unreduced chromophores in the n = 1, 2 products and the doubly reduced chromophores are isolated from the singly reduced chromophores in the n = 4, 5 products.

The slight dependence of the RR frequencies of the unreduced chromophores on metal and charge is consistent with the predicted effects of back-bonding between the metal and unreduced chromophores. Those frequencies that do show a dependence on M in the three M5COOEt^{2+} complexes follow the energy ordering $E_{\text{vib}}(\text{Fe}) > E_{\text{vib}}(\text{Ru}) > E_{\text{vib}}(\text{Os})$. This is consistent with the presence of back-bonding since the greater the back-bonding, the greater the antibonding character of the ground state. The frequency shifts cannot be rationalized as a reduced mass effect (G matrix effect) due to the metal since the vibrational frequencies for the three different M(bpy)$_3^{2+}$ systems do not display the differences that the substituted complexes do. Thus, the RR spectra of the n = 0 substituted complexes provide evidence for the presence of back-bonding, but the role of back-bonding is apparently limited to the unreduced chromophores in the 5,5′-complexes since only these vibrations show a metal dependence.

Summary and Conclusions

The 5,5′-substituted bipyridine complexes of iron, ruthenium, and osmium exhibit spectroscopic behavior that is clearly indicative of single-ligand localized *redox* orbitals for the entire (n = 1 ... 6) redox series. The presence of back-bonding in the unreduced systems is indicated by the metal dependence of the vibrational frequencies in the RR spectra. The back-bonding appears to be limited to the unreduced chromophores since only the vibrational energies of the unreduced ligands shift upon reduction while those of the reduced ligands remain constant. The lack of metal character in the redox orbitals is indicated by the similarity of the absorption and vibrational spectra for the reduced complexes regardless of the type of metal center.

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Registry No. Fe5COOEt$^+$, 102869-07-8; Fe5COOEt, 102869-08-9; Fe5COOEt$^-$, 102869-09-0; Fe5COOEt^{2-}, 102869-10-3; Fe5COOEt^{3-}, 102869-11-4; Fe5COOEt^{4-}, 102869-12-5; Fe5COOEt^{2+}, 102869-13-6; Os5COOEt^{2+}, 102869-14-7; Os5COOEt$^+$, 102869-15-8; Os5COOEt, 102869-16-9; Os5COOEt$^-$, 102869-17-0; Os5COOEt^{2-}, 102869-18-1; Os5COOEt^{3-}, 102869-19-2; Os5COOEt^{4-}, 102869-20-5; Ru5Ph^{2+}, 102869-21-6; Ru5Ph$^+$, 102869-22-7; Ru5Ph, 102869-23-8; Ru5Ph$^-$, 102869-24-9; Ru5Ph^{2-}, 102869-25-0; Ru5Ph^{3-}, 102869-26-1; Ru5Ph^{4-}, 102869-27-2; Os5Ph^{2+}, 102869-28-3; Os5Ph$^+$, 102869-29-4; Os5Ph, 102869-30-7; Os5Ph$^-$, 102869-31-8; Os5Ph^{2-}, 102919-93-7; Os5Ph^{3-}, 102919-94-8.