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Photochemical NO release from nitrosyl Ru^{II} complexes with C-bound imidazoles

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ABSTRACT

The series of nitrosyl complexes *trans*-$[Ru(NH_3)_4L(NO)]Cl_3$, L = caffeine, theophylline, imidazole and benzoimidazole in position trans to NO were prepared and their photochemical properties studied. All complexes showed nitric oxide (NO) release under light irradiation at 330–440 nm. Quantum yields for $[Ru(NH_3)_4L(H_2O)]^{3+}$ formation ($\phi_{Ru(III)}$) were sensitive to the natures of L, λ_{irr} and pH. The major product of the irradiation of *trans*-$[Ru(NH_3)_4L(NO^+)]^{3+}$ is the *trans*-$[Ru^{III}(NH_3)_4L(Cl)]^{2+}$ and NO as suggested by UV–Vis, electrochemical, and FTIR techniques.

1. Introduction

In recent years, a great number of studies concerned with NO activity in biological systems have been published [1–6]. In this field, ruthenium complexes have been studied as NO scavengers, or reciprocally, their nitrosyl complexes have been investigated as NO delivery systems toward biological targets [7–20], with regard to the design and evaluation of a number of new transition metal complexes as NO carriers for biological applications [21–26]. Consequently, metalonitrosyl complexes as agents potentially capable of releasing NO in vivo have recently become an active area of research [15,27–31]. One strategy is to employ a precursor that displays relatively low thermal reactivity, but is photochemically active, to yield NO when subjected to electronic excitation [10,32]. In this context, the chemical and photochemical reactions of various metal nitrosyl complexes and of related species are being investigated [10,15,27–29,32,33] with the goal of developing models for NO delivery agents in pharmaceutical applications. Complexes of the type *trans*-$[Ru(NH_3)_4(L)NO^+]^{3+}$ are robust in aqueous solution and are easily activated to release NO through electrochemical [15,28,34,35], chemical [15,36] or photochemical monoelectronic reduction. In this area, the photochemical behavior of several nitrosyl metal complexes and related species [15,37,38] have been reported. An interesting system is that of ruthenium ammines, which can be modified to exhibit desired properties [12,39]. Franco et al. [15,32] reported on the photochemical behavior of some nitrosyl complexes of the type *trans*-$[Ru(NH_3)_4L(NO)]^{3+}$ (L = 4-pic, imN, L-hist, py, nic, pz, isn, 4-acpy and $P(OEt)_3$). They observed that the photolysis at higher energy than 310–370 nm light leads to the dissociation of NO and *trans*-$[Ru(NH_3)_4L(H_2O)]^{3+}$ as products, Eq. (1). However, the photochemistry of most nitrosyl ruthenium complexes, which could act as NO delivery agents under light stimulation, have been described mainly in acidic medium [15,32,33,38], due to the nitro–nitrosyl equilibrium in basic solution

$$trans\text{-}[Ru^{(II)}(NH_3)_4L(NO^+)]^{3+} \xrightarrow{h\nu} trans\text{-}[Ru^{(III)}(NH_3)_4L(H_2O)]^{3+} + NO^0 \quad (1)$$

Contrarily, Richter-Addo have observed that the irradiation of some iron–porphyrin containing nitrosyl and nitro ligands, at $300 < \lambda < 500$ nm, induces the linkage isomerism of both nitro and nitrosyl ligands [40,41]. In these systems it was observed a shift in the νNO around 150 cm^{-1} suggesting such isomerism [40,41].

In a previous article [34], we showed that the complexes *trans*-$[Ru(NH_3)_4L(NO)]Cl_3$ (L = C-bonded imidazole, C-bonded caffeine and C-bonded theophiline) are stable at physiological pH but rapidly release NO after NO^+/NO reduction. This article describes the photochemical properties of the *trans*-$[Ru(NH_3)_4L(NO)]^{3+}$ complexes where L is carbon-bound imidazole, caffeine and theophylline (Fig. 1).

2. Experimental

Ultrahigh purity water purified with a Millipore system was used throughout. $RuCl_3 \cdot (H_2O)_x$, imidazole, caffeine, benzoimidazole and theophylline were obtained from Aldrich and used without

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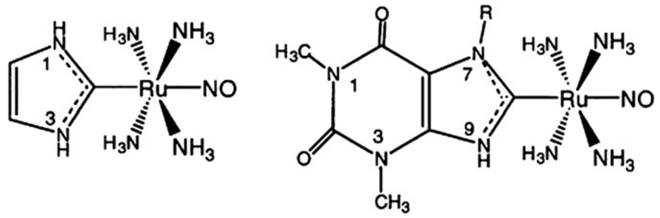

Fig. 1. Structures of (A) *trans*-$[Ru(NH_3)_4(imidazole)(NO)]^{3+}$ and (B) R = H *trans*-$[Ru(NH_3)_4(theophylline)(NO)]^{3+}$, R = CH_3 *trans*-$[Ru(NH_3)_4(caffeine)(NO)]^{3+}$.

further purification. *trans*-$[Ru(NH_3)_4L(NO)]Cl_3$ (L = imidazole, caffeine, theophylline and benzoimidazole) [34,35] complexes were prepared according to literature procedures. *Anal.* Calc. for imidazole: C, 9.63; H, 4.28; N, 26.23. Found: C, 9.62; H, 4.32; N, 26.20%. *Anal.* Calc. for caffeine: C, 19.21; H, 4.40; N, 25.21. Found: C, 19.02; H, 4.43; N, 24.98%. *Anal.* Calc. for theophylline: C, 17.28; H, 4.12; N, 25.94. Found: C, 17.02; H, 4.18; N, 25.75%. *Anal.* Calc. for benzoimidazole: C, 11.20; H, 2.40; N, 13.00. Found: C, 10.95; H, 2.36; N, 13.23%.

The electrochemical experiments were performed at room temperature by using Ag/AgCl (BAS, 3.50 mol L^{-1} KCl) as reference electrode.

UV–Vis spectra were recorded on an HP-8453 diode-array spectrophotometer. ^1H and ^{13}C NMR spectra were obtained in 5 mm NMR tubes on a Bruker 300 MHz FT spectrometer in D_2O. IR spectra were obtained in KBr pellets on a Shimadzu 283-B FT-IR spectrophotometer.

Photolysis experiments were carried out at 25.0 ± 0.3 °C in 1.0 cm path length quartz cells capped with a rubber septum. The complexes solutions were prepared in an 0.10 mol L^{-1} of NaCl to form the characterized product as *trans*-$[Ru(NH_3)_4LCl]^{2+}$. The solutions (10^{-4} mol L^{-1} initial complex concentration) were deaerated by bubbling with argon prior to photolysis and stirred during irradiation. The solutions were photolyzed to approximately 5% reaction to minimize inner filter effects. Simultaneous dark reactions were carried out with identical solutions. As analyzed from their UV–Vis spectra, these samples were stable in the dark on a time scale longer than that of the photochemical experiments. Photoproducts were identified by UV–Vis and voltammetric measurements by comparison with the respective data of separately prepared ruthenium complexes. Quantitative analyses were made by monitoring electronic spectral changes, and it was assumed that the quantum yield for appearance of product is equal to that of disappearance of the starting material, consistent with the stoichiometry indicated in Eq. (1). Quantum yields were determined from initial spectral changes, monitoring the appearance of the *trans*-$[Ru(NH_3)_4LCl]^{2+}$ species, and were plotted versus reaction percentage and extrapolated back to 0% reaction to minimize inner filter effects. The reported quantum yields are the average of, at least, three independent experiments.

3. Results and discussion

Studies of the electronic structure and electronic spectroscopy of transition metal nitrosyl compounds have been directed towards establishing the link between the molecular orbital description and the physical and chemical properties, especially for these complexes as metallodrugs and in catalysis [42]. The absorption spectra of the compounds presented here showed bands at 260 and 300 nm (Fig. 2) attributed to $\pi \rightarrow \pi^*$ transitions on the aromatic ligands, and at 446 and 456 nm, which are assigned to $\pi^*(NO) \leftarrow d\pi(Ru^{II})$ metal to ligand charge-transfer (MLCT) transitions. These assignments are taken by analogy to those observed for *trans*-$[Ru(NH_3)_5(NO)]^{3+}$ and related complexes [15,28,43]. Consistent with this assignment, these bands shifted to lower energy with increasing pH as the imidazole proton was ionized, thereby increasing electronic density on the Ru^{II}.

Fig. 2 presents typical changes in the UV–vis spectra of a solution of *trans*-$[Ru(NH_3)_4L(NO)]^{3+}$ during the photolysis. The appearance of the LMCT band in the visible region for all complexes at different pHs values (Table 1) is clearly observed, typical of the *trans*-$[Ru(NH_3)_4LCl]^{2+}$ species generated after the release of NO, since the photolysis experiments were carried out in chloride medium [44]. Also, a change in color is observed from yellow to purple for caffeine and theophylline complexes, characteristic of the Ru^{III} species [44].

The release of NO as a photoproduct was confirmed by differential pulse voltammetry (DPV). Fig. 3 shows the differential pulse voltammogram obtained after 330 nm irradiation of *trans*-$[Ru(NH_3)_4(caffeine)(NO)]^{3+}$. The anodic process observed at 0.80 V was assigned to the oxidation of the released NO. This process was not observed when the solution of *trans*-$[Ru(NH_3)_4(caffeine)(NO)]Cl_3$ was kept in the dark. Moreover, well-defined waves appeared at potentials 0.114, 0.168, −0.083 and 0.053 V for L = caffeine, theophylline, imidazole and benzoimidazole, respectively. This wave is assigned to the $Ru^{II} \rightarrow Ru^{III}$ oxidation process for *trans*-$[Ru(NH_3)_4LCl]^{2+}$, which must be generated as a result of dissociation of NO from the original compound [34]. The same behavior was found for several nitrosyl compounds reported in the literature [12,45–48].

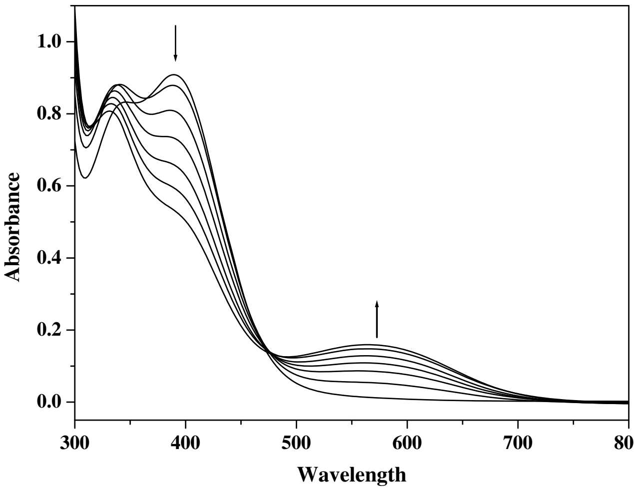

Fig. 2. Spectral changes of the absorption spectrum accompanying photolysis of *trans*-$[Ru(NH_3)_4(theophylline)(NO)]^{3+}$ in phosphate buffer solution, pH 7.1, μ = 1.0 mol L^{-1}, λ_{irr} = 330 nm.

Table 1
UV–Vis spectra data for *trans*-$[Ru(NH_3)_4LCl]^{2+}$ in different pHs values

L	pH	λ (nm)
Caffeine	3.4	569
	4.4	605
	7.1	648
Theophylline	3.4	564
	4.4	577
	7.1	603
Imidazole	3.4	449
	4.4	474
	7.1	476
Benzoimidazole	3.4	443
	4.4	475
	7.1	498

The process at +0.8 V is attributed the free $NO^0 \rightarrow NO^+$ oxidation [28]. In addition, the photolysis of the compound *trans*-$[Ru(NH_3)_4(caffeine)(NO)]^{3+}$ dispersed in KBr was performed and monitored by IR spectroscopy (Fig. 4). Comparison of the IR spectra acquired before and after irradiation showed a decrease in the intensity of the νNO^+ peak at 1905 cm^{-1} and the appearance of a new peak at 1870 cm^{-1}, which can be assigned to νNO^0 stretching mode [6,15,49]. The spectrum of the final product, after exhaustive photolysis, is identical for the *trans*-$[Ru(NH_3)_4(caffeine)(Cl)]Cl_2$ (compared with an authentic sample) in agreement with the formation of the Ru^{III} species upon photolysis. Also, a change in color is observed during the irradiation of the complexes from yellow to purple for L = caffeine and theophylline and from yellow to orange for L = imidazole. These colors are characteristic of the *trans*-$[Ru(NH_3)_4(L)(Cl)]^{2+}$ complex ion. There are several studies in the literature concerning the photochemical studies of the metal–nitrosyl complexes. Several authors [12,45,47,48,50,51] have carried out photochemical studies of several ruthenium nitrosyl complexes and had observed that the irradiation at

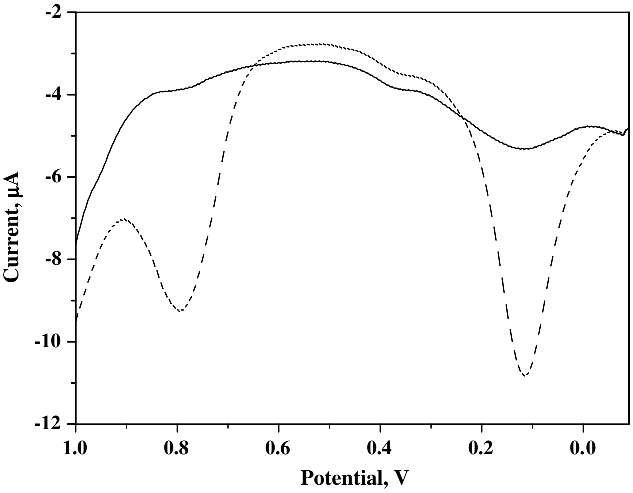

Fig. 3. Differential pulse voltammogram of *trans*-$[Ru(NH_3)_4(caffeine)(NO)]^{3+}$ in KCl solution, pH 7.0; μ = 1 mol L^{-1} at a glassy carbon electrode with platinum wire as an auxiliary electrode and SCE as the reference electrode. The voltammogram was taken after irradiation at 330 nm. Solid line: starting material, dashed line: after irradiation. Potential scan started at −0.1 V with anodic sweep.

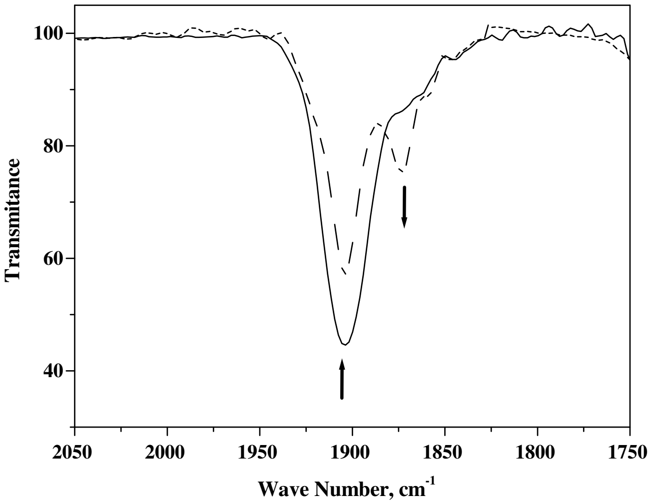

Fig. 4. Infrared spectra changes of *trans*-$[Ru(NH_3)_4(caffeine)(NO)]^{3+}$ dispersed in KBr as function of the irradiation process under 330 nm. Solid line: starting material, dashed line: after photolysis.

Table 2
Quantum yield values (Ru^{III}) for the photolysis of *trans*-$[Ru(NH_3)_4L(NO)]^{3+}$ in aqueous solution

L	λ_{Irr} (nm)	pH	ϕ_{Ru}^{III}
Caffeine	330	3.4	0.51 ± 0.05
	330	4.4	0.40 ± 0.05
	330	7.1	0.21 ± 0.05
	410	3.4	0.20 ± 0.05
	410	4.4	0.16 ± 0.05
	410	7.1	0.11 ± 0.05
	440	3.4	0.20 ± 0.05
	440	4.4	0.15 ± 0.05
	440	7.1	0.11 ± 0.05
Theophylline	330	3.4	0.68 ± 0.05
	330	4.4	0.41 ± 0.05
	330	7.1	0.25 ± 0.05
	410	3.4	0.32 ± 0.05
	410	4.4	0.30 ± 0.05
	410	7.1	0.28 ± 0.05
	440	3.4	0.28 ± 0.05
	440	4.4	0.25 ± 0.05
	440	7.1	0.14 ± 0.05
Imidazole	330	3.4	0.25 ± 0.05
	330	4.4	0.30 ± 0.05
	330	7.1	0.35 ± 0.05
	410	3.4	0.12 ± 0.05
	410	4.4	0.13 ± 0.05
	410	7.1	0.15 ± 0.05
	440	3.4	0.030 ± 0.05
	440	4.4	0.030 ± 0.05
	440	7.1	0.050 ± 0.05
Benzoimidazole	330	3.4	0.0050 ± 0.05
	330	4.4	0.0060 ± 0.05
	330	7.1	0.0070 ± 0.05

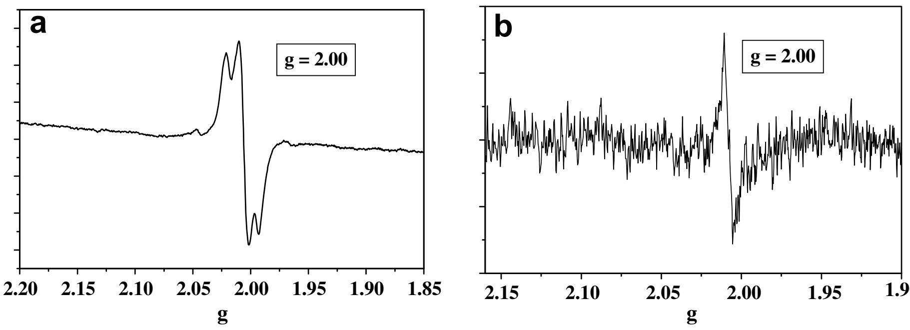

Fig. 5. EPR spectrum of (a) *trans*-$[Ru(NH_3)_4(caffeine)(NO)]^{3+}$ complex, λ_{irr} = 355 nm and (b) *trans*-$[Ru(NH_3)_4(theophylline)(NO)]^{3+}$ complex, λ_{irr} = 440 nm, in water/ethylenеglycol (50%) solution, and 144 K.

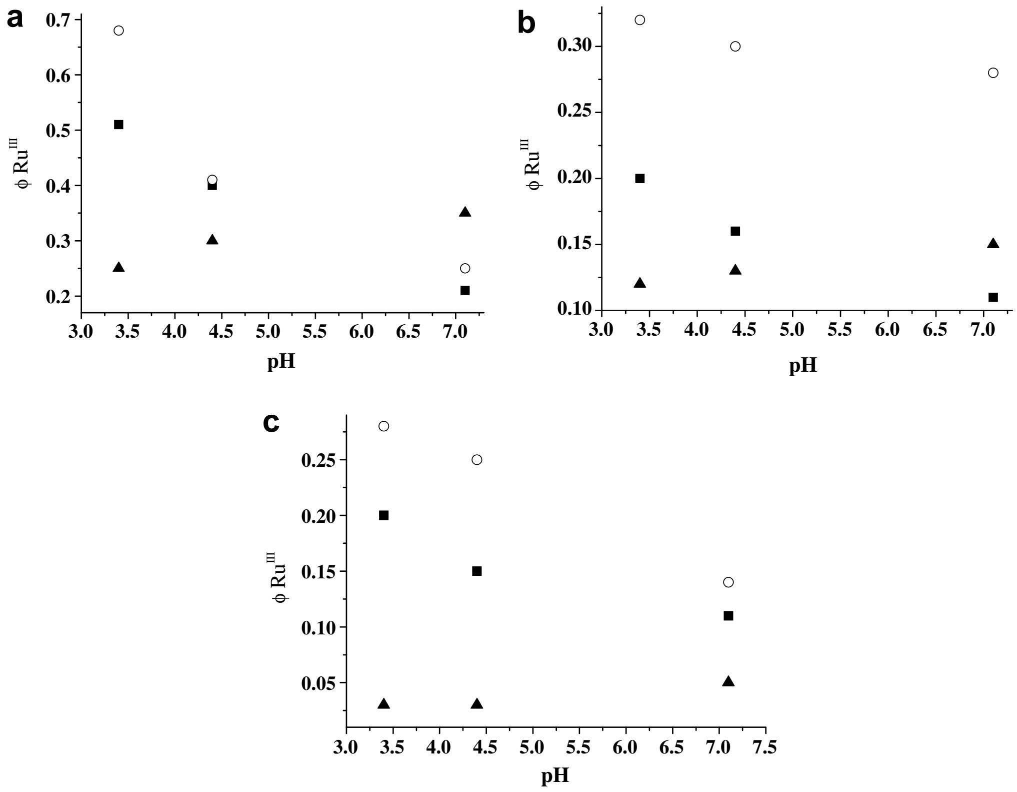

Fig. 6. Plot of ØRu^{III} vs pH for the of *trans*-$[Ru(NH_3)_4L(NO)]^{3+}$ in aqueous solution. ■L = caffeine, ○L = theophylline, ▲L = imidazole. (a) $\lambda_{irr} = 330$ nm, (b) $\lambda_{irr} = 410$ nm and (c) $\lambda_{irr} = 440$ nm.

$300 < \lambda < 500$ nm range produces the NO release from the starting material leading to the formation of the Ru^{III}-solvent species. The data collected in this work suggest that the title complexes behave by a similar mechanism.

Fig. 5 shows the *in situ* EPR spectrum of a solution containing the *trans*-$[Ru(NH_3)_4L(NO)]^{3+}$ after irradiation at 355 nm for L = caffeine and 440 nm for L = theophylline revealing the presence of a paramagnetic photoproduct. The $g = 2.00$ value and observation of the hyperfine splitting in the EPR spectrum of *trans*-$[Ru(NH_3)_4(\text{caffeine})(NO)]^{3+}$ after irradiation suggest the formation of a paramagnetic species containing the reduced nitric oxide radical coordinated to the metal center [52].

Reduction of coordinated NO$^+$ in *trans*-$[Ru^{II}Cl(NO^+)(\text{cyclam})]^{2+}$ [49] results in *trans*-$[Ru^{II}Cl(\text{cyclam})(NO^0)]^+$, which undergoes a relatively fast chloride labilization ($k = 2.0\ s^{-1}$ at 8 °C) resulting in *trans*-$[Ru^{II}(H_2O)(\text{cyclam})(NO^0)]^{2+}$, which in turn releases NO^0 slowly ($k = 6.4 \times 10^{-4}\ s^{-1}$ at 25 °C). DFT calculations for several RuNO complexes have shown [32,53,54] that the ($d\pi \rightarrow NO^+$) MLCT transitions lie around 330 and 450 nm, consequently the photoproducts after irradiation in this range should be *trans*-$[Ru^{III}(NH_3)_4L(H_2O)]^{3+}$ and NO. Consequently, since, in these experiments, the complexes were irradiated in a ($d\pi \rightarrow NO^+$) MLCT band, it is believed that the observed EPR spectra correspond to coordinated NO^0 radical rather than that of a solvated one [39].

3.1. Quantum yields

Table 2 and Fig. 6a–c summarize the quantum yields for the photoreaction depicted in Eq. (1) determined from changes in the absorption spectrum of the aqueous solution of *trans*-$[Ru(NH_3)_4L(NO)]^{3+}$ when irradiated with 330–440 nm light. ϕ_{Ru}^{III} and ϕ_{NO} are assumed to be the same and are sensitive to the natures of L, λ_{Irr} and pH.

The lowest quantum yield was found for the complex, where L = benzoimidazole, the worst π-acceptor, and the highest quantum yield was observed for L = theophylline, the best π-acceptor. The irradiation of the complex, where L is benzoimidazole with light at $\lambda_{irr} > 350$ nm did not lead to observable photochemistry under the conditions used. Similar behavior was observed for other complexes, where L is a strong σ-donor such as ImN, L-Hist, py and Isn [32].

For the compounds with L = caffeine and theophylline a decrease in ϕ_{NO} was observed with an increase in the pH of the photolyzed solution. This can probably be explained by the more pronounced π-acceptor character of the protonated L ligand increasing the relative charge on the Ru^{II}, thereby making it more difficult to transfer electron density from Ru^{II} to NO$^+$ through a MLCT transition (see Fig. 6).

4. Conclusion

We have shown that the photolysis of *trans*-$[Ru(NH_3)_4L(NO)]Cl_3$, where L is caffeine, theophylline, imidazole and benzoimidazole, produces NO when it is irradiated with light at 330–440 nm range. The major product of the irradiation of *trans*-$[Ru(NH_3)_4L(NO^+)]^{3+}$ is an paramagnetic intermediate that in chloride aqueous solution releases NO to produce *trans*-$[Ru(NH_3)_4L(Cl)]^{2+}$. The quantum yield observed for the NO formation involved in the photolysis of *trans*-$[Ru(NH_3)_4L(NO)]^{3+}$ decreases with the π acceptor character of L, trans to NO$^+$, which is consistent with an increase in charge on NO$^+$.

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