condition, can be affected by different degrees of cage effect.

In contrast to the case of $[Co(CN)_6]^{3-}$,[34] the $[Fe(CN)_5(N\frown N)]^{3-}$ system reveals the presence of an efficient cage effect, even in aqueous solution. In this latter case, an adequate bidentate diamine ligand, linking together a suitable reaction partner, quite efficiently competes with the rapid geminate recombination by means of a specific molecular organization. A propitious location of the uncoordinated amine group reduces the probability of back reaction, preventing the rapid recombination of the quasi-dissociated species, before the attack of the solvent molecule.

It is interesting to contrast the effect observed in this work with that presented by a supramolecular structure formed by the association of the hexacyanocobaltate(III) anion with polyammonium macrocyclic receptors.[35,36] In this latter system, the adducts obtained prevented some CN^- groups from escaping when the Co–CN bonds were temporarily broken as a consequence of photoexcitation. Althought the effect is just the opposite, the present work has also shown that the use of a $N\frown N$ chelating ligand can direct the photosubstitution reactions toward a specific product, under appropriate experimental conditions, modifying what has been considered to be the typical photochemical pattern of pentacyanoferrate(II) complexes. Furthermore, its reactivity can also be controlled by means of suitable ligands taking into account factors such as shape, size, and binding-site arrangement.

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Synthesis and Spectroscopic Properties of Zeolite-Entrapped Bis-Heteroleptic Ruthenium(II) Polypyridine Complexes

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A convenient method for the preparation of polypyridine complexes of Ru(II) within the supercages of zeolite Y is reported. The bis-heteroleptic trisligated species $Ru^{2+}(bpy)_2(bpz)^{2+}$–Y and $Ru^{2+}(bpy)_2(dmb)^{2+}$–Y have been obtained and characterized by electronic absorption and resonance Raman spectroscopies. Two methods of zeolite matrix destruction have been used to extract the zeolite-entrapped complexes. Depending on experimental conditions, a blue byproduct can be formed in the zeolite supercages. Preliminary evidence suggests that this compound is properly formulated as $Ru^{3+}(bpy)_2(X)O-$ (where X is unspecified) bound to the supercage interior wall via an oxygen atom donated by the zeolite.

Introduction

The intense interest in the photophysics and photochemistry of polypyridine complexes of divalent ruthenium continues in view of their potential utility in solar energy conversion schemes.[1–4] Incorporation of these and other photoactive species into organized molecular assemblies may provide an effective means to eliminate inherent problems involving photodegradation[5,6] and undesirable rapid back-electron-transfer reactions.[7,8]

One early effort to incorporate tris(2,2′-bipyridyl)ruthenium(II) $[Ru(bpy)_3^{2+}]$ into an organized assembly was made by Lunsford and co-workers, who described a method for the synthesis of $Ru(bpy)_3^{2+}$ within the cavities of Y-type zeolites.[9,10] Entrapment within the ~13-Å cavity did not significantly alter the absorption or emission spectra and led to only a small decrease in the excited-state lifetime.[9–11] Following this early lead, Faulkner and co-workers, using 366-nm excitation, demonstrated photoelectron transfer from $Ru(bpy)_3^{2+}$–zeolite X to N,N,N',N'-tetramethyl-*p*-phenylenediamine ions, $TMPD^+$, in the surrounding medium.[12] More recently, Dutta and co-workers have studied photoelectron transfer from $Ru(bpy)_3^{2+}$–zeolite Y to methyl viologen, MV^{2+} (the latter being located in neighboring cages), and have determined that back electron transfer is retarded, the $MV^{\bullet+}$ product being stable for over 1 h.[13]

The readily available zeolites possess a chemically and structurally well-defined framework and are therefore attractive for organization of photoactive redox components, as the above studies demonstrate. We have also considered the potential utility of this structurally rigid, highly electronegative cavity for alteration of the photochemical and photophysical properties of cavity-entrapped complexes.

In principle, the structurally diverse bipyridines may be employed to synthesize complexes of varying size and functionality while retaining the readily available and structurally well-defined zeolite-Y framework. In order to evaluate the potential of this approach, we have undertaken a systematic study of such systems and herein report a relatively convenient and effective method for the preparation of zeolite-Y-entrapped heteroleptic polypyridine complexes of ruthenium(II).

Experimental Section

A. Materials. A research sample of zeolite Y was generously provided by Union Carbide Corp. 2,2′-Bipyridine, 4,4′-dimethyl-2,2′-bipyridine, and 2,2′-bipyrazine (Aldrich Chemical Co.) were sublimed prior to use. $Ru(NH_3)_6Cl_3$ was obtained from Alfa Inorganics. Zeolite samples were

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precleaned by oxidation under flow of oxygen at 500 °C for 4 h.[11] Samples were extensively washed with a 10% NaCl solution and deionized water.

B. Preparation of Compounds. Ruthenium-Loaded Zeolite (Ru-$(NH_3)_6^{3+}$-Y). This was prepared, according to Lunsford et al.,[9,10] by equilibrating 2 g of Na–Y in 0.6 L of deionized water which contained 50 mg of $Ru(NH_3)_6Cl_3$. After 24 h, the suspension was filtered and $Ru(NH_3)_6^{3+}$-Y was washed with approximately 200 mL of deionized water.

Zeolite-Entrapped Tris(2,2'-bipyridine)ruthenium(II) $(Ru(bpy)_3^{2+}$-Y). This was prepared by a slight modification of the method described by Lunsford and co-workers.[9,10] A 0.50-g sample of $Ru(NH_3)_6^{3+}$-Y was suspended in approximately 10 mL of an ethanol solution containing 50 mg of bipyridine, and the suspension was stirred for 24 h. The suspension was then transferred to a 15 mm × 10 cm Pyrex tube fitted with a vacuum stopcock, and the ethanol was removed by evaporation. The tube was filled three times with nitrogen and evacuated at $10^{-5}–10^{-3}$ Torr for 5 min. The evacuated tube was then partially immersed in a hot oil bath and heated at 180–200 °C for 24 h. While the temperature was maintained, the tube was evacuated for 6 h in order to remove excess ligand. After cooling, the tube was opened and the bright orange solid was suspended in water. The suspension was filtered and the orange solid washed with approximately 200 mL of 10% (w/v) NaCl solution in water in order to remove the surface-adsorbed $Ru(bpy)_3^{2+}$. The orange solid was further washed with approximately 100 mL of 95% ethanol and approximately 200 mL of deionized water. Ethanol washings were checked (ultraviolet absorption spectrum) for free bipyridine. Finally, the solid was dried in air at room temperature.

Zeolite–Entrapped Bis(2,2'-bipyridine)ruthenium(II) $(Ru(bpy)_2^{2+}$-Y). A 0.50-g sample of $Ru(NH_3)_6^{3+}$-Y was suspended in approximately 10 mL of an ethanol solution of 50 mg of bipyridine and handled as described above with the exception that the temperature of the oil bath was maintained at 90 °C. During the first hour of heating, the solid gradually became violet. After 24 h of heating, the sample was purified as described above.

Zeolite-Entrapped Bis(2,2'-bipyridine)(L)ruthenium(II) $(Ru(bpy)_2$-(L)-Y). Bipyrazine (bpz) and 4,4'-dimethyl-2,2'-bipyridine (dmb) were used as L ligands. In both cases the experimental procedure was the same, leading to $Ru(bpy)_2(bpz)^{2+}$-Y and $Ru(bpy)_2(dmb)^{2+}$-Y, respectively. A 0.5-g sample of $Ru(bpy)_2^{2+}$-Y was suspended in approximately 10 mL of the ethanol solution of 40 mg of bpz or dmb, and the samples were handled as described above. The samples were heated at 180–200 °C for 24 h. During heating, the solids became yellow-orange. The resulting solids were purified as described above.

C. Extraction of Complexes from the Zeolite Matrix. 1. Hydrofluoric Acid Method. A method for dissolution of the zeolite matrix is based on a previously reported protocol.[14] A 0.050-g sample of $RuL_nL'_{3-n}^{2+}$-Y was suspended in 4 mL of a solution composed of 20 parts H_2O and 1 part 50% HF. After several minutes the suspension clarified, yielding an orange solution. The solution was then brought to pH 7 with a 2 M KOH solution and centrifuged to remove residual solids. The orange solution was drawn off with a Pasteur pipet and reduced to dryness with a Buchi Rotavap. The residue was dissolved in ethanol, and the resulting sample was purified by chromatography on Sephadex LH20 resin using 95% ethanol as an eluent. Finally, the resultant sample was analyzed by TLC on an aluminum oxide plate with an eluent composed of EtOH, H_2O, and HOAc (49:49:2). This method was used for dissolution of $Ru(bpy)_3$-Y, $Ru(bpy)_2$-Y, and $Ru(bpy)_2(dmb)^{2+}$-Y.

2. Citric Acid Method. A 0.20-g sample of the zeolite-entrapped complex $RuL_nL'_{3-n}^{2+}$-Y was suspended in 5 mL of 20% citric acid. After the suspension was stirred for 12 h, it was brought to pH 7 with a 2 M KOH solution and centrifuged. The resulting orange solution was decanted, and the excess citrate was removed from the solution by chromatographing the sample on Dowex AG 1-X8 resin (hydroxyl form). The chloride form of the Dowex resin was converted to the hydroxyl form by washing with a 10% solution of NaOH followed by water. The sample was chromatographed using water as the eluent. Finally, the sample was condensed on a Buchi Rotavap. The purity of the sample was evaluated by TLC as described above. This method was used in the case of $Ru(bpy)_2(bpz)^{2+}$-Y because the complex proved to be unstable in the HF solution.

D. Spectroscopic Measurements. 1. Electronic Absorption Spectra. Electronic absorption spectra were obtained with a Hewlett-Packard Model 8452A diode array spectrophotometer. The solid samples were mixed with a few drops of mineral oil. The resulting pastes were diluted with additional oil, and the samples were placed in a 1-cm quartz cuvette. Spectra were obtained in the absorbance mode.

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2. Resonance Raman Spectra. Ground-state Raman spectra were obtained using a conventional Raman spectrophotometer (Spex Model 1403 double monochromator equipped with a Spex Model DM1B controller and a Hamamatsu R928 photomultiplier tube) with 457.9-nm excitation from a Spectra-Physics Model 2025-05 argon ion laser. Excitation of 441.7 nm was obtained from a Liconix Model 4240NB He–Cd laser, while 647.1-nm excitation was obtained from a Spectra-Physics Model 164 krypton ion laser. Spectra of the zeolite-entrapped compounds were obtained from solid samples in rotating NMR tubes. Spectra of the compounds extracted from the zeolite matrix were obtained from aqueus solutions in the same manner. The laser beam was focused onto the sample by using a glass lens, and the scattered light was collected with a 135° backscattering geometry and a conventional two-lens (glass) collecting system.

Results and Discussion

A. Synthesis. 1. The Tris-Homoleptic Complex. The preparation of the zeolite-entrapped trisligated complexes described here represents only a slight modification of the procedure described by Lunsford and co-workers.[9,10] The most important difference is the inclusion of the aqueous NaCl wash.[11] We have found that extensive Soxhlet extraction of the product is insufficient to remove all surface-bound complex. The last traces are removed only upon washing with the 10% NaCl solution.

2. Tris-Heteroleptic Complexes. In preparing the samples of $Ru(bpy)_3^{2+}$-Y, we noted color changes from white to violet to orange during the first hour of heating. The gradual change in color of the sample led us to suspect that it would be possible to stop the reaction at the stage where only the bis complex was formed and prompted us to attempt the preparation of $Ru(bpy)_2^{2+}$-Y.

Several variations in the procedure for the preparation of the bis-homoleptic complexes were investigated. In some cases, samples were heated at 90 °C for long periods (up to several days) and then cooled and washed according to the described procedure. Even in the presence of a large excess of ligand, we have found that maintaining the temperature at ∼90 °C produces only the entrapped bisligated species. The presence of this species has been confirmed by electronic absorption and resonance Raman spectroscopies. Thus, spectra of the independently prepared bisligated complex obtained in aqueous solution are virtually identical to those of the compound obtained in the zeolite. The RR spectrum of the zeolite-entrapped complex is virtually identical to those obtained when ammonia is the second ligand.[15] However, as pointed by Caswell et al.,[16] the spectral changes upon substitution of ammonia by water are expected to be quite small. Thus, although we suspect the presence of ammonia in the first coordination sphere, we cannot completely exclude the possibility of other ligands such as H_2O. We note that trace amounts of surface-bound trisligated species are formed during this 90 °C heating step, as evidenced by slight luminescence in the aqueous NaCl wash, but these are easily removed by the washing step. However, it is important to emphasize that it is essential to adequately remove (heating under vacuum and ethanol washing) the excess free ligand from the RuL_2^{2+}-Y product. If this is not effectively accomplished, some ligand combinations may give rise to zeolite-entrapped tris-homoleptic (or unwanted tris-heteroleptic) complexes during the final (high temperature) treatment.

We note that if $Ru(NH_3)_6^{3+}$-Y is dry-mixed with bipyridine and the mixture is then handled as described in the section concerning preparation of $Ru(bpy)_2^{2+}$-Y, a blue-violet product is obtained, rather than the violet one. Figure 1B shows the electronic absorption spectrum of $Ru(bpy)_2^{2+}$-Y prepared from the ethanol-soaked sample (i.e., the violet product) whereas Figure 1A shows the electronic absorption spectrum of $Ru(bpy)_2^{2+}$-Y prepared from the dry-mixed sample (i.e., the blue-violet). Note the increase in intensity of the band at ca. 606 nm. The nature of this byproduct is discussed later.

Treatment of the violet product with an excess of either bpz or dmb results in the formation of pure bis-heteroleptic zeolite-

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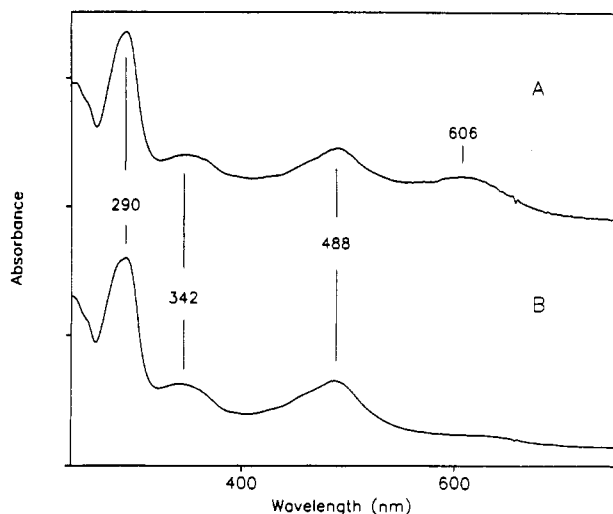
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Figure 1. Electronic spectra of Nujol suspensions of $Ru(bpy)_2^{2+}$–Y prepared from dry-mixed reagents (trace A) and ethanol-presoaked reagents (trace B).
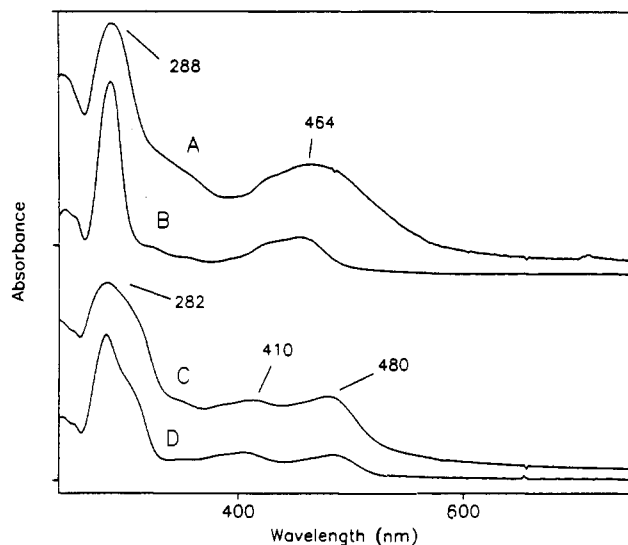

Figure 2. Electronic spectra of Nujol suspensions of zeolite-entrapped complexes and aqueous solutions of independently synthesized complexes: trace A, $Ru(bpy)_2(dmb)^{2+}$–Y; trace B, independently synthesized $Ru(bpy)_2(dmb)^{2+}$; trace C, $Ru(bpy)_2(bpz)^{2+}$–Y; trace D, independently synthesized $Ru(bpy)_2(bpz)^{2+}$.

Figure 3. Resonance Raman spectra of $Ru(bpy)_2(bpz)^{2+}$ with 441.7-nm excitation: zeolite-entrapped complex (trace A); zeolite-extracted complex (trace B); independently synthesized complex (trace C).

Figure 4. Resonance Raman spectra of $Ru(bpy)_2(dmb)^{2+}$ with 457.9-nm excitation: zeolite-entrapped complex (trace A); zeolite-extracted complex (trace B); independently synthesized complex (trace C).

entrapped complexes. The electronic absorption spectra are shown in Figure 2, along with those of aqueous solutions of authentic mixed-ligand complexes (i.e., independently synthesized). At this point, it is necessary to mention the fact that attempts to prepare $Ru(bpz)_2(bpy)$–Y and $Ru(dmb)_2(bpy)$–Y were unsuccessful. While in the latter case it is reasonable to suggest that this failure is the result of excessive steric bulk, we currently can offer no explanation for the lack of success in the case of the former complex.

B. Spectroscopic Characterization. The electronic absorption spectra of the zeolite-entrapped complexes show no significant differences in the positions of the absorption maxima compared to the spectra of the solution-phase complexes. However, the zeolite-entrapped species gave broadened electronic absorption bands.

The resonance Raman spectra of $Ru(bpy)_2(bpz)^{2+}$–Y, $Ru(bpy)_2(bpz)^{2+}$ extracted from the zeolite matrix, and a solution of the independently prepared complex are shown in Figure 3. The analogous resonance Raman spectra of $Ru(bpy)_2(dmb)$ are presented in Figure 4. In both cases, there are only minor frequency shifts (0–7 cm^{-1}) between bands in the spectra of the free and zeolite-entrapped complexes. However, the intensities of the Raman bands undergo significant changes upon incorpo-
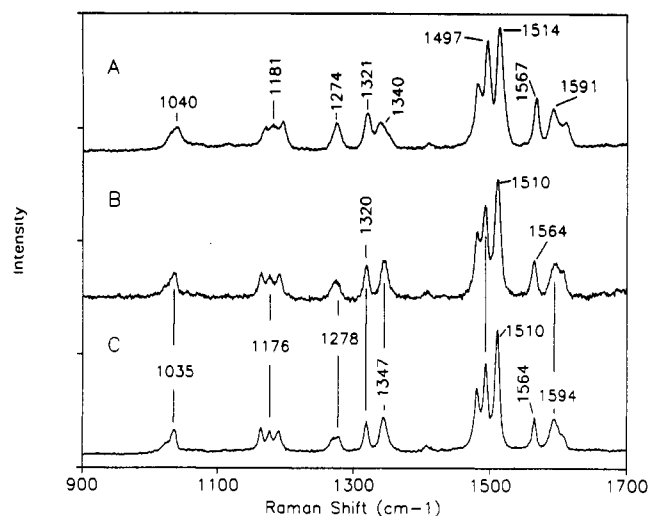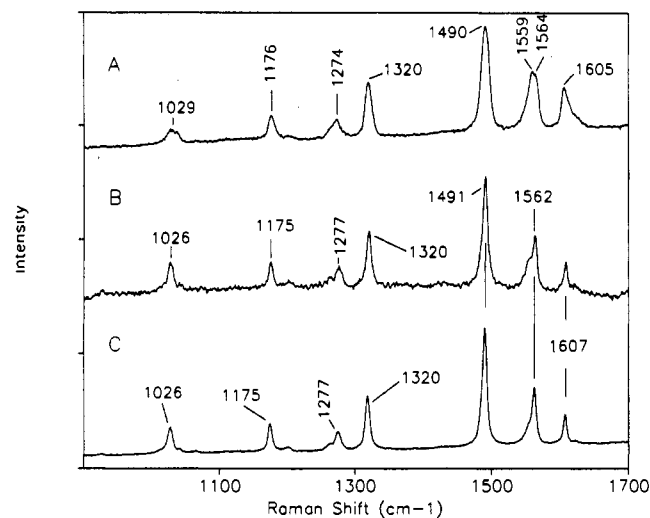
ration of the complexes in zeolite supercages. That these effects are due to the environment in the zeolite supercage and not to a modification of the parent compound is confirmed by the observation that the spectra of the extracted complexes are virtually identical to those prepared outside of the zeolite. Furthermore, we also note that, in TLC experiments (on the $Ru(bpy)_2(bpz)$–Y extract) wherein the tris-homoleptic species yielded R_f values of 0.9 and 0.5, only a single spot having an R_f value of 0.6 was obtained.

C. Nature of the Blue Byproduct. When the $Ru(bpy)_2^{2+}$ was extracted from the zeolite matrix (see Experimental Section), the resultant residual solid was blue. Figure 5 presents the resonance Raman spectra of the blue-violet zeolite sample (whose electronic absorption spectrum is shown in Figure 1A) and the blue solid from the extraction (trace C). Trace A of Figure 5 shows the RR spectrum obtained with 488-nm excitation (i.e., in resonance with the 488-nm absorption band) whereas trace B presents the RR spectrum obtained with 647-nm excitation (i.e., in resonance with the 606-nm absorption maximum of the component under consideration). These results suggest that the blue compound is a bipyridine–transition-metal complex. The possibility of complexation with metals other than ruthenium was eliminated, since when bpy ligand was added to the zeolite sample with no Ru^{2+} ions and the mixture was heated to 200 °C, there was no change in the electronic absorption spectrum of the sample. When the
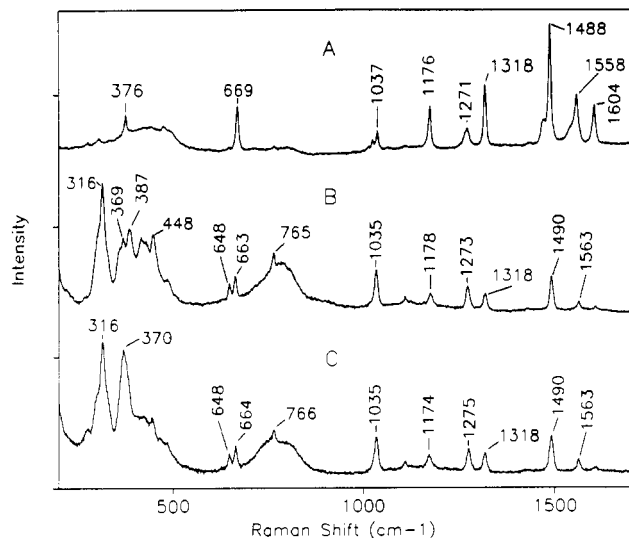
Figure 5. Resonance Raman spectra of the blue-violet zeolite sample with 488.0-nm excitation (trace A), the blue-violet zeolite sample with 647.1-nm excitation (trace B), and the solid from the extraction with 647.1-nm excitation (trace C).
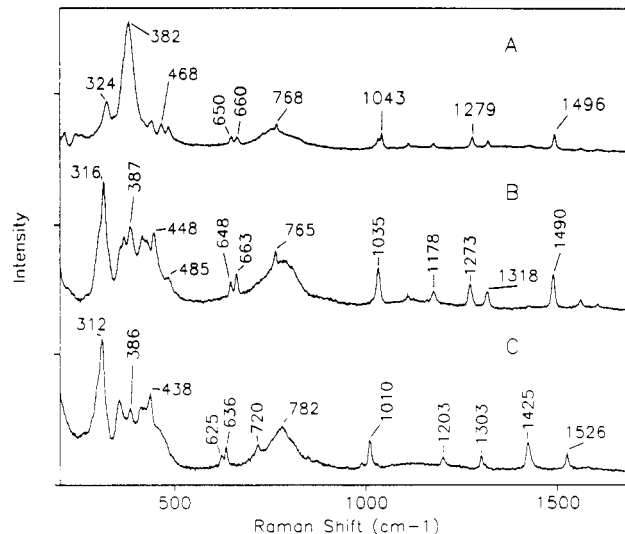

Figure 6. Resonance Raman spectra (with 647.1-nm excitation) of the green solution (trace A), the blue-violet zeolite sample (trace B), and the blue-violet zeolite sample prepared from the perdeuteriated bipyridine (trace C).

blue-violet sample was heated without additional bpy to 200 °C, it became violet and its electronic absorption spectrum became identical to that of pure $Ru(bpy)_2^{2+}$-Y. Resonance Raman spectra of the blue-violet and violet samples obtained with 488-nm excitation are virtually identical. However, when 647-nm excitation was used, a spectrum could only be obtained from the blue-violet sample. We conclude that the blue-violet sample is in reality a composite of two species. Indeed, the violet eluent from an originally blue-violet sample has no absorption in the 600-nm region. Meyer and co-workers have reported the preparation of a blue complex whose formula is $[(bpy)_2(H_2O)RuORu(H_2O)(bpy)_2)]^{4+}$ and which has an electronic absorption maximum at 640 nm.[17,18] The similarity of the visible absorption bands in Meyer's compound and ours leads us to suspect that we have formed a Ru(III) species. Although a complex such as that reported by Meyer is too large to conveniently fit into the zeolite supercage, the zeolite framework may serve as a source of oxygen and we might envision a complex such as $(Al)SiORu(bpy)_2(H_2O)^{2+}$, ruthenium being bound via an oxygen atom to the zeolite surface. The existence of a Ru(III) species is further indicated by the observation that we can produce $Ru(bpy)_2^{2+}$-Y by heating the compound to 200 °C, i.e., completing the reduction of the ruthenium.

In order to elucidate the nature of this blue byproduct, we have compared its RR spectra to that of the compound reported by Meyer and co-workers.[17,18] As is shown in Figure 6, the RR

spectrum of the green solution[19] (trace A) is quite similar to that of the blue zeolite sample, with the major differences occurring in the region between 100 and 500 cm^{-1}. The strongest feature in trace A (382 cm^{-1}) can be reasonably assigned to the Ru–O–Ru stretching mode.[20] In trace B this feature disappears and is replaced by a strong band occurring at 316 cm^{-1}, whereas the high-frequency bipyridine-based modes are virtually unaltered. This strong feature at 316 cm^{-1} is assigned to the Ru–O–Si(Al) stretching mode. This assignment is supported by the fact that, upon perdeuteration of the bipyridine ligands (trace C), this feature shifted by only 4 cm^{-1} whereas all other bands exhibited shifts comparable to those observed when comparing $Ru(bpy)_3^{2+}$ to $Ru(bpy-d_8)_3^{2+}$.

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(19) Because the pure blue compound is difficult to obtain, we have prepared the green solution using a slightly modified procedure reported by Weaver et al.[17] The electronic absorption spectrum of the green solution presents a strong absorption band at 640 nm and a weak one at ~480 nm, the latter electronic absorption band being probably an indication of unreacted $Ru(bpy)_2(H_2O)_2^{2+}$.

(20) (a) Stretching frequencies of metal–oxygen bonds in μ-oxo dimers are found in the low-frequency region (~300–500 cm^{-1}). For example, ν_s(Fe–O–Fe) for a heme oxo dimer occurs at 363 cm^{-1} (see ref 20b).
(b) Crisanti, M. C.; Spiro, T. G.; English, D. S.; Hendrickson, D. N.; Suslick, K. S. *Inorg. Chem.* **1984**, 3897.