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Inorganica Chimica Acta 355 (2003) 191–196

Inorganica Chimica Acta

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Control of NO release by light irradiation from nitrosyl–ruthenium complexes containing polypyridyl ligands

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Received 26 February 2003; accepted 25 April 2003

Abstract

The series of nitrosyl complexes *cis*-$[RuL(bpy)_2NO]^{3+}$ (bpy = bipyridine; L = pyridine, 4-picoline, 4-acetylpyridine) were prepared and studied by laser plash-photolysis. All the studied complexes showed nitric oxide (NO) release under light irradiation at 355 nm account by NO measured made by a NO sensor. The quantum yields for NO release was determined with a laser flash-photolysis apparatus (Continuum Q-switched Nd-YAG laser). The major product of the irradiation of *cis*-$[RuL(bpy)_2(NO)]^{3+}$ is an intermediate which was suggested to be *cis*-$[Ru^{III}L(bpy)_2(NO^{\bullet})]^{3+}$ that in aqueous solution release NO to produce *cis*-$[RuL(bpy)_2(OH)]^{2+}$.

Keywords: Nitric oxide; Nitrosyl–ruthenium complexes; Metalonitrosyl

1. Introduction

Nitric oxide (NO) has emerged as an important molecule involved in initiating or regulating numerous biological processes. The endogenous mediator character of NO has been implicated in the range from regulation of cardiovascular function to participation in memory [1–4]. Since the initial discovery that the endothelium-derived relaxing factor is NO [5], the main goal of many scientific researches has been focused on elucidating the mechanisms that regulate NO synthesis and understanding the physiological and pathophysiological consequences of biological NO production. These multiple effects of NO in biological systems have resulted in intense investigation into the mechanisms of NO-mediated events. Because of its short half-life in biological systems and the inherent challenges of studying its role in the body, there is a great number of agents that release NO in a controlled manner in living systems [6] and could also be potentially developed as therapeutic agents [7–9].

Most of the known NO donor systems involve the formation of NO by either simple dissociation or by a complex series of reaction, often requiring metabolism in the cell [10]. Therefore it's important to produce compounds that can be trigged to release NO when subjected to any external or internal stimulation [11]. One of the possibilities is to use light irradiation in the appropriated wavelength on metalonitrosyl complexes, which are compounds potentially capable of release NO [12]. In this way, a special class of metal complexes, which has received considerable attention, is iron–sulfur–nitrosyl cluster anions that could release NO thermally or photochemically [13]. The photochemical experiment conducted with classical compounds as $[Fe_4S_3(NO)_7]^-$ showed relatively small quantum yield for the NO production. Another group of light sensitive compounds is the chloro nitrosyl–ruthenium complexes [14]. The $[RuCl_3NO]$ and $K_2[RuCl_5NO]$ are thermally stable but photolabile, releasing NO under UV light exposure. The quantum yield for those ruthenium

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doi:10.1016/S0020-1693(03)00271-8

complexes on the irradiation in the range 300–350 nm varies from 0.06 to 0.012 mol einstein^{-1}. In the course of probing photochemical NO releaser, a series of nitrosyl porphyrin complexes has been synthesized and the photochemical pathway described [15–18]. Among them Hoshino and co-workers reported that NO complexes of Co(II) and Mn(II) meso-tetraphenylporphyrins undergo efficient photodenitrosylation [15,16]. Similar observation has been made by Ford and co-workers involving $[Ru^{II}(P)(NO)(NO_2)]^{2+}$ [17,18] where P is octaethylporphyrin or tetra(*m*-tolyl)porphyrin ligand. For those nitrosyl nitrito–ruthenium complexes they found at least two main pathways involving NO and NO_2^- photolabilisation.

Despite numerous investigations of nitrosyl ruthenium photochemistry, many questions concerning the electronic effect under photoreactivity are still not completely understood. The *trans*-$[RuL(NH_3)_4NO]^{3+}$, for example, showed low NO photolabilisation [19], although our studies conducted with *cis*-$[RuCl(bpy)_2NO]^{2+}$ showed higher quantum yield, around 0.98 mol einstein^{-1} [8]. We believe that the electronic effect under the nitrosyl group should affect the NO reactivity. To answer these and many other questions we have synthesized a series of *cis*-$[RuL(bpy)_2NO]^{3+}$ complex where L could be pyridine (py), 4-picoline (4-pic) and 4-acetylpyridine (4-acpy) and systematically studied the photoreactivity using laser flash-photolysis coupled to a NO sensor. The π-acceptor character of the L ligand was taken as main factor in the nitrosyl compounds, responsible for the observed photoreactivity of *cis*-$[RuL(bpy)_2NO]^{3+}$. The mechanism pathway we have been proposed was mainly based on the experimental observations on the spectroscopy properties and the chronoamperometry studies using NO sensor.

2. Experimental

2.1. Apparatus

The ultraviolet–visible (UV–Vis) spectra were recorded on a Hitachi U-3501 and Genesys-2 apparatus from Spectronic. Infrared (IR) spectra were recorded on a protegé 460 series FT-IR spectrometer. The pH measurements were made using a 430 pH meter from Corning. The photolysis was carried out using a laser flash-photolysis apparatus consisting of a Continuum Q-switched Nd-YAG laser (Continuum, Santa Clara, CA) with excitation provided by the third harmonic at $\lambda = 355$ nm. The pulse length was 8 ns, the beam diameter incident on the sample was 6 mm, and the repetition rate was 10 Hz. The pulse energy was typically 10 mJ pulse^{-1} as measured with a Field Master power-meter with an L-30V head.

2.2. Chemicals and reagents

$RuCl_3 \cdot 3H_2O$, 2,2′-bipyridine (bpy), py, 4-pic, 4-acpy were purchased as high purity reagents from Aldrich Chemicals and potassium ferrioxalate was purchased from Fisher Scientific Co. and used as supplied. Doubly distilled H_2O was used for all experiments. The recrystallized complex salt *cis*-$[RuL(bpy)_2(NO)](PF_6)_3$ ($L = $ 4-pic, py and 4-acpy) was prepared as previously published [20]. The complex salt *cis*-$[RuL(bpy)_2(H_2O)](PF_6)_2$ (L = 4-pic, py and 4-acpy) was prepared as previously described for *cis*-$[Ru(bpy)_2(py)(H_2O)](PF_6)_2$ [21]. The *cis*-$[RuL(bpy)_2(NO)](PF_6)_3$ complex was characterized by IR for L = 4-pic (ν_{NO} 1944 cm^{-1}), L = py (ν_{NO} 1947 cm^{-1}), L = 4-acpy (ν_{NO} 1943 cm^{-1}) and by UV–Vis for L = 4-pic (332 nm, $\log \varepsilon = 3.67$; 300 nm $\log \varepsilon = 4.09$), py (334 nm, $\log \varepsilon = 3.70$; 300 nm, $\log \varepsilon = 4.17$), 4-acpy (336 nm, $\log \varepsilon = 3.77$; 300 nm $\log \varepsilon = 4.29$) in 0.1 M HCl. In the photochemical experiment the buffer solution was kept constant with NaTFA/HTFA (TFA = trifluoroacetate) at pH 2.0 and ionic strength of 0.1 M adjusted with KCl.

2.3. NO measurements with the ISO-NO NO-meter and the DUO-18 acquisition board

NO release was measured with an ISO-NOP NO meter from World Precision Instruments. The sensitivity of this apparatus ranges from 1 nM to 20 μM, with a 2 mm sensor, which directly detects NO concentration by an amperometric technique.

The calibration curve was constructed by dilutions of NO stock solution. NO gas was purchased from Oxigênio do Brasil and passed through a 10 M KOH solution to remove any trace of NO_2^- specie. NO stock solution was prepared by degassing aqueous TFA buffer solution (pH 2.0) following by the introduction of NO as previously described [22]. The NO concentrations were calculated according to reported molar fraction solubility of NO (1.9 mM at 25 °C) [23], that was confirmed by titration with $KMnO_4$ as previously described [24].

The 1-cm pathlength quartz cell containing the sample solution was routinely thermostated at 25.0 ± 0.1 °C. The sample solution was stirred continuously during the flash-photolysis experiment and the NO measurements were made with the electrode positioned outside the light path to avoid any photoelectric interference. The output of the sensor was recorded with an IBM-PC computer linked to a DUO-18 acquisition board from WPI.

2.4. Quantum yield measurements

Light intensities were determined by the classical potassium ferrioxalate actinometry procedure before each photolysis experiments. The NO quantum yields production were calculated based on NO concentrations obtained by NO meter measurement. For most runs the initial concentration of *cis*-[RuL(bpy)$_2$(NO)](PF$_6$)$_3$ was approximately 1.4×10^{-4} M. After equilibration to the cell holder temperature, photolysis was begun by irradiating the sample for a period of time ranging from 0 to 30 s with increments of 5 s. The calculated ϕ_t values obtained in the range studies, were plotted versus t. These plots were linear, with a negative slope, for the first 40% of the reaction. The extrapolated spectroscopic quantum yield at $t = 0$ was taken as Φ_{NO} for the photoaquation of NO from *cis*-[RuL(bpy)$_2$(NO)]$^{3+}$ compounds. Evaluation of Φ_{NO} at $t = 0$ eliminates possible complications resulting from secondary photolysis of primary reaction product [25–27].

3. Results

In a previous work we reported a flash-photolysis study on *cis*-[RuCl(bpy)$_2$(NO)]$^{2+}$ in aqueous solution at room temperature [8]. We concluded therefrom that NO was dissociated from its ligand site with formation of *cis*-[RuCl(bpy)$_2$(OH)]$^{+}$. Here we describe complementary study on the related species *cis*-[RuL(bpy)$_2$NO]$^{3+}$ where L is py, 4-pic and 4-acpy. The photolysis of *cis*-[RuL(bpy)$_2$NO]$^{3+}$ type complex was carried out in trifluoroacetic buffer solution pH 2.0 to avoid *cis*-[RuL(bpy)$_2$NO$_2$]$^{+}$ formation as a product of nucleophilic attack for OH^{-}, as previously described [20]. In the photochemical experiment, the resulting electronic spectrum appearing immediately after laser irradiation at 355 nm as showed in the Fig. 1 for *cis*-[Ru(4-pic)(bpy)$_2$NO]$^{3+}$ is as an example of *cis*-[RuL(bpy)$_2$NO]$^{3+}$ complex. Clearly we have seen that the photoreactivity of the nitrosyl complex was accompanied by a change in the UV–Vis spectrum, with a decrease in absorption at the 330 nm region, and an increase in absorption at the 288 and 430 nm regions for all studied complexes.

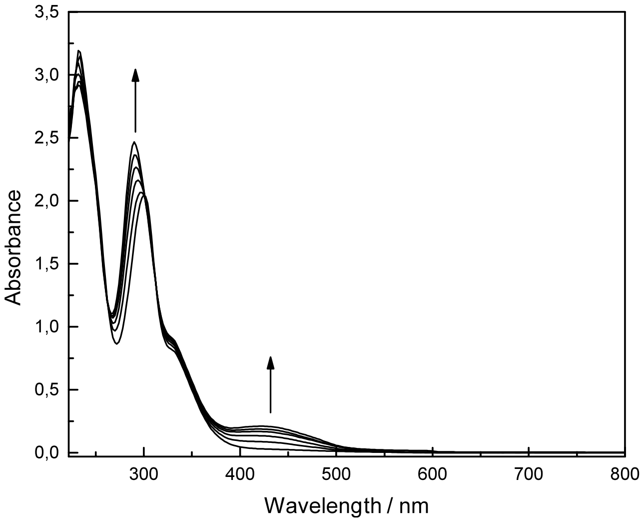


Fig. 1. Electronic spectra of 1.64×10^{-4} M *cis*-[Ru(4-pic)(bpy)$_2$(NO)]$^{3+}$ at pH 2.0 TFA buffer solution during flash-photolysis with 355 nm light irradiation.

The NO release from *cis*-[RuL(bpy)$_2$NO]$^{3+}$ during the photolysis at 355 nm was supported in situ by NO detection based on the chronoamperogram of NO release showed in the Fig. 2. Quantitative NO concentrations could be estimated from these signals by comparison to the NO calibration curve. The quantum yield Φ_{NO} for *cis*-[Ru(4-pic)(bpy)$_2$NO]$^{3+}$ at 355 nm photolysis are reported in Fig. 3. The calculated quantum yield for NO release measured after the irradiation of the series of *cis*-[RuL(bpy)$_2$NO]$^{3+}$ compounds was 0.17±0.02, 0.16±0.02, 0.07±0.01 for mol einstein^{-1} 4-pic, py and 4-acpy, respectively.

The primary product for the photolysis of *cis*-[RuL(bpy)$_2$NO]$^{3+}$ involves the formation of an intermediate which the electronic spectrum has showed dependence on time function. In order to pursue the details of this reaction, an aqueous solution of *cis*-[RuL(bpy)$_2$NO]$^{3+}$ complex where L is py, 4-pic and 4-acpy was irradiated continuously in cycles of 20 s at 355 nm light leading to the final photoproduct. The resulting electronic spectrum shows a band in a visible region that decreased in time function (Fig. 4).

4. Discussion

One of the currently investigated problems related to the electronic structure of nitrosyl–ruthenium complexes is the degree of α and π bonding contributions of co-ligands to NO release in the metal ion coordina-

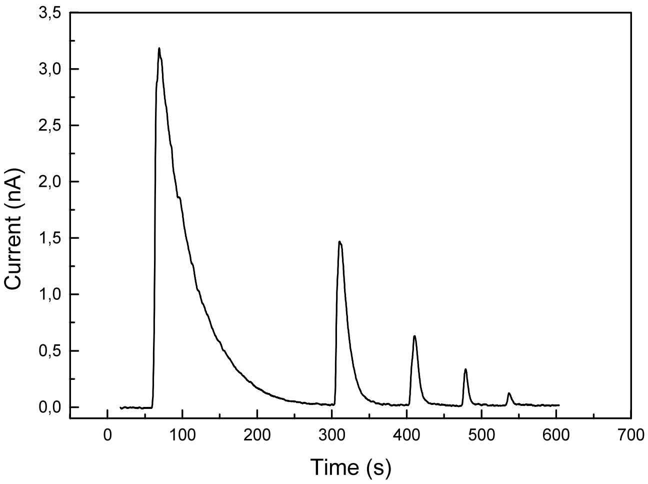


Fig. 2. Chronoamperogram of NO released by photolysis of 1.64×10^{-4} M *cis*-[Ru(4-pic)(bpy)$_2$(NO)]$^{3+}$ at pH 2.0 TFA buffer solution using 355 nm light irradiation.

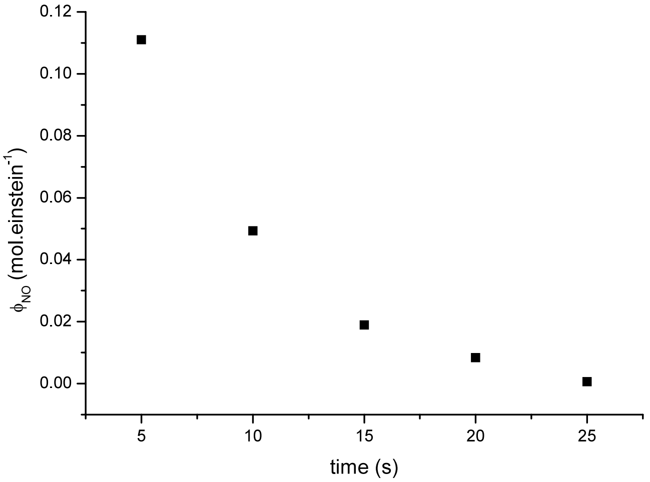


Fig. 3. Plot of ϕ(NO) versus time for *cis*-$[Ru(4\text{-}pic)(bpy)_2(NO)]^{3+}$ during flash-photolysis with 355 nm light irradiation.

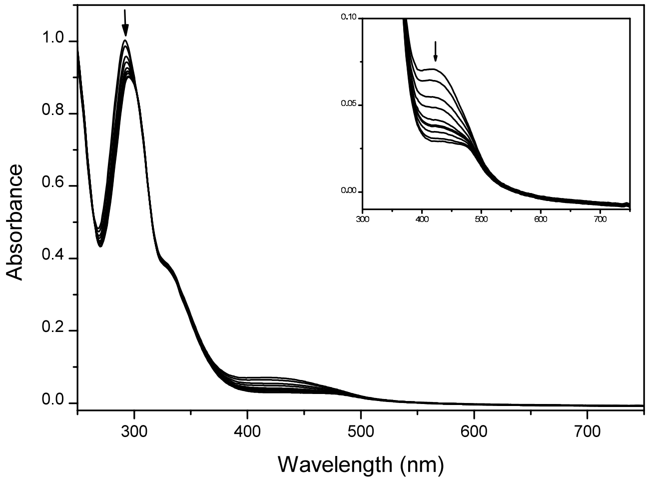


Fig. 4. Decay of absorbance in 420 nm region formed after laser flash-photolysis of *cis*-$[Ru(bpy)_2(4\text{-}acpy)NO]^{3+}$ at pH 2.0 in TFA buffer solution.

tion sphere [28–30]. An interesting approach to study this question is based on the synthesis and evaluation of a series of compounds where the electron density under nitrosyl ligand was changed by different co-ligand L in $[RuL_5NO]^{n+}$ type complex. In order to understand the electronic effect under nitrosyl ligand, we have synthesized and performed the photochemistry studies of *cis*-$[RuL(bpy)_2NO]^{3+}$, where L is py, 4-pic and 4-acpy.

The quantum yield of NO release (Φ_{NO}) for *cis*-$[RuL(bpy)_2NO]^{3+}$ decreases as the π-acceptor character of L increases, which is consistent with the decrease of electron density under nitrosyl ligand. Assuming that the metal ligand charge transfer between Ru(II) and NO^+ occurs at 330 nm for *cis*-$[Ru^{II}L(bpy)_2NO^+]^{3+}$ complex, the irradiation in this region could easily generate *cis*-$[Ru^{III}L(bpy)_2NO^{\bullet}]^{3+}$ at excited state. Since the transient is formally $Ru^{III}–NO^{\bullet}$, the substitution reaction is expected to occur considering many of the reports that present the NO° specie as a labile ligand for ruthenium(III) complex [8,19,31–34]. In that case, we expected that the quantum yield for the NO production should be higher as stronger is the back-bonding $d_\pi\{Ru(II)\text{-}\pi^*(NO^+)\}$. Our results indicated a higher quantum yield for *cis*-$[Ru(4\text{-}pic)(bpy)_2NO]^{3+}$ in *cis*-$[RuL(bpy)_2NO]^{3+}$ series for the NO photorealease, what is consistent with the nature of the π-acceptor character of 'L', which increases as 4-pic < py < 4-acpy [20]. These results clearly demonstrate that the electron density under nitrosyl ligand in *cis*-$[RuL(bpy)_2NO]^{3+}$ complex increases in the same order that the π-acceptor character of 'L' decreases. Similar conclusion could be observed considering electrochemical data previously described by this class of compounds [20].

In the photodissociation pathway, formation of NO radical was preceded by an increase and subsequent decay of absorption at 290 and 430 nm, whose successive decayings were recorded (Fig. 4). This may be assigned to the ligand photoisomerization of *cis*-$[Ru^{II}L(bpy)_2NO^+]^{3+}$ producing *cis*-$[Ru^{II}L(bpy)_2ON^+]^{3+}$ specie and the absorbance fading could be interpreted as NO^+ release with posterior consumption via various pathways [35]. Although the NO linkage isomer have not been noticed in aqueous solutions, some isonitrosyl complexes have been generated as low temperature photoproducts in the solid state derived from the corresponding NO complexes [36–38]. The resulting electronic spectrum of the photoproduct of *cis*-$[Ru^{II}L(bpy)_2NO^+]^{3+}$ after approximately 40 min shows some similarities with the electronic spectrum of the *cis*-$[Ru^{II}L(bpy)_2H_2O]^{2+}$ complex (Fig. 5). Although unequivocal assignment of the substitution was not

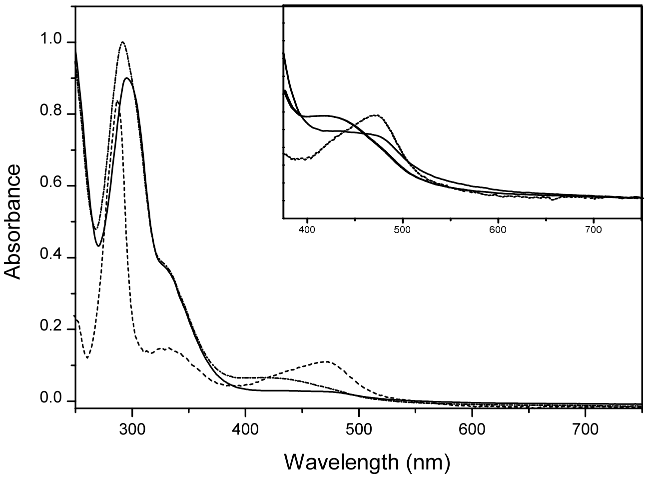


Fig. 5. Electronic spectra in UV–Vis region of *cis*-$[Ru^{II}(4\text{-}pic)(bpy)_2(H_2O)]^{2+}$ (dashed line), *cis*-$[Ru(4\text{-}pic)(bpy)_2(NO)]^{3+}$ after flash-photolysis at 355 nm (dot-dashed line) and *cis*-$[Ru(4\text{-}pic)(bpy)_2(NO)]^{3+}$ after approximately 40 min of flash-photolysis at 355 nm (line).

possible, the electronic spectrum of the photoproduct suggesting the decay occurs by a chemical reaction.

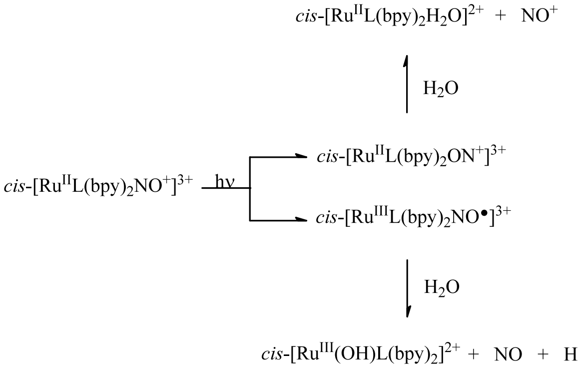
The overall light-induced process can be represented by Scheme 1.

The assumption of *cis*-$[Ru^{III}(OH)L(bpy)_2]^{2+}$ formation from the photolytic product of *cis*-$[RuL(bpy)_2(NO)]^{3+}$ is based mainly on the electrochemical behavior of *cis*-$[Ru^{II}L(bpy)_2(H_2O)]^{2+}$. The results of differential pulse voltammetry on aqueous solution containing *cis*-$[Ru^{II}L(bpy)_2(H_2O)]^{2+}$ for the expected Ru(III)/(II) couple are pH-dependent. The dependence of the potentials as a function of pH are shown in the Ep_a–pH diagram in Fig. 6 for *cis*-$[Ru^{II}(py)(bpy)_2(H_2O)]^{2+}$ as an example of *cis*-$[RuL(bpy)_2(NO)]^{3+}$ compounds, where L was 4-pic, py and 4-acpy.

In the diagram (Fig. 6) the linear relation shows how the potential of Ru(III)/(II) varies with pH. The line is drawn according to the Nernst equation with slope of 0 or 59 mV/pH unit corresponding to proton to electron ratios 0 and 1.0. This pH dependence allows one to obtain the pK_a values for the *cis*-$[Ru^{II}L(bpy)_2(H_2O)]^{2+}$ specie. The observed pK_a for the *cis*-$[RuL(bpy)_2H_2O]^{2+}$ complex where L is py, 4-pic and 4-acpy is 10.6, 11.2, 11.5 and for *cis*-$[RuL(bpy)_2H_2O]^{3+}$ it is 1.6, 1.2 and 1.4, respectively. Controlled potential oxidation of *cis*-$[Ru^{II}L(bpy)_2(H_2O)]^{2+}$ in a trifluoroacetic buffer solution pH 2.0 yields a specie with no absorption in visible region which is consistent with its formulation as *cis*-$[Ru^{III}L(bpy)_2(OH)]^{2+}$.

5. Conclusion

We have shown that the photolysis of *cis*-$[RuL(bpy)_2(NO)]^{3+}$ complex where L is py, 4-pic and 4-acpy produces NO when it is irradiated with laser at 355 nm. The major product of the irradiation of *cis*-$[RuL(bpy)_2(NO)]^{3+}$ is an intermediate which was suggested to be *cis*-$[Ru^{III}L(bpy)_2(NO^\bullet)]^{3+}$ that in aqueous solution releases NO to produce *cis*-$[RuL(bpy)_2(OH)]^{2+}$. The photochemical pathway was suggested based on the monitoring NO with NO sensor during light irradiation. The quantum yield observed for the NO formation involved in the photolysis of *cis*-$[RuL(bpy)_2(NO)]^{3+}$ decreases with the π acceptor character of L increase. It is consistent with the increase of electron density under NO^+.



Scheme 1.

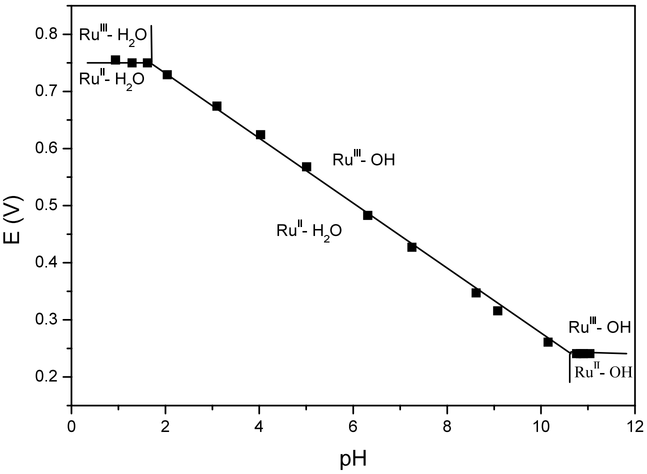


Fig. 6. pH potential regions of stability for different oxidation states of *cis*-$[Ru(H_2O)(bpy)_2(py)]^{+}$ complex. The vertical lines in the various E versus pH regions show the pK_a values.

Acknowledgements

The authors thank the Brazilian agencies CAPES and FAPESP for their financial support.

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