would result in additional (albeit nine-membered) rings. Although the effect of nine-membered rings on the stability of the metal complex might be small, it should be positive. BCPA would obviously bond to lanthanons more tenaciously than PMDTA if its fifth carboxylate O were involved in chelation. This is apparently not the case since the lanthanide–BCPA stability constants are approximately 10-fold less stable than their PMDTA counterparts. The trend of stability with BCPA complexes mimics the trend observed with PMDTA rather than that characteristic of EEDTA[9] and BPETA chelates, in which additional rings are formed, making the structure less flexible.

The experimental conditions for BCPA are different from those of BPETA. Both ^{241}Am and ^{155}Eu were eluted, coincidentally, under necessarily more basic conditions. The results are shown in Figure 3. Preliminary elutions with 25 column volumes of 0.04 M BCPA solution at pHs of 3.0, 4.0, 5.0, and 6.0 were insufficient to remove the Am and Eu tracers from the resin bed. The higher pH requirements reflect the 1000-fold lower affinity of BCPA (compared to BPETA) for trivalent cations.

Registry No. $H_3CN(CH_2CH_2CH_2NH_2)_2$, 105-83-9; $O(CH_2CH_2CN)_2$, 1656-48-0; $O(CH_2CH_2CH_2NH_2)_2$, 2157-24-6; BPEDTA, 87720-52-3; BCPA, 89378-46-1.

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Photosubstitution Reactions of $Ru(bpy)_2XY^{n+}$ Complexes

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The quantum yields for the photosubstitution of a series of $Ru(bpy)_2XY^{n+}$ complexes have been measured. The ligands X and Y span the range of the spectrochemical series from Cl^- to CO. The correlation between the energy of the lowest energy charge-transfer transition and the quantum yield is discussed in terms of the energies of MLCT and d–d excited states.

Introduction

The photoreactivity of ruthenium(II) complexes of the type $Ru(bpy)_2XY^{n+}$, where bpy = 2,2′-bipyridine and X and Y = any monodentate ligand, has been noted since the publication of a series of synthetic papers by Bosnich, Dwyer, and coworkers.[1] The photoreactions usually involve loss of the monodentate ligands according to reactions 1 and 2. In

$$Ru(bpy)_2XY^{n+} + S \xrightarrow{h\nu} Ru(bpy)_2YS^{p+} + X \quad (1)$$

$$Ru(bpy)_2YS^{p+} + S \xrightarrow{h\nu} Ru(bpy)_2S_2^{q+} + Y \quad (2)$$

coordinating solvents S will usually be a solvent molecule, while in poor coordinating, low dielectric constant solvents S may be the counterion, added anions, or residual water in the solvent.[2,3] These reactions have proven to be of some synthetic utility.[3]

The $Ru(bpy)_3^{2+}$ ion may also be placed in this series of complexes. The $Ru(bpy)_3^{2+}$ ion, however, is substantially less photoreactive, and this has been shown to be a result of efficient ring reclosure after the primary photochemical event.[4] Numerous studies[5] have resulted in a reasonably well-defined description of the excited-state manifold of $Ru(bpy)_3^{2+}$. This description has been successfully extended[6–8] to some $Ru(bpy)_2XY^{n+}$ complexes to explain the temperature dependence of the emission lifetime.

With this description in mind we have embarked on a study of those aspects of the excited-state manifold that play an important role in the photochemical reactions in the series of complexes $Ru(bpy)_2XY^{n+}$. The following is a report of an interesting correlation between quantum yield for photosubstitution and the energy of the major visible charge-transfer transition.

Experimental Section

Materials. All of the ruthenium complexes except those containing carbon monoxide were prepared as PF_6^- salts from *cis*-$Ru(bpy)_2Cl_2$ by standard literature procedures.[1,9] The complexes were purified by column chromatography on alumina. Purity was judged by cyclic voltammetry and NMR and visible spectroscopy. Dichloromethane was dried over molecular sieves. Tetrabutylammonium chloride and all other reagents were used as received.

$[Ru(bpy)_2(CO)_2](PF_6)_2$. This complex was prepared by a slight modification of the procedure described by Choudhury and coworkers.[10] A solution of dichloromethane containing 0.38 g of $Ru(bpy)_2Cl_2$ (0.78 mmol) and 0.6 g of $AgSbF_6$ (1.75 mmol) was heated to 80 °C in an an autoclave pressurized with carbon monoxide (4 atm). After 48 h the solid material obtained by filtration of the reaction mixture was extracted with acetone. The volume of acetone was reduced to less than 5 mL in a rotary evaporator and the product recovered by adding the acetone solution dropwise to ethyl ether followed by filtration and air drying. The product was further purified

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Table I. Charge-Transfer Maxima, Emission Maxima, $E_{1/2}$(II/III), and Quantum Yields for the Photoanation of *cis*-$Ru(bpy)_2XY^{n+}$ Complexes

no.	XY	ϕ(photoanation)[a]	abs λ_{max},[a] $cm^{-1} \times 10^3$	emission 0-0,[b] $cm^{-1} \times 10^3$	$E_{1/2}$(II/III),[c] V
1	(pyridine)Cl	0.04	19.8	15.15	0.79
2	(4-acetylpyridine)Cl	0.07	20.2	15.31	0.82
3	(*N*-methylimidazole)$_2$	<0.001	20.7	15.57	0.94
4	(imidazole)$_2$	<0.001	20.5	15.92	1.02
5	$(CH_3CN)Cl$	0.12	20.8	15.96	0.86
6	(pyridine)$_2$	0.20	22.03	17.10	1.30
7	(4,4′-bpy)$_2$	0.20	22.37	17.32	1.32
8	(4-acetylpyridine)$_2$	0.29	22.62	17.36	1.45
9	(3-iodopyridine)$_2$	0.24	22.62	17.40	1.36
10	(pyridazine)$_2$	0.06	22.73	17.48	1.42
11	$(P(C_6H_5)_2CH_3)_2$	~0	23.31	18.28	1.52
12	$(CH_3CN)_2$	0.31	23.47	18.45	1.44
13	(CO)Cl	0.045		no emission	1.55
14	$(CO)_2$	0.05	32.78	22.57	>1.9

[a] Determined in dichloromethane. [b] Highest energy maxima at 77 K in 1:1 methanol-ethanol glass. [c] Determined in CH_3CN with TBAH vs. SSCE.

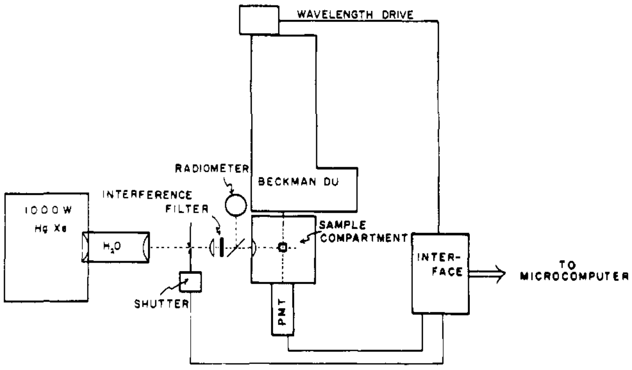

Figure 1. Equipment used for the determination of quantum yields.

by dissolving in acetone and precipitating as the chloride salt with saturated LiCl solution. The chloride salt was recovered by filtration and dissolved in water. A concentrated solution of NH_4PF_6 was added dropwise until no further precipitation occurred. The final product was filtered out, washed with 2-propanol and then diethyl ether, and air-dried. The IR and UV spectra match those reported earlier.[10]

[Ru(bpy)(CO)Cl]PF$_6$. This complex was prepared in a manner identical with that for $[Ru(bpy)_2(CO)_2](PF_6)_2$ except the reaction time was reduced to 24 h. The dichloromethane was removed from the reaction mixture by rotary evaporation and the remaining solid extracted with acetone. The acetone solution was passed through a short column (2 cm × 2.5 cm i.d.) of alumina (Fisher) to remove the unwanted $[Ru(bpy)_2(CO)_2](PF_6)_2$. Purity was judged by comparison of IR and UV spectra.[10]

Photolyses. The equipment used to determine the quantum yields for photosubstitution is illustrated in Figure 1. The equipment provides for monochromatic irradiation of the sample, continuous measurement of the incident flux, and periodic spectrophotometric analysis of the sample. All of these activities as well as data storage and refinement were coordinated by a Commodore PET microcomputer and appropriate interfacing circuitry. The irradiation source was composed of a 1000-W Hg-Xe arc lamp housed in a Schoeffel Instruments Model LH 151 universal lamp housing and powdered by a LPS 255 power supply. The beam was lowered to bench top height by two mirrors (2 in. × 2 in.), passed through a shutter, a collimating lens, an interference filter, and a beam splitter, and finally partially focused on the sample by a second lens. The incident flux was monitored by an Oriel 7072 radiometer with a vacuum photodiode detector. The beam splitter used was from Melles Griot (03 BTF001) and directed approximately 23% of the beam at 436 nm to the photodiode detector. The radiometer readings were calibrated by using Reinecke Salt actinometry.[11] The linearity was verified by monitoring the fluorescence of $Ru(bpy)_3^{2+}$ as a function of incident flux as measured by the radiometer. Variations in flux were obtained by using a Wilks comb type beam attenuator. Calibrations were repeated throughout the experiments as were determinations of the quantum yield for $Ru(bpy)_2(py)_2^{2+}$ photoanation to ensure against radiometer detector fatigue. Sample analysis was performed with a spectrophotometer at right angles to the irradiation beam. The spectrophotometer was constructed from the monochromator and lamp housing of a Beckman DU single-beam spectrophotometer. The detector was a IP28A photomultiplier. Scanning capabilities were provided by adding a stepper motor drive to the wavelength wheel of the monochromator. An empirically determined function enabled the computer to position the monochromator at any wavelength or any number of different wavelengths. Care was taken, however, not to operate over a wavelength range that required changes in the monochromators slits. Typical experiments involved wavelengths in the range of 400-560 nm. Absorbance data were determined from photomultiplier voltages that were digitized with a 7109 12-bit A/D converter and read by the computer. Zero and 100% transmittance measurements were collected before each run. The operation of this aspect of the equipment was verified by comparisons of spectra taken on a Cary 14 spectrophotometer. The sample (3 mL) was held in a 1-cm^2 fluorescence cell. The sample solutions were deaerated with argon and stirred magnetically.

Quantum yields were determined from plots of effective quantum yields ([products] or [reactants]/total absorbed photons) vs. extent of reaction. These plots were linear, and the intercepts were taken to be equal to the actual quantum yield for the reaction. The effective quantum yields were determined from absorbance data taken at several wavelengths; λ_{max} for reactant, λ_{max} for product, and 436 nm (the wavelength of irradiation) were typically used. Effective quantum yields based on the appearance of products and the disappearance of reactants were used to determine the actual quantum yields. The concentrations of products and reactants were determined by using simultaneous equations. A minimum of six determinations, including random variations in [Cl^-] and [complex], was used to arrive at the final value of the quantum yield. No systematic variations in quantum yield were noted. Measurements of the absorbance changes upon irradiation were superimposable for samples made from the same stock solutions. The standard deviations of the quantum yields were less than 10% and were limited by the extinction coefficients and the sensitivity of the simultaneous equations to errors in the extinction coefficients.

The quantum yields for photosubstitution of $Ru(bpy)_2(CO)Cl^+$ were determined as above except a 313-nm irradiation beam was employed. The beam splitter, in this instance, was replaced by a quartz plate, and actinometry was performed by using the ferrioxalate method.[12] Spectrophotometric analysis was carried out at wavelengths above 400 nm by monitoring the appearance of $Ru(bpy)_2Cl_2$. The quantum yield for $Ru(bpy)_2(py)_2^{2+}$ was also determined with the apparatus configured in this way and found to be the same, within experimental error, as that determined with 436-nm irradiation.[13] We have been

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(13) py = pyridine; Me_2bpy = 4,4′-dimethyl-2,2′-bipyridine; phen = *o*-phenanthroline.

Table II. Charge-Transfer Maxima and Quantum Yield for Photoaquation of *cis*-$Ru(bpy)_2L_2^{2+}$ Complexes Determined in 1 M H_2SO_4

no.	L_2	ϕ(photoaquation)	abs λ_{max}, $cm^{-1} \times 10^3$
18	H_2O (trans)	0.026	20.20
19	H_2O (cis)	0.045	20.83
20	pyrazole	0.20	21.37
21	pyridine	0.26	21.93
22	acetonitrile	0.44	23.64

unable, at this time, to accurately determine the quantum yield for photosubstitution of $Ru(bpy)_2(CO)_2^{2+}$ because of a competitive reaction with residual water in the solvent. The value given in Table I is based on the appearance of $Ru(bpy)_2Cl_2$, which is limited by the photoreactivity of $Ru(bpy)_2(CO)Cl^+$.

Equipment. UV-visible absorption spectra were obtained with a Cary 14 spectrophotometer. Electrochemical measurements were carried out at 22 ±2 °C in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. A home-built ramp generator,[14] a HI-TEK Instruments potentiostat, and a Houston Model 164 X-Y recorder were used in conjunction with a platinum-bead working electrode, a platinum-wire auxiliary electrode, and a saturated sodium chloride calomel (SSCE) reference electrode. Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer. NMR spectra were obtained on a Varian EM 360 or a JEOL FX90Q NMR spectrometer. Emission spectra were recorded on a Perkin-Elmer Model 360-40 spectrofluorimeter with 3600 Data Station.

Results

The photosubstitution reactions of $Ru(bpy)_2L_2^{2+}$ complexes in CH_2Cl_2 in the presence of excess $(C_4H_9)_4NCl$ proceed according to reactions 3 and 4. The quantum yields for these

$$Ru(bpy)_2X_2^{2+} + Cl^- \xrightarrow{h\nu} Ru(bpy)_2XCl^+ + X \quad (3)$$

$$Ru(bpy)_2XCl^+ + Cl^- \xrightarrow{h\nu} Ru(bpy)_2Cl_2 + X \quad (4)$$

reactions are reported in Table II. Only the cis isomers have been examined at this time. In most cases, given a particular X, reactions 3 and 4 were completely separable since the quantum yields for reaction 4 were generally a factor of 2 smaller than those of reaction 3. The simplicity of the reaction is supported in these cases by the fact that only a single set of isosbestic points was noted when spectra were recorded as a function of irradiation time. In the cases where the quantum yields for reaction 3 were on the order of 0.3, reactions 3 and 4 were not separable. Fortunately, the contribution from reaction 4 is small enough in the initial stages of the overall photolysis to allow accurate determinations of the quantum yields. Quantum yields of reaction 4 were determined independently by starting with pure monochloro complexes in all cases. Again, isosbestic points were evident when spectra were recorded as a function of irradiation time.

Thermal reactions equivalent to (3) and (4) do not proceed to a measureable degree in solutions up to 8 h old. No evidence for thermal reactions with O_2 was found.

The quantum yields were independent of Cl^- concentration over the range 5×10^{-4}–1×10^{-2} M. Previous studies[3] indicated further that the efficiencies were also independent of the nature of the incoming ligand if that ligand was a singly charged anion. A single set of measurements of the photoreactivity of $Ru(bpy)_2(py)_2^{2+}$ using 313-nm irradiation suggests that the yields are also independent of irradiation wavelength. The photoreactivity of $Ru(bpy)_2(H_2O)_2^{2+}$ has also been shown to be wavelength independent.[2]

The stereochemical nature of these reactions was established by comparison to known compounds. In particular, when the photolyses of the cis isomers were followed spectrophotometrically, changes in the spectra were consistent only with the appearance of cis products. The trans isomers all show MLCT absorption bands that are typically 10–15 nm lower in energy than the corresponding cis isomers and, therefore, would have been readily identifiable.[15] In addition, *trans*-$Ru(bpy)_2Cl_2$ is completely insoluble in dichloromethane as well as most other organic solvents. Extensive photolyses of bulk samples have previously been shown to yield only cis products.[3]

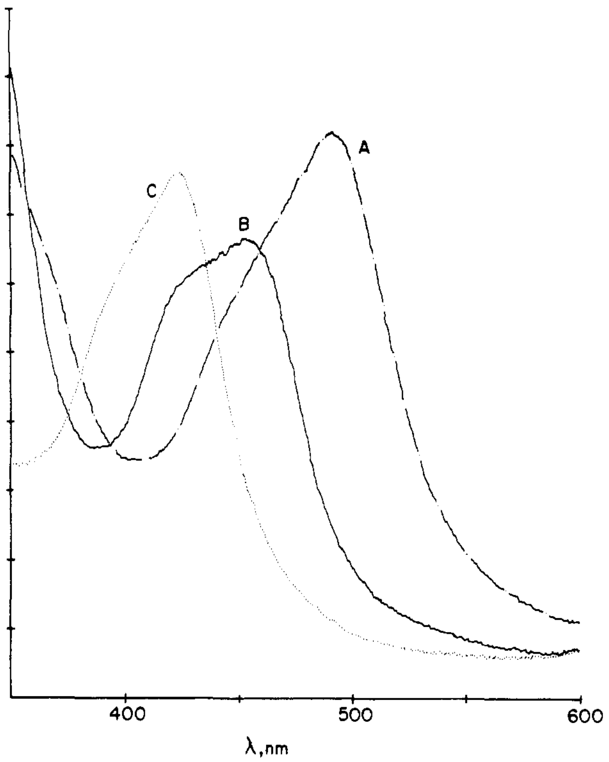

Figure 2. Absorption spectra of (A) $Ru(bpy)_2(imidazole)_2^{2+}$, (B) $Ru(bpy)_2(pyridine)_2^{2+}$, and (C) $Ru(bpy)_2(CH_3CN)_2^{2+}$ in dichloromethane.

Photolyses were also carried out on several complexes in aqueous 1 M H_2SO_4. In these cases the reaction observed corresponds to eq 5. Product analysis was again carried out

$$Ru(bpy)_2L_2^{2+} + H_2O \xrightarrow{h\nu} Ru(bpy)_2L(OH_2)^{2+} + L \quad (5)$$

by comparison to known samples and by bulk photolyses. In addition, samples of $[Ru(Me_2bpy)_2(py)_2]Cl_2$ were photolyzed and monitored by using NMR spectroscopy.[13] No evidence for the formation of trans isomers was observed.

The only two verified examples in which isomerization occurs are $Ru(bpy)_2(OH_2)_2^{2+}$ and $Ru(bpy)_2Cl_2$. In the case of $Ru(bpy)_2(OH_2)_2^{2+}$, a photostationary state is reached in which the concentrations of cis and trans isomers are comparable.[2] The quantum yields for the diaquo cases used in the following discussion are for the disappearance of the starting isomer.

The complex *cis*-$Ru(bpy)_2Cl_2$ also isomerizes to the trans isomer upon irradiation, but because the trans isomer is insoluble,[15] no quantum yield data could be obtained. The photolyses were carried out in 6 M HCl to ensure that $Ru(bpy)_2Cl_2$ was the predominate species in solution. We cannot rule out the possibility that $Ru(bpy)_2(OH_2)_2^{2+}$ or $Ru(bpy)_2(OH_2)Cl^+$ are the photoreactants and the trans photoproducts subsequently react with Cl^- to form *trans*-$Ru(bpy)_2Cl_2$. The thermal substitution reactions are known to proceed with stereoretention. The estimated equilibrium constant[16] and

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[14] Woodward, W. S.; Rocklin, R. D.; Murray, R. W. *Chem. Biomed. Environ. Instrum.* **1979**, *9*, 25.

[15] Durham, B.; Walsh, J. L. *Inorg. Chem.* **1982**, *21*, 329.

[16] Davies, N. R.; Mullins, T. L. *Aust. J. Chem.* **1968**, *21*, 915.

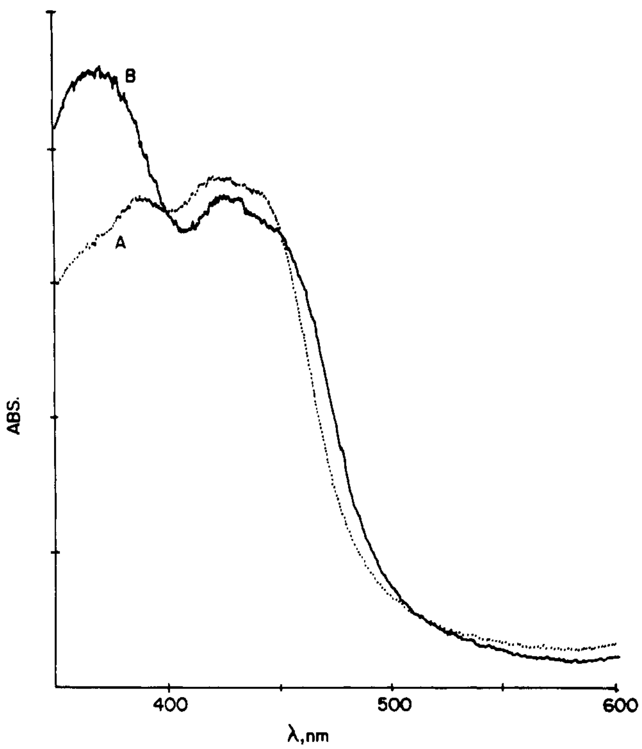

Figure 3. Absorption spectra of (A) Ru(bpy)$_2$(4-acetylpyridine)$_2{}^{2+}$ and (B) Ru(bpy)$_2$(4,4′-bpy)$_2{}^{2+}$ in dichloromethane.

expected photoreactivity of Ru(bpy)$_2$(OH$_2$)$_2{}^{2+}$ and Ru(bpy)$_2$(OH$_2$)Cl$^+$, however, strongly support the contention that *cis*-Ru(bpy)$_2$Cl$_2$ is the photoreactant.

Most members of the series exhibit absorption spectra that are very similar to that of Ru(bpy)$_3{}^{2+}$. Specifically, the visible spectra are dominated by single absorption bands that are clearly composed of two major transitions. Some representative spectra are shown in Figure 2. The quantum yields appear to correlate closely with the energies of the visible transitions. The lowest energy transition, which in most cases has the highest extinction coefficient, seems to show the best correlation. The energies of these transitions are listed in Tables I and II for measurements in dichloromethane and aqueous 1 M H$_2$SO$_4$, respectively.

In a few cases, notably the complexes containing substituted pyridines, an additional transition at higher energy was observed. The tail of this absorption band overlaps the normally observed visible bands in such a way at to alter the expected relative intensities (see Figure 3). Also exceptional are the complexes containing metal carbonyls. They exhibit only near-UV transitions that are not easily compared to the remaining complexes of the series.

The emission spectra of the series of complexes under consideration were determined in 1:1 methanol–ethanol glasses at 77 K. In all cases, except those containing carbon monoxide, an emission spectrum similar in structure to that displayed by Ru(bpy)$_3{}^{2+}$ was observed. Two maxima were clearly distinguishable under these conditions with energy differences of approximately 1.3 × 10^3 cm^{-1} in each case. The maxima for the highest energy transition are reported in Table I. The complex Ru(bpy)$_2$(CO)Cl$^+$ showed no emission, and Ru(bpy)$_2$(CO)$_2{}^{2+}$ showed an emission spectrum that was clearly of a different nature from that displayed by the remaining members of the series.

Discussion

The most remarkable feature of the photoreactivity of Ru(bpy)$_2$XY^{n+} complexes is the correlation between quantum yield for photosubstitution and the energy of the lowest energy charge-transfer transition (correlation coefficient 0.93). The quantum yields correlate equally well with the emission energies and $E_{1/2}$(II/III) couples of the complexes (correlation coefficient 0.92 and 0.99, respectively). The correlations are illustrated in Figures 4–6. The numbering scheme is the same as that used in Table I.

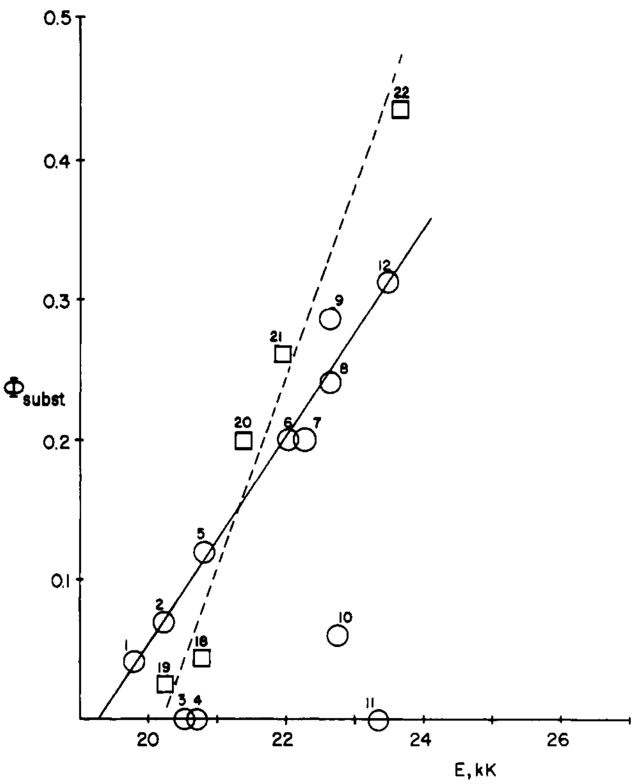

Figure 4. Correlation of quantum yield for the photosubstitution of Ru(bpy)$_2$XY^{n+} in (a) dichloromethane in the presence of excess (C$_4$H$_9$)$_4$NCl (—) and (b) 1 M H$_2$SO$_4$ (- -) with the lowest energy charge-transfer maxima measured in the respective solvents. See Tables I and II for numbering scheme.

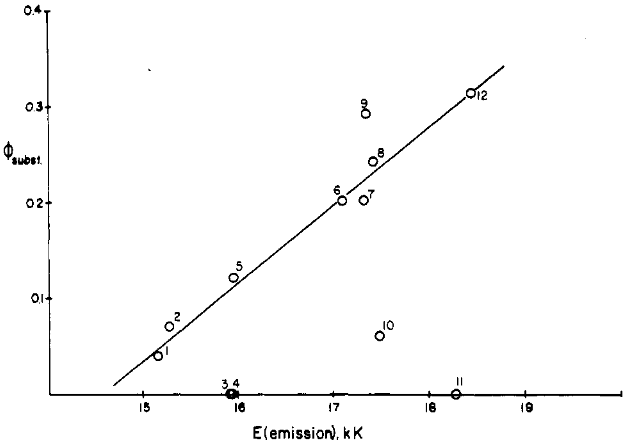

Figure 5. Correlation of quantum yield for the photoanation of Ru(bpy)$_2$XY^{n+} in dichloromethane in the presence of excess (C$_4$H$_9$)$_4$NCl with emission maxima measured at 77 K in a 1:1 methanol–ethanol glass.

The absorption and emission spectra of the complexes investigated, with a few exceptions, strongly resemble those exhibited by Ru(bpy)$_3{}^{2+}$. Crosby and co-workers[8] have carried out extensive studies of the luminescence emitted by some of the complexes in Table I, in addition to many others, and have assigned the transition involved as π*(bpy) → d in every case. Other investigators have observed spectral similarities among complexes of the type employed in this study and have noted correlations between emission energies and charge-transfer absorption energies. Some specifics of the spectral similarities

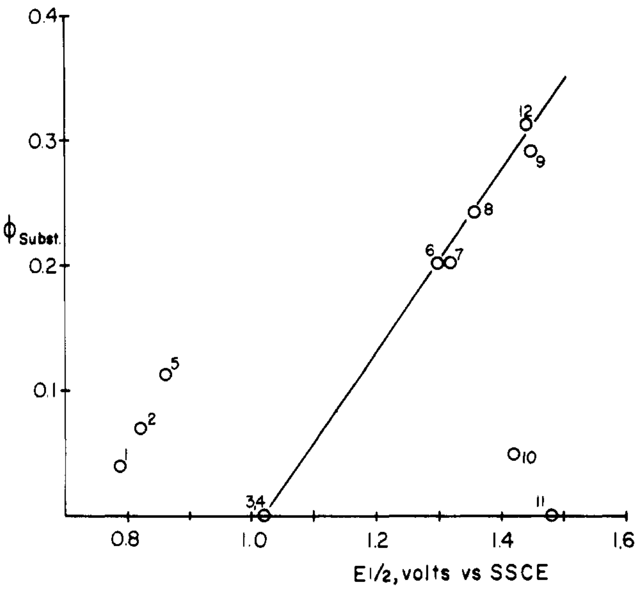

Figure 6. Correlation of quantum yield for the photoanation of $Ru(bpy)_2XY^{n+}$ in dichloromethane in the presence of excess $(C_4H_9)_4NCl$ with $E_{1/2}$ for the II/III couples.

include (1) nearly constant differences between the emission energy and the absorption energy ((4.96 ± 0.17) × 10^3 cm^{-1} in Table I), (2) similar energy spacing in the vibrational progression of the emission spectra, and (3) nearly identical UV spectra dominated by bipyridine-localized transitions.

The existence of the correlation between $E_{1/2}$(II/III) and the quantum yield is not surprising given the fact that a correlation between [$E_{1/2}$(II/III) − $E_{1/2}$($Ru(bpy^-)$/Ru(bpy))] and the emission energy had been previously noted.[17] The correlation is somewhat simplified with the complexes employed in this study since the $E_{1/2}$($Ru(bpy^-)$/Ru(bpy)) are essentially constant (−1.33 to −1.37 V vs. SCE) for dicationic complexes. Such relations are not unique to ruthenium bipyridyl complexes and have been noted with some metallophthalocyanines.[18] The origins of such relations can be traced to the similarities of the electrochemical process, i.e., removal of a t_{2g} electron and reduction of the coordinated ligand and the charge-transfer transitions. The departure of the chloro complexes from the line in Figure 6 can be attributed to important solvation energies in the $E_{1/2}$ values.

It is apparent from the interrelations of emission energy, absorption energies, and the electrochemical potentials that the bipyridine orbitals play a dominant role in the spectroscopy of $Ru(bpy)_2XY^{n+}$ complexes and, by inference, in their photochemistry. Specifically, the lowest energy excited state in all of these complexes probably derives from the electronic configuration $d^5\pi^*(bpy)^1$. The remaining monodentate ligands in these complexes have a profound influence over the energy of the lowest energy electronic state but do not appear to alter the nature of this state. The complexes containing carbonyl ligands are exceptions and will be discussed later in this section.

The correlations with quantum yields illustrated in Figures 4–6 appear to be consistent with the photochemical picture proposed by Watts and co-workers[5e] for $Ru(bpy)_3^{2+}$. The model suggests that photosubstitution in $Ru(bpy)_3^{2+}$ is a result of thermal population of a d–d excited state from lower energy charge-transfer states. It would appear that, for the series of complexes in Table I, the efficiency of populating the d–d excited state from the characteristic lowest energy charge-transfer state is a strong function of the remaining monodentate ligands. The most obvious mechanism by which this can occur is by reducing the energy difference between the CT and d–d excited states. Unfortunately, the energies of the appropriate states will be a function, to varying degrees, of all of the ligands because of the very low symmetry. However, given (1) the invariance of the vibrational progression in the emission spectra, (2) the large variation in $E_{1/2}$(II/III) but very small variation in $E_{1/2}$($Ru(bpy)^-$)/R(bpy)), and (3) the nearly constant bipyridine-localized transitions observed in the ultraviolet region, it is reasonable to attribute variations in visible absorption and emission energy primarily to variations in the energies of the more metal-like $t_{2g}(d\pi)$ molecular orbitals and only secondarily to variations in the energies of the more bipyridine-like t_{2g}^* molecular orbitals. We have, for simplicity of discussion, retained the symmetry labels of an octahedral environment around ruthenium and thus treat various orbitals as groups derived from the highly symmetric case. Figure 7 is drawn with this simplification in mind.

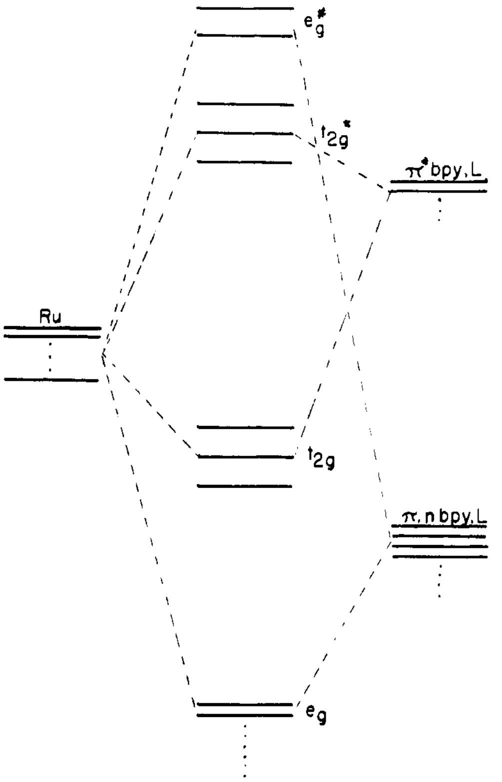

Figure 7. Simplified molecular orbital diagram of $Ru(bpy)_2XY^{n+}$ complexes.

The nearly constant energy difference between the emission maxima and the absorption maxima, despite the uncertainty created by using room-temperature absorption maxima instead of E_{0-0}'s, suggests further that the lowest energy absorbing state is fundamentally the same in all cases and is related in the same fashion to the emitting state. In keeping with Kober and Meyer's analysis of the $Ru(bpy)_3^{2+}$ spectrum, designation of the absorbing and emitting states as singlet and triplet is appropriate.[19] The above reasoning must also lead to the conclusion that the energy of the d–d excited state responsible for photosubstitution must also be strongly dependent on the nature of the two monodentate ligands. It is difficult, at this time, to predict the effect of the monodentate ligands on the energy of d–d excited states since there are no good measures of σ-bonding abilities of the ligands used in this study. There is one factor, the electron density around the metal, that is influenced by the energy of all the metal orbitals. It is clear from the trend in $E_{1/2}$(II/III) that, as the monodentate ligands are replaced by increasingly better π acceptors, the electron

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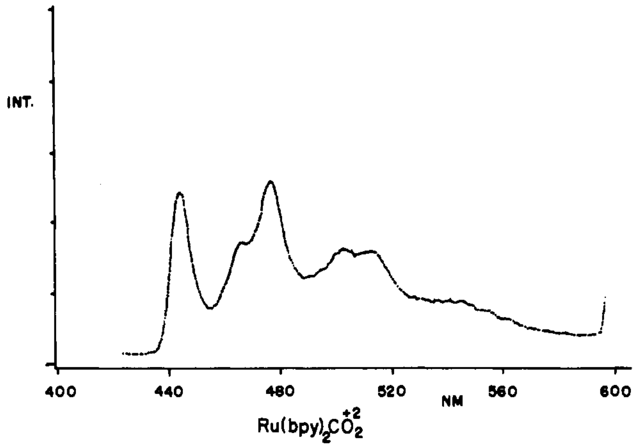

Figure 8. Emission spectrum of $Ru(bpy)_2(CO)_2^{2+}$ in 1:1 methanol–ethanol glass at 77 K with 303-nm excitation.

density on the metal is reduced. Given the probable diversity of σ-bonding capabilities of the monodentate ligand and the contrasting smooth dependence of quantum efficiency on $E_{1/2}$(II/III), the charge of the metal could, in fact, be the dominant factor that determines the energy of the d–d excited state.

An alternative rationalization of the relation between quantum yield for photosubstitution and the nature of the monodentate ligands X and Y is also in keeping with the original proposal of Watts and co-workers but places the emphasis not on the population of the approriate excited state but, instead, on the activation process that precedes loss of the coordinated ligand. If we treat photosubstitution as a dissociative process from the excited state, then the activation process will be strongly dependent on the energy of bond breaking. The parameters that determine the Ru–L bond energies are the same parameters that determine the excited-state energies; thus, the above correlations with quantum yield would, if this mechanism is correct, be coincidental. Preliminary measurements indicate a substantial temperature dependence of the quantum yields given in Table I, and we are currently in the process of gathering accurate activation energies in order to address the correctness of this alternate mechanism.

The quantum yields for photosubstitution for some of the complexes of interest have also been measured in acidic aqueous solution. A similar correlation to that observed in dichloromethane was noted and is also illustrated in Figure 4. The existence of the correlation and the similarity in slope in both media confirm the idea that the quantum efficiencies for substitution are dictated by excited-state properties and are affected in only minor ways by processes subsequent to the photochemical step such as cage recombination.

There are some notable exceptions to the correlations presented thus far. These exceptions include $Ru(bpy)_2(pyridazine)_2^{2+}$, $Ru(bpy)_2(P(C_6H_5)_2CH_3)_2^{2+}$, and complexes containing CO. The first of these exceptions, $Ru(bpy)_2(pyridazine)_2^{2+}$, is substantially less photoreactive than expected. The low efficiency, however, may simply be a manifestation of efficient cage recombination. Pyridazine has two adjacent nitrogen atoms that may prove competitive with substitution by an incoming ligand. The complex $Ru(bpy)_2(P(C_6H_5)_2CH_3)_2^{2+}$ seems to be representative of complexes containing PR_3 ligands ($P(C_6H_5)_3$ and $P(C_6H_5)(CH_3)_2$ have also been examined) that are photosubstitutionally inert. The complexes, however, do exhibit the characteristic emission spectra at 77 K. No explanation for this anomalous behavior is available at the present time.

The carbonyl complexes appear to be cases in which the monodentate ligands have a sufficiently strong influence over the orbital energies as to change the nature of the lowest lying excited state or the ground state. The complex $Ru(bpy)_2(CO)_2^{2+}$, for example, shows no room-temperature emission but at 77 K exhibits the highly structured emission spectrum illustrated in Figure 8. Surprisingly, the emission spectrum is essentially superimposable in structure and energy to that of $Rh(bpy)_2(phen)^{3+}$, which has been assigned as a π^*(bpy) $\rightarrow$ π(bpy) transition.[20] It appears then that, independent of the relative energies of the t_{2g}^* and $e_g^*(d\sigma)$ orbitals, the $t_{2g}(d\pi)$ orbitals are stabilized to such an extent that they are now lower in energy than the π orbitals of bipyridine. The similarities in emission spectra of the rhodium and ruthenium complexes support the idea that the energies of the $t_{2g}^*(d\pi)$ orbitals, which involve bipyridine predominantly, are not sensitive to the nature of the monodentate ligands.

The complex $Ru(bpy)_2(CO)Cl^+$ exhibits no emission even at 77 K and has a low quantum yield for photosubstitution. An attractive rationalization in this case may be that the ordering of the t_{2g}^* and e_g^* orbitals are reversed. This interpretation is inconsistent with a low quantum yield and with the emission spectrum observed with $Ru(bpy)_2(CO)_2^{2+}$. We have noted that the emission efficiency of the monochloro complexes, in general, are substantially smaller than those exhibited by complexes with two neutral ligands. The lack of emission in $Ru(bpy)_2(CO)Cl^+$ may be a result of an enhancement of this trend. The low quantum yields for photosubstitution may, in turn, result from an inability to adequately populate the d–d excited state because of competitive quenching pathways.

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Supplementary Material Available: A table of the extinction coefficients used to calculate the quantum yields (2 pages). Ordering information is given on any current masthead page.