



ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 122 (1999) 103–108

Journal of
Photochemistry
and
Photobiology
A: Chemistry

Photochemical reactions of pentaammine(cyanopyridine)ruthenium(II) complexes, $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$ ^{1,2}

Maristela Silva Martinez^{a,b}, Érica Cristina de Oliveira^a, Elia Tfouni^{a,*}

^aDepartamento de Química, Faculdade de Filosofia Ciências e Letras de Ribeirão Preto, Universidade de São Paulo. Av. dos Bandeirantes, 3900, 14040-901, Ribeirão Preto SP, Brazil

^bInstituto de Química de São Carlos, Universidade de São Paulo, São Carlos SP, Brazil

Received 7 July 1998; received in revised form 27 October 1998; accepted 21 December 1998

Abstract

Photolyses of nitrile bonded $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$ complexes (L = 2-cyanopyridine (2-NCpy); 3-cyanopyridine (3-NCpy); or 4-cyanopyridine (4-NCpy)) at 365, 404, and 436 nm, were studied in aqueous solution, and lead exclusively to ammonia and cyanopyridine photoaquation. No linkage isomerization to yield the pyridinyl bonded complexes occurs, suggesting that the kinetic control observed for thermal reactions of Ru(II) amines with nitriles are also operative for the possible transients and intermediates formed following deactivation of the excited states. Ligands photoaquation showed irradiation wavelength independent quantum yields. The 2-NCpy and 3-NCpy complexes have higher L quantum yields and the 4-NCpy have higher ammonia quantum yield. Initial excitation in the ¹MLCT (metal to ligand charge transfer) energy range, is followed by competitive internal conversion and intersystem crossing to one ³LF (ligand field) state or one ³LF manifold of excited states of the same configuration, and of lowest energies, from which photoaquation occurs. The results suggest that these states for 2-NCpy and 3-NCpy complexes have more contribution from the z^2 orbital, while for 4-NCpy the $x^2 - y^2$ have larger contribution. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Photolyses; Photoaquation; Thermal reactions; Quantum yields

1. Introduction

Ruthenium amines with azine ligands have metal to ligand charge transfer (MLCT) and ligand field (LF) as lowest energy excited states (LEES), with comparable energies [1–11]. These complexes undergo photosubstitution reactions when the LEES is LF in character, and which is ³LF. When the LEES is MLCT in character the complexes are relatively unreactive. This behavior laid the basis for the ‘tuning model’ which also holds for other ruthenium(II) amines [1–8].

The photochemical behavior of ruthenium(II) amines with other π unsaturated ligands have also been examined [3–8,12,13], however, with nitrile ligands, only the acetonitrile (acn) and benzonitrile (bnz) complexes have been reported [1,2,14–17]. The photosubstitution of pyridine (py) in $[\text{Ru}(\text{NH}_3)_5\text{py}]^{2+}$ shows pH dependent quantum

yields, which were explained by the formation of a η^2 -bonded py–Ru(II) intermediate. A relatively long-lived intermediate was also detected given further support to this hypothesis [18].

Similar intermediates were proposed to occur upon the Ru(III) reduction of the amido bonded $[(\text{NH}_3)_5\text{Ru}^{\text{III}}\text{NHC}(\text{O})\text{-py}]^{2+}$ to form the pyridinyl bonded $[(\text{NH}_3)_5\text{Ru}^{\text{II}}\text{pyCONH}_2]^{2+}$ (pyCONH₂ = nicotinamide or isonicotinamide) [19]. More recently [20], both linkage isomerizations, amido to pyridinyl and pyridinyl to amido, were reported to occur for the Ru(III) complex $[\text{Ru}(\text{edta})(\text{isn})]^-$, with the same type of intermediate being claimed, as a possibility, without further evidences.

The ground state reaction of $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$ with 2-cyanopyridine (2-NCpy), 3-cyanopyridine (3-NCpy), or 4-cyanopyridine (4-NCpy) yields different products, depending on the medium pH [21,22]. At low pHs, the nitrile bonded $[\text{Ru}(\text{NH}_3)_5(\text{NCpy})]^{2+}$ complexes are exclusively formed, whereas at high pH (~6.0), a mixture of pyridinyl bonded and the nitrile bonded complexes results. A kinetic control was reported to be responsible for this behavior [21]. An interesting illustration of the kinetic control seems to be the behavior of acrilamide and acrylonitrile complexes of

*Corresponding author. Fax: +55-16-633-8151; e-mail: eltouni@usp.br

¹Presented in part at the XXXII International Conference on Coordination Chemistry, Santiago de Chile, Chile, August 1997.

²Taken in part from: Maristela Silva Martinez, M. D.Sc. Thesis, Instituto de Química de São Carlos, Universidade de São Paulo, São Carlos, SP, Brazil, 1997.

pentaammineruthenium. The amido bonded complex of acrilamide $[(\text{NH}_3)_5\text{Ru}^{\text{III}}(\text{acrilamido})]$ undergoes, upon reduction to Ru(II), a linkage isomerization reaction to form the η^2 -bonded acrilamido complex of Ru(II) [23]. On the other hand, reactions of $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$ with the amphiphilic acrylonitrile yielded the nitrile bonded complex without any evidence of a η^2 -bonded one, in agreement with a preference for nitrile bonds [24,25]. Another example of such a preference comes from the pentaammineruthenium(II) complex of 2-cyanoethyldiphenylphosphine, where the nitrile bonded complex is formed rather than the phosphine bonded of higher back-bonding and strong ligand field site [26]. Considering the amphiphilic character of cyanopyridines, the preferential nitrile site for coordination in amphiphilic ligands, and the above isomerization reactions occurring through η^2 -bonded intermediates, the possible occurrence of isomerization reactions from nitrile to pyridinyl bonded cyanopyridines complexes derived from photochemical reactions is worth examining. As a matter of fact, in an earlier qualitative experiment, irradiation of the nitrile bonded $[\text{Ru}(\text{NH}_3)_5(4\text{-NCpy})]^{2+}$ resulted in the formation of a species which presumably could be the pyridinyl bonded complex. On the other hand, in latter flash photolysis experiments [27], this isomerization and the possible intermediate were not observed. However, it should be pointed out that in this latter case, monitoring of the intermediates, of unknown spectra, was done within a few selected wavelengths.

Thus, taking into account these peculiarities and the fact that the acn and bzn complexes were the only ammine Ru(II) nitrile complexes the photochemistry of which was so far examined in detail, we decided to examine the photosubstitution reactions of $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$ (L = 2-cyanopyridine (2-NCpy), 3-cyanopyridine (3-NCpy) or 4-cyanopyridine (4-NCpy)) in aqueous solutions, which are described in this paper.

2. Experimental

2.1. Chemicals and reagents

$\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ (Aldrich), 2-cyanopyridine (Aldrich), 3-cyanopyridine (Aldrich) and 4-cyanopyridine (Aldrich) were used for the Ru–cyanopyridines complexes syntheses. NaBF_4 was recrystallized from hot water. Ethanol and acetone were purified before use [28]. Ether was purified as described [29]. Doubly distilled water was used throughout this work. All other materials were reagent grade and were used without further purification.

2.2. Ruthenium complexes syntheses

$[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and $[\text{Ru}(\text{NH}_3)_5\text{L}](\text{BF}_4)_2$ (L = 2-cyanopyridine (2-NCpy), 3-cyanopyridine (3-NCpy) or 4-cyanopyridine (4-NCpy)) were synthesized according to literature

procedures [21,22] with some modifications [30]. Typically, 100 mg (0.34 mmol) of $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ were dissolved, with continuous argon bubbling, in 5 ml of a deaerated acidic aqueous solution of trifluoroacetic acid (TFA) (pH \sim 2) with a gentle heating (\sim 50°C) to aid the dissolution. The solution was let to cool down, and, then, with continuous argon bubbling and protection from light, Zn(Hg) was added. After reduction, an acidic (pH 0.2; TFA) solution of the ligand (144 mg (1.19 mmol) of 2- or 4-NCpy, or 300 mg (2.88 mmol) of 3-NCpy, in 3 ml), was added. The mixture was allowed to react for ca. 30 min with continuous argon bubbling in the dark, and, then, it was filtered over a freshly prepared, deaerated, and filtered NaBF_4 (0.2 g, 0.2 ml) solution. The resulting mixture was kept in a vacuum desiccator, over silica gel, under reduced pressure, until formation of a precipitate, which was collected by filtration and purified as follows. The collected solid was dissolved in hot water (\sim 70°C) and the solution cooled in an ice-bath. The formed precipitate was collected by filtration, washed with ethanol and vacuum dried. Yields averaged 65–70%. The UV–Vis spectral and redox potentials data of the complexes agree with the reported values [21,30,31].

2.3. Spectra

Electronic spectra were recorded at room temperature with a HP8452A Hewlett Packard recording spectrophotometer using quartz cells.

2.4. Photolyses procedures

These are quite similar to previously described procedures [1,2,32]. Irradiations at 365, 404, 436 nm were carried out by using an Osram 150 W/I Xenon lamp in an Oriel Model 8500 universal arc lamp source with an Oriel interference filter for monochromatization (band pass \sim 10 nm), an infrared filter, and a thermostated cell holder. Photolyses were carried out in aqueous solution of \sim 10⁻⁴ mol/l Ru(II) complex concentration at pH \sim 4.5 (with HCl). Ferrioxalate actinometry was used for light intensity measurements at 365 and 404 nm and Reinecke ion actinometry was used at 436 nm [33]. Solutions for photolyses and dark reactions were prepared and deaerated with purified argon and transferred to 1.0 cm path length quartz cells. During photolysis, the solution was stirred by a small magnetic bar in the cell. All photolysis were carried out at (25.0 \pm 0.1)°C. The reactions under photolysis were monitored periodically by recording their UV–Vis spectra. The absorbance changes were used to determine the cyanopyridine aquation quantum yields [1,2]. Analogous reactions mixtures allowed to react in the dark, under the same conditions of the photolyzed solutions, displayed either no observable or just negligible spectral changes, which were taken into account for quantum yields calculations. Secondary photolysis was minimized by limiting the extent of the reaction up to 10% and by extrapolating stepwise quantum yields to 0% reaction [34].

Ammonia quantum yields were calculated by pH changes which were measured with a PM600 Analion digital pHmeter calibrated with commercial standard buffers.

3. Results and discussion

Table 1 summarizes the photosubstitution quantum yields and some relevant electronic spectral data of $\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{L}$ complexes studied in this work.

3.1. Spectra

The $\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{L}$ complexes have MLCT and LF excited states as lowest energy excited states with similar energies. The lowest energy bands observed in their UV–Vis spectra is MLCT in nature. The expected LF absorption bands are assumed to be obscured by these much more intense MLCT bands, based on the following reasoning. The lowest energy LF bands of $\text{Co}(\text{NH}_3)_6^{3+}$ [35], $\text{Co}(\text{NH}_3)_5(\text{py-x})^{3+}$ (py-x = substituted pyridine) [36] and $\text{Co}(\text{NH}_3)_5(\text{NCpy})^{3+}$ (NCpy = 2-NCpy, 3-NCpy or 4-NCpy) [37], all are in the 469–475 nm range, indicating that all these ligands have essentially the same LF strength. Given that the lowest energy LF band of $\text{Ru}(\text{NH}_3)_6^{3+}$ is at 390 nm [38,39], the LF bands of $\text{Ru}(\text{NH}_3)_5(\text{NCpy})^{2+}$ should be very close to this wavelength. The much more intense MLCT bands which lie nearby 400 nm in the nitrile bonded $\text{Ru}(\text{NH}_3)_5(\text{NCpy})^{2+}$ will obscure the LF bands.

3.2. Photolysis

Irradiation of deaerated acidic (pH \sim 4.5) aqueous solutions of $[\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{L}]$ (L = 2-NCpy, 3-NCpy or 4-NCpy), in the MLCT bands energy range, with lights of 365, 404 or 436 nm, leads to a decrease of the MLCT bands (Fig. 1). At this pH, no MLCT bands due to the protonated complexes are observed, in accordance with their $\text{p}K_a$'s which are 0.8, 1.75 and 2.72, respectively [40].

Oxidation of the complex to its Ru(III) analog would also lead to bleaching of the MLCT absorption band, and, for

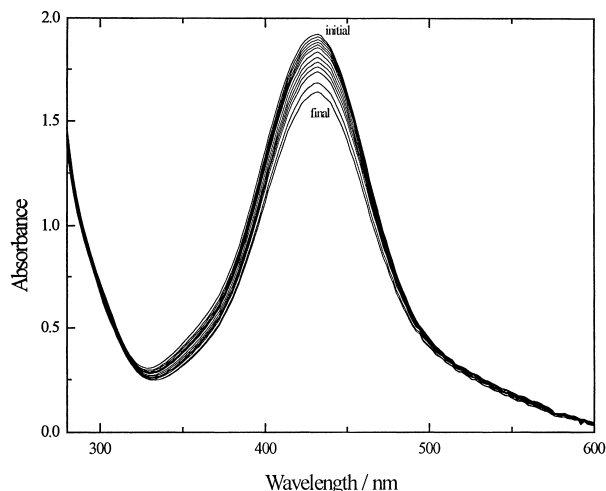


Fig. 1. Spectral changes upon irradiation at 404 nm of an aqueous solution of $[\text{Ru}(\text{NH}_3)_5(4\text{-NCpy})]^{2+}$ in 0.2 mol/l NaCl at pH 3.96, adjusted with HCl; temperature (25 ± 0.5)°C; 1.0 cm cell pathlength; $t = 60$ min.

these cyanopyridine complexes, it would may eventually lead to the appearance of LMCT bands in the 300–400 nm, which were not observed under the photolysis runs. These LMCT bands would appear as a result of the hydrolysis of the coordinated nitrile to amide in the Ru(III) complex formed after any eventual oxidation of the $\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{L}$ complex [41–43]. Photolysis of the $\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{L}$ complexes also leads to $[\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{H}_2\text{O}]^{2+}$. This complex, in the presence of the added Cl^- , would lead to $[\text{Ru}^{\text{II}}\text{Cl}(\text{NH}_3)_5]^+$, which can be oxidized to $[\text{Ru}^{\text{III}}\text{Cl}(\text{NH}_3)_5]^{2+}$ [44–46], giving rise to Cl–Ru(III) LMCT bands, which would lie nearby 350 nm [47,48]. Since no bands appear in this region during photolysis, oxidation can be ruled out, and the MLCT decrease can be ascribed to the photoaquation of the cyanopyridine ligand.

The pyridinyl bonded complexes $[\text{Ru}(\text{NH}_3)_5(\text{pyCN})]^{2+}$ and the binuclear complexes $[(\text{NH}_3)_5\text{Ru}(\text{pyCN})\text{-Ru}(\text{NH}_3)_5]^{4+}$ show MLCT bands at lower energies than those of the respective nitrile bonded complex [49]. Since upon irradiation there is no other spectral change, but the decrease of the MLCT band, then the linkage isomer

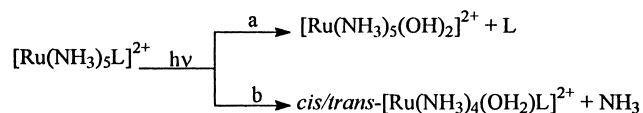
Table 1
MLCT spectral data and photosubstitution quantum yields^a of $[\text{Ru}(\text{NH}_3)_5(\text{NCpy})]^{2+}$ in aqueous solution

L	$\lambda_{\text{max}}/\text{nm}$ (log ϵ)	$\lambda_{\text{irr}}/\text{nm}$	$\Phi/10^{-3}$		
			NCpy	NH_3	Total
$[\text{Ru}(\text{NH}_3)_5(3\text{-NCpy})]^{2+}$	400 (3.98)	365	89 ± 2	67 ± 1	156 ± 3
		404	84 ± 1	67 ± 1	151 ± 2
		436	88 ± 1	78 ± 2	166 ± 3
$[\text{Ru}(\text{NH}_3)_5(2\text{-NCpy})]^{2+}$	406 (3.97)	365	71 ± 1	56 ± 2	127 ± 3
		404	72 ± 2	40 ± 1	112 ± 3
		436	65 ± 2	58 ± 1	123 ± 3
$[\text{Ru}(\text{NH}_3)_5(4\text{-NCpy})]^{2+}$	424 (4.04)	365	16 ± 1	37 ± 1	51 ± 2
		404	18 ± 1	35 ± 2	53 ± 3
		436	16 ± 1	28 ± 1	44 ± 2

^a Average of at least three independent determinations.

pyridinyl bonded and the bridged complexes are not being formed.

Thus, the only occurring reactions should be photosubstitution reactions, according to the following equation.



pH monitoring of the photolysis runs revealed pH increases upon irradiation, which should come from ammonia photoaquation, based on the following reasoning. The ligands pK_a 's are 1.86, 1.36 and -0.26 for 4-NCpy, 3-NCpy and 2-NCpy, respectively [50]. Considering that all runs were performed in solutions of pH ~ 4.0 , the released cyanopyridine ligands are not protonated at this pH, and, then, could not be responsible for the pH increase. The photoproducts $[\text{Ru}(\text{NH}_3)_5(\text{OH}_2)]^{2+}$ and $[\text{Ru}(\text{NH}_3)_4(\text{OH}_2)(\text{NCpy})]^{2+}$ do not interfere with pH measurements. The $[\text{Ru}(\text{NH}_3)_5(\text{OH}_2)]^{2+}$ has a pK_a of ~ 13.1 [51]. Changing one *trans* ammonia for the strong π acceptor ligand isonicotinamide, in $[\text{Ru}(\text{NH}_3)_4(\text{OH}_2)(\text{isn})]^{2+}$, results in a pK_a of the coordinated water of ~ 11.7 , in $[\text{Ru}(\text{NH}_3)_4(\text{OH}_2)(\text{isn})]^{2+}$ [51]. Changing isn for cyanopyridine, with back-bonding strength similar to isn, in $[\text{Ru}(\text{NH}_3)_4(\text{OH}_2)(\text{NCpy})]^{2+}$, is not expected to result in pK_a changes large enough to interfere with measurements at pH ~ 4 . Protonation of the coordinated cyanopyridine in $[\text{Ru}(\text{NH}_3)_4(\text{OH}_2)(\text{NCpy})]^{2+}$ is ruled out. No absorptions due to strongly absorbing MLCT bands of protonated complexes appear in the spectra under photolysis. Thus, in addition, since, photooxidation, which might involve pH changes, is not occurring, then only ammonia photoaquation can be responsible for the pH increase. Hence, a straightforward way to calculate ammonia aquation quantum yields was using the pH changes.

Cyanopyridine aquation quantum yields were calculated from spectral measurements, as done in other related systems [1,2,9,10]. Since cyanopyridine photoaquation is essentially the pathway responsible for the decreases in the MLCT absorptions of the $[\text{Ru}(\text{NH}_3)_5(\text{NCpy})]^{2+}$ complexes ($\epsilon \sim 10^4 \text{ mol}^{-1} \text{ l cm}^{-1}$) [21], the photoproduct of the cyanopyridine photoaquation is $[\text{Ru}(\text{NH}_3)_5(\text{OH}_2)]^{2+}$, which has negligible absorbance ($\lambda_{\text{max}} = 415 \text{ nm}$; $\epsilon = 40 \text{ mol}^{-1} \text{ l cm}^{-1}$) [39] in the λ_{irr} studied. The also occurring ammonia photoaquation results in the tetraammine ion complexes $[\text{Ru}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{NCpy})]^{2+}$, the spectra of which are not known, and which, very likely, have MLCT maxima and molar absorptivities very similar to those of the parent complexes, but not identical. Thus, ammonia photoaquation, can, presumably, result in a slight decrease in the absorption at the $[\text{Ru}(\text{NH}_3)_5(\text{NCpy})]^{2+}$ complexes MLCT maxima. As a result, the quantum yields of NCpy photoaquation calculated from MLCT absorbance decreases are, in fact, upper limits, but reasonably close to the real values, and good enough to establish photoreaction patterns.

At least conceivably, linkage isomerization reactions to form the pyridinyl bonded complexes were expected to occur, eventually through η^2 -bonded intermediates, as in the pyridine, pyridinecarboxamide, and acrilamide systems [1,2,18,19,23]. In those cases, evidence for such a type of intermediates and isomerization was drew: (a) from the final products, taking into account kinetic arguments in the case of amide complexes [19,23], and (b) from the pH independent quantum yields and the existence of a long-lived intermediate in the case of the py complex [1,2,18].

The existence of similar intermediates, as a result of one of the possible decay routes of the excited state(s) of the $[\text{Ru}(\text{NH}_3)_5(\text{NCpy})]^{2+}$ complexes, was not examined in this work. Earlier flash photolysis experiments, with a $>10 \mu\text{s}$ dead time, irradiating $[\text{Ru}(\text{NH}_3)_5(4\text{-NCpy})]^{2+}$ in the visible range, and monitoring at 425 and 510 nm, did not show any absorptions at these wavelengths, which could be due to η^2 -bonded intermediates [27]. In the present case, results come from steady state photolysis, and even faster techniques would be needed to follow the fate of the excited states and detect eventual resulting intermediates. The absence of linkage isomerization does not necessarily rule out such intermediates. These intermediates could have lifetimes shorter than $10 \mu\text{s}$ and/or could absorb at wavelengths different from 425 and 510 nm. Furthermore, if such intermediates were formed, they had not proceeded to isomerization, reacting back to initial products and/or decaying through other routes.

The photoreactions observed in the $[\text{Ru}(\text{NH}_3)_5(\text{NCpy})]^{2+}$ system should come from the lowest energy triplet ligand field excited states ^3LF and follow the 'tuning model', as occurs for other Ru(II)-ammine complexes [1–11,32,52,53].

The decrease in the total lower quantum yields from 2-NCpy and 3-NCpy to 4-NCpy complexes follows the order of decreasing MLCT energy. Considering that the three ligands have the same ligand-field strength, and not taking into account the splitting of the d_π orbitals from symmetry lowering or back-bonding, decay to the ground state would be favored in the last case, which would imply in a decrease in the photochemical quantum yields, as occurs for $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$ (L = pyridine; pyrazine; or 4-phenylpyridine) [1,2,11].

Examination of the products quantum yields shows that for the 4-py ligands [1,2], ammonia photosubstitution is predominant in most cases, but not in $[\text{Ru}(\text{NH}_3)_5(3,5\text{-Cl}_2\text{py})]^{2+}$. For the 4-NCpy complex, ammonia photosubstitution is predominant, whereas for the 2-NCpy and 3-NCpy complexes, NCpy photoaquation is the major photochemical pathway. The reason for this behavior is not clear and may involve slight differences in the electronic structures of the complexes, among others.

Some considerations concerning the splitting of the d orbitals can be made. For the Ru(II) complexes *trans*- $[\text{Ru}(\text{NH}_3)_4(\text{P}(\text{OR})_3)\text{L}]^{2+}$ (L = P(OR)₃ or CO), the T_{1g} states of octahedral parentage are split into A_2 and E under C_{4v}

symmetry [12,54]. The $^1A_1 \rightarrow ^1E$ transition involves depopulation of xz , yz orbitals and population of the z^2 orbital, and the $^1A_1 \rightarrow ^1A_2$ transition involves depopulation of the xy and population of the $x^2 - y^2$ orbitals. Thus, in electronic terms alone, the E state would lead to labilization of ligands in the z axis, and A_2 would lead to labilization of ligands in the x and y axis, i.e., ammonia. The resulting quantum yields and ratios would, then, reflect the different energy splittings for each complex combined with different deactivation pathways competitive with those leading to photoaquation. This splitting is high enough, in the *trans*- $[Ru(NH_3)_4(P(OR)_3)L]^{2+}$ ($L = P(OR)_3$ or CO) complexes, which have strong LF ligands with high back-bonding ability, in the z axis, in order to display quantum yields dependences on the wavelength of irradiation, as illustrated by the exclusive ammonia aquation under irradiation with light corresponding to the A_2 state of lower energy in these complexes [12,54]. Considering that the LF absorption bands are obscured by the much more intense MLCT bands, a direct evaluation of possible energy splittings and energies is not attainable for the $[Ru(NH_3)_5(NCpy)]^{2+}$ complexes. However, some information can be get from the photochemical data. The results for these cyanopyridine complexes do not show a quantum yield dependence on the irradiation wavelength energy range examined. This may mean that the back-bonding effect is less important for the nitriles than for the former ligands, as also spectral and redox potentials data for these complexes show [12,21,22,54]. The results indicate that very likely, initial excitation into the 1MLCT energy range, is followed by competitive internal conversion and intersystem crossing to one 3LF state or one 3LF manifold of excited states of the same configuration, and of lowest energies, from which deactivation includes photoaquation. The results suggest that these states for the 2-NCpy and 3-NCpy complexes have more contribution from the z^2 orbital, while that of 4-NCpy have more contribution from the $x^2 - y^2$ orbital.

Acknowledgements

This work was supported in part by grants from the PADCT program, CNPq, CAPES, and FAPESP. M.S. and E.C.O. acknowledge fellowships from CAPES. E.T. acknowledges a fellowship from CNPq. The authors thank Profs. P.C. Ford and A.B.P. Lever for helpful discussions.

References

- [1] G. Malouf, P.C. Ford, J. Am. Chem. Soc. 99 (1977) 7213.
- [2] G. Malouf, Ph.D. Thesis, University of California, Santa Barbara, 1977.
- [3] P.C. Ford, J.D. Petersen, R.E. Hintze, Coord. Chem. Rev. 14 (1974) 67.
- [4] P.C. Ford, R.E. Hintze, J.D. Petersen, in: A.W. Adamson, P.D. Fleischauer (Eds.), Concepts of Inorganic Photochemistry, Chap. 5, Wiley, New York, 1975.
- [5] P.C. Ford, G. Malouf, J.D. Petersen, V. Durante, ACS Adv. Chem. 150 (1976) 187.
- [6] P.C. Ford, ACS Adv. Chem. 168 (1978) 73.
- [7] P.C. Ford, Rev. Chem. Intern. 2 (1979) 267.
- [8] P.C. Ford, D. Wink, J. Dibenedetto, Prog. Inorg. Chem. 30 (1983) 213.
- [9] R.M. Carlos, M.G. Neumann, E. Tfouni, Inorg. Chem. 35 (1996) 2229.
- [10] R.M. Carlos, E. Tfouni, M.G. Neumann, J. Photochem. Photobiol. A 103 (1997) 121.
- [11] J.R. Winkler, T.L. Netzel, C. Creutz, N. Sutin, J. Am. Chem. Soc. 109 (1987) 2381.
- [12] S.E. Mazzetto, L.M.A. Plicas, E. Tfouni, D.W. Franco, Inorg. Chem. 31 (1992) 516.
- [13] L.M.A. Plicas, D.Sc. Thesis, Instituto de Química de São Carlos, Universidade de São Paulo, São Carlos, SP, Brazil, 1995.
- [14] P.C. Ford, D.H. Stuermer, D.P. McDonald, J. Am. Chem. Soc. 91 (1969) 6209.
- [15] R.E. Hintze, P.C. Ford, J. Am. Chem. Soc. 97 (1975) 2664.
- [16] D.A. Chaisson, Master's Dissertation, University of California, Santa Barbara, 1971.
- [17] P.C. Ford, D.A. Chaisson, D.H. Stuermer, J.D. Petersen, D.P. McDonald, P.C. Ford, J. Am. Chem. Soc. 94 (1972) 6665.
- [18] V.A. Durante, P.C. Ford, Inorg. Chem. 18 (1979) 588.
- [19] M.H. Chou, B.S. Brunschwig, C. Creutz, N. Sutin, A. Yeh, R.C. Chang, C.T. Lin, Inorg. Chem. 31 (1992) 5347.
- [20] D. Chatterjee, H.C. Bajaj, J. Chem. Soc., Dalton Trans. (1995) 3415.
- [21] R.E. Clarke, P.C. Ford, Inorg. Chem. 9 (1970) 495.
- [22] P.C. Ford, R.E. Clarke, Inorg. Chem. 9 (1970) 227.
- [23] N.E. Katz, E. Fagalde, Inorg. Chem. 32 (1993) 5391.
- [24] P.C. Ford, R.D. Foust Jr., R.E. Clarke, Inorg. Chem. 9 (1970) 1933.
- [25] R.D. Foust Jr., P.C. Ford, J. Am. Chem. Soc. 94 (1972) 5686.
- [26] W. Caetano, J.J.F. Alves, B.S. Lima Neto, D.W. Franco, Polyhedron 14 (1995) 1295.
- [27] V.A. Durante, Ph.D. Thesis, University of California, Santa Barbara, CA, 1977.
- [28] A.I. Vogel, in: Química Orgânica: Análise Orgânica Qualitativa, vol. 1, 3rd ed., Livro Técnico SA, Rio de Janeiro, Brazil, 1971.
- [29] R.S. Silva, E. Tfouni, Inorg. Chem. 31 (1992) 3313.
- [30] Z.N. Rocha, D.Sc. Thesis, UNESP, Araraquara, SP, Brazil, 1995.
- [31] H.Y. Hung, W.J. Chen, C.C. Yang, A. Yeh, Inorg. Chem. 30 (1991) 1862.
- [32] E. Tfouni, P.C. Ford, Inorg. Chem. 19 (1980) 72.
- [33] J.F. Rabek, in: Experimental Methods in Photochemistry and Photophysics, Wiley, New York, 1986.
- [34] J.D. Petersen, R.J. Watts, P.C. Ford, J. Am. Chem. Soc. 98 (1976) 3188.
- [35] A.W. Adamson, A.H. Sporer, J. Am. Chem. Soc. 80 (1958) 3865.
- [36] F. Nordmeyer, H. Taube, J. Am. Chem. Soc. 90 (1968) 1162.
- [37] R.J. Balahura, Can. J. Chem. 52 (1974) 1762.
- [38] H.H. Schmidtke, D. Garthoff, Helv. Chim. Acta 49 (1966) 2039.
- [39] T. Matsubara, S. Efrima, H.I. Metiu, P.C. Ford, J. Chem. Soc., Faraday Trans. II 75 (1979) 390.
- [40] R.E. Clarke, P.C. Ford, Inorg. Chem. 9 (1970) 495.
- [41] Z.N. Rocha, G. Chiericato, Jr., E. Tfouni, ACS Adv. Chem. Ser. 253 (1997) 297, and references therein.
- [42] A.W. Zanella, P.C. Ford, Inorg. Chem. 14 (1975) 42.
- [43] M.H. Chou, D.J. Szalda, C. Creutz, N. Sutin, Inorg. Chem. 33 (1994) 1674.
- [44] R.E. Hintze, P.C. Ford, J. Am. Chem. Soc. 97 (1975) 2664.
- [45] T. Matsubara, P.C. Ford, Inorg. Chem. 17 (1978) 1747.
- [46] C.M. Elson, I.J. Itzokovitch, J. McKenney, J.A. Page, Can. J. Chem. 53 (1975) 2922.

- [47] A.B.P. Lever, in: *Inorganic Electronic Spectroscopy*, 2nd ed., Elsevier, Amsterdam, 1984, and references therein.
- [48] S.E. Boggs, R.E. Clarke, P.C. Ford, *Inorg. Chim. Acta* 247 (1996) 129.
- [49] D.E. Richardson, H. Taube, *J. Am. Chem. Soc.* 105 (1983) 40.
- [50] S.F. Mason, *J. Chem. Soc.* (1959) 1247.
- [51] C.G. Kuhen, H. Taube, *J. Am. Chem. Soc.* 98 (1976) 689.
- [52] L.A. Pavanin, Z.N. Rocha, E. Giesbrecht, E. Tfouni, *Inorg. Chem.* 30 (1991) 2185.
- [53] M. Silva, E. Tfouni, *Inorg. Chem.* 36 (1997) 274.
- [54] S.E. Mazzetto, E. Tfouni, D.W. Franco, *Inorg. Chem.* 35 (1996) 3509.