

I, are nearly identical with those observed for doublet 1 of the unoxidized sample. It is due to the  $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{3+}$  complex located in the center of the zeolite supercages. Parameters for doublet 2 are also comparable to those of doublet 2, Figure 6a, and are again assigned to low-spin iron(II) species. Since the abundance of this doublet has not changed following  $\text{Cl}_2$  treatment, within the uncertainty limits, it appears that these species are not available for oxidation. Indeed, the Fe(II) ions of the  $\pi$ -type complex proposed for the unoxidized sample should not be accessible to  $\text{Cl}_2$  because they would be shielded by both of the complexes on either side of the 12-membered ring. Doublet 3 is also relatively unchanged following oxidation and remains assigned to an uncomplexed, high-spin Fe(III) species.

Doublet 4 of Figure 6b exhibits new parameters (Table I), and a low-spin iron(III) tris(bipyridine) complex is assumed to be responsible for it. The very small IS of this species as well as the large QS value is characteristic of low-spin Fe(I-II).<sup>12</sup> The sum of the abundance of doublets 1 and 4 agrees fairly well with the amount of tris(bipyridine) complex in the original  $[\text{Fe}^{\text{II}}(\text{bpy})_3]-\text{Y}(13)$  sample. A chlorine oxidation efficiency of 33% is calculated from their abundance in agreement with the 34% value calculated from the diffuse-reflectance data. We assume that the trivalent iron complex experiences perturbations, possibly through  $\pi$  bonding of its bipyridine ligands to the doublet 2 Fe(II) ion, in much the same way as its divalent counterpart. Comparison of the EPR data (Table II) for the high- and low-loading trivalent complex tends to confirm this assumption.

## Conclusions

Stable tris(2,2'-bipyridine)iron(II) complexes may be synthesized selectively upon exposure of  $\text{Fe}^{\text{II}}-\text{Y}$  zeolites to the ligand at 200 °C. The reaction is most effective at iron loadings less than that necessary for formation of one complex per lattice supercage. The zeolite environment appears to exhibit a higher degree of negative charge density than that of aqueous solution phases or doped powder matrices. Any excess, uncomplexed Fe(II) in the zeolite is forced from the supercage by the bulky bipyridine complex. At higher loadings the excess Fe(II) may possibly form  $\pi$ -type complexes with the bipyridine ligands of the tris complex, perhaps bridging two such complexes in adjacent supercages. This proposed dual function for the bpy ligands should reduce their interaction with the central iron atom of the tris complex.

At lower loadings chlorine gas oxidizes the divalent tris(bipyridine) complex with close to 90% efficiency. Since only partial oxidation is observed at higher loadings, it appears that either diffusion of the chlorine to the excess Fe(II) is inhibited or perhaps there is no space for the formation of chlorine ions at the oxidation sites. The iron(III) complexes also appear to be influenced by the higher negative charge density within the zeolite as compared to a doped powder sample.

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**Registry No.**  $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$ , 15025-74-8;  $[\text{Fe}^{\text{III}}(\text{bpy})_3]^{3+}$ , 18661-69-3.

Contribution from the Department of Chemistry, City University of New York, Queens College, Flushing, New York 11367

## Resonance Raman Spectra of Ruthenium(II) Complexes of Bipyridine and Substituted Bipyridines: Ground- and Excited-State Properties

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Resonance-enhanced Raman vibrational spectra are reported for  $\text{Ru}(\text{bpy})_3^{2+}$  and trissubstituted complexes of bipyridine substituted at the ring 4-position,  $\text{Ru}(4-\text{Xbpy})_3^{2+}$ :  $\text{X} = \text{NO}_2$ ,  $\text{OEt}$  ( $n = 2$ );  $\text{X} = \text{PEt}_3$  ( $n = 5$ ). For comparison, spectra of  $\text{Ru}(\text{bpy})_2\text{Cl}_2$ ,  $\text{Ru}(4,4'-\text{Me}_2\text{bpy})_3^{2+}$ , and  $\text{Ru}(4,4'-(\text{NO}_2)_2\text{bpy})_2\text{Cl}_2$  are presented and analyzed. Analysis of the resonance Raman spectra for this series provides evidence for the nature of the bipyridine ring substituent effects on the electronic properties of the complexes. The ground-state properties are perturbed as shown by frequency shifts and the appearance of additional resonance-enhanced Raman bands. In addition, the variation in the relative intensities of the resonance-enhanced Raman bands can be related to the polarization of the excited state for the metal to ligand charge-transfer bands in resonance due to electronic effects of the substituents.

## Introduction

Considerable recent interest has arisen concerning the photochemical properties of trissubstituted metal complexes of 2,2'-bipyridine and various derivatives,<sup>1-4</sup> particularly for ruthenium(II) and its analogues iron(II) and osmium(II). Of particular interest are the unusual excited-state redox properties of such species, which have been employed<sup>5,6</sup> in various photochemical systems to generate molecular hydrogen.

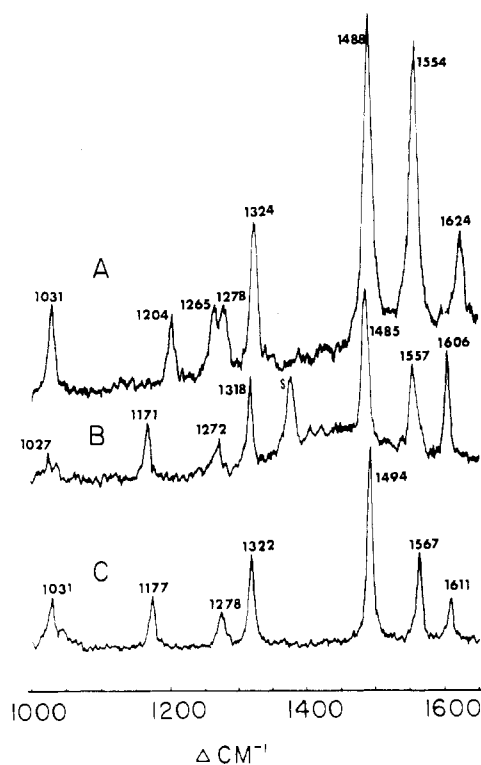
Numerous studies of the electronic absorption and emission spectra of the  $\text{M}(\text{bpy})_3^{2+}$  complexes ( $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ ) have appeared,<sup>7-10</sup> and the assignment of the principal visible ab-

sorption bands as metal ( $t_2$ ) to ligand ( $\pi^*$ ) charge transfer in origin is generally accepted, although more detailed assignments<sup>11</sup> have recently been presented.

Resonance-enhanced Raman vibrational spectra are diagnostic of the nature of electronic transitions,<sup>12,13</sup> since they reveal the normal modes most intimately coupled to the electronic transition in resonance. Resonance-enhanced Raman vibrational spectra of  $\text{Ru}(\text{bpy})_3^{2+}$  have been reported,<sup>14</sup> as well as time-resolved resonance Raman spectra (RRS) of

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**Figure 1.** Resonance Raman spectra of (A) 0.76 mM  $\text{Ru}(4,4'\text{-Me}_2\text{bpy})_3^{2+}$  in water, 457.9-nm excitation, (B) 1.0 mM  $\text{Ru}(\text{bpy})_2\text{Cl}_2$  in acetonitrile, 488.0-nm excitation, and (C) 0.5 mM  $\text{Ru}(\text{bpy})_3^{2+}$  in water, 457.9-nm excitation. Instrumental settings: 1.0  $\text{cm}^{-1}/\text{s}$  scan speed, 0.1-s time constant, 1000 counts/s full scale, 5–6  $\text{cm}^{-1}$  spectral slit width. S designates the solvent band for acetonitrile.

its excited state. These studies reveal the altered character of the bipyridine  $\pi$  system in the excited state. In both the ground and the excited state, the most strongly enhanced normal modes lie in the 1000–1700  $\text{cm}^{-1}$  region and correspond to vibrations of the coordinated bipyridine ligand. This is consistent with spectral assignments that specify charge transfer as the origin of the absorption bands in resonance.

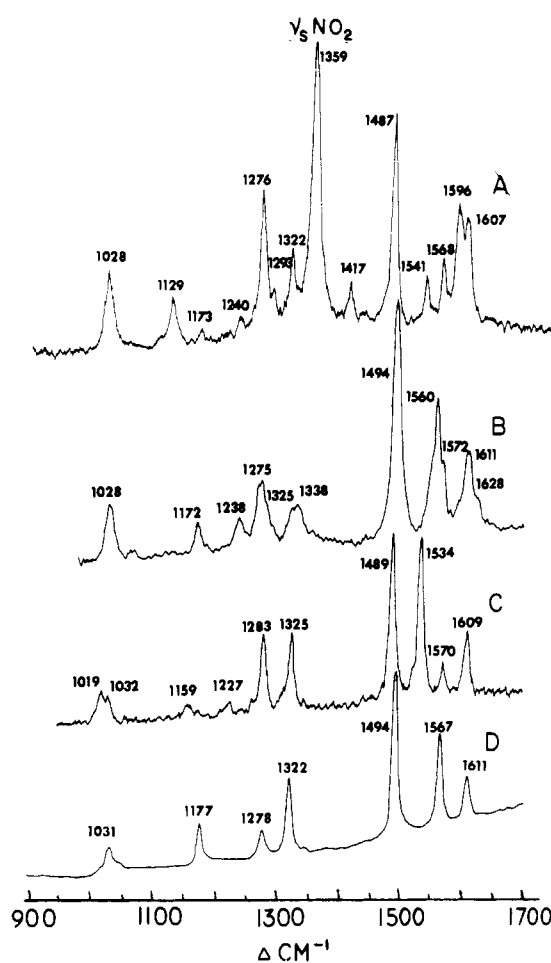
The nature of the excited state is also revealed<sup>12,13</sup> by the normal modes that are subject to the greatest resonance enhancement. The degree of this enhancement in Raman scattering intensity is related to the tendency of each normal mode to distort the molecule toward the excited-state equilibrium geometry.

The substitution of various groups into the bipyridine ring system has been shown<sup>3</sup> to significantly shift the visible absorption bands of the trisubstituted complexes of ruthenium(II), as well as the emission spectra,<sup>15</sup> and to alter the electrochemical properties.<sup>3,15</sup> The resonance-enhanced Raman vibrational spectra of such species are of interest in further comparing both ground- and excited-state properties of such complexes with those of the parent compound,  $\text{Ru}(\text{bpy})_3^{2+}$ .

We report here the resonance-enhanced Raman spectra of selected complexes of the formula  $\text{Ru}(4\text{-Xbpy})_3^{n+}$ , where X represents ethoxy ( $n = 2$ ), triethylphosphonium ( $n = 5$ ), and nitro ( $n = 2$ ). We also report the spectra for the related complexes  $\text{Ru}(\text{bpy})_2\text{Cl}_2$  and  $\text{Ru}(4,4'\text{-(NO}_2)_2\text{bpy})_2\text{Cl}_2$  as well as those of  $\text{Ru}(4,4'\text{-Me}_2\text{bpy})_3^{2+}$ . The Raman frequencies of 2,2'-bipyridine in carbon disulfide and hydrochloric acid and in the solid state are presented for comparison.

### Experimental Section

The ruthenium complexes were prepared and characterized by previously published methods.<sup>3,8,10</sup> The 4-ethoxybipyridine complex



**Figure 2.** Resonance Raman spectra in aqueous solution: (A) 0.34 mM  $\text{Ru}(4\text{-NO}_2\text{bpy})_3^{2+}$ , 488.0-nm excitation; (B) 0.34 mM  $\text{Ru}(4\text{-OEtbpy})_3^{2+}$ , 457.9-nm excitation; (C) 0.25 mM  $\text{Ru}(4\text{-PEt}_3^+\text{bpy})_3^{3+}$ , 457.9-nm excitation; (D) 0.31 mM  $\text{Ru}(\text{bpy})_3^{2+}$ , 457.9-nm excitation. Instrumental settings: (A) and (C) 1.0  $\text{cm}^{-1}/\text{s}$  scan speed, 0.1-s time constant, 1000 counts/s full scale, 5–6  $\text{cm}^{-1}$  spectral slit width; (B) same as (A) and (C), except 0.5  $\text{cm}^{-1}/\text{s}$  scan speed and 1.0-s time constant; (D) same as (A) and (C), except 10000 counts/s full scale.

was formed from the 4-nitro-substituted tris complex in 95% ethanol–water. The change in Raman spectrum most clearly indicated the loss of the substituted nitro group. The Raman spectrum of the new complex is consistent with the proposed<sup>15</sup> formulation as an ethoxy-substituted bipyridine complex, as previously described.

Raman spectra were obtained for solutions in water or acetonitrile. A typical complex concentration was 0.5 mM. Spectra were run in glass capillary cells (1 mm i.d.) with use of transverse excitation from an argon ion or argon-pumped dye (Rhodamine 6G) laser. The Raman spectrometer consists of a Spex 14018 double monochromator, an RCA C31034 photomultiplier tube, and Pacific Precision Instruments photon-counting equipment. Specific conditions are given in the figure captions.

### Results and Discussion

**Resonance Raman Spectra.** The resonance-enhanced Raman vibrational spectra for the compounds studied are displayed in Figures 1 and 2. The optical spectra are displayed in Figure 3. The excitation wavelengths used for the spectra displayed were 457.9- and 488.0-nm lines of an argon ion laser, as indicated, depending on which was closer to the visible absorption maximum. In general, these spectra are indicative of the relative intensity pattern found for any excitation within the range of available argon- or dye-laser (Rhodamine 6G) frequencies that falls within the absorption band at a point where the absorbance is half-maximum or higher. Typical maximum resonance enhancements, relative to the symmetric stretch of sulfate ( $\nu_1$ , 981  $\text{cm}^{-1}$ ) present as an internal standard

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Table I. Observed Raman Frequencies (900–1700  $\text{cm}^{-1}$ ) for Bipyridine and Ruthenium(II) Complexes of Bipyridine and Substituted Bipyridines

Ru(bpy) <sub>3</sub> <sup>2+</sup>	Ru(bpy) <sub>2</sub> Cl <sub>2</sub>	Ru(4,4'-Me <sub>2</sub> bpy) <sub>3</sub> <sup>2+</sup>	Ru(4-OEtbpy) <sub>3</sub> <sup>2+</sup>	Ru(4-PEt <sub>3</sub> <sup>+</sup> bpy) <sub>3</sub> <sup>5+</sup>	Ru(4-NO <sub>2</sub> bpy) <sub>3</sub> <sup>2+</sup>	Ru(4,4'-(NO <sub>2</sub> ) <sub>2</sub> bpy) <sub>2</sub> Cl <sub>2</sub>	bpy/CS <sub>2</sub>	bpy/HCl <sup>b</sup>	assignts <sup>c</sup>
1611 <sup>a</sup>	1606 <sup>b</sup>	1624 <sup>a</sup>	1628 <sup>a</sup> 1611	1609 <sup>a</sup>	1607 <sup>b</sup>	1604 <sup>b</sup>	1615 w <sup>b</sup>	1655 w, sh 1623 m, sh 1615 m	C=C str
1567	1557	1554	1572 1560	1570 1534	1596 1568 1541	1588 1534	1596 s 1577 s	1592 m 1576 m 1536 vw	C=C str
1494	1485	1488	1494	1489	1487	1467 1445	1484 m 1448 m	1476 vw 1464 w 1439 vw	C=N str
1322	1318	1324	1338 1325	1325	1322	1350	1314 w 1303 m	1327 vs	C=N str
1278	1272	1278 1265	1275 1238	1283 1227	1293 1276 1240	1256	1237 m 1213 vw	1255 m	C-C inter-ring str
1177	1171	1204	1172	1159	1173 1129		1148 vw 1179 vw 1164 vw	1179 vw	C-H bend in plane
1031	1027	1031	1028	1032 1019	1028	1134 1040 1020	1046 m 997 vs	1013 m 1000 m	ring breathing

<sup>a</sup> Laser excitation at 457.9 nm. <sup>b</sup> Laser excitation at 488.0 nm. <sup>c</sup> Approximate group frequency correlations as explained in text.

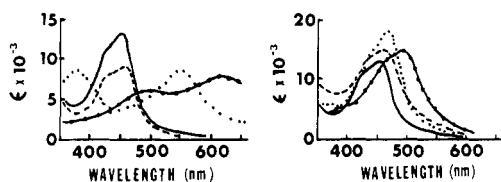


Figure 3. Visible absorption spectra, in aqueous solution unless otherwise noted, of complexes for which Raman results are reported. Left: Ru(bpy)<sub>3</sub><sup>2+</sup> (—); Ru(4,4'-Me<sub>2</sub>bpy)<sub>3</sub><sup>2+</sup> (---); Ru(bpy)<sub>2</sub>Cl<sub>2</sub> in acetonitrile (···); Ru(4,4'-(NO<sub>2</sub>)<sub>2</sub>bpy)<sub>2</sub>Cl<sub>2</sub> in acetonitrile (— · —). Right: Ru(bpy)<sub>3</sub><sup>2+</sup> (—); Ru(4-OEtbpy)<sub>3</sub><sup>2+</sup> (---); Ru(4-PEt<sub>3</sub><sup>+</sup>bpy)<sub>3</sub><sup>5+</sup> (···); Ru(4-NO<sub>2</sub>bpy)<sub>3</sub><sup>2+</sup> (— · —).

at 1 M concentration, are as follows: Ru(4-PEt<sub>3</sub><sup>+</sup>bpy)<sub>3</sub><sup>5+</sup> 1489- $\text{cm}^{-1}$  mode,  $1.6 \times 10^5$ ; Ru(4-NO<sub>2</sub>bpy)<sub>3</sub><sup>2+</sup> 1487- $\text{cm}^{-1}$  mode,  $2.2 \times 10^5$ , 1359- $\text{cm}^{-1}$  mode  $3.0 \times 10^5$ . For Ru(bpy)<sub>2</sub>Cl<sub>2</sub> and Ru(4,4'-(NO<sub>2</sub>)<sub>2</sub>bpy)<sub>2</sub>Cl<sub>2</sub>, Raman excitation within both the argon- and dye-laser ranges were used to excite resonance Raman spectra. The qualitative features of spectra obtained in each region were not significantly different.

Table I lists the observed frequencies for the ruthenium complexes as well as those for 2,2'-bipyridine under various conditions. The geometry<sup>16</sup> in the solid state and in carbon disulfide is trans or transoid, while the geometry in hydrochloric acid, for the monoprotonated form, is cisoid and should most closely approximate the geometry for coordinated bipyridine.

**Normal-Mode Analysis. Ru(bpy)<sub>3</sub><sup>2+</sup>.** Complete normal-coordinate calculations have been performed<sup>16</sup> for bipyridine, as well as its 1:1 complex with palladium dichloride, with the employment of infrared data. Using the assignments of Struik and Walter, we can suggest the probable normal modes of coordinated bipyridine that appear in the resonance-enhanced Raman spectra of the parent compound of the series studied here, Ru(bpy)<sub>3</sub><sup>2+</sup>.

Using a localized C<sub>2v</sub> symmetry for the coordinated bipyridine, including the ruthenium (Figure 4), we expect a maximum of 20 totally symmetric modes. Polarization studies show that only totally symmetric modes are observed for all the compounds studied in the region below 1700  $\text{cm}^{-1}$ .

These 20 totally symmetric modes may be broken down into 12 stretching modes, 4 C-H, 1 Ru-N, 4 C-C, 2 C-N, and

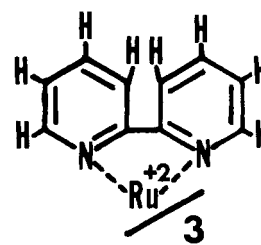


Figure 4. Coordination geometry (C<sub>2v</sub>) of Ru-bipyridine centers assumed in the discussion of vibrational analysis.

1 inter-ring C-C stretch, 4 C-H in-plane deformations, and 4 ring angle deformations, also in plane. The C-H stretching modes are not expected to show resonance enhancement, since the C-H  $\sigma$ -bonding system is not coupled electronically to the chromophoric  $\pi$  system of the bipyridine. No Raman bands in the C-H stretching region are in fact observed. There is also no strong evidence of Ru-N stretching modes in the low-frequency region below about 500  $\text{cm}^{-1}$ . This again is not without precedence since Ru-N bonding distances may not be significantly altered in the excited state, resulting in little resonance enhancement.

The four ring-angle deformation modes are expected below about 1000  $\text{cm}^{-1}$ , and there are observed some weak to very weak Raman bands, particularly one between 660 and 670  $\text{cm}^{-1}$  for the various derivatives but at 668  $\text{cm}^{-1}$  for the parent compound, Ru(bpy)<sub>3</sub><sup>2+</sup>. These modes are apparently not subject to significant resonance enhancement. This is further demonstrated by the relatively low intensity in the metal complex resonance Raman spectra of the ring "breathing" mode, which appears just above 1000  $\text{cm}^{-1}$  and is quite intense in the nonresonance spectrum of bipyridine in HCl.

Of the 11 remaining totally symmetric modes, the C-H deformations should contribute primarily to frequencies below about 1200  $\text{cm}^{-1}$  and the C-C and C-N stretching modes to frequencies above 1200  $\text{cm}^{-1}$ . A number of modes are of course highly mixed, but to the extent that C-H deformation coordinates contribute to a mode, one would expect less resonance enhancement. In the spectra reported here, the Raman bands above 1300  $\text{cm}^{-1}$  are generally the most intense. Suggested assignments for the seven (or possibly eight) resonance-enhanced Raman bands in the region above about 1000  $\text{cm}^{-1}$  for the parent compound are included in Table I. The most intense band at 1494  $\text{cm}^{-1}$ , which remains nearly as

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intense in the other spectra reported here and shows a frequency range of only about  $9\text{ cm}^{-1}$ , is assigned to C–N stretch, along with another band at  $1322\text{ cm}^{-1}$ , which again varies little in frequency or relative intensity throughout the series of compounds. Since substitutions are at the ring 4-position, the C–N modes are spatially remote and may be expected to couple least strongly with substituent modes. The band at  $1278\text{ cm}^{-1}$  is assigned to the C–C inter-ring stretch, after Strukl and Walter and because this mode is assigned<sup>17</sup> in this region for biphenyl and substituted biphenyls. This mode is relatively constant in frequency for all complexes studied.

Less intense bands at  $1031$  (with shoulder) and  $1177\text{ cm}^{-1}$  are assigned as ring breathing and C–H deformation mixed with some stretching. The  $1177\text{-cm}^{-1}$  mode shows appreciable variation, from  $1159\text{ cm}^{-1}$  in  $\text{Ru}(4\text{-PEt}_3^+\text{bpy})_3^{5+}$  to  $1204\text{ cm}^{-1}$  in  $\text{Ru}(4,4'\text{-Me}_2\text{bpy})_3^{2+}$ . Finally, the  $1567\text{-}$  and  $1611\text{-cm}^{-1}$  modes are associated with C–C stretching on the periphery of the bipyridine ring system. These bands are split and shifted most by position-4 substitutions.

**$\text{Ru}(4,4'\text{-Me}_2\text{bpy})_3^{2+}$  and  $\text{Ru}(\text{bpy})_2\text{Cl}_2$ .** For the bisubstituted bipyridine complex, the observed resonance-enhanced Raman spectra (Figure 1B) are quite similar for  $488\text{-}$  and  $570\text{-nm}$  excitation, on either side of the  $550\text{-nm}$  visible absorption peak. The band pattern is almost identical with that of the tris complex, with lower frequencies ( $4\text{--}10\text{ cm}^{-1}$ ).

Upon asymmetric substitution, at the 4- and 4'-positions of the bipyridine, the resonance Raman spectrum (Figure 1A) of the trissubstituted complex is again quite similar to that of the unsubstituted ligand complex. The  $1611\text{-cm}^{-1}$  peak shifts to  $1624\text{ cm}^{-1}$  and the  $1567\text{-cm}^{-1}$  peak to  $1554\text{ cm}^{-1}$ . Two peaks are observed near  $1278\text{ cm}^{-1}$ , at  $1278$  and  $1265\text{ cm}^{-1}$ , and the  $1177\text{-cm}^{-1}$  band is shifted to  $1204\text{ cm}^{-1}$ . The new band at  $1265\text{ cm}^{-1}$  is probably due to mixing of the C–C stretch for the methyl substituent with resonance-enhanced ring stretching modes, resulting in an enhancement of the otherwise uncoupled substituent stretches. The symmetric substitution produces only a single new resonance-enhanced band, due to this mixing with resonance-enhanced modes of higher frequency, probably ring C–C stretch. Asymmetric substitutions (i.e., in one ring only) can result in a larger number of observed modes, due to the removal of the degeneracy of the internal coordinate sets of the two ring systems as well as the mechanism just discussed. This will be actually observed to the extent that the degeneracy is in fact removed, if the substituent alters bonding in one ring with respect to that of another or if coupling occurs with resonance-enhanced normal coordinates within the single ring system.

**4-Substituted Bipyridine Complexes of Ruthenium.** The ethoxy substituent is, of the three studied here, the least perturbing with respect to the  $\pi$  system of the ligand (the absorption maximum is shifted to  $460\text{ nm}$ , from  $448\text{ nm}$  in the parent tris complex). The resonance Raman spectrum (Figure 2B) is most affected in the  $1150\text{--}1350\text{ cm}^{-1}$  region, where new modes at  $1238$  and  $1338\text{ cm}^{-1}$  appear. The  $1275\text{-}$  and  $1325\text{-cm}^{-1}$  bands correspond to peaks in the parent compound. Mixing of Ph–O–R stretching can account<sup>17</sup> for the appearance of a new band in this region, possibly that at  $1238\text{ cm}^{-1}$ . The splitting of the  $1550\text{--}1650\text{ cm}^{-1}$  C–C stretching modes is probably due to the slight electronic asymmetry induced by the ethoxy group with respect to the adjacent C–C bonds in the substituted ring. The  $1494\text{-cm}^{-1}$  C–N mode is relatively unaffected.

The triethylphosphonium substitution at the 4-position perturbs the  $1500\text{--}1650\text{ cm}^{-1}$  region most in the resonance Raman spectrum (Figure 2C) of the tris complex. A band at  $1534\text{ cm}^{-1}$  is now comparable in intensity to the  $1489\text{-cm}^{-1}$

C–N stretch, whereas a mode at  $1570\text{ cm}^{-1}$ , shifted little from the position in the parent complex spectrum, shows much lower relative intensity. The maximum in the visible absorption spectrum is now shifted to  $466\text{ nm}$ , and the positive charge at the 4-position might be expected to polarize the charge-transfer transition toward the C–C bond region at the periphery of the bipyridine ring that is substituted. The lower frequency ( $1534\text{ cm}^{-1}$ ) may reflect significant alteration of the C–C bonding due to  $\sigma$  charge withdrawal by the triethylphosphonium. Unshifted bands in this region indicate a lack of effect on similar coordinates in the unsubstituted ring of the bipyridine. C–N stretch and C–C inter-ring stretch are similar in frequency for both the substituted and the unsubstituted rings and show no splitting. The high resonance intensity of the C–C band at  $1534\text{ cm}^{-1}$  suggests an excited-state geometry in which more charge is transferred to the substituted ring and to a position further out on the ring system.

In the resonance-enhanced Raman vibrational spectrum for the 4-nitro-substituted compound (Figure 2A) more new resonance-enhanced bands are observed than for any of the other compounds. By far the most striking feature of the Raman spectrum is a band at  $1359\text{ cm}^{-1}$ , which dominates the spectrum. This can be assigned as the symmetric stretch of the nitro substituent by analogy to other nitro-substituted aromatics<sup>18</sup> such as nitrobenzene, where the band is observed at  $1345\text{ cm}^{-1}$ . The large resonance enhancement, coupled with the observed red shift of the visible charge-transfer band to  $486\text{ nm}$ , indicates the extent of coupling of the nitro group with the aromatic  $\pi$  system of bipyridine. Indeed, the extent of polarization of the charge-transfer transition toward the nitro-substituted ring must be quite large. Another mode at  $1596\text{ cm}^{-1}$  may be due to mixing of the asymmetric nitro stretch ( $1510\text{ cm}^{-1}$  in nitrobenzene) with ring C–C stretch. As with the triethylphosphonium-substituted compound, the greatest frequency shifts occur in the peripheral C–C modes of the nitro-substituted ring. A band is observed at  $1541\text{ cm}^{-1}$  in addition to that at  $1596\text{ cm}^{-1}$ , while bands at  $1607$  and  $1568\text{ cm}^{-1}$  are relatively unshifted from the positions in  $\text{Ru}(\text{bpy})_3^{2+}$  spectra. A band at  $1417\text{ cm}^{-1}$  is assigned to the ring– $\text{NO}_2$  stretch and is resonance enhanced due to strong coupling with the bipyridine  $\pi$  system.

**$\text{Ru}(4,4'\text{-NO}_2\text{bpy})_2\text{Cl}_2$ .** The dinitro-substituted compound exhibits a resonance Raman spectrum (Table I) that is completely dominated by the  $1350\text{-cm}^{-1}$  nitro symmetric stretch. Even the "invariant" C–N stretch in the  $1490\text{-cm}^{-1}$  region is no longer evident, but a much weaker band at  $1467\text{ cm}^{-1}$  is observed. Other bipyridine modes can be assigned, but they are significantly shifted from their positions in the parent complex. The conjugative electronic withdrawal of the nitro group on each ring is now dominant in effecting charge transfer to the periphery and onto the nitro groups.

**Interpretation of Visible Electronic Transitions.** The generally accepted assignment<sup>7–11</sup> for the  $450\text{-nm}$  visible absorption band of  $\text{Ru}(\text{bpy})_3^{2+}$  as metal ( $t_2$ ) to ligand ( $\pi^*$ ) charge transfer is, as already mentioned, quite in keeping with the observation of bipyridine ring vibrations in the resonance Raman scattering upon excitation near the peak maximum. The same is generally true for the series of 4-substituted bipyridine complexes reported here. For the bisubstituted  $\text{Ru}(\text{bpy})_2\text{Cl}_2$ , in which the optical spectrum is quite altered, with bands at  $375$  and  $551\text{ nm}$  in acetonitrile, the resonance Raman results indicate that the  $550\text{-nm}$  band terminates in a  $\pi^*$  orbital that must be nearly identical with that found for the  $450\text{-nm}$  charge-transfer band of  $\text{Ru}(\text{bpy})_3^{2+}$ . The same vibrational modes are resonance enhanced with excitation to

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the high- (488 nm) or low-frequency (570 nm) side of the maximum. In addition, the relative intensities of these modes are very similar to those found for  $\text{Ru}(\text{bpy})_3^{2+}$ . This further indicates the similarity of the excited-state geometries.

From the resonance Raman spectrum of  $\text{Ru}(4,4'\text{-Me}_2\text{bpy})_3^{2+}$  we note the small effect of symmetric (4,4') substitution on the frequencies of the resonance-enhanced Raman modes. Upon asymmetric substitution (i.e., one ring only), one observes the emergence of a pattern in which the Raman frequencies of one ring of the bipyridine system remain relatively unshifted as compared to those of the parent compound, whereas the substituted ring results in some shifted frequencies as well as additional resonance-enhanced bands due to mixing of substituent modes with resonance-enhanced ring modes. Of course, not all modes in the substituted-ring system are altered. In particular, the C-N stretching mode at about  $1488\text{ cm}^{-1}$  seems quite invariant throughout the series of compounds with the exception of the 4,4'-dinitro compound. When such a dual set of observed modes exists, it gives rise to the possibility of following the transfer of charge onto the bipyridine ring system in the excited state as influenced by various substituents.

A comparison of the resonance Raman spectra for the parent compound and the ethoxy-substituted compound shows little change in the pattern of relative intensities even though new modes are observed due to the substitution. For the triethylphosphonium-substituted compound a very intense mode at  $1534\text{ cm}^{-1}$  due to peripheral C-C stretch indicates the transfer of charge in the direction of the substituted ring system. The  $1489\text{-cm}^{-1}$  band is equally intense but, along with the  $1609\text{-cm}^{-1}$  mode, is apparently not sufficiently shifted from the unsubstituted ring value to allow a distinction. Note the low intensity of the  $1570\text{-cm}^{-1}$  mode, which is assigned to the peripheral C-C stretch of the unsubstituted ring (corre-

sponding to the  $1534\text{-cm}^{-1}$  band).

In the nitro-substituted compound, the coupling of the strongly electron-withdrawing nitro group with the bipyridine  $\pi$  system has an even more dramatic effect on the resonance Raman spectrum. The dominance of the intense symmetric nitro stretching mode at  $1359\text{ cm}^{-1}$  is unique among the spectra reported here and indicates that the nitro moiety is part of the chromophoric system. A great deal of charge must be transferred to the nitro group in the excited state, and this has been proposed<sup>15</sup> as an explanation for the unique absence of detectable luminescence for this substituted bipyridine complex of ruthenium(II). Because the nitro group can couple well with solvent (e.g., through hydrogen bonding), this may provide a facile, rapid pathway for vibrational depopulation of the excited state. The observed shift of only the nitro stretch to  $1352\text{ cm}^{-1}$  in ethanol is further evidence of this type of solvent interaction.

As demonstrated by this study, the investigation of the resonance Raman spectra of an appropriate series of complexes of a metal with substituted ligands can provide insight concerning the nature of the electronic transitions for such a series. In addition, certain properties of the excited states may be inferred from such an analysis.

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**Registry No.**  $\text{Ru}(\text{bpy})_3^{2+}$ , 15158-62-0;  $\text{Ru}(\text{bpy})_2\text{Cl}_2$ , 15746-57-3;  $\text{Ru}(4,4'\text{-Me}_2\text{bpy})_3^{2+}$ , 32881-03-1;  $\text{Ru}(4\text{-OEtbpy})_3^{2+}$ , 80106-00-9;  $\text{Ru}(4\text{-PEt}_3^+\text{bpy})_3^{3+}$ , 73891-49-3;  $\text{Ru}(4\text{-NO}_2\text{bpy})_3^{2+}$ , 73891-47-1;  $\text{Ru}(4,4'\text{-(NO}_2)_2\text{bpy})_2\text{Cl}_2$ , 73891-51-7;  $\text{bpy}$ , 366-18-7.

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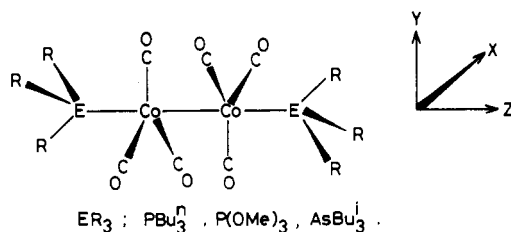
## Electron Spin Resonance Study of Anion Radicals of Dicobalt Carbonyl Derivatives, $\text{Co}_2(\text{CO})_6(\text{ER}_3)_2$ ( $\text{ER}_3 = \text{P-}n\text{-Bu}_3$ , $\text{P}(\text{OMe})_3$ , and $\text{As-}i\text{-Bu}_3$ )

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Anion radicals of  $\text{Co}_2(\text{CO})_6(\text{ER}_3)_2$  ( $\text{ER}_3 = \text{P-}n\text{-Bu}_3$ ,  $\text{P}(\text{OMe})_3$ , and  $\text{As-}i\text{-Bu}_3$ ) are generated by exposure of 2-methyltetrahydrofuran solutions of their parent neutral complexes to  $^{60}\text{Co}$   $\gamma$  rays at 77 K and examined with ESR. The odd electron is accommodated in the intermetallic  $\sigma^*$  MO. The odd-electron densities on cobalt orbitals have small dependence on the axial ligand:  $\rho(\text{Co } d_z) = 0.31\text{--}0.32$  and  $\rho(\text{Co } 4s) = 0.010\text{--}0.015$ . The odd-electron density on the central atom of the axial ligand is 0.10 for the phosphine complex and 0.05–0.06 for the phosphite and the arsine complexes. This ligand dependence of the odd-electron distribution is interpreted with an orbital interaction scheme corresponding to a competitive sharing of the odd electron on the cobalt atoms between the lone pair orbitals on the axial and equatorial ligands. Carbonyl  $\pi^*$  and cobalt  $4p_z$  orbitals are suggested to not be important contaminants in the intermetallic  $\sigma^*$  orbital. Anion radicals of dimanganese decacarbonyl derivatives are predicted to have a possibility of an axial ligand dependence of the odd-electron distribution different from that of the present dicobalt anions on a basis of an LCAO–Hartree–Fock–Slater calculation.

The cobalt complexes  $\text{Co}_2(\text{CO})_6(\text{ER}_3)_2$  ( $\text{ER}_3 = \text{P-}n\text{-Bu}_3$ ,  $\text{P}(\text{OMe})_3$ , and  $\text{As-}i\text{-Bu}_3$ ) have a nonbridged  $D_{3d}$  geometry with an intermetallic single bond.<sup>1</sup> Manning<sup>1a</sup> suggested that the



$\text{CoC}$  stretching frequencies of this class of complexes correlate with  $\pi$ -acceptor properties of the axial ligands as in the case of dimanganese decacarbonyl derivatives.<sup>2</sup> Gray and his co-workers<sup>3</sup> have investigated their electronic spectra with conclusions that the intense absorptions at 393 and 360 nm of  $\text{Co}_2(\text{CO})_6(\text{PPh}_3)_2$  and  $\text{Co}_2(\text{CO})_6[\text{P}(\text{OMe})_3]_2$ , respectively, are due to the intermetallic  $\sigma\text{--}\sigma^*$  transition. Poe and Jackson<sup>4</sup>

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