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Studies of Zeolite Entrapped Ruthenium Polypyridine Complexes

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Abstract

There is an intense interest in designing molecular systems which will absorb visible sunlight, initiate an electron transfer process, and ultimately convert the solar energy to useful chemical energy of fuels such as hydrogen produced from water. The zeolite-entrapped polypyridine complexes of divalent ruthenium hold promise as efficient photocatalysts for net charge separation and such efficiencies are further enhanced by organized incorporation of donor and acceptor components. This paper deals with the synthesis and spectroscopic investigation of zeolite-entrapped ruthenium polypyridine complexes which may be useful in the development of solar energy conversion schemes. The sensitizer molecules, such as $Ru(bpy)_3^{2+}$ (bpy = 2,2'-bipyridine), are entrapped within the supercages of structurally well-defined zeolite Y by the so called "ship in a bottle" synthesis, which eliminates the undesirable diffusion of the complex and inhibits the wasteful back-electron transfer reaction. This complex has a dimension of ~12Å, which is too large to introduce through a 7.4 Å window opening. Once the complex is formed in the supercage, it cannot escape through the windows and is effectively entrapped within the supercage. The zeolite-entrapped ruthenium complexes are characterized by diffuse reflectance, electronic absorption, electronic emission, and resonance Raman (RR) spectroscopy, as well as excited state lifetime measurements. A brief summary of the synthetic and characterization procedure of the zeolite-entrapped ruthenium polypyridine complexes is presented here. Emphasis is given on the author's work, although a discussion of some of the important contributions made by other workers is also included. This study clearly demonstrates that entrapment of ruthenium complex within the supercage of Y-zeolite can alter inherent photophysical properties of the complex in an advantageous manner.

Introduction

Photosynthesis is the process that converts solar energy into chemical energy and maintains life on earth (Lawlor, 1993). Only a very small fraction (~0.05%) of the huge amount of solar energy available is converted by green plants in photosynthesis, and the rest of the energy is wasted. For the last two decades there has been an intense interest in designing molecular systems that mimic photosynthesis. The strategy has been to design a molecular assembly that will absorb visible light, that will initiate an electron transfer process, ultimately the solar energy is used to cleave water to produce hydrogen fuel (Kalyanasundaram, 1987; Parmon and Zamarev, 1989). The inexhaustible solar energy can be converted to environmentally clean fuels by assembling a molecular suprastructure.

There are three basic phenomena that control the use of light energy: energy capture, energy transfer, and photoinitiated electron transfer. A synthetic photocatalytic system that can produce hydrogen by the reduction of water is shown in Scheme 1. In this scheme the excited state molecule S* (S is the sensitizer molecule which absorbs the visible light) reacts with the acceptor molecule A forming S+ and A-. The reduced A- intermediate can transfer the electron to water via an appropriate catalyst, leading to the production of hydrogen. The sensitizer, S, is then regenerated by the electrons provided by a donor (another ruthenium complex or a sacrificial electron donor such as EDTA), D, to form D+, which is then available to convert H_2O to O_2.

$$S \xrightarrow{h\nu} S^*$$

$$S^* + A \longrightarrow S^+ + A^-$$
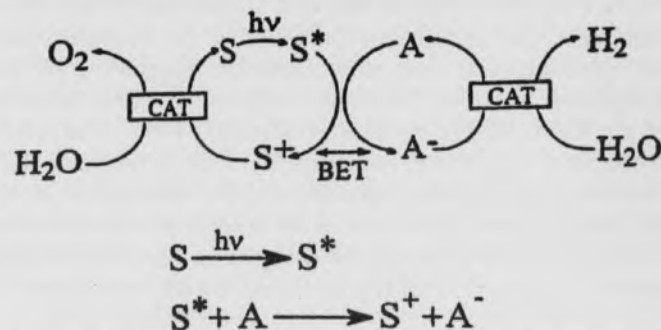
Scheme 1. Photocatalytic system for splitting of water (S = sensitizer, A = acceptor, BET = back electron transfer, CAT = catalyst).

In order to make Scheme 1 practical, several issues need to be resolved. The issues of concern are: (1) proper choice of sensitizer (S) from the view point of absorption of sunlight; (2) production of a reasonably long excited state lifetime of S* so that it can react with A; (3) separation of S+ and A- from each other to minimize back electron transfer; (4) suitable ground and excited state potential of the redox species so that some useful chemistry can be carried out; and (5) regeneration of the photochemical cycle.

Many attempts have been made (Ramamurthy, 1991) to overcome these problems and to make Scheme 1 practical. Several classes of molecules have been shown to possess the necessary properties to serve as effective photosensitizers for such schemes. The most promising are

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those based on polypyridine complexes of divalent ruthenium (i.e, $Ru(bpy)_3^{2+}$ and related complexes; Kalyanasundaram, 1982), various metal complexes of porphyrins (Persaud et al., 1987), and phthalocyanines (Darwent et al., 1982). Even though suitable photosensitizers are available in terms of excited state lifetime, other fundamental problems need to be solved. Simple homogeneous systems such as liquid solutions are not suitable for solar devices because of the random character of molecular thermal motion, uncontrolled diffusion, and the lack of a barrier to prevent wasteful back reaction.

There is an intense interest in designing effective organizational strategies to overcome the above-mentioned problems. These strategies include synthesis of covalently linked redox assemblies as well as the incorporation of the photoactive species into larger spatially well-organized media such as modified glass surfaces or microheterogeneous systems (Gafney, 1990) such as micelles, colloids, lipids, or polymers. One of the most interesting attempts reported so far is the use of highly ordered host materials such as zeolites (Turbeville et al., 1992; Dutta and Turbeville, 1992). The sensitizer molecules such as $Ru(bpy)_3^{2+}$ (bpy = 2,2'-bipyridine) are entrapped within the supercages of structurally well defined zeolite Y (Turbeville et al., 1992; Dutta and Turbeville, 1992), which eliminates the undesirable diffusion of the complex, and the photophysical and photochemical properties of the complexes can be favorably influenced (Maruszewski et al., 1993; Maruszewski and Kincaid, 1995). Electronic absorption, electronic emission, as well as excited state lifetime measurements provide valuable information about the photophysical properties of the complexes in solution as well as for zeolite entrapped complexes, and such studies clearly document modifications upon zeolite entrapment.

Materials and Methods

Structure of Zeolites.—Zeolites are crystalline aluminosilicates of sodium, potassium, or calcium. The general chemical composition can be expressed by the formula $M_{2/n} \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$ (Breck, 1974), where n is the charge of the cation and x is usually ≥ 2. The structural framework is assembled by sharing the corner of the SiO_4 and AlO_4 tetrahedra in a three dimensional network. The cations M^{n+} occupy extra framework positions and balance the negative charge of the AlO_4 unit of the framework. The internal structure of the zeolite is composed of interconnecting cages and channels. The channels and void spaces of the three dimensional zeolites are usually occupied by cations and water molecules.

Under typical conditions, water molecules fill the interior volume of zeolites. The water molecules can be removed by heating without any structural change, which is in contrast to other hydrated compounds. In the dehydrated

zeolites, the empty channels can be filled with other molecules. Another useful feature of the zeolites is that the M^{n+} cations can be readily ion exchanged with other cations in aqueous media. The size of the supercages and size of the channels in zeolites vary from 2 to 13 Å and extend in a regular fashion throughout the structure. The internal architecture of zeolite makes it suitable for spatial arrangement of molecules. The steric and electrostatic constraints imposed by the supercages and channels may change the photophysical and photochemical properties of entrapped molecules, sometimes in an advantageous manner.

There are 34 known naturally occurring zeolite minerals and about 100 types of synthetic zeolites. Only a few of them are of practical use because the others are structurally unstable upon dehydration. The 6 most commonly examined zeolites as hosts for photocatalytic systems are zeolites X, Y, A, and L, mordenite, and ZSM-5. The synthetic analogue of the mineral faujasite is known as zeolite X or Y depending on the ratio of Si/Al in the framework. The unit cell of this zeolite is cubic and contains 192 (Si, Al)O_4 tetrahedra as
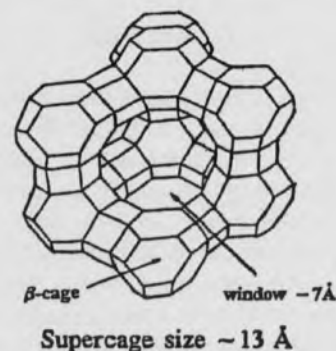

β-cage   window ~7Å

Supercage size ~13 Å

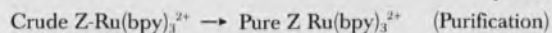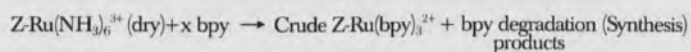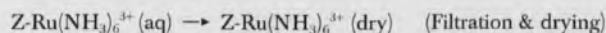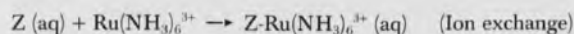Fig. 1. The structure of a zeolite-Y supercage.

shown in Fig. 1. The basic unit is formed by sodalite cages connected in a tetrahedral arrangement by double-6-ring (D6R) units, which produce the largest supercages of internal diameter ~13 Å and a window opening of ~ 7.4 Å. This large supercage makes it a very attractive host for immobilized photochemical reactants. The Na^+ cation present in this zeolite can easily be ion-exchanged with a wide variety of ions having dimensions less than the 7.4 Å window opening of the supercages.

Among all the zeolites, zeolite Y has the largest void space, which is 50% of the dehydrated crystal. It is thermally stable up to 700°C. Zeolite X has a Si/Al ratio of 1:1.4 and zeolite Y has a ratio of 1.4:3. Zeolite A has no natural counterpart and can be synthesized in the laboratory. In the framework Si and Al atoms are repeating alternately with

a Si/Al ratio typically of 1. The framework is made up of sodalite cages which are connected via double four-membered rings to form a supercage of diameter 11.4 Å and window size of 4.1 Å. Zeolite L is a one-dimensional tunnel-like framework, and Mordenite is a one-dimensional 12-membered ring system. Among all the stable zeolites, zeolite Y is an attractive one for the entrapment of a sensitizer molecule for carrying out photochemical reactions. The one-dimensional zeolites are not suitable for the entrapment. The internal diameter and window sizes are not suitable for the entrapment of the sensitizer for some of the zeolites. The popularity of zeolite Y arises from its ready availability, rigid framework structure, the largest void space of any known zeolite, and it is used in this research work as a host.

Assembly within Zeolite.–There are several strategies used to introduce the molecules of interest into the zeolites, depending on the nature and size of the molecular species. Positively charged species can be ion exchanged into the zeolite if they are small enough to penetrate through the window openings. Neutral molecules can be transported in vapor phase or via a solvent into the dehydrated zeolites. Using both of these strategies, it is possible to assemble a molecule inside the zeolite supercages that is then too large to escape via the 7.4 Å window opening. This so-called "ship in a bottle" synthesis is a 2-step process. The first step is the ion exchange with the desired cation, and the second step is the addition of the ligand followed by a thermal treatment to form the complex. One of the most impressive examples is the synthesis of zeolite (Z)-entrapped $Ru(bpy)_3^{2+}$ complex reported in the pioneering work of DeWilde and coworkers (1980). This molecule has a dimension of ~12 Å, which is too large to introduce through the window opening. Once it is formed, it cannot escape through the 7.4 Å windows and is effectively entrapped within the supercage. The reaction scheme is shown below:

$Z\ (aq) + Ru(NH_3)_6^{3+} \longrightarrow Z\text{-}Ru(NH_3)_6^{3+}\ (aq)$ (Ion exchange)

$Z\text{-}Ru(NH_3)_6^{3+}\ (aq) \longrightarrow Z\text{-}Ru(NH_3)_6^{3+}\ (dry)$ (Filtration & drying)

$Z\text{-}Ru(NH_3)_6^{3+}\ (dry) + x\ bpy \longrightarrow$ Crude $Z\text{-}Ru(bpy)_3^{2+}$ + bpy degradation (Synthesis) products

Crude $Z\text{-}Ru(bpy)_3^{2+} \longrightarrow$ Pure $Z\ Ru(bpy)_3^{2+}$ (Purification)

The calcinated (pre-cleaned from organic impurities by oxidation under flow of oxygen at 500°C for 5 hours) zeolite sample (Z) is loaded with $Ru(NH_3)_6^{3+}$ by ion exchange from aqueous solution and then filtered and dried under vacuum. The color of the solid changes from white to yellow when heated at high temperature (~200°C) with excess bipyridine (bpy) in a sealed tube. Surface adsorbed $Ru(bpy)_3^{2+}$ is removed by washing extensively with 10% NaCl solution, and excess ligand can be removed by extensive soxhlet extraction with ethanol. The zeolite entrapped

complex is characterized by diffuse reflectance, electronic absorption, electronic emission, and resonance Raman (RR) spectroscopy.

Maruszewski and coworkers (1991, 1993, and 1995) and Bhuiyan and Kincaid (1999, and 2001) developed an extended approach to synthesize mixed-ligand complexes of ruthenium(II) within zeolite Y. In this procedure the bis complex, $Z\text{-}RuL_2^{2+}$ (L = polypyridine ligand), is first synthesized within zeolite by heating at a relatively low temperature (~90°C). Then the third ligand is inserted at higher temperature (~200°C). The integrity of the material is confirmed by spectroscopic methods. The ability to generate zeolite-entrapped, tris-ligated, heteroleptic complexes opens up many more possibilities for synthesis of a wide range of complexes. More importantly, this type of heteroleptic complex is very useful for the construction of zeolite-based organized molecular assemblies, which can effectively reduce the rate of wasteful back-electron transfer and increase the net charge separation efficiency.

Maruszewski and Kincaid (1995) demonstrated that upon the entrapment of $Ru(bpy)_2(daf)^{2+}$ (daf = diazafluorene) within the Y-zeolite supercages, an increase in the energy of the ^3dd state is observed. In solution this complex is essentially non-emitting because of its very low-lying ^3dd state (E_{dd}=2271 cm^{-1}). Upon entrapment within the zeolite supercage, the complex exhibits easily detectable emissions and a dramatically increased ^3MLCT(metal-to-ligand charge transfer-state) lifetime at room temperature. By conducting lifetime measurements at many temperatures, it was shown that the increased lifetime of the entrapped complex results from zeolite-induced destabilization (by ~ 1700 cm^{-1}) of the ^3dd state. It was concluded that both steric and electrostatic interactions of the entrapped species change the photophysical properties of the complexes.

One fundamental question which arises concerns the size limitation imposed by the 7Å window opening on the polypyridine ligands, which can be efficiently delivered to the intra-zeolitic ruthenium ions. In order to address this issue, efforts have been made to prepare the zeolite-entrapped ruthenium complex of terpyridine: i.e., $Z\text{-}Ru(tpy)_2^{2+}$ (Bhuiyan and Kincaid, 1998). Having established the feasibility of utilizing ligands the size of terpyridine, we (Bhuiyan and Kincaid, 1999) took another project to employ the commonly used bridging ligand 2,3-bis(2-pyridyl) pyrazine (dpp) to demonstrate the possibility that covalently-linked binuclear complexes may be formed within the three-dimensional intrazeolitic framework. The synthesis of $Z\text{-}Ru(bpy)_2dpp^{2+}$ was successfully accomplished, and the spectroscopic and photophysical properties of this material were throughly documented (Bhuiyan and Kincaid, 1999). Structures of some of the complexes synthesized inside zeolite Y are shown in Fig. 2.
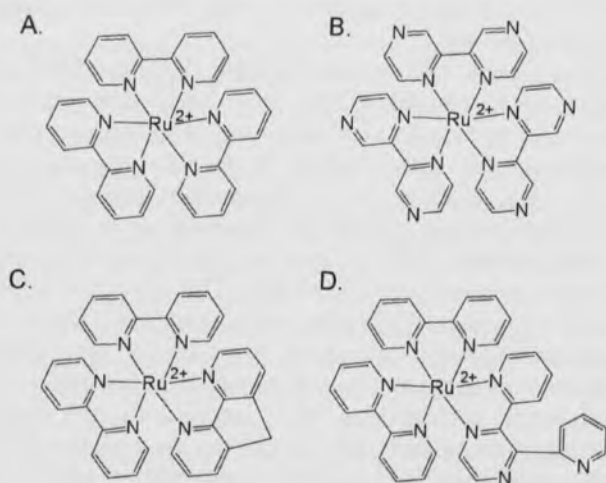
There are examples of large, transition-metal

Fig. 2. Structure of metal complexes synthesized in zeolite Y supercages (A) Ru(bpy)₃2+ (B) Ru(bpz)₃2+ (C) Ru(bpy)₂(daf)2+ (D) Ru(bpy)₂(dpp)2+ where bpy = 2,2'-bipyridine, bpz = 2,2'-bipyrazine, daf = 4,5-diazafluorene, dpp = 2,3-bis(2-pyridyl)pyrazine

complexes entrapped in the supercages of zeolite Y, such as iron (II) phthalocyanine (Herron, 1988) and zinc porphyrazine (Szulbinski and Kincaid, 1998). In these substances, the large guest molecules are presumably distorted from their planar configuration since the dimensions of the ligands (i.d. 14-15 Å) exceed the diameter of the zeolite supercages. The selectivity and activity of a metal phthalocyanine catalyst is enhanced with its inclusion in the zeolite cavity.

Persaud and coworkers (1987) reported the construction of a zeolite-based, multicomponent, photocatalytic assembly, which provides spatial organization of the electron donor and acceptor. A one-dimensional tunnel-like zeolite L was used as a host in that work. Small platinum clusters were formed inside the zeolite channel, and then the channel was loaded with a large amount of methyl viologen acceptor (MV^{2+}). The zinc porphyrin photosensitizer, $(ZnTMPy)^{4+}$, was too large to enter the 7Å zeolite channels, but it was strongly adsorbed on the outer surface. In the presence of a sacrificial electron donor (EDTA), this system was capable of photocatalytic generation of hydrogen from water. Upon photolysis, the electron transfer from zinc porphyrin to the acceptor methyl viologen (MV^{2+}) forming the $MV^{+\cdot}$ radical and the photosensitizer was regenerated by the sacrificial electron donor (EDTA), which prevents back electron transfer. Electron transfer along the chain of included MV^{2+} cations ultimately leads to the reduction of water to hydrogen in the presence of the included platinum catalyst.

Dutta and Turbeville (1992) reported the photoinduced electron transfer between the zeolite-entrapped $Ru(bpy)_3^{2+}$ and an acceptor, methyl viologen (MV^{2+}), located in neighboring cages. In this photoredox study, Z-$Ru(bpy)_3^{2+}$ was synthesized, and then MV^{2+} was ion exchanged at high loadings such that each supercage contained two MV^{2+} ions. Upon photolysis under anaerobic conditions, the orange pellet turned blue in color, indicating the formation of the $MV^{+\cdot}$ radical. The presence of the methyl viologen radical was confirmed by diffuse reflectance and time resolved resonance Raman (TR^3) spectroscopy. This blue species was stable for several hours under anaerobic conditions. The results were interpreted to indicate that the back electron transfer was retarded, and the photogenerated $MV^{+\cdot}$ transfers its electron to more remote MV^{2+} acceptors.

Results and Discussion

Synthesis and Characterization of Zeolite-Entrapped Bis-Terpyridine Ruthenium(II).—The results of detailed studies of the photophysical properties of a range of zeolite entrapped complexes demonstrates that the most important effect of entrapment of such complexes within the Y-zeolite supercages is an increase in the energy of the so-called "ligand-field" (^3dd) state (Maruszewski and Kincaid, 1995). The referenced study, demonstrated the effectiveness of zeolite entrapment in eliminating the LF (ligand-field)-state destabilization pathway, and prompted us (Bhuiyan and Kincaid, 1998) to undertake the study of zeolite-entrapped complexes of terpyridine (tpy). In free solution the bis-tpy complex, $Ru(tpy)_2^{2+}$, is essentially non-luminescent with a very short lifetime (~250 ps) at room temperature (Winkler et al., 1987). The origin of this short lifetime has been debated. The results of our previous study (Bhuiyan and Kincaid, 1998) revealed that the increased LF-state destabilization in this complex is comparable to that observed upon zeolite-Y-entrapped $Ru(bpy)_2daf^{2+}$ and nicely demonstrated the concept that zeolite entrapment provides a useful strategy for advantageous manipulation of the photophysical properties of such systems.

The zeolite sample was purified by calcinations (Incavo and Dutta, 1990). The zeolite-entrapped complex, Z-$Ru(tpy)_2^{2+}$, was prepared by a modification of a method previously developed in Kincaid's laboratory (Bhuiyan and Kincaid, 1998; Maruszewski et al., 1991), which is based on the pioneering work of DeWilde and coworkers (1980) and Quayle and Lunsford (1982). Spectroscopic measurements indicated that Z-$Ru(tpy)_2^{2+}$ was formed. The integrity of the zeolite-entrapped sample was confirmed by RR, electronic absorption, and emission spectra. The zeolite-entrapped complex was extracted from the zeolite matrix by the hydrofluoric acid method (Maruszewski et al., 1991). The reference complex, $[Ru(tpy)_2](PF_6)_2$, was prepared following the procedure of Maestri and coworkers (1995).
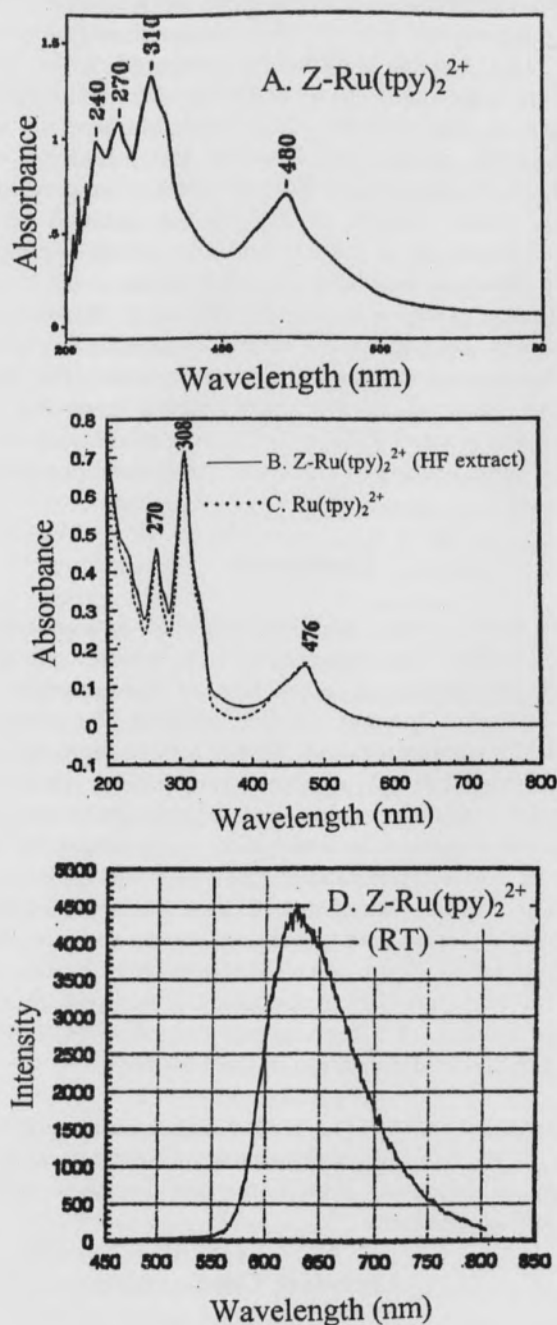
Fig. 3. Absorption and emission spectra of Ru(tpy)$_2$2+ complex.

The electronic absorption and emission spectra of the bis-terpyridine complex in various forms are given in Fig. 3. The absorption spectrum of the independently synthesized complex in acetonitrile solution (trace C) matches that reported in the literature (Maestri et al., 1995). The absorption spectrum of the zeolite-entrapped complex

(trace A) as well as the liberated complex that is obtained following dissolution of the zeolite matrix (trace B) shows no significant differences in the positions of the absorption maxima compared to the spectrum of the independently prepared solution-phase complex (trace C). The very intense bands in the UV region can be assigned to ligand-centered $\pi \rightarrow \pi^*$ transitions. The relatively intense and broad absorption band in the visible region, which is responsible for the deep red color, is due to spin allowed $d \rightarrow \pi^*$ metal-to-ligand charge-transfer (MLCT) transitions (Stone and Crosby, 1981). At room temperature, Ru(tpy)$_2^{2+}$ is practically non-luminescent, but upon entrapment in zeolite, there is a dramatic increase in luminescence (trace d) at room temperature. The RR spectra of the complex in solution and that of the zeolite-entrapped species are in good agreement (Bhuiyan and Kincaid, 1998). The spectral pattern does not significantly change upon entrapment of the complex into the zeolite matrix. There are only slight shifts observed for the zeolite entrapped complex relative to the solution-phase complex.

Effects on Photophysical Properties.—The ^{3}MLCT-state lifetime of Ru(tpy)$_2^{2+}$ in solution is too short (250 ps at room temperature) in comparison with the other ruthenium-polypyridine complexes (Winkler et al., 1987). However, the luminescence of the zeolite-entrapped sample at room temperature has an associated lifetime of 140 ns in aqueous suspension (Bhuiyan and Kincaid, 1998). As expected, excited-state lifetimes obtained at low temperatures increase with decreasing temperature, reaching 844 ns at -50°C. As is
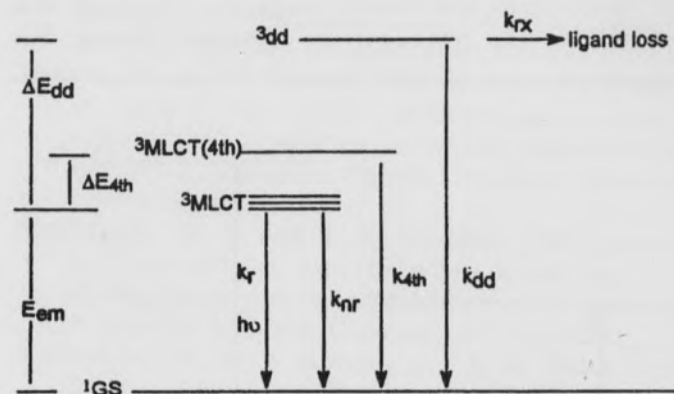

Fig. 4. Schematic representation of the excited-state deactivation pathways in ruthenium polypyridine complexes.

summarized in Fig. 4, the lowest energy ^{3}MLCT states of ruthenium(II)-polypyridine complexes may relax to the ground state via a number of pathways, including

population of two thermally accessible upper states whose participation can be documented by analysis of lifetime data acquired over a range of temperatures (Allen et al., 1984; Sykora and Kincaid, 1995). For most cases, a single thermal term (eq 2) is adequate to fit the experimental temperature-dependent lifetime data, but in some cases it is necessary to use two thermal terms (eq 1) in order to fit the experimental data (Maruszewski et al., 1993; Maruszewski and Kincaid, 1995; Sykora and Kincaid, 1995; Bhuiyan and Kincaid, 1998; Bhuiyan and Kincaid, 1999). The excited state lifetimes (T) are given by

$$1/T = k_{total} = k_r + k_{nr} + k_{dd}\,exp(^-\Delta E_{dd}/kT) + k_{dd}\,exp(^-\Delta E_{4th}/kT) \qquad (1)$$

$$1/T = k_{total} = k_r + k_{nr} + k_{dd}\,ex\,(^-\Delta E_{dd}/kT) \qquad (2)$$

In equations 1 and 2, k_r and k_{nr} are the rate constants for direct radiative and nonradiative decays. The deactivation rate constant of the thermally populated (^{3}dd) states is designated k_{dd}. ΔE_{dd} is the energy gap between the ^{3}dd states and the ^{3}MLCT-emitting states. The deactivation-rate constant, k_{4th}, is associated with an additional low lying ^{3}MLCT state (the so-called fourth MLCT state), which may be thermally populated as a consequence of the small magnitude of ΔE_{4th} (typically 600-900 cm^{-1}; Maruszewski et al., 1993; Maruszewski and Kincaid, 1995; Sykora and Kincaid, 1995; Bhuiyan and Kincaid, 1998; Bhuiyan and Kincaid, 1999).

Both equations (equations 1 and 2) were tested (Bhuiyan and Kincaid, 1998) in an attempt to reproduce the observed data. Analysis of the curves reveals that the monoexponential model (single thermal term) does not satisfactorily reproduce the observed lifetime data.

However, introduction of the second thermal term yields excellent agreement between the calculated and observed curves. The kinetic parameters obtained from both models are quite similar to those obtained for the majority of complexes (Maruszewski et al., 1993; Maruszewski and Kincaid, 1995; Sykora and Kincaid, 1995; Bhuiyan and Kincaid, 1998; Bhuiyan and Kincaid, 1999). Comparison of the ΔE_{dd} values (shown in Fig. 5) for solution phase Ru(tpy)$_2{}^{2+}$ (Clark et al., 1991) and the zeolite-entrapped complex (Bhuiyan and Kincaid, 1998) shows a substantial increase upon zeolite entrapment (1181 cm^{-1}). This increase in E_{dd} values accounts for the dramatic increase in lifetime and emission intensity upon zeolite entrapment. The steric constraint induced by the rigid zeolite cage on the electronically excited Z-Ru(tpy)$_2{}^{2+}$ results in destabilization of the LF state, leading to a decrease in thermal population of this state.

Conclusions

This study clearly demonstrates that entrapment of Ru(tpy)$_2{}^{2+}$ within the supercage of Y zeolite can alter inherent photophysical properties of the complex in an advantageous manner. In free solution this complex is practically nonluminescent, having a very short excited-state lifetime (250 ps) at room temperature. However, entrapment within the zeolite supercage results in dramatic increases in emission intensity and excited-state lifetime (140 ns) at room temperature. The observed temperature dependence of the excited-state lifetime has been modeled by a kinetic equation with two thermal terms corresponding to the population of the so-called fourth ^{3}MLCT state and the ligand field state (LF), respectively. It is shown that the increased lifetime of the entrapped complex results from zeolite-induced destabilization of the LF state.

Literature Cited

Allen, G H, R P White, D. P. Rillema, and T J Meyer. 1984. Synthetic control of excited-state properties. Tris-chelate complexes containing the ligands 2,2'-bipyrazine, 2,2'-bipyridine, and 2,2'bipyrimidine. Journal of the American Chemical Society 106:2613-2620.

Bhuiyan, A A and J R Kincaid. 1998. Synthesis and photophysical properties of zeolite-entrapped bisterpyridine ruthenium(II). Dramatic consequences of ligand-field-state destabilization. Inorganic Chemistry 37:2525-2530.
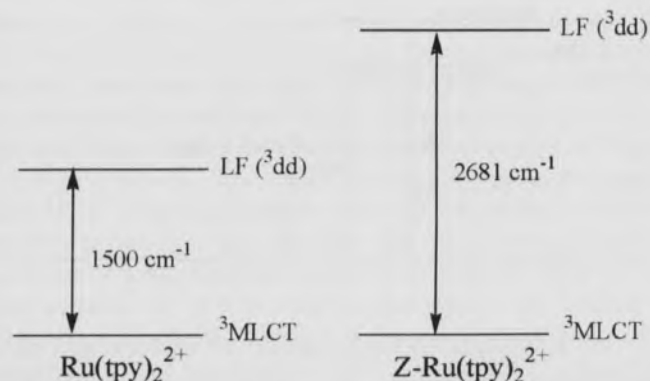
Fig. 5. Energy gap (Edd) diagram for solution-phase Ru(tpy)₂2+complex and zeolite-entrapped Z-Ru(tpy)₂2+ complex.

Bhuiyan, A A and J R Kincaid. 1999. Synthesis and spectroscopic characterization of a zeolite-entrapped Ru(bpy)$_2$(dpp)$^{2+}$ complex. Inorganic Chemistry 38:4759-4764.

Bhuiyan, A A and J R Kincaid. 2001. Zeolite-based organized molecular assemblies. Photophysical characterization and documentation of donor oxidation upon photosensitized charge separation. Inorganic Chemistry 40:4464-4471.

Breck, D W. 1974. Zeolite Molecular Sieves: Structure, Chemistry and Use. Wiley, New York. 275 pp.

Clark, R H, K I G Ann, and R M David. 1991. Phenyl substituents and excited-state lifetimes in ruthenium(II) terpyridyls. Inorganic Chemistry 30:538-541.

Darwent, J R, P Douglas, A Harriman, G Porter, and M C Richoux. 1982. Metal phthalocyanines and porphyrins as photosensitizers for reduction of water to hydrogen. Coordination Chemistry Reviews 44:83-126.

DeWilde, W, G Peeters, and J H Lunsford. 1980. Synthesis and spectroscopic properties of tris(2,2'-bipyridine)ruthenium(II) in zeolite Y. The Journal of Physical Chemistry 84:2306-2310.

Dutta, P K and W Turbeville. 1992. Intrazeolitic photoinduced redox reactions between tris(2,2'-bipyridine)ruthenium(2+) and methylviologen. The Journal of Physical Chemistry 96:9410-9416.

Gafney, H D. 1990. Spectral, photophysical and photochemical properties of tris(2,2'-bipyridine) ruthenium(2+) on porous Vycor glass. Coordination Chemistry Reviews 104:113-142.

Herron, N. 1988. The selective partial oxidation of alkanes using zeolite based catalysts. Phthalocyanine "ship-in-bottle" species. The Journal of Coordination Chemistry 19:25-38.

Incavo, J A and P K Dutta. 1990. Zeolite host-guest interactions: optical spectroscopic properties of tris(bipyridine)ruthenium(II) in zeolite Y cages. The Journal of Physical Chemistry 94:3075-3081.

Kalyanasundaram, K. 1982. Photophysics, photochemistry and solar energy conversion with tris(bipyridyl) ruthenium(II) and its analogs. Coordination Chemistry Reviews 46:219-244.

Kalyanasundaram, K. 1987. Photochemistry in Micro-heterogeneous Systems. Academic Press, New York. 388 pp.

Lawlor, D W. 1993. Photosynthesis: Molecular, Physiological and Environmental Processes, 2nd ed. Longman, Essex, England. 292 pp.

Maestri, M, N Armaroli, V Balzani, E C Constable, and A M W C Thompson. 1995. Complexes of the ruthenium(II)-2,2':6',2"-terpyridine family. Effect of electron-accepting and donating substituents on the photophysical and electrochemical properties. Inorganic Chemistry 34:2759-2767.

Maruszewski, K, D P Strommen, and J R Kincaid. 1993. Zeolite-entrapped ruthenium (II) complexes with bipyridine and related ligands. Elimination of ligand-field-state deactivation and increase in 3MLCT state lifetimes. Journal of the American Chemical Society 115:8345-8350.

Maruszewski, K and J R Kincaid. 1995. Dramatic increase of 3MLCT state lifetime of a ruthenium(II) polypyridine complex upon entrapment within Y-zeolite supercages. Inorganic Chemistry 34:2002-2006.

Maruszewski, K, D P Strommen, K Handrich, and J R Kincaid. 1991. Synthesis and spectroscopic properties of zeolite-entrapped bis-heteroleptic ruthenium(II) polypyridine complexes. Inorganic Chemistry 30:4579-4582.

Parmon, V N and K I Zamarev. 1989. Pp. 565-602, In Photocatalysis: Fundamentals and Applications (N. Serpone and E. Pelizzetti eds.). Wiley, New York. 38 pp.

Persaud, L, A J Bard, A Campion, M A Fox, T E Mallouk, S E Webber, and J M White. 1987. Photochemical hydrogen evolution via singlet-state electron-transfer quenching of zinc tetra(N-methyl-4-pyridyl)porphyrin cations in a zeolite L based system. Journal of the American Chemical Society 109:7309-7314.

Quayle, W H and J H Lunsford. 1982. Tris(2,2'-bipyridine)ruthenium(III) in zeolite Y: characterization and reduction on exposure to water. Inorganic Chemistry 21:97-103.

Ramamurthy, V Ed. 1991. Photochemistry in Organized and Constrained Media. VCH, New York. 210 pp.

Stone, ML and G A Crosby. 1981. Charge transfer luminescence from ruthenium(II) complexes containing tridentate ligands. Chemical Physics Letters 79:169-173.

Sykora, M. and J R Kincaid. 1995. Synthetic manipulation of excited state decay pathways in a series of ruthenium(II) complexes containing bipyrazine and substituted bipyridine ligands. Inorganic Chemistry 34:5852-5856.

Szulbinski, W S and J R Kincaid. 1998. Synthesis and spectroscopic characterization of zinc tetra (3,4-pyridine)porphyrazine entrapped within the supercages of Y-zeolite. Inorganic Chemistry 37:5014-5020.

Turbeville, W, D S Robins, and P K Dutta. 1992. Zeolite-entrapped tris(2,2'-bipyridene)ruthenium(2+): intermolecular structural and dynamic effects. The Journal of Physcial Chemistry 96:5024-5029.

Winkler, J R, T L Netzel, C Creutz, and N Sutin. 1987. Direct observation of metal-to-ligand charge transfer (MLCT) excited states of pentaammine-ruthenium(II) complexes. Journal of the American Chemical Society 109:2381-2392.