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The sensitization of the ligand-field state of the hexaammineruthenium(II) complex ion by organic compounds

Rose Maria Carlos [a,b], Elia Tfouni [b], Miguel G. Neumann [c,*]

[a] *Instituto de Química de Araraquara, Universidade Estadual Paulista "Julio de Mesquita", Araraquara SP, Brazil*

[b] *Departamento de Química, Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto, Universidade de São Paulo, Av. dos Bandeirantes, 3900-14040 Riberão Preto SP, Brazil*

[c] *Instituto de Química de São Carlos, Universidade de São Paulo, Caixa Postal 780, 13560 São Carlos SP, Brazil*

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Abstract

The sensitized photolysis of $[Ru(NH_3)_6]^{2+}$ by the organic dye rhodamine B and biacetyl was studied under conditions in which only the sensitizer absorbs. The reaction products resulting from ammonia aquation and Ru(II) to Ru(III) oxidation are the same for direct and sensitized photolysis. The energy transfer rate constant, calculated from the fluorescence quenching of rhodamine B, is similar to that estimated from the limiting quantum yield of the photosensitized photoaquation of the complex. Both reactions originate from a common reactive low-lying ligand-field (LF) state, which is also responsible for the direct photolysis reactions. This state, which leads directly to photoaquation, seems to have a certain charge transfer to solvent (CTTS) character, which is responsible for the photo-oxidation products. Sensitization is effective with rhodamine B (17 450 cm^{-1}) and biacetyl (19 000 cm^{-1}), whereas no reaction is observed with neutral red (16 900 cm^{-1}). These results show that the excited state responsible for the photochemical reactions lies in the energy range between 16 900 cm^{-1} and 17 700 cm^{-1} and possesses spin–orbit character.

Keywords: Ru(II) complexes; Sensitization

1. Introduction

Extensive studies have been made of $[Ru(NH_3)_5L]^{2+}$ and $[Ru(NH_3)_4L_2]^{2+}$, where L represents a nitrogen-containing aromatic heterocycle, such as pyridine (py) or substituted pyridine (py-X) [1–19]. These compounds have been well characterized, and their thermal [20–25] and photochemical [1–19] reactivities have been investigated. Metal-to-ligand back-bonding has been shown to make an important contribution to the properties of these complexes. The low-spin d^6 configuration of these complexes provides filled orbitals of the right symmetry to interact with relatively low-energy, unoccupied π^* orbitals of the ligand (L). A notable feature of the UV–visible spectra of these complexes is the strong absorption assigned to metal-to-ligand charge transfer (MLCT) transitions $\pi^* \leftarrow t_{2g}$ [1–25]. The energies of these transitions vary with the ability of the ligand to act as a π-acceptor. Studies of complexes in which L is a substituted pyridine have shown that electron-releasing substituents increase the energy of the transition, whereas electron-withdrawing substituents decrease this energy [1–3,5–13,20–23]. This is also the expected order for a charge transfer from metal to ligand.

The photochemical behaviour of $[Ru(NH_3)_5py]^{2+}$ in aqueous solution has been investigated at wavelengths corresponding to the Ru(II) to pyridine charge transfer band [1–13,16–19]. In this case, the photoaquation of both NH_3 and pyridine shows low quantum efficiency and is ascribed to a certain contribution of ligand-field (LF) character to the lowest excited state. The thermal stability of both Ru(II)- and Ru(III)-ammine complexes seems to be inconsistent with the large lability of the Ru–pyridine charge transfer state [26–29]. Thus there is no reason to expect an MLCT excited state of $[Ru(NH_3)_5py]^{2+}$ to undergo easy ligand substitution. On the other hand, LF states are strongly labile [26–29]. In addition, $[Ru(NH_3)_5py]^{2+}$ complexes of substituted pyridine, such as $[Ru(NH_3)_5(\text{formyl-py})]^{2+}$, present very little photosubstitution [11–13]. From these results, Malouf and Ford [12] proposed the "excited state tuning" model.

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[*] Corresponding author. Tel.: +55 16 274 9167; fax: +55 16 274 9205; e-mail: neumann@iqsc.sc.usp.br

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In this model, it is assumed that the reactive excited state responsible for the photochemical behaviour of $[Ru(NH_3)_5L]^{2+}$ is the lower energy LF state.

Recent energy transfer studies [18] from singlet and triplet donors to $[Ru(NH_3)_5py]^{2+}$ are consistent with the "excited state tuning" model, and indicate that the LF excited state precursor of the observed photosubstitution in this complex lies near 16 900 cm^{-1}. LF bands are observed for Ru(II) complexes with saturated ligands [30,31] and for the isoelectronic, but harder to oxidize, Rh(III) complexes with the same ligands [32–34]. The case in which Ru(II) is bonded to saturated ligands is exemplified [31] by the $[Ru(NH_3)_6]^{2+}$ ion which has a low-intensity band at 390 nm. It should be noted that direct LF photolysis of the $[Ru(NH_3)_6]^{2+}$ ion in aqueous solution leads to a substitutional behaviour (0.2 mol $einstein^{-1}$), consistent with the general observation that the LF excitation of low-spin d^6 complexes leads to substitutional processes for heavier transition metals [30].

Since ammonia cannot participate in back-bonding, a comparison of the energies for both ammonia and pyridine on Ru(II) should provide a direct measure of the contribution of back-bonding to the interaction of Ru(II) with the latter base. In this context, the sensitization studies described here for $[Ru(NH_3)_6]^{2+}$ are designed to test the feasibility of direct sensitization of the LF state, and to examine the effects of back-bonding from Ru(II) to pyridine on the energy of the MLCT state of the $[Ru(NH_3)_5py]^{2+}$ complex ion.

2. Experimental details

2.1. Chemicals

$[Ru(NH_3)_6]^{2+}$ was prepared by boiling a solution of $RuCl_3 \cdot nH_2O$ with NH_4OH in the presence of zinc powder according to the literature [30]. Rhodamine B (Aldrich) was recrystallized twice from ethyl ether and air dried. Neutral red and biacetyl (2,3-butanedione) were obtained from Aldrich and were used without further purification. Solutions for photolysis and luminescence studies were prepared using doubly distilled water containing NaCl (0.2 M) at pH 3.0 (HCl, 10^{-3} M). Solutions were deaerated with argon previously passed through a chromous bubbler. Reinecke's salt [35] $(NH_4)[Cr(NH_3)_2(SCN)_4]$ (Eastman) was converted to the potassium salt by recrystallization from KNO_3 solution, prior to being used for actinometry at 519 nm. Potassium(trisoxalate)ferrate(III), used in actinometry at 405 nm, was prepared according to Calvert and Pitts [36].

2.2. Instruments

Monochromatic irradiation at 405 nm and 519 nm was performed as described elsewhere [18]. The progress of the photoreactions was monitored spectrophotometrically on an HP model 8452A diode array spectrometer. Emission spectra were recorded with an Aminco-Bowman spectrofluorometer model J4-8960A, with a high-pressure xenon lamp and an IP28 type photomultiplier. Electrochemical data were obtained using a PAR model 273 potentiostat/galvanostat, a plotting system recorder and an IBM XT microcomputer. Measurements were carried out in NaCl (0.2 M) at pH 3.0 (HCl, 10^{-3} M), using a cell containing AgCl/Ag (−17 mV vs. saturated calomel electrode (SCE)) as the reference electrode, Pt wire as the auxiliary electrode and a glassy carbon electrode with an area of 0.082 cm^2 as the working electrode, at scan rates of 0.1 s^{-1}. The concentrations of the solutions were 1×10^{-4} M for $[Ru(NH_3)_6]^{2+}$ and 1×10^{-4} M for the dyes.

2.3. Procedures

Solutions for direct and sensitized photolysis of $[Ru(NH_3)_6]^{2+}$ were prepared as follows. A weighed amount of the complex was dissolved in a solution of approximately 1×10^{-5} M of the sensitizer in NaCl (0.2 M) at pH 3.0 (HCl, 10^{-3} M). The solutions were deaerated by bubbling with argon prior to photolysis, and stirred during irradiation. The solutions were photolysed up to approximately 5% conversion in 1.0 cm or 0.5 cm path length cells at 25 °C. The quantum yields of photo-oxidation of Ru(II) to Ru(III) and photosubstitution of coordinated ammonia were obtained from spectral data as described in Ref. [30]. Analogous samples were allowed to react in the dark, under the same conditions as the photolysed solutions, in order to correct the quantum yields.

3. Results

3.1. Absorption and emission data

Data on the absorption and emission spectra of rhodamine B, neutral red, biacetyl and the acceptor $[Ru(NH_3)_6]^{2+}$ are given in Table 1. The observed absorption bands of $[Ru(NH_3)_6]^{2+}$ at 275, 390 and 310 nm correspond to the charge transfer to solvent (CTTS) and LF transitions, ${}^1T_{1g} \leftarrow {}^1A_{1g}$ and ${}^1T_{2g} \leftarrow {}^1A_{1g}$ respectively, according to Matsubara et al. [31]. The forbidden low-energy triplet LF band (${}^3T_{1g} \leftarrow {}^1A_{1g}$) reported [18] to occur at 17 700 cm^{-1} was not observed in solution. Biacetyl presents both fluorescence and phosphorescence in aqueous solution. The ruthenium complex does not emit in solution even at low temperature.

3.2. Direct photolysis of $[Ru(NH_3)_6]^{2+}$

The photolyses in this work were performed using solutions of $[Ru(NH_3)_6]^{2+}$ ((1–2) × 10^{-3} M) in NaCl (0.2 M) at pH 3.0 (HCl, 10^{-3} M). Irradiation with 405 nm light produced ammonia aquation ($\Phi_{aq} = 0.29 \pm 0.06$ mol $einstein^{-1}$) and Ru(II) to Ru(III) photo-oxidation ($\Phi_{ox} = 0.035 \pm 0.004$ mol $einstein^{-1}$), in good agreement

Table 1
Absorption and emission data of the sensitizers and $[Ru(NH_3)_6]^{2+}$

Compound	λ_{abs} (nm) (ϵ ($M^{-1}cm^{-1}$))	λ_{irr} (nm)	λ_{em} (nm)	Emission
Rhodamine B	554 (99 000)	520	578	Fluorescence
Neutral red	531 (24 000)	510	625	Fluorescence
Biacetyl	404 (9.0)	404	470	Fluorescence
			525	Phosphorescence
$[Ru(NH_3)_6]^{2+}$	275 (640)			
	390 (35)			
	310 (<35)			

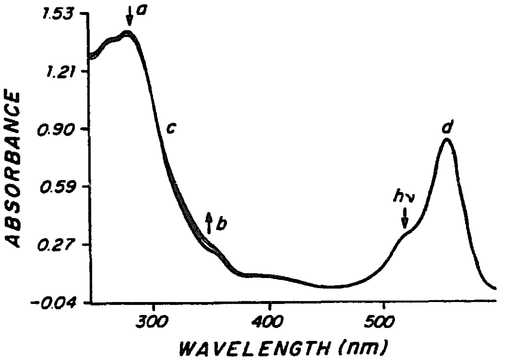

Fig. 1. Spectral changes of an aqueous solution of rhodamine B (1×10^{-5} M) and $[Ru(NH_3)_6]^{2+}$ (2×10^{-3} M) in NaCl (0.2 M) at pH 3.0 (HCl, 10^{-3} M) on irradiation at 520 nm.

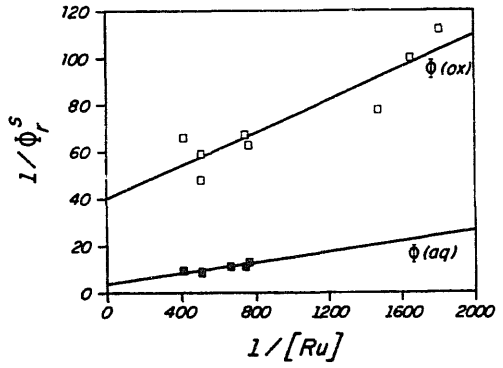

Fig. 2. Quantum yields of ammonia aquation (a) and Ru(II) to Ru(III) oxidation (b) of $[Ru(NH_3)_6]^{2+}$ photosensitized by rhodamine B.

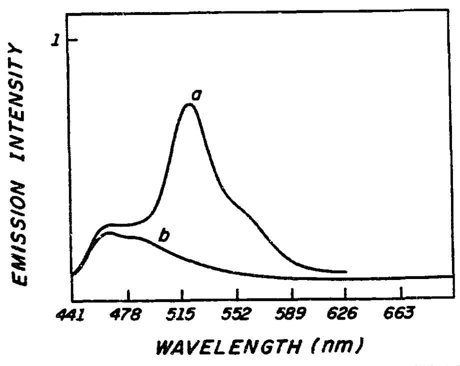

Fig. 3. Emission spectrum of biacetyl (0.30 M) in NaCl (0.2 M) at pH 3.0 (HCl, 10^{-3} M): (a) biacetyl alone; (b) in the presence of $[Ru(NH_3)_6]^{2+}$ (5.6×10^{-4} M).

with the results of Matsubara and Ford [30] for photolysis at longer wavelengths ($\Phi_{aq}=0.26$ and $\Phi_{ox}=0.035$).

3.3. Sensitized photolysis of $[Ru(NH_3)_6]^{2+}$

The sensitization experiments were performed by irradiation at 520 nm where only the sensitizers absorb. The rhodamine B concentration was 1×10^{-5} M, and the $[Ru(NH_3)_6]^{2+}$ concentration was varied in the range 5×10^{-4}–3×10^{-3} M. The irradiation of solutions containing both rhodamine B and the complex caused spectral variations which matched exactly those found in direct photolysis, i.e. an increase in absorbance around 330 nm and a decrease at 300 nm, with an isosbestic point at 290 nm corresponding to the conversion of $[Ru(NH_3)_6]^{2+}$ to $[Ru(NH_3)_5Cl]^{2+}$. No change was observed in the absorption band of rhodamine B at 554 nm (Fig. 1).

The quantum yield of the photosensitized reaction increased with increasing complex concentration, as can be seen in Fig. 2. The limiting quantum yields of the sensitized reactions (Φ_{lim}) were obtained from the intercepts of the double reciprocal plots. These values were 0.29 ± 0.09 mol einstein^{-1} for photoaquation and 0.026 ± 0.01 mol einstein^{-1} for photo-oxidation. The rate constant for energy transfer, calculated from the product of the slope of the plot for photoaquation and Φ_{lim} (using $\tau_D=10^{-9}$ s), was 1.5×10^{11} $M^{-1}s^{-1}$.

3.4. Luminescence studies

Excitation at 510 nm of aqueous solutions of rhodamine B resulted in an intense fluorescence emission band at 578 nm. The emission intensity of the dye decreased with increasing complex concentration. The fluorescence quenching data yielded a Stern–Volmer quenching constant K_{SV} of 410 M^{-1}, which corresponds to an energy transfer rate constant of 2.0×10^{11} M^{-1} s^{-1} for the rhodamine B–$[Ru(NH_3)_6]^{2+}$ system. In contrast, the addition of 1×10^{-4}–3×10^{-3} M of the ruthenium(II) complex had no effect on the fluorescence of neutral red.

Excitation of deaerated solutions of biacetyl (0.3 M) at 400 nm produced a low-intensity fluorescence band at 470 nm and a very intense phosphorescence band with a maximum around 525 nm. The phosphorescence of biacetyl was completely quenched in the presence of $[Ru(NH_3)_6]^{2+}$ (5.6×10^{-4} M), whereas the fluorescence was practically unaffected by the complex (Fig. 3).

4. Discussion

4.1. The mechanism of the quenching process

There are several possible mechanisms for energy transfer in fluid solutions [37]:

1. donor emission followed by re-absorption by the acceptor;
2. collisional exchange energy transfer from the luminescent state of the donor to the reactive excited state of the complex;
3. excited state reversible electron transfer followed by chemical generation of the excited state;
4. dipole–dipole Förster resonance energy transfer.

The observed rate constants for energy transfer from rhodamine B and biacetyl to the $[Ru(NH_3)_6]^{2+}$ complex ion are always higher than 10^{11} M^{-1} s^{-1}, i.e. well above the diffusional limit for reactions in aqueous solutions, indicating that the energy transfer cannot involve collisional processes. Therefore sensitization probably occurs via a Förster energy transfer mechanism. Furthermore, as the sensitization of the $[Ru(NH_3)_6]^{2+}$ complex is obtained by quenching of the rhodamine B fluorescence and biacetyl phosphorescence, no spin restrictions seem to be present in the process, as predicted for Förster-type energy transfer.

The possibility of "trivial" sensitization can also be eliminated because the $[Ru(NH_3)_6]^{2+}$ complex does not absorb appreciably at the emission wavelengths of the sensitizers (see Table 1).

In addition to the high quenching rate constants, a reversible electron transfer process, i.e.

$$^{*}\text{Dye} + [Ru(NH_3)_6]^{2+} \rightarrow {}^{*}\{\text{Dye}^{-} \,|\, [Ru(NH_3)_6]^{3+}\} \rightarrow \text{Dye} + {}^{*}[Ru(NH_3)_6]^{2+} \qquad (1)$$

can be ruled out on thermodynamic grounds [37]. The energies of reductive quenching of the excited singlet states of the dyes by the Ru(II) complex can be evaluated as 1.66 V for rhodamine B and 2.58 V for neutral red, using 0.21 V for the oxidation of the complex and 1.45 and 2.37 V for the reduction of the excited dyes. The potentials involved in the electron back-transfer reactions are 0.50 and 0.06 V for rhodamine B and neutral red respectively. Although the photoreduction of the dye by the complex is possible, the energy involved in the electron back-transfer (0.50 and 0.06 V) is not sufficient to excite the Ru(II) complex.

Furthermore, the photochemical stability of the dyes in the presence of the complex (no spectral changes during photolysis and the same products in the photosensitized and direct photolysis of the complex) demonstrates that an electron transfer pathway for energy transfer is not a probable explanation for the observed reactions. Thus the sensitization experiments demonstrate that the dominant quenching mechanism for $[Ru(NH_3)_6]^{2+}$ is energy transfer.

4.2. The excited states involved in the photoreaction

The direct photolysis of $[Ru(NH_3)_6]^{2+}$ at wavelengths above 400 nm, which mainly reach the lowest spin-allowed excited LF state, leads almost exclusively to ammonia aquation ($\Phi_{aq}=0.29$), although some photo-oxidation is also observed ($\Phi_{ox}=0.035$). Similar quantum yields are obtained from rhodamine B photosensitization of $[Ru(NH_3)_6]^{2+}$, indicating a common reactive state in both cases. As the energy provided by the sensitization of rhodamine B (17 450 cm^{-1}) or biacetyl (19 000 cm^{-1}) is lower than that of the state reached by direct photolysis (approximately 24 000 cm^{-1}), the reactive state should be of lower energy than the $^{1}T_{1g}$ state, probably the corresponding triplet, or a spin–orbit state derived from it ($^{1,3}T_{1g}$). The energy estimated for this triplet is 17 700 cm^{-1} [18], but it is not observed in absorption experiments. The actual reactive state will be somewhat lower due to the mixing of the states with different spin, as shown by the sensitization by rhodamine B (17 450 cm^{-1}) (Fig. 4).

The similarity between the values of Φ_{lim} and the product yields from direct photolysis indicates that intersystem crossing between the lowest energy LF singlet excited state reached by irradiation and the reactive state occurs with nearly unit efficiency, i.e. $\Phi_{ISC}\sim1.0$, and that the reaction mechanism passes through the same reactive state. In addition, it can be seen that the k_{et} value estimated from the quenching of rhodamine fluorescence is similar to that obtained from the limiting quantum yield of photoaquation, indicating that the sensitization reaction excites directly the $^{1,3}T_{1g}$ state. A smaller yield of photo-oxidation is also found (about 10%), as in direct photolysis, originating from the CTTS character of the reactive state.

When irradiating $[Ru(NH_3)_6]^{2+}$ at shorter wavelengths (214–280 nm), photo-oxidation predominates over photoa-

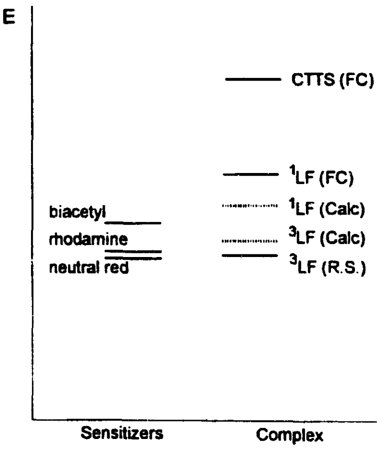

Fig. 4. Energy levels for the $[Ru(NH_3)_6]^{2+}$ ion and the sensitizers: FC, Franck–Condon (vertical) energies; Calc, calculated energies; R.S., reactive state.

quation and, at 280 nm, the observed quantum yields are $\Phi_{ox} = 0.25$ mol einstein^{-1} and $\Phi_{aq} = 0.04$ mol einstein^{-1} [30,31]. This proves that the reactive state in this case must be different from that for long-wavelength irradiation. The absorption of the complex ion found at 275 nm corresponds to a CTTS band with rather high energy (approximately 36 300 cm^{-1}), and it is assumed that this is the reactive state which leads to the oxidation of the complex ion. In a manner parallel to that postulated for the reactive state for photoaquation, this state includes a certain LF character responsible for the small photoaquation quantum yield.

4.3. Energy of the reactive LF excited state of $[Ru(NH_3)_6]^{2+}$

Considering that the singlet state of rhodamine B (17 450 cm^{-1}) is quenched by the complex, whereas no quenching of neutral red (16 900 cm^{-1}) is observed, it can be concluded that the energy of the sensitized excited state precursor of the photoaquation reaction of $[Ru(NH_3)_6]^{2+}$ lies between 16 900 and 17 700 cm^{-1}.

It is interesting that the energy range for sensitization of $[Ru(NH_3)_6]^{2+}$ is the same as that found [18] for the sensitization of the reactive excited state of $[Ru(NH_3)_5py]^{2+}$. Similarly, the reflectance spectrum of solid $[Ru(NH_3)_5py]^{2+}$ presents a broad shoulder with a maximum around 385 nm, close to the absorption maximum for $[Ru(NH_3)_6]^{2+}$ at 390 nm. These observations lead to the question of back-bonding effects for pyridine on the MLCT energy in $[Ru(NH_3)_5py]^{2+}$.

Since pyridine is a poorer σ-donor than ammonia, it is also expected to be a weaker field ligand [38]. The failure to observe a wavelength displacement of the LF absorption band between the complexes with these two ligands may be associated with the π-acceptor ability of pyridine. Thus the results of absorption and sensitization of $[Ru(NH_3)_6]^{2+}$ and $[Ru(NH_3)_5py]^{2+}$ seem to reflect an approximate cancellation of the expected opposing influences of the pyridine ligand σ-donor and π-acceptor abilities in the ground and excited states.

In support of the above arguments, the absorption and emission spectra of other d^6 metal complexes give results similar to those observed for the Ru(II) complexes. For the low-spin d^6 complexes $[ML_6]^{2+}$, two spin-allowed LF bands are expected ($^1T_{1g} \leftarrow {}^1A_{1g}$ and $^1T_{2g} \leftarrow {}^1A_{1g}$), whereas for $[ML_5py]^{2+}$ systems with nearly C_{4v} symmetry, these bands correspond to the ^1E_a ($^1A_2 \leftarrow {}^1A_1$) and ^1E_b ($^1B_2 \leftarrow {}^1A_1$) symmetries respectively [32,39]. However, band splitting in the latter case is often undetectable and the observed λ_{max} depends on the average LF. For example, the absorption maxima for $[Rh(NH_3)_6]^{3+}$ and $[Rh(NH_3)_5py]^{3+}$ are at 302 and 305 nm respectively, indicating that pyridine is placed near to ammonia in the spectrochemical series [33]. Similarly, LF emission from $[Rh(NH_3)_6]^{3+}$ and $[Rh(NH_3)_5py]^{3+}$ shows comparable energies (16 400 and 16 300 cm^{-1} respectively) [32]. When comparing the results for NH$_3$ and pyridine ligands in Ru(II) and Rh(III) complexes, it must be considered that the same spectral behaviour is obtained for both metals, notwithstanding that Rh(III) complexes do not exhibit back-bonding interactions. This proves again that the back-bonding effects in Ru(II)–pyridine interactions are not important.

Qualitatively, it is possible to take the difference in energy between the reactive excited states of $[Ru(NH_3)_6]^{2+}$ and $[Ru(NH_3)_5py]^{2+}$ ions, i.e. $17\,700 - 16\,900 = 800$ cm^{-1}, as the approximate contribution of the back-bonding of the pyridine ligand in the Ru(II) complex. This value indicates that the back-bonding effect for pyridine is small in the excited state and suggests that it will not be large for the ground state. The back-bonding contribution in $[Ru(NH_3)_5py]^{2+}$ and *cis*- and *trans*-$[Ru(NH_3)_4(py)_2]^{2+}$ complexes has been estimated to be 1200 cm^{-1} by molecular orbital calculations based on symmetry and overlap arguments [39]. Thus, evidence from experimental data and theoretical calculations leads to back-bonding energies of the order of 1000 cm^{-1} for both the excited and ground states, proving that these effects are not very important in the Ru(II)–pyridine interaction. Recently published calculations, using ZINDO-95 [40], of the relative contributions of the π(py)–dπ and dπ–π^*(py) interactions are consistent with these results.

5. Conclusions

The sensitized photolysis of $[Ru(NH_3)_6]^{2+}$ leads to products and quantum yields similar to those for direct photolysis. The high photoaquation quantum yields obtained in the sensitization experiments and the observation of $\Phi_{ISC} \approx 1.0$ indicate that transitions between the CTTS and LF manifolds are restricted. It is proposed that the reactive state reached after irradiation at wavelengths corresponding to the LF absorption bands of $[Ru(NH_3)_6]^{2+}$ is the lowest energy LF state. The small oxidation quantum yield observed is ascribed to the small CTTS character of this state.

Sensitization is effective with rhodamine B (17 450 cm^{-1}) and biacetyl (19 000 cm^{-1}), whereas no reaction is observed with neutral red (16 900 cm^{-1}), demonstrating that the excited state responsible for the photochemical reactions lies between 16 900 and 17 700 cm^{-1}.

The energy of the reactive state of $[Ru(NH_3)_6]^{2+}$ is in the same range as that found for the sensitized photoreactions of $[Ru(NH_3)_5py]^{2+}$ [18]. A simple consideration which may be used to accommodate these results is that back-bonding effects are small for pyridine and, therefore, the smaller σ-donor ability of pyridine is largely compensated by the increase in the π-acceptor ability.

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