Ligand Field Photochemistry of Pentacyanoferrate(II) Complexes with Diamine Ligands: Influence of the Chelating Ligands and the Role of Neighboring Group Effects on the Photoinduced Ring Closure Process

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A series of pentacyanoferrate(II) complexes with bidentate diamine ligands, [Fe(CN)$_5$(N⌒N)]$^{3-}$, where N⌒N is 1,2-diaminoethane, *N,N*-diethyl-1,2-diaminoethane, 2-((2-aminoethyl)amino)ethanol, 1,2-diaminopropane, 1,2-diamino-2-methylpropane, 1,3-diaminopropane, 2-amino-5-(diethylamino)pentane, 1,6-diaminohexane, or 1,2-diaminobenzene, was studied in the presence of an excess of the free ligand in solution. In this condition, the photodissociation of L becomes ineffective, and only the photolabilization of a cyanide can be observed, yielding the corresponding tetracyanoferrate(II) complexes. The quantum yields for photosubstitution of cyanide range from 0.11 to 0.025 for photolyses at 365 nm and are dependent on the N⌒N chain length of the aliphatic diamines. The presence of bulky substituents in one of the amine groups has little influence on the photoinduced ring closure efficiency. However, methyl substituents on the carbon chain of the chelating ligand cause an increase in the quantum yield. The variation of the quantum yield with the different ligands permits comparison of several effects such as metric, topological, chelating, and neighboring group effects on the photoreactivity of the series.

Introduction

The photochemistry of pentacyanoferrate(II) complexes, [Fe(CN)$_5$L]$^{3-}$, exhibits the photolabilization of either L or CN$^-$, depending on the experimental conditions.[1-10] Recently, we reported the photosubstitution behavior[9] of some inert [Fe(CN)$_5$L]$^{3-}$ complexes, where L = PPh$_3$, AsPh$_3$, SbPh$_3$, P(OCH$_3$)$_3$, and CO, which do not display metal-to-ligand charge-transfer (MLCT) bands in the visible region, allowing direct access to the ligand field (LF) excited states. Ligand field excitation of these complexes results in labilization of L (eq 1) toward substitution

$$[Fe(CN)_5L]^{3-} + mpz^+ \xrightarrow{h\nu} [Fe(CN)_5mpz]^{2-} + L \quad (1)$$
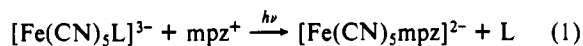
by the *N*-methylpyrazinium ion (mpz$^+$) with quantum yields (Φ) around 0.15, except for the carbonyl complex, where Φ = 0.38.

This difference in the quantum yields was ascribed to a distinct energy level scheme for each class of complexes. In the former class of complexes, ^{3}E state is the lowest one, while in the carbonyl derivative the ligand has a field strength stronger than that of CN$^-$, and the lowest excited state is the ^{3}A$_2$ level. This interpretation is also in accord with the photochemical results obtained by other groups.[1-3]

The labilization of the ligand L, considered to be the only typical photochemical pattern for [Fe(CN)$_5$L]$^{n-}$, has already been reported by Figard and Petersen[4] for pentacyanoferrate(II) complexes with aromatic nitrogen ligands. Such complexes present a metal-to-ligand charge-transfer transition, and upon irradiation in this band, the magnitude of the quantum yields is dependent on whether the LF (0.1 < Φ < 1.0) or MLCT (Φ < 0.05) excited state is lowest in energy.

The photosubstitution of a cyanide ligand, although expected to be less favored than that of a neutral ligand,[11] was observed for the first time in our previous work[6] with the (1,2-diaminoethane)pentacyanoferrate(II) complex (eq 2) and subsequently with other diamine-ligand complexes.[7,10]

The presence of a bidentate ligand, such as 1,2-diaminoethane,

$$[(NC)_5Fe\text{---}N⌒N]^{3-} \xrightarrow{h\nu} \left[(NC)_4Fe\left\langle\begin{array}{c}N\\N\end{array}\right\rangle\right]^{2-} + CN^- \quad (2)$$
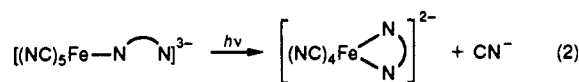
which has an amine group available to enter a vacant coordination site, yielding the corresponding chelated tetracyanoferrate(II) complex, was essential in order to observe the photosubstitution of the cyanide ion with quantum yields comparable to those for substitution of L.[4,9]

In this work, a systematic study on the photochemistry of [Fe(CN)$_5$(N⌒N)]$^{3-}$ (N⌒N is 1,2-diaminoethane, **en**; *N,N*-diethyl-1,2-diaminoethane, **deten**; 2-((2-aminoethyl)amino)ethanol, **aeaet**; 1,2-diaminopropane, **pn**; 1,2-diamino-2-methylpropane, **mpn**; 1,3-diaminopropane, **tn**; 2-amino-5-(diethylamino)pentane, **adeap**; 1,6-diaminohexane, **dahex**; or 1,2-diaminobenzene, **dab**) has been carried out with the aim of investigating the influence of the chelate ring size, the substituent effects, and the presence of sterically hindered groups in the ligands on the efficiency of the ring closure process.

Experimental Section

Materials. Na$_3$[Fe(CN)$_5$NH$_3$]·3H$_2$O was synthesized from Na$_2$[Fe(CN)$_5$NO]·2H$_2$O (Merck) by slight modifications of the method of Brauer[12] and recrystallized several times from saturated aqueous ammonia solution at 0 °C. The [Fe(CN)$_5$L]$^{3-}$ complexes were generated in solution by reacting the aquapentacyanoferrate(II) ion, obtained by the aquation of the [Fe(CN)$_5$NH$_3$]$^{3-}$ ion, with a large excess of the corresponding ligand L. All ligands (Aldrich Chemical Co.) were either distilled under reduced pressure (liquids) or used as supplied (solids). The Na$_2$[Fe(CN)$_4$(N⌒N)] complexes were prepared as described by Goto et al.[13-15] Potassium tris(oxalate)ferrate(III) was prepared and purified according to the literature procedure[16] from reagent grade potassium oxalate and FeCl$_3$. The *N*-methylpyrazinium iodide was synthesized and recrystallized according to the method described by Bahner and Norton[17] by the reaction of methyl iodide (Aldrich) with pyrazine (Aldrich) in benzene solution.

Physical Measurements and Procedures. The photolysis of the complexes was carried out with an Oriel 200 W Hg(Xe) arc lamp powered by an Oriel universal power supply. Monochromatic irradiation was obtained by passing the beam through a quartz collimating lens and a 365-nm Oriel interference filter with a bandpass of 10 nm. The beam was interrupted by means of an Oriel Shutter Control. Light intensities were determined by tris(oxalate)ferrate(III) actinometry before and after each photolysis run.

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Table I. Spectra Data for the d–d Transition for Substituted Diamine–Cyanoferrate(II) Complexes, in Aqueous Solution[d]

L		$[(CN)_5FeL]^{3-}$ λ_{max}/nm	$[(CN)_4FeL]^{2-}$ λ_{max}/nm
en	H₂N⌢NH₂	395 (4.6)[a]	393 (3.5)[a]
deten	H₂N⌢NEt₂	398 (4.6)	391 (4.6)
aeaet	H₂N⌢NH⌢OH	400 (4.2)	383 (5.2)
pn	Me / H₂N⌢NH₂	398 (4.7)	392 (4.1)[b]
mpn	Me / Me / H₂N⌢NH₂	399 (4.6)	389 (4.7)
tn	H₂N⌢⌢NH₂	395 (4.5)	392 (4.6)[c]
adeap	Me / H₂N⌢⌢⌢NEt₂	397 (4.6)	389 (4.8)
dahex	H₂N⌢⌢⌢⌢NH₂	398 (4.9)	413 (4.5)
dab	C₆H₄(NH₂)₂	410 (4.5)	404 –

[a] Reference 6. [b] Reference 13. [c] Reference 15. [d] The number in parentheses indicates the molar absorption/10^{-2} M⁻¹ cm⁻¹.

All the experiments were performed at 25.0 °C, in a 5.00 cm path length quartz cell, in the presence of an excess of the free ligand. The concentrations of the complexes (3.4 × 10⁻³ to 6.0 × 10⁻³ M) were adjusted to yield optical densities greater than 2 at 365 nm to assure that all the incident light was absorbed. The solution was continuously stirred during the irradiation. Net conversions of starting material ranged from 2.1% to 12.4%. The contribution of thermal reaction was negligible and controlled by the use of a dark sample prepared in an identical manner.

At least two distinct analytical procedures were employed for obtaining quantum yield values for each photolysis run in order to check internal consistency. Several quantum yield determinations were made for each set of conditions until at least four values with comparable data were collected, within experimental error.

The concentrations of residual [Fe(CN)₅L]³⁻ and of photogenerated [Fe(CN)₄L]²⁻ were determined spectrophotometrically after carrying out a ligand-exchange reaction with a large excess of pyrazinamide and/or the methylpyrazinium ion, for at least 40 min in the dark. The [Fe(CN)₄L]²⁻ ion was also isolated by ion-exchange chromatography and identified by conversion to the corresponding tetracyanodiimine complexes,[13–15,18] as described previously.[6]

Absorbance measurements were recorded on a HP 8451A diode array spectrophotometer or a Beckman DU-70 spectrophotometer.

Results

Electronic Spectra. The electronic spectra of aqueous solutions of the pentacyanoferrate(II) complexes with diamines exhibit an absorption band which has been previously ascribed to a d–d transition from the $^1A_1$ ground state to the $^1E(1)$ excited state, in C_{4v} symmetry.[19] The spectra of tetracyanoferrate(II) complexes with chelated diamines are very similar to those of the pentacyanoferrates(II) and can be assigned as LF $^1A_1 \rightarrow {}^1B_1$ or $^1A_1 \rightarrow {}^1B_2$ transitions in C_{2v} symmetry.

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Table II. Quantum Yields for the Ring Closure Process of the Substituted (Diamine)pentacyanoferrate(II) Complexes, [Fe(CN)₅N⌢N]³⁻ in Aqueous Solution at λ_{exc} = 365 nm[b]

complex	L	$\Phi \pm 0.002$	[L]/[complex]
1	en	0.084 (6)	10
		0.087 (5)[a]	10
2	deten	0.087 (6)	10
3	aeaet	0.088 (7)	11
4	pn	0.095 (8)	11
		0.093 (4)	25
5	mpn	0.100 (6)	10
6	tn	0.110 (7)	17
		0.120 (4)	35
7	adeap	0.059 (7)	9
8	dahex	0.025 (8)	10
9	dab	0.100 (5)	10

[a] Reference 6. [b] The number in parentheses indicates the number of independent runs in each data set.

The absorption maxima and corresponding molar absorbances, listed in Table I, are similar to those for ligand field transitions of other cyanoferrate(II) complexes.[13–15,20–23]

Quantum Yields. The [Fe(CN)₅(N⌢N)]³⁻ complexes are labile toward substitution of the N⌢N ligand. Because of this, both the thermal and the photochemical reaction (3) is annuled by rapid back-reaction in the presence of a large exces of free N⌢N ligand.

$$[Fe(CN)_5N\frown N]^{3-} + H_2O \rightarrow [Fe(CN)_5H_2O]^{3-} + N\frown N \quad (3)$$
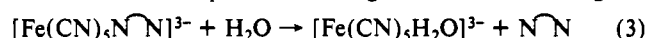
Under these experimental conditions, the [Fe(CN)₅(N⌢N)]³⁻ complexes seem to be essentially insensitive to photolysis, since no spectral change can be detected during the irradiation time. However, by using an alternate analytical procedure, based on the distinct reactivity of cyanoferrate species, as discussed below, one can detect the formation of the tetracyanoferrate(II) species with a bidentate N⌢N ligand resulting from photolabilization of the cyanide ion followed by ring closure process (see eq 2). The apparent photoinertness is due to the similar absorptivities in the same spectral region, as one can see in Table I, exhibited by both the starting complex and the photoproduct.

Although direct spectral analysis is precluded, the extent of the photochemical reaction can be determined by means of a differential spectrum after selective conversion of [Fe(CN)₅(N⌢N)]³⁻ into a highly absorbing species, e.g., by reacting the labile pentacyanoferrate(II) ion with pyrazinamide ([Fe(CN)₅(pz)-CONH₂]³⁻, λ_{max} = 490 nm, ϵ = 4.3 × 10³ M⁻¹ cm⁻¹) or with methylpyrazinium ([Fe(CN)₅mpz]²⁻, λ_{max} = 660 nm, ϵ = 12.3 × 10³ M⁻¹ cm⁻¹). Since the tetracyanoferrate(II) species are stable and inert toward substitution, they do not react with those ligands and can be isolated by ion exchange and further characterized by oxidative dehydrogenation with hexacyanoferrate(III) at pH 12.5 to form the corresponding dark red tetracyanodiimine complexes.[18]

The average quantum yields, measured by at least two analytical methods, are reported in Table II. Net conversions were kept to a minimum in order to prevent secondary photoreactions and to obtain reliable quantum yields. After 15% photolysis one may observe an apparent decrease of the quantum yields due to a parallel photodecomposition of the tetracyano species.

The irradiation of the (1,2-diaminobenzene)pentacyanoferrate(II) complex showed a peculiar behavior, with the appearance of a new band at 580 nm. Figure 1 presents typical spectral changes observed during photolysis of an air-equilibrated solution. No spectral variation can be observed in a deoxygenated solution, but a prompt reaction takes place when the irradiated solution is exposed to air, producing a fast color change of the solution from yellow to deep blue.

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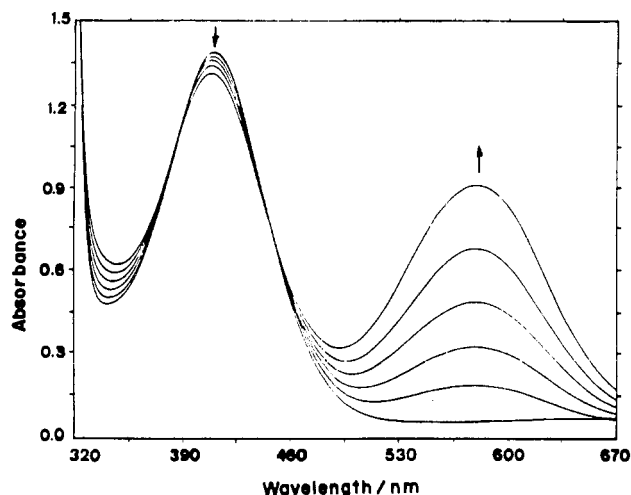
Figure 1. Absorption spectral changes observed during 365-nm photolysis of $[Fe(CN)_5dab]^{3-}$ (5.8×10^{-3} M) in aqueous solutions containing excess ligand. [dab] = 6.0×10^{-2} M. Δt_{irr} = 210 s.

The data for the 1,2-diaminoethane derivatives (Table II, entries 1–3) show that the presence of relatively bulky substituents in one of the terminal NH_2 groups of the diamine has little influence on the photoinduced ring closure process. However, methyl groups in the carbon chain of the N͡N chelating ligand increase the quantum yield (Table II, entries 4 and 5). It is noteworthy that the quantum yield for the photosubstitution of CN^- is dependent on the N͡N chain length of the aliphatic diamines, and their values ranged from 0.11 to 0.025 (Table II, entries 1 and 6–8). The maximum value is reached for a six-membered ring, and then it decays progressively as the carbon chain increases (Table II, entries 6–8).

Discussion

The (1,2-Diaminobenzene)pentacyanoferrate(II) System. In air-equilibrated solution, the observed behavior clearly points to a thermal reaction with oxygen subsequent to the photochemical ring closure process. The blue species detected, previously described by Christoph and Goedken,[24] is (1,2-benzoquinonediimine)tetracyanoferrate, $[Fe(CN)_4(bqdi)]^{2-}$, formed according to eq 4. Similar reactions are known for other 1,2-diaminobenzene

$$\lambda_{max} = 580 \text{ nm}, \quad \varepsilon = 12.5 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$$

(4)
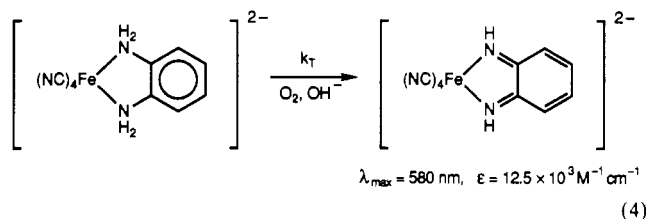
complexes.[25-28] As far as we are aware, the photochemical ring closure in deaerated $[Fe(CN)_5(dab)]^{3-}$ solutions is the only way to obtain the $[Fe(CN)_4(dab)]^{2-}$ complex instead of $[Fe(CN)_4(bqdi)]^{2-}$. Attempts to use the formation of the blue species to measure the quantum yields led to erratic results, since the reaction rate with oxygen was either too slow or not quantitative. Irradiation under an O_2 atmosphere resulted in a blue compound, which gradually precipitated. This precipitate is apparently derived from oxidation of the excess free ligand itself, which is known to be unstable at room temperature or in concentrated solution, decomposing to produce 2-aminophenoxazin-3-one and 2,3-diaminophenazine, as the main nonpolymeric products.[29-31]
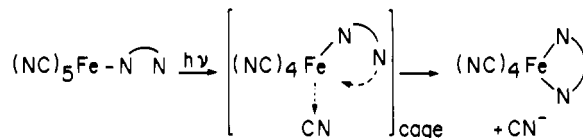

Figure 2. Schematic representation of the neighboring group effect in the ring closure process.

Photochemical Reactivities. The magnitude of the measured quantum yields is strongly influenced by the nature of the N͡N ligands, all of which are highly flexible. This quantum yield variation could be related to a metric (*or relative size*) factor, in addition to a topological (*or linking*) factor, and emphasizes the important role of molecular organization[32] prior to the occurrence of the photochemical process.[33]

In this work, the topological effect is the result of the presence of an additional amine group, available for coordination, linked to the $[Fe(CN)_5]^{3-}$ moiety in the bidentate N͡N ligands. The free NH_2 group may assist the dissociation of a cyanide from the metal by forming an incipient chelating ring in the excited state, according to the scheme represented in Figure 2. This ring closure process, which is accomplished by the unchelated amine group in the proximity of the coordination sphere, may also preclude geminate recombination prior to cage escape, allowing complete dissociation of the cyanide ion. In fact, depending on the experimental conditions,[34] the presence of a vacant coordination site on the metal could lead to species with reactivities high enough to allow recombination, preventing the detection of the primary event. These hypotheses also explain why the photosubstitution of the cyanide ion has not been detected during steady-state photolysis studies employing monodentate ligands.

Complementing the topological factor, the metric factor determines how efficiently these effects may act on the photosubstitution of the cyanide ion. As indicated in Table II, the 1,3-diaminopropane complex exhibits the highest quantum yield values. In fact, the N͡N trimethylene chain is found to give the best geometrical fit, facilitating the ring closure process after the labilization of the cyanide ion.

A good illustration of this end-to-end distance effect (*metric factor*) can be seen for N͡N = 1,6-diaminohexane, where the quantum yield is 0.025. This result is very similar to that obtained upon irradiation of $[Fe(CN)_5H_2O]^{3-}$ in the presence of phenanthroline, which can only coordinate as a bidentate ligand because of the ring rigidity and, consequently, cannot present a neighboring group effect.[6] The low quantum yield for the 1,6-diaminohexane complex reveals a pronounced decrease of the ring closure process. Conformational factors and the larger N͡N distance in this complex make the topological factor negligible by locating the dangling amine group far away. This situation becomes quasi-equivalent to that of a free ligand having random motion in solution, permitting an appreciable recombination of the geminate products during the very short lifetime of the solvent cage. This is in fact a trivial ring size effect: six-membered rings are easy to form; nine-membered rings are nearly impossible to prepare by unactivated ring closure reactions.

The present study shows the fundamental role of the neighboring group effect for detecting by conventional steady-state photolysis, short-lived intermediates and/or reactions which take place from an excited state. Thus, the observation of the photolabilization of CN^- from $[Fe(CN)_5(N\!\frown\!N)]^{3-}$ was made possible because of this preorganization. It also shows that the photosubstitution quantum yields, measured in a given experimental

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

In contrast to the case of [Co(CN)$_6$]$^{3-}$,[34] the [Fe(CN)$_5$(N̑N̑)]$^{3-}$ 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 N̑N̑ 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+}$–zeolite Y to methyl viologen, MV^{2+} (the latter being located in neighboring cages), and have determined that back electron transfer is retarded, the MV$^{•+}$ 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$_3$)$_6$Cl$_3$ was obtained from Alfa Inorganics. Zeolite samples were

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