

EFFECT OF CHELATE RING SIZE ON THE PHOTOANATION REACTION OF POLYPYRIDINE RUTHENIUM COMPLEXES

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Summary

Several new polypyridine ligands (L) with two pyridine rings linked by methylene bridges of different lengths have been synthesized. The corresponding $[\text{Ru}(\text{bpy})_2\text{L}]^{2+}$ (bpy \equiv bipyridine) complexes have been prepared and their photophysical and photochemical properties examined. The low temperature (77 K) emission properties of the new complexes are similar to those of $[\text{Ru}(\text{bpy})_3]^{2+}$; at higher temperatures their emission intensities are significantly decreased. In organic solvents, photoanation is efficient for all of the new complexes. In the case of $[\text{Ru}(\text{bpy})_2\text{DPE}]^{2+}$ (DPE \equiv 1,2-di(2-pyridyl)ethane), substitution of the first pyridine occurs thermally in 0.01 M Cl^- (solvent, CH_2Cl_2) and in H_2SO_4 so that photoanation of the second pyridine could be directly studied. For the six-membered chelate ring $[\text{Ru}(\text{bpy})_2\text{DPM}]^{2+}$ (DPM \equiv di(2-pyridyl)methane) reclosure of the chelate ring competes with photoanation only in polar solvents where ion pairing is not significant.

1. Introduction

In contrast to the extensive photophysical studies of polypyridine ruthenium(II) complexes (for example see ref. 1, which gives a number of review articles; the field is too extensive to list all the important references), photochemical studies have been sparse. The sequence of events for the photoanation of these complexes has only recently been delineated [2]. This apparent neglect of photochemical processes in such an extensively studied system undoubtedly results from the very inefficient photoanation reaction of *tris*(2,2'-bipyridine)ruthenium(II), $[\text{Ru}(\text{bpy})_3]^{2+}$, in water. However, the photochemical efficiency can be drastically increased in organic solvents such as dimethylformamide (DMF) and CH_2Cl_2 .

Any understanding of the photoanation process in $[\text{Ru}(\text{bpy})_3]^{2+}$ must begin with its photophysical behavior. Numerous studies have led to the model shown in Fig. 1 [1]. The intense absorption band in the visible

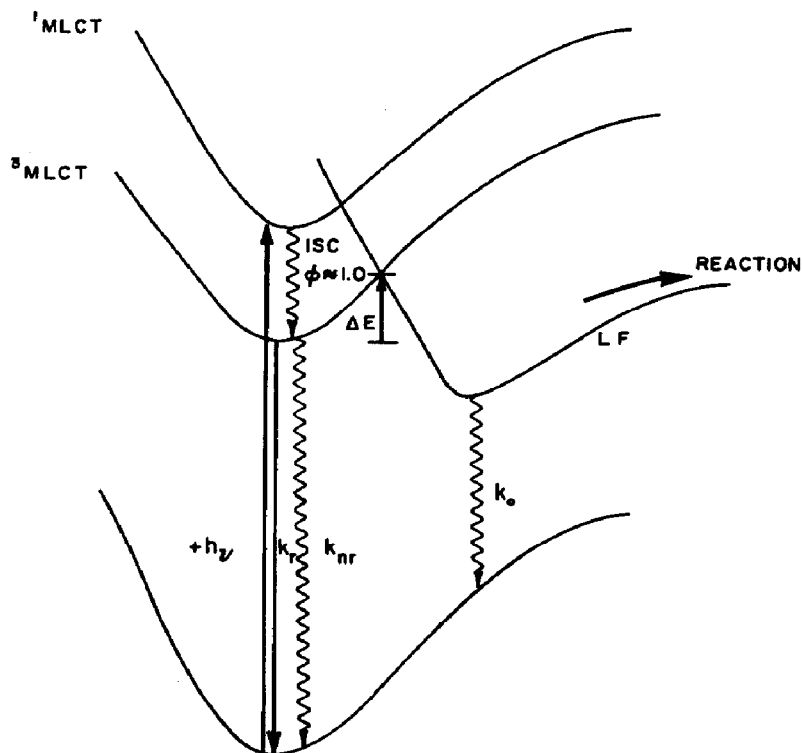


Fig. 1. Photophysical processes of $[\text{Ru}(\text{bpy})_3]^{2+}$.

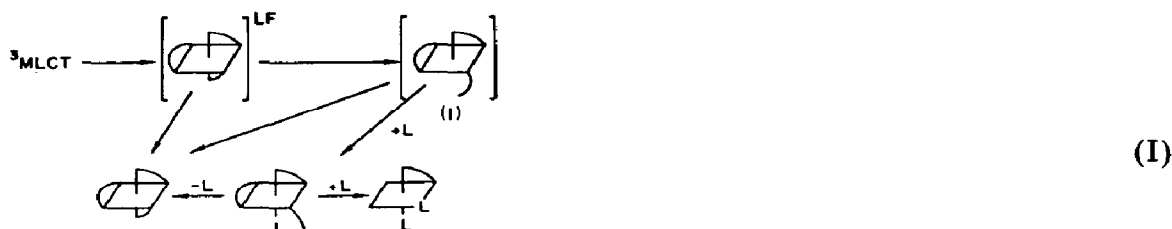
region ($\lambda_{\text{max}} \approx 450 \text{ nm}$) has been assigned as a metal-to-ligand charge transfer (MLCT) transition [3 - 14]. The initially produced MLCT state apparently has predominately singlet character but readily decays to the corresponding triplet state with unit efficiency [15]. The large spin-orbit coupling expected in these complexes raises questions as to the validity of these spin quantum numbers [16]. However, most photophysical features of $[\text{Ru}(\text{bpy})_3]^{2+}$ can be rationalized in terms of a model which assumes D_3 symmetry and incorporates spin-orbit coupling for the $d^5\text{Ru}(\text{III})$ core [17].

Once formed, the $^3\text{MLCT}$ state decays via three processes: radiative decay (k_r), radiationless decay (k_{nr}) and thermal population of a higher lying ligand field (LF) state ($k_e e^{-\Delta E/RT}$). The value for k_r is typically of the order of $5 \times 10^4 \text{ s}^{-1}$. The radiationless rate constant k_{nr} has been related to the energy difference between the initial ($^3\text{MLCT}$) and final (ground) states [18]. Indeed, it is possible to predict the value of this rate constant by knowing the 0-0 band for the phosphorescence [19]. Finally, the characterization of the higher lying excited state as an LF state is based upon the facts that (1) it is non-luminescent, (2) it undergoes rapid radiationless decay and (3) it results in a photoanation reaction [20]. For $[\text{Ru}(\text{bpy})_3]^{2+}$, the activation energy for population of this LF state has been evaluated as approximately 3600 cm^{-1} [21].

The early photochemical studies indicated only very low photoanation quantum yields. For example, van Houten and Watts reported quantum yields of nearly zero in water but this rose to 1.8×10^{-3} in 1.0 M HCl [20]. Similarly, low photochemical quantum yields were obtained with $[\text{Ru}(\text{bpy})_3](\text{NCS})_2$ in DMF [22]. However, a dramatic increase in the photoanation reaction is apparent in CH_2Cl_2 solution [23].

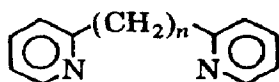
Recently the details of this photochemical reaction have been clarified by Meyer *et al.* [2, 24]. The photophysical and photochemical behavior of $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{bpy})_2(\text{py})_2]^{2+}$ ($\text{py} \equiv \text{pyridine}$) were examined in water and CH_2Cl_2 . Photophysically, the two complexes displayed similar behavior and, most importantly, the efficiency for population of the LF state was found to be similar for both complexes at 298 K. In contrast, the photoanation process was very different for the two complexes. The quantum yields were high (about 0.3) for $[\text{Ru}(\text{bpy})_2(\text{py})_2]^{2+}$ in both water and CH_2Cl_2 , whereas $[\text{Ru}(\text{bpy})_3]^{2+}$ displayed a high efficiency only in CH_2Cl_2 .

These results have been rationalized within the framework of the model presented in reaction (I). Population of the LF state results in either decay



to the ground state or formation of a pentacoordinated intermediate (I). The intermediate will in turn decay to the ground state or be trapped by another ligand (L). The key to understanding the photoanation efficiency is the partitioning of I between products and starting material. For $[\text{Ru}(\text{bpy})_2(\text{py})_2]^{2+}$, a complexed pyridine is lost and the partitioning is dictated by the relative concentrations of pyridine and L. However, the pentacoordinated intermediate obtained from $[\text{Ru}(\text{bpy})_3]^{2+}$ will have a tendency to rechelate. Consequently, only when L is a very effective ligand and then only when it is close to the cation will capture of the intermediate be competitive with ring closure. In CH_2Cl_2 , with charged ligands such as Cl^- , Br^- , NCS^- etc., ion pairs exist and the intimate contact between $[\text{Ru}(\text{bpy})_3]^{2+}$ and the anion promotes the photoanation. In water, the cation and anion(s) are well solvated and ring closure dominates.

To examine further the partitioning of the pentacoordinated intermediate, a series of ligands with two pyridines linked by methylene bridges of varying lengths were prepared. The corresponding $[\text{Ru}(\text{bpy})_2\text{L}]^{2+}$ complexes below



- $n = 0$: bpy
 $n = 1$: DPM
 $n = 2$: DPE
 $n = \infty$: (pic)₂

were prepared and their photophysical and photochemical properties compared with the case of $[\text{Ru}(\text{bpy})_2(\text{pic})_2]^{2+}$ (pic \equiv 4-picoline), where $n = \infty$.

2. Experimental details

2.1. Materials

The ligands were either commercially available or could be prepared by literature methods. Dipyridylmethane was obtained by the Wolff–Kishner reduction of dipyridylketone. Dipyridylethane was prepared by the procedure reported in ref. 25. The complexes were prepared by heating $[\text{Ru}(\text{bpy})_2]\text{Cl}_2$ [26] with an excess of the ligand in EtOH (Et \equiv ethyl) for several hours. The complexes were precipitated as the PF_6^- salt and purified by repeated recrystallization from water–acetone or MeOH–toluene (Me \equiv methyl). Satisfactory elemental analyses were obtained for all new complexes.

The CH_2Cl_2 was reagent grade and used without further purification. For $[\text{Ru}(\text{bpy})_3]^{2+}$, it was determined that purification of CH_2Cl_2 by literature methods [27] did not significantly affect the emission quantum yield or lifetime. The remaining organic solvents (EtOH, MeOH and MeCN) were purified by literature methods [27]. Water was distilled from KMnO_4 and then redistilled in an all-glass apparatus.

2.2. Emission spectra

All emission spectra were recorded using an SLM 4800 spectrofluorometer and were corrected for photomultiplier response. The low temperature (77 K) spectra were recorded in an EtOH–MeOH (4:1 by volume) glass and the intensities were determined relative to $[\text{Ru}(\text{bpy})_3]^{2+}$ ($\phi = 0.376$) [28]. The emission spectra at higher temperatures were recorded in degassed solvents (at least five freeze–pump–thaw cycles). For the latter spectra, the variable temperatures were maintained by flowing precooled N_2 gas through the sample holder; the sample temperature was determined by a copper–constantan thermocouple.

2.3. Lifetimes

All lifetimes were determined by means of the single-photon counting method [29] with samples prepared as described above.

2.4. Quantum yields

The disappearance of the starting material was followed by absorption spectroscopy using a modified Cary 14 spectrometer that allowed right-angle excitation. Samples (3 ml) of the solvent were degassed and the solid complex added just prior to the experiment. Care was exercised to prevent the introduction of O₂ and to keep the sample in the dark. The excitation source was a 150 W Xe-Hg lamp and the band at 436 nm was isolated with an interference filter. The actinometry was accomplished using ferrioxalate.

The quantum yields were determined in the reaction's initial stages while an isosbestic point (IP) was still maintained. The extinction coefficients for [Ru(bpy)₂(pic)₂]²⁺, [Ru(bpy)₂(pic)H₂O]²⁺, [Ru(bpy)(pic)Cl]⁺ and *cis*-[Ru(bpy)₂(H₂O)₂]²⁺ were evaluated in the appropriate solvents. The preparations of these complexes were similar to those of the corresponding pyridine complexes (see ref. 30). For [Ru(bpy)₂DPM]²⁺, the intermediate complexes could not be prepared by the usual methods. Consequently, the required extinction coefficients for the photoproducts were estimated by examining [Ru(bpy)₂DPE]²⁺; this complex was found to be thermally unstable in both CH₂Cl₂ (0.01 M tetrabutylammonium chloride (TBACl)) and in 1 N H₂SO₄. A known concentration of [Ru(bpy)₂DPE]²⁺ was prepared in CH₂Cl₂ or H₂O and the extinction coefficient at 450 nm determined. Next, either TBACl or H₂SO₄ was added and the [Ru(bpy)₂DPE]²⁺ was quantitatively converted to either the monochloro or the monoquo complex and the extinction coefficient evaluated. For [Ru(bpy)₂DPM]²⁺, the same *ratio* of the extinction coefficients for the initial complex and the monosubstituted complex was assumed. As a check, this procedure was applied to [Ru(bpy)₂(pic)₂]²⁺ and the extinction coefficients compared with those directly determined. The observed error was 27% so that a systematic error in the quantum yield for [Ru(bpy)₂DPM]²⁺ may be present.

3. Results

The quantum yields and lifetimes for the complexes at 77 K are shown in Table 1. All emission spectra displayed a well-defined vibrational fine structure similar to that of [Ru(bpy)₃]²⁺. Upon warming, this fine structure is lost for all the complexes and a drastic decrease in the quantum yields for emission is noted, with the exception of [Ru(bpy)₃]²⁺.

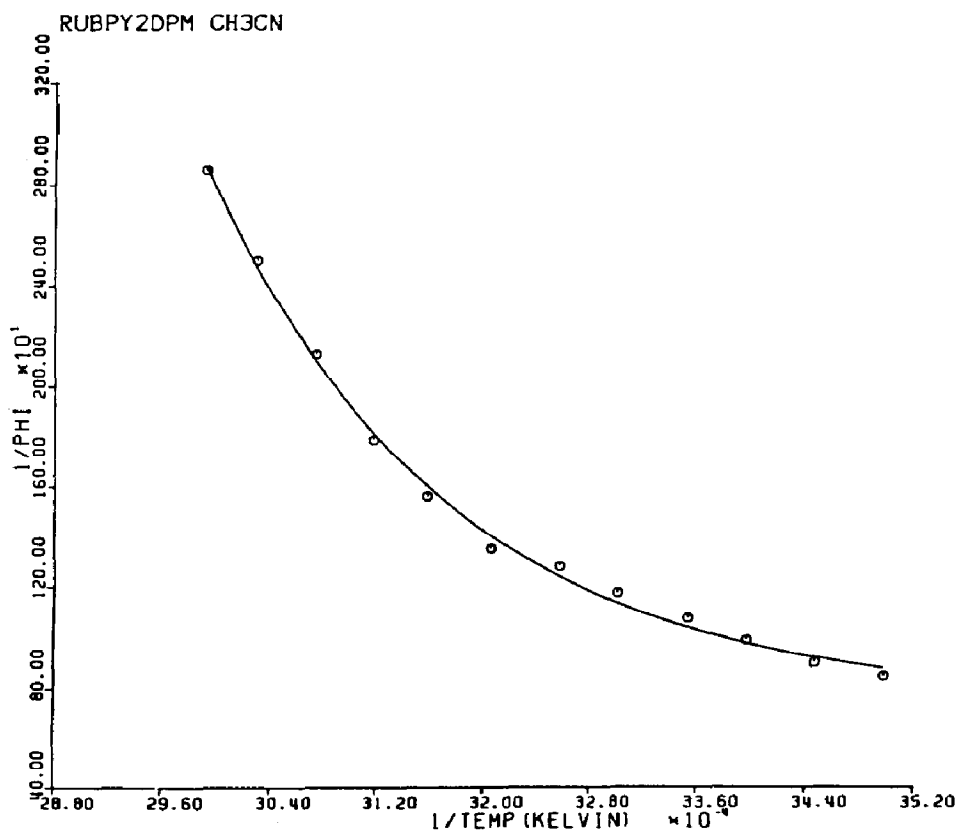
For [Ru(bpy)₂L]²⁺ (L ≡ (pic)₂ or DPM), the temperature dependence of the emission intensity was determined over the range 100 - 270 K. As previously suggested, the non-linear Arrhenius plot was fitted to eqn. (1) in order to evaluate the quantum yield of LF production at 298 K [2, 20, 21].

$$\frac{1}{\phi} = \frac{k_r + k_{nr}}{k_r} + \frac{k_0}{k_r} e^{-\Delta E/RT} = k + k' e^{-\Delta E/RT} \quad (1)$$

TABLE 1

Emission properties of the ruthenium complexes at 77 K

Complex	λ_{\max} (nm)	ϕ^a	τ^a (μs)	$k_r \times 10^4{}^b$	$k_{nr} \times 10^5{}^c$
[Ru(bpy) ₃] ²⁺	578	0.376 ^d	5.2 ^d	7.2	1.2
[Ru(bpy) ₂ (pic) ₂] ²⁺	592	0.41	5.6	7.3	1.1
[Ru(bpy) ₂ DPM] ²⁺	584	0.56	7.2	7.7	0.6
[Ru(bpy) ₂ DPE] ²⁺	605	0.11	7.5	1.5	1.2

^aAt 77 K in EtOH–MeOH (4:1 by volume).^bCalculated from $k_r = \phi/\tau$.^cCalculated from $k_{nr} = 1/\tau - k_r$.^dSee ref. 28.Fig. 2. Inverse dependence of emission intensity ($1/\text{PHI}$) and temperature for $[\text{Ru}(\text{bpy})_2\text{DPM}]^{2+}$.

A representative plot for $[\text{Ru}(\text{bpy})_2(\text{pic})_2]^{2+}$ is shown in Fig. 2. For both $[\text{Ru}(\text{bpy})_2(\text{pic})_2]^{2+}$ and $[\text{Ru}(\text{bpy})_2\text{DPM}]^{2+}$, the efficiency of LF production is nearly unity at 298 K. The emission from $[\text{Ru}(\text{bpy})_2\text{DPE}]^{2+}$ was so

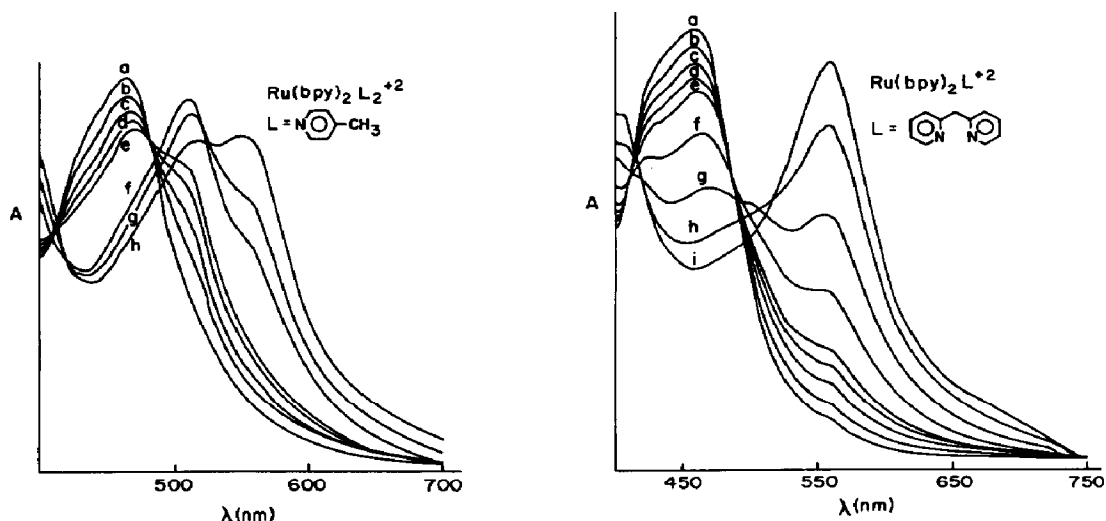


Fig. 3. Absorption spectra during the photolysis of $[Ru(bpy)_2(pic)_2]^{2+}$ in 0.01 M TBACl- CH_2Cl_2 . The photolysis times (in seconds) are: curve a, 0; curve b, 15; curve c, 30; curve d, 45; curve e, 60; curve f, 360; curve g, 600; curve h, 1200.

Fig. 4. Absorption spectra during the photolysis of $[Ru(bpy)_2DPM]^{2+}$ in 0.01 M TBACl- CH_2Cl_2 . The photolysis times (in seconds) are: curve a, 0; curve b, 15; curve c, 30; curve d, 45; curve e, 60; curve f, 120; curve g, 240; curve h, 360; curve i, 600.

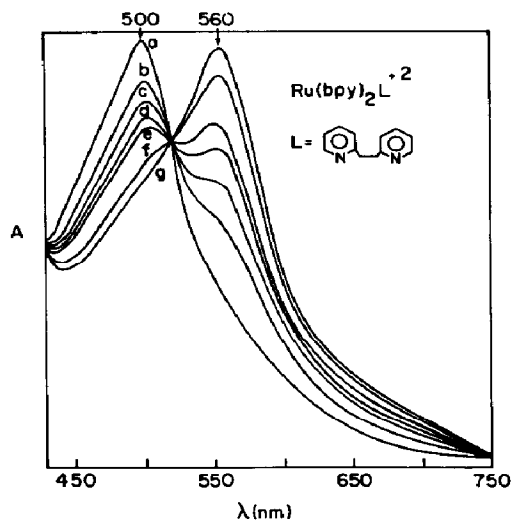


Fig. 5. Absorption spectra during the photolysis of $[Ru(bpy)_2Cl(py-CH_2CH_2-py)]^+$ in 0.01 M TBACl- CH_2Cl_2 . The photolysis times (in seconds) are: curve a, 0; curve b, 15; curve c, 30; curve d, 45; curve e, 60; curve f, 120; curve g, 180.

weak above the solvent phase transition (95 - 110 K) that a similar study was not attempted.

All complexes were extremely photolabile in CH_2Cl_2 and MeCN when a strongly complexing ligand was present. The disappearance of the four complexes in 0.01 M TBACl- CH_2Cl_2 could be easily followed by absorption spectroscopy as shown in Figs. 3 - 6. In the case of $[Ru(bpy)_2DPE]^{2+}$, the

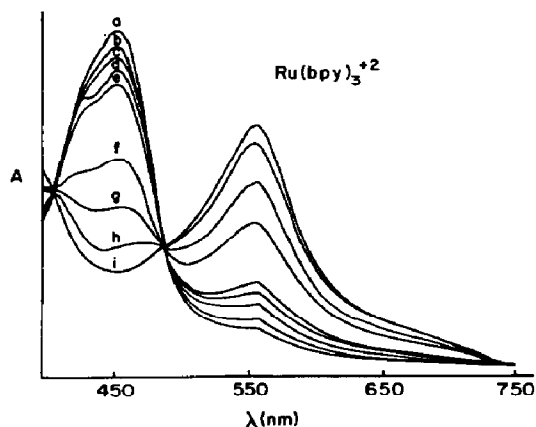


Fig. 6. Absorption spectra during the photolysis of $[\text{Ru}(\text{bpy})_3]^{2+}$ in 0.01 M TBACl- CH_2Cl_2 . The photolysis times (in seconds) are: curve a, 0; curve b, 15; curve c, 30; curve d, 45; curve e, 60; curve f, 180; curve g, 300; curve h, 600; curve i, 1200.

complex was stable in CH_2Cl_2 in the dark but was rapidly transformed in the presence of Cl^- to a product which had an absorption maximum at 504 nm and was stable in the dark for at least 1 h. The absorption spectra after extensive photolysis of all four complexes were identical and matched the absorption spectrum of $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$. The quantum yields were determined only during the initial stages of the reaction (not more than 10% completion) and are displayed in Table 2.

Similar results were obtained using 0.01 M TBACl in MeCN. However, in this solvent $[\text{Ru}(\text{bpy})_2\text{DPE}]^{2+}$ was stable in the dark and had photochemical behavior quite similar to that of $[\text{Ru}(\text{bpy})_2\text{L}]^{2+}$ ($\text{L} \equiv \text{pic}_2$ and DPM). The quantum yields under these conditions are presented in Table 2.

In 1 N H_2SO_4 , $[\text{Ru}(\text{bpy})_3]^{2+}$ was photostable ($\phi < 1 \times 10^{-4}$) while both $[\text{Ru}(\text{bpy})_2\text{pic}_2]^{2+}$ and $[\text{Ru}(\text{bpy})_2\text{DPM}]^{2+}$ underwent photoanation. The

TABLE 2

Quantum yields for photolysis of ruthenium complexes and for the production of the higher lying LF state

Complex	CH_2Cl_2		CH_3CN		1 N H_2SO_4	
	ϕ^a	ϕ_{LF}^b	ϕ^a	ϕ_{LF}^b	ϕ^a	ϕ_{LF}^b
$[\text{Ru}(\text{bpy})_3]^{2+}$	0.04	0.93 ^c	0.003	0.54 ^c	$> 1 \times 10^{-4}$	0.22 ^c
$[\text{Ru}(\text{bpy})(\text{pic})_2]^{2+}$	0.17	1.0	0.21	1.0	0.24	1.0
$[\text{Ru}(\text{bpy})_2\text{DPM}]^{2+}$	0.21	1.0	0.24	1.0	0.04	1.0
$[\text{Ru}(\text{bpy})_2\text{DPE}]^{2+}$	0.58 ^d	—	0.18	—	$< 0.3^d$	—

^aPhotoanation quantum yield.

^bQuantum yield for LF production.

^cSee ref. 2.

^dPhotolysis of intermediate complex — see text.

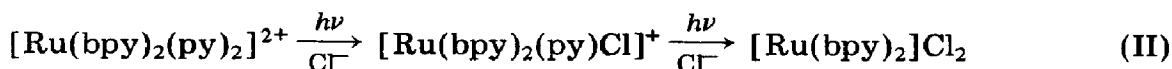
quantum yields are shown in Table 2. As in CH_2Cl_2 (0.01 M TBACl), $[\text{Ru}(\text{bpy})_2\text{DPE}]^{2+}$ was unstable in this medium, solvolyzing to the mono-aquo complex.

4. Discussion

The absorption and emission spectra of the four complexes are unremarkable. In all cases, the intense MLCT band occurs near 450 nm. The low temperature emission spectra reveal that $[\text{Ru}(\text{bpy})_2\text{DPE}]^{2+}$ has an unusually low radiative rate constant. The cause of this is at present unknown. At 298 K, $[\text{Ru}(\text{bpy})_2\text{L}]^{2+}$ ($\text{L} \equiv (\text{pic})_2$, DPM or DPE) displayed essentially no emission; this is a characteristic of complexes that have ligands weaker than bipyridine in the spectrochemical series [31].

Population of the LF state is one important decay pathway of the $^3\text{MLCT}$ state. As noted previously, the emission lifetime and intensity show a temperature dependence that has been ascribed to the population of this LF state. For $[\text{Ru}(\text{bpy})_3]^{2+}$, previously reported results indicate that, depending upon the solvent, 20% - 90% of the $^3\text{MLCT}$ excited states are deactivated by thermal conversion to the LF state [2]. For $[\text{Ru}(\text{bpy})_2(\text{pic})_2]^{2+}$ and $[\text{Ru}(\text{bpy})_2\text{DPM}]^{2+}$ essentially 100% of the excitation energy is dissipated via production of the LF state. The estimated quantum yields for LF production are shown in Table 2.

In the early stages of the $[\text{Ru}(\text{bpy})_2(\text{pic})_2]^{2+}$ photolysis in 0.01 M TBACl- CH_2Cl_2 an IP at 481 nm becomes apparent as the initial product which absorbs at 508 nm accumulates (Fig. 3). After a significant quantity of the exciting light is absorbed by this intermediate the IP is lost and a second species which has an absorption maximum at 550 nm appears. Similar behavior has been observed previously for $[\text{Ru}(\text{bpy})_2(\text{py})_2]^{2+}$ and the sequence shown in reaction (II) was proposed [24, 32]. This same mechanism is assumed to be operative in the present example.



Virtually identical behavior is found for $[\text{Ru}(\text{bpy})_2\text{DPM}]^{2+}$. The spectrum in Fig. 4 shows the initial IP; this is subsequently lost as the intermediate complex begins to absorb a significant fraction of the incident radiation. Interestingly, the quantum yield for formation of the first intermediate is as large as the corresponding value for $[\text{Ru}(\text{bpy})_2(\text{pic})_2]^{2+}$. Apparently, the ring closure is not particularly important in the collapse of this pentacoordinated intermediate under these conditions.

The $[\text{Ru}(\text{bpy})_2\text{DPE}]^{2+}$ complex is thermally unstable and within several minutes produces a species with an absorption maximum at 504 nm. This product, which is similar to the initial photoproduct of the last two complexes (*i.e.* $[\text{Ru}(\text{bpy})_2\text{ClpyCH}_2\text{CH}_2\text{py}]^+$) is relatively stable in the dark (about 1 h) but can be readily photolyzed to $[\text{Ru}(\text{bpy})_2]\text{Cl}_2$. An IP is main-

tained throughout the photolysis (Fig. 5), which is indicative of a direct relationship between reactant and product. The quantum yield for the loss of the second pyridine is substantially larger than that for the loss of the first ligand in $[\text{Ru}(\text{bpy})_2\text{DPM}]^{2+}$. In contrast, the second step in reaction (II) has a low quantum yield [32]. This difference may result from increased steric strain in the case of DPE.

As shown in Fig. 6, an IP is maintained throughout the photolysis of $[\text{Ru}(\text{bpy})_3]^{2+}$. The intermediate complex cannot be detected; apparently, this reverts back to $[\text{Ru}(\text{bpy})_3]^{2+}$ or proceeds to $[\text{Ru}(\text{bpy})_2]\text{Cl}_2$. The IP maintained throughout the photoreaction indicates that these decay pathways are thermal and reasonably rapid. Quantitatively, this photoreaction occurs with a lower quantum yield than the previous three complexes. The LF state is formed very readily in CH_2Cl_2 (yield, about 93%) [2]. Thus the difference in quantum yield is not due to population of the LF state. A second possible factor dictating the low quantum yield is capture of the pentacoordinated intermediate. However, the cations must certainly be paired in 0.01 M Cl^- - CH_2Cl_2 and capture of this intermediate is expected to be fast. Thus, the ultimate fate of the initially produced complex ($[\text{Ru}(\text{bpy})_2\text{Cl}(\text{bpy})]^+$) must be responsible for the fourfold decrease in the photoanation quantum yield of $[\text{Ru}(\text{bpy})_3]^{2+}$. This complex can rapidly reform $[\text{Ru}(\text{bpy})_3]^{2+}$, a process that apparently is much less significant in the other three complexes.

All four complexes are thermally stable in 0.01 M TBACl (solvent, MeCN) but do undergo photoanation. In this solvent, the qualitative behavior of all four complexes is similar in that initially an IP occurs as an intermediate complex with an absorption maximum at 490 nm accumulates. The identity of this new complex is probably $[\text{Ru}(\text{bpy})_2\text{Cl}(\text{py}-(\text{CH}_2)_n-\text{py})]^+$ although $[\text{Ru}(\text{bpy})_2\text{ClMeCN}]^+$ cannot be dismissed [33]. The IP is lost upon further photolysis and absorption due to $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ appears. Extensive photolysis results in complete conversion to $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ for all four complexes.

The quantum yields for the initial photoanation are shown in Table 2. The most dramatic decrease in this quantum yield is noted for $[\text{Ru}(\text{bpy})_3]^{2+}$. This loss of efficiency is due to decreased ion pairing in MeCN so that capture of the pentacoordinated intermediate is decreased. This seems to be important only in the five-membered ring $[\text{Ru}(\text{bpy})_3]^{2+}$, as the quantum yield is still high for the six-membered ring $[\text{Ru}(\text{bpy})_2\text{DPM}]^{2+}$.

In 1 N H_2SO_4 , $[\text{Ru}(\text{bpy})_3]^{2+}$ is photostable ($\phi < 1 \times 10^{-4}$). Under the same conditions, $[\text{Ru}(\text{bpy})_2(\text{pic})_2]^{2+}$ readily undergoes photoanation to $[\text{Ru}(\text{bpy})_2(\text{pic})\text{H}_2\text{O}]^{2+}$. The observed behavior is quantitatively similar to that observed for $[\text{Ru}(\text{bpy})_2(\text{py})_2]^{2+}$ [32]. However, a different behavior is now noted for $[\text{Ru}(\text{bpy})_2\text{DPM}]^{2+}$. Photolysis of this complex results in the production of a species with an absorption spectrum identical with that of $[\text{Ru}(\text{bpy})_2(\text{H}_2\text{O})_2]^{2+}$. Furthermore, an IP at 476 nm is maintained *throughout* the photolysis. This behavior is qualitatively similar to that observed for $[\text{Ru}(\text{bpy})_3]^{2+}$ in CH_2Cl_2 (0.01 M TBACl). This indicates that the monoquo

complex is not a stable intermediate and that once formed it rapidly decays either back to the starting complex or on to $[\text{Ru}(\text{bpy})_2(\text{H}_2\text{O})_2]^{2+}$. Apparently, the rate of reclosure for the six-membered chelate ring is slow and this process can compete with trapping of the intermediate only in solvents where ion pairing is not extensive. Further support for this argument is provided by the fact that photolysis occurs at essentially the same rate in H_2O and 1 N H_2SO_4 for $[\text{Ru}(\text{bpy})_2(\text{pic})_2]^{2+}$ but is substantially slower for $[\text{Ru}(\text{bpy})_2\text{DPM}]^{2+}$ in H_2O .

Finally, $[\text{Ru}(\text{bpy})_2\text{DPE}]^{2+}$ is thermally unstable in 1 N H_2SO_4 , decomposing to the monoquo complex in less than 1 min. The quantum yield for photolysis of the intermediate complex to $[\text{Ru}(\text{bpy})_2(\text{H}_2\text{O})_2]^{2+}$ is reasonably high. Again, this contrasts with the behavior of $[\text{Ru}(\text{bpy})_2(\text{py})\text{H}_2\text{O}]^{2+}$ which undergoes photosubstitution of the pyridine only very slowly.

5. Conclusions

The photoanation quantum yield for ruthenium(II) complexes is determined by the competition between chelate ring reclosure and trapping of the pentacoordinated intermediate by an external ligand. For a five-membered chelate ring, the external ligand must be spatially proximate (ion paired) to the complex in order to compete effectively. In contrast, reclosure of six-membered chelate rings is a kinetically slower process. In this case, ring closure can compete with external ligand scavenging only when ion pairing is not extensive. Further studies designed to measure the rate constant for ring closure in these systems are currently underway.

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