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Photochemical reactions of *trans*-$[Ru(NH_3)_4L(NO)]^{3+}$ complexes ☆

Rose M. Carlos [a], Alessander A. Ferro [c,1], Hildo A.S. Silva [a], Maria G. Gomes [a], Simone S.S. Borges [a], Peter C. Ford [b], Elia Tfouni [c,*], Douglas W. Franco [a,*]

[a] *Instituto de Química de São Carlos, IQSC–USP, Av. do Trabalhador Sãocarlense, 400 – CP 780, 135666-590, São Carlos, SP, Brazil*
[b] *Department of Chemistry and Biochemistry, University of California, Santa Barbara, Santa Barbara, CA 93106-9510, USA*
[c] *Departamento de Química, FFCLRP–USP, Av. dos Bandeirantes, 3900, 14040 – 901, Ribeirão Preto, SP, Brazil*

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Abstract

The photochemical behavior of a series of *trans*-$[Ru(NH_3)_4L(NO)]^{3+}$ complexes, where L = nitrogen bound imidazole, L-histidine, 4-picoline, pyridine, nicotinamide, pyrazine, 4-acetylpyridine, or triethylphosphite is reported. In addition to ligand localized absorption bands (<300 nm), the electronic spectra of these complexes are dominated by relatively low intensity bands assigned as ligand field (LF) and metal to ligand ($d_\pi \rightarrow NO$) charge transfer (MLCT) transitions. Irradiation of aqueous solutions of these complexes with near-UV light (300–370 nm) labilizes NO, i.e.,

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

Quantum yields for $[Ru(NH_3)_4L(H_2O)]^{3+}$ formation ($\phi_{Ru(III)}$) are sensitive to the natures of L, λ_{irr} and pH. The lowest quantum yields ($\lambda_{irr} = 310$ nm) were found for L = imidazole (0.03) and L-histidine (0.04), while much higher values were found for $L = P(OEt)_3$ (0.30). Irradiation at longer wavelengths does not induce photochemical reactivity. These results are interpreted in terms of the expected reactivities of $d_\pi \rightarrow NO$ MLCT state in these systems.

Keywords: Ruthenium nitrosyl photochemistry; Nitric oxide; Nitrosyl; Nitric oxide donors; Ruthenium ammines

1. Introduction

It is now well recognized that nitric oxide (also known as nitrogen monoxide) has important roles in mammalian biology. It serves as a bioregulator of blood pressure, as a neurotransmitter and as a toxic agent formed in immune response to pathogens among other roles [1]. The initial studies have led to a plethora of studies concerning other possible biological roles for NO. Also of interest are the interactions of NO and related species with biologically important targets, the search for nitric oxide scavengers, and the design of compounds for therapeutic NO delivery from different donors, thermally or through activation with light [2–17].

In the last context, the chemical and photochemical reactions of various metal nitrosyl complexes and of related species are being investigated [6–17] with the goal of developing models for NO delivery agents in pharmaceutical applications. The physiological functions of NO are complicated and depend on thermodynamic, kinetic, and concentration considerations [2a,2b], and high or low NO concentrations can be either beneficial or harmful; depending on the specific

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* Corresponding authors. Tel.: +55166023748; fax: +55166331851.
E-mail addresses: ford@chem.ucsb.edu (P.C. Ford), eltfouni@usp.br (E. Tfouni), douglas@iqsc.sc.usp.br (D.W. Franco).

[1] Present address: Faculdade de Tecnologia e Ciências de Feira de Santana, Rua Artêmia Pires Freitas, s/n, SIM, 44.115-000, Feira de Santana, BA, Brazil.

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circumstances. Thus, there is a continuing need for controlled and site specific NO scavengers and NO delivery agents. As a consequence, there is considerable interest in stable compounds that can, with minimal toxic effects, release NO in vivo. In this context, water soluble ruthenium am(m)ine nitrosyls provide the basis for a systematic study and are shown to have tunable reactivities toward NO release [8–13]. Recent in vivo experiments demonstrated that these are able to release NO after being reduced biologically, resulting in blood pressure suppression. Furthermore, these ruthenium complexes were less toxic than sodium nitroprusside, which is an NO donor used as a vasodilator in hypertensive emergencies [15–17].

Although other ruthenium nitrosyl and related complexes have been studied as potential NO delivery agents, there has been little systematic study of a series of related compounds in this regard. The *trans*-$[Ru(NH_3)_4L(NO)]^{3+}$ complexes constitute a system where L can be systematically varied in order to tune the desired NO properties [8–17]. Such an investigation can contribute to the fundamental understanding necessary to design systems with tunable thermal and photochemical properties for specific applications.

Preliminary photochemical experiments have shown that aqueous solutions of certain *trans*-$[Ru(NH_3)_4L(NO)]^{3+}$complexes are photoactive toward near-UV excitation to give *trans*-$[Ru(NH_3)_4L(H_2O)]^{3+}$ and NO as products [8,9]:

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

This article describes the photochemical properties of the *trans*-$[Ru(NH_3)_4L(NO)]^{3+}$ complexes where L is nitrogen bound imidazole (imN), L-Histidine (L-Hist), 4-picoline (4-pic), pyridine (py), 4-acetylpyridine (4-acpy), pyrazine (pz), nicotinamide (nic), and triethylphosphite ($P(OEt)_3$).

2. Experimental

2.1. Materials and reagents

Ruthenium trichloride ($RuCl_3 \cdot nH_2O$) (Strem or Aldrich) was the starting material for ruthenium complex syntheses. HPLC grade solvents were used, except acetone, ethyl ether and ethanol, which were purified according to the literature [18]. Doubly distilled water was used throughout. All other materials were reagent grade. The Ru(II) complexes *trans*-$[Ru(NH_3)_4L(NO)]^{3+}$ (L = imN, L-Hist, py, nic, and pz) were prepared from *trans*-$[Ru(NH_3)_4L(SO_4)]^+$ by the room temperature reaction of the corresponding sulfate complexes with $NaNO_2$ in acidic medium, or by reacting *trans*-$[Ru(NH_3)_4L(H_2O)]^{2+}$, generated from the reduction of the corresponding Ru(III) sulfate, with NO^+ generated by $NaNO_2$ in acidic medium, as described elsewhere [9,10]. The new complexes *trans*-$[Ru(NH_3)_4L(NO)]$ $(BF_4)_3$ (L = 4-acpy and 4-pic) were prepared by both methods, with 70% yields; *Anal.* Calc. (Found) for the 4-acpy complex: C, 13.79 (13.34); N, 13.78 (13.59); H, 3.14 (3.06)%, and for the 4-pic complex: C, 13.0 (13.0); N, 15.2 (14.9); H, 3.46 (3.4)%. The *trans*-$[Ru(NH_3)_4(P(OEt)_3)(NO)]$ $(PF_6)_3$ complex was synthesized by direct reaction of *trans*-$[Ru(NH_3)_4$ $(P(OEt)_3)(H_2O)]^{2+}$ with nitrous acid [19], with 60% yield; *Anal.* Calc. (Found): C, 9.00 (8.98); N, 8.75 (8.85); H, 3.37 (3.47); Ru, 12.63 (12.30)%. The electronic spectra of the anticipated photoproducts *trans*-$[Ru^{III}(NH_3)_4L(H_2O)]^{3+}$ were obtained by reduction of *trans*-$[Ru(NH_3)_4L(SO_4)]^+$ with Zn/Hg in aqueous deaerated $\sim 1.0 \times 10^{-2}$ M CF_3COOH solution followed by addition of a slight excess (10–15% the stoichiometric amount) of hydrogen peroxide, followed by pH adjustment to the pH of photolysis.

Potassium trisoxalatoferrate(III) was prepared according to Calvert and Pitts [20] for use as a chemical actinometer.

2.2. Instruments

Monochromatic irradiations at 310, 313, 330, 334, 370, 410, 450 and 480 nm were carried out using a 200 W or a 150 W Xenon lamp in models 68805 or 6253, respectively, Oriel Universal Arc Lamp Source. The irradiation wavelengths were selected with Oriel interference filters for photolysis at the appropriate wavelengths. The interference filters had an average band pass of 10 nm and the collimated beam intensities ranged from 4×10^{-8} to 1×10^{-9} einstein^{-1} cm^{-2} as determined by ferrioxalate actinometry. The progress of the photoreactions was monitored spectrophotometrically on a Hitachi model U-2000 or HP8452A diode array spectrophotometers. The ESR frozen aqueous solution spectra of the reactants and products were recorded on a Brucker model ESP 300 E EPR spectrometer at 77 K. A polarographic analyzer/stripping voltammeter Model 264A from Princeton Applied Research (PARC) attached to a microcomputer employing Microquímica electrochemical software and a model 273 PARC potentiostat/galvanostat were used for the electrochemical measurements. The electrochemical cells used were of the conventional three electrode type with an aqueous saturated calomel electrode (SCE) as a reference electrode and glassy-carbon and Pt wire as working and auxiliary electrodes, respectively. Emission spectra were recorded with an Aminco-Bowman spectrofluorimeter model J4-8960A, with a high-pressure xenon lamp and an IP28 type photomultiplier. Infrared spectra were recorded in a 1600 FTIR Perkin–Elmer spectrophotometer in KBr pellets.

2.3. Procedures

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 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 voltammetric measurements by comparison with respective data of separately prepared ruthenium complexes. Quantitative analyses were made 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 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

3.1. Syntheses and spectroscopic properties

The syntheses of the previously unreported complexes *trans*-$[Ru(NH_3)_4(4\text{-acpy})(NO)]^{3+}$ (**I**) and *trans*-$[Ru(NH_3)_4(4\text{-pic})(NO)]^{3+}$ (**II**) followed the general procedures described for other *trans*-$[Ru(NH_3)_4L(NO)]^{3+}$ (L = py, pz, nic, L-Hist, imN) [9,10]. The physical properties, such as electrochemical and spectral, are similar to those with L = py, pz, nic, L-Hist, imN [8]. Crystallographic structural studies [8] have confirmed the *trans* configuration for such complexes with the ammines in the equatorial plane and the linear nitrosyl and L in the axial positions and suggest a nitrosonium character for NO [8]. All are ESR silent, consistent with a diamagnetic $[Ru^{II}(NO^+)]$ core. The infrared spectra (KBr pellets) of *trans*-$[Ru(NH_3)_4L(NO)](BF_4)_3$ each displayed a single ν_{NO} band at 1930 and 1934 cm^{-1} for **I** and **II**, respectively, consistent with the nitrosyl configuration with a NO triple bond. The reduction potentials of the coordinated nitrosyl in the **I** and **II** complexes, in aqueous solution, were determined to be –0.108 and +0.002 V versus NHE for 4-pic and 4-acpy, respectively, falling in the range found for the other *trans*-$[Ru(NH_3)_4L(NO)]^{3+}$ complexes [8–10].

The electronic absorption spectra of the nitrosyl ruthenium ammine complexes, *trans*-$[Ru(NH_3)_4L(NO)]^{3+}$, are quite different from those of analogous ruthenium(II) complexes $[Ru(NH_3)_5L]^{2+}$ and *trans*-$[Ru(NH_3)_4LL']^{2+}$ without the nitrosyl ligand [21–23]. The spectra of the latter complexes show intense metal to ligand charge transfer (MLCT) absorption bands in the visible when L and/or L′ are aromatic heterocycles such as pyridines or pyrazine. However, the spectra of the nitrosyl complexes (e.g., *trans*-$[Ru(NH_3)_4(4\text{-acpy})(NO)]^{3+}$, Fig. 1) do not display analogous MLCT bands, even when a pyridine or pyrazine is present in the coordination sphere. Table 1 summarizes the relevant spectral features of the complexes studied here. The absorption spectra of all the *trans*-$[Ru(NH_3)_4L(NO)]^{3+}$ complexes are similar and consist of several sets of bands, strong $\pi\pi^*$ ligand localized transitions below 300 nm, broad bands centered around 330 nm and ~400–500 nm and, in some cases, a band at >500 nm. (The spectrum of aqueous *trans*-$[Ru(NH_3)_4(pz)(NO)]^{3+}$ was previously reported to have λ_{max} at 302, 468 and 584 nm [10], but reexamination of the spectrum with a higher concentration showed the lowest energy band to be centered at 508 nm.)

Theoretical computational studies [11,24] of several *trans*-$[Ru(NH_3)_4L(NO)]^{3+}$ ions have addressed the electronic absorption spectra. The seven to ten calculated transitions involve ligand field (LF) (d–d), ligand-to-ligand charge transfer (LLCT) ($L \rightarrow NO^+$), internal ligand (IL) ($L \rightarrow L$), MLCT (Ru $d_\pi \rightarrow NO^+$) and MLCT ($Ru \rightarrow L$) transitions. The transitions that should be involved in the photochemistry reported here are centered around 330 nm and 450 nm. According to the calculations, absorptions at 300–350 nm involve LF and Ru $d_\pi \rightarrow$ NO MLCT transitions; and that at ~400–500 nm involves a Ru $d_\pi \rightarrow$ NO MLCT transition.

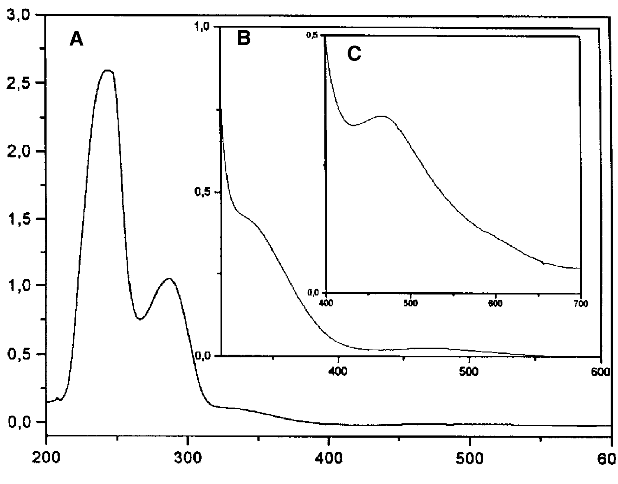

Fig. 1. Absorption spectra of *trans*-$[Ru(NH_3)_4(4\text{-acpy})(NO)]^{3+}$ complex in CF_3COOH/CF_3COONa solution pH 2.0, $\mu = 0.1$ mol l^{-1}. (A) 2.9×10^{-4} mol l^{-1}; (B) 1.2×10^{-3} mol l^{-1}; (C) 8.7×10^{-3} mol l^{-1}.

Table 1
UV–Vis spectral data for *trans*-$[Ru(NH_3)_4L(NO)]^{3+}$ in aqueous solution[a]

L	λ_{max} (nm) (ε/L mol^{-1} cm^{-1})
imN[b,c]	233 (9300); 324 (1000); 460 (40)
L-Hist[b,d]	242 (2200); 294sh (3700); 336sh (600); 461 (40)
4-pic[e,f]	239 (11 200)[g]; 262 (3550)[g]; 325 (220); 460 (20)
py[b,h]	231 (9100); 267 (2300); 324 (160); 47 (23)
nic[b,i,j]	224 (9400)[g]; 242 (3500)[g]; 272 (2500)[g]; 320 (160); 485 (23)
pz[k,l]	230 (10 000); 276 (4400); 302 (660)[g];468 (40)[g]; 508 (40); 584 (43)[g]
4-acpy[b,m]	238 (19 000); 286 (3700); 330 (340); 464 (40)
$P(OEt)_3$	260 (1400); 316 (216)

[a] Values previously reported [9,10] were either from experimental absorption peaks or result of Gaussian deconvolution. Values reported here are from experimental absorption peaks, except where noted.

[b] In 0.1 M CF_3COOH.

[c] $[Ru] = 4.5 \times 10^{-4}$, 1.7×10^{-4} and 4.3×10^{-3} mol l^{-1}.

[d] $[Ru] = 5.4 \times 10^{-3}$ and 1.2×10^{-2}mol l^{-1}.

[e] In CF_3COOH/CF_3COONa solution pH 3.0, $\mu = 0.1$ mol l^{-1}.

[f] $[Ru] = 9.4 \times 10^{-5}$ and 5.1×10^{-3} mol l^{-1}.

[g] From Gaussian deconvolution.

[h] $[Ru] = 1.0 \times 10^{-4}$ and 1.0×10^{-3} mol l^{-1}.

[i] The 224 nm value was reported as doubtful for possible interference from electrolyte absorption [9].

[j] $[Ru] = 8.6 \times 10^{-5}$ mol l^{-1}.

[k] In pH 3.96 CF_3COOH solution.

[l] $[Ru] = 1.0 \times 10^{-4}$, 1×10^{-4}, 7.3×10^{-4}, and 8.0×10^{-3} mol l^{-1}.

[m] $[Ru] = 2.9 \times 10^{-4}$, 1.2×10^{-3} and 8.7×10^{-3} mol l^{-1}.

3.2. Photochemical studies

All the complexes described are robust in solution and in the solid state and only undergo NO release upon photolysis. In a preliminary investigation with *trans*-$[Ru(NH_3)_4L(NO)]^{3+}$ (L = py and nic), it was observed that photolyses at higher energy (310–370 nm) light leads to the formation of NO and $[Ru(NH_3)_4L(H_2O)]^{3+}$ as products Eq. (1) [9]. Similar photochemical behavior is found for the other complexes reported here, but irradiation with $\lambda_{irr} \geqslant 380$ nm does not lead to observable photochemistry under the conditions used (25 °C).

$$\textit{trans-}[Ru(NH_3)_4L(NO)]^{3+} \xrightarrow{h\nu} \textit{trans-}[Ru(NH_3)_4L(H_2O)]^{3+} + NO \qquad (1)$$

At pH ~6.0, the Ru(III) products are largely in the hydroxo form Eq. (2). The aqua and hydroxo products were identified by comparing the UV–Vis spectra, electrochemical and EPR data with those of authentic samples of previously characterized *trans*-$[Ru(NH_3)_4L(OH_2)]^{3+}$ and *trans*-$[Ru(NH_3)_4L(OH)]^{2+}$ [25]. Formation of Ru(II) complexes, such as *trans*-$Ru(NH_3)_4L(OH_2)]^{2+}$, can easily be ruled out, since these would have strong MLCT bands in the visible range ($\varepsilon > \sim 8 \times 10^3$).

$$\textit{trans-}[Ru(NH_3)_4L(H_2O)]^{3+} \rightleftharpoons \textit{trans-}[Ru(NH_3)_4L(OH)]^{2+} + H^+ \qquad (2)$$

The EPR spectrum of the photolysis solutions at pH 2 indicates the presence of a paramagnetic photoproduct (Fig. 2). Although free NO is paramagnetic, its aqueous solution spectrum does not exhibit an EPR signal [13]. Furthermore, excited states generated in 25 °C solution would not live long enough to be detected by EPR. Thus, the paramagnetic species observed in the photolyzed solutions of *trans*-$[Ru(NH_3)_4L(NO)]^{3+}$ must be *trans*-$[Ru(NH_3)_4L(H_2O)]^{3+}$ and this is confirmed by spectral simulation and comparison with an authentic sample of this species.

The formation of NO as a photoproduct was confirmed using a nitric oxide selective electrode and by differential pulse polarography (DPP). Fig. 3 shows the differential pulse polarogram obtained after 330 nm irradiation of *trans*-$[Ru(NH_3)_4(4\text{-pic})(NO)]^{3+}$. The anodic peak observed at 0.80 V was assigned to the oxidation of the released NO. This was not observed when the so-

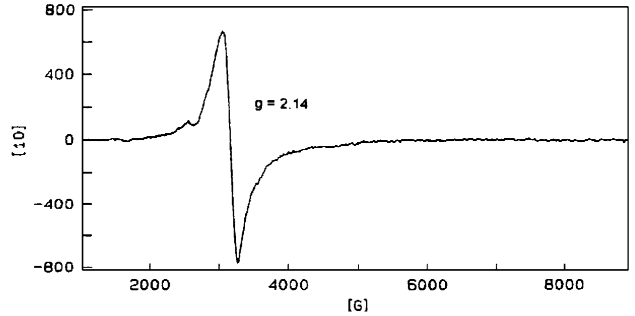

Fig. 2. EPR spectrum of *trans*-$[Ru(NH_3)_4(py)(NO)]^{3+}$ complex in KCl solution, pH 4.34, $\mu = 0.1$ mol l^{-1} after 4% complex irradiation at 330 nm.

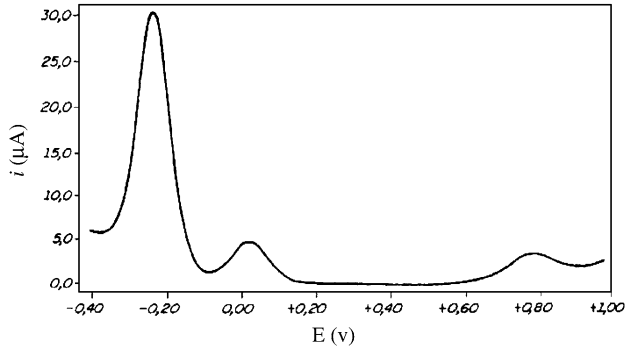

Fig. 3. Differential pulse voltammogram of *trans*-$[Ru(NH_3)_4(py)(NO)]^{3+}$ complex in KCl solution, pH 4.34; $\mu = 0.1$ mol l^{-1} at glassy-carbon electrode with platinum wire as an auxiliary electrode and SCE as the reference electrode. The voltammogram was taken after 4% complex irradiation at 330 nm.

lution of *trans*-$[Ru(NH_3)_4(4\text{-pic})(NO)](PF_6)_3$ was kept in the dark.

Fig. 4 illustrates typical electronic spectral changes accompanying photolysis of aqueous *trans*-$[Ru(NH_3)_4(4\text{-acpy})(NO)]^{3+}$ at pH 2. These reactions occur quite smoothly and photolyses were allowed to proceed up to the limit of 5% conversion. There is an increase in absorbance around 330 nm and the spectral changes are consistent with the formation of *trans*-$[Ru(NH_3)_4(4\text{-acpy})(H_2O)]^{3+}$.

Thus, extensive data from three independent techniques show that irradiation of aqueous *trans*-$[Ru(NH_3)_4L(NO)]^{3+}$ gives *trans*-$[Ru(NH_3)_4L(H_2O)]^{3+}$ and NO as the only observable products at pH 2.0, and 25 °C Eq. (1). Increasing the solution pH results in increasing concentrations of *trans*-$[Ru(NH_3)_4L(OH)]^{3+}$, which become dominant about pH 6 owing to the equilibrium indicated by Eq. (2).

3.3. Quantum yields

Table 2 summarizes the quantum yields for the photoreaction depicted in Eq. (1) determined from changes in the optical spectra of aqueous solutions of, initially, *trans*-$[Ru(NH_3)_4L(NO)]^{3+}$, when irradiated with 300–370 nm light. $\Phi_{Ru(III)}$ ($\phi_{Ru(III)}$ and ϕ_{NO} are assumed to be the same) is somewhat sensitive to the nature of L, and over the series 4-pic, L-hist, py, nic, 4-acpy, pz, $P(OEt)_3$ at pH 2.0 the quantum yields span an order of magnitude. The lowest quantum yields are found for the complexes, where L is a strong σ-donor such as imN or L-hist, while the highest $\Phi_{Ru(III)}$ observed for $L = P(OEt)_3$, is a good π-acceptor. The $\Phi_{Ru(III)}$ values correlate roughly with the formal Ru(III)/Ru(II) reduction potentials for the *trans*-$[Ru(NH_3)_4L(H_2O)]^{3+}$, which range from –0.30 V (versus Ag/AgCl) for L = L-Hist to +0.46 V for $L = P(OEt)_3$. The quantum yields are also pH dependent (Table 3).

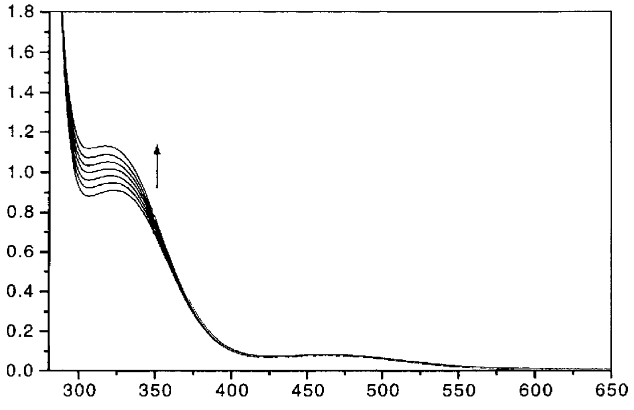

Fig. 4. Spectral changes of the absorption spectrum accompanying photolysis of *trans*-$[Ru(NH_3)_4(4\text{-acpy})(NO)]^{3+}$ in CF_3COOH/CF_3COONa solution pH 3.0, $\mu = 0.1$ mol l^{-1}, $\lambda_{irr} = 330$ nm.

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

L	λ_{irr} (nm)	pH	$\Phi_{Ru(III)}$
4-pic	310	2.0	0.06 ± 0.01
	330	2.0	0.08 ± 0.01
	370	2.0	0.04 ± 0.02
	410	2.0	<0.001
	480	2.0	<0.001
imN	313	2.13	0.042 ± 0.002
	330	2.13	0.033 ± 0.004
	370	2.13	0.017 ± 0.003
L-Hist	313	2.13	0.045 ± 0.003
	334	2.13	0.039 ± 0.005
	370	2.13	0.022 ± 0.002
py	310	3.0	0.17 ± 0.01
	330	3.0	0.10 ± 0.01
	370	4.5	0.07 ± 0.02
nic	310	2.0	0.07 ± 0.01
	334	2.0	0.08 ± 0.01
	370	2.0	<0.001
	480	2.0	<0.001
pz	313	2.13	0.13 ± 0.03
	334	2.13	0.10 ± 0.01
	370	2.13	0.07 ± 0.01
	450	2.0	<0.01
isn	310	3.0	0.04 ± 0.01
	330	3.0	0.05 ± 0.01
	370	3.0	<0.01
4-acpy	313	2.13	0.10 ± 0.02
	334	2.13	0.07 ± 0.01
	370	2.13	0.04 ± 0.02
$P(OEt)_3$	310	2.0	0.30 ± 0.05

The photochemical behavior of *trans*-$[Ru(NH_3)_4L(NO)]^{3+}$ is completely different from that of other Ru(II) ammines [8,21], for which MLCT and LF states, the order of which can be tuned, are the lowest energy excited states (LEES). For the latter complexes, ligand photosubstitution is the major photochemical pathway, and this is usually attributed to the ligand field excited states [21]. Photooxidation of Ru(II) to Ru(III) has been observed for UV irradiation into charge transfer to solvent (CTTS) states. However, with the nitrosyl ruthenium complexes, visualizing these as $Ru^{II}(NO^+)$ complexes as described above leads to the view that the photoreaction depicted in Eq. (1) represents photooxidation of the metal center simultaneous with ligand (NO) labilization.

Among the UV–Vis transitions predicted by earlier DFT calculations [24], the ($d_\pi \rightarrow NO^+$) MLCT transitions around 330 and 450 nm would appear to be logical predecessors of the *trans*-$[Ru^{III}(NH_3)_4L(OH_2)]^{3+}$ and NO products. While there is also an LF transition around 330 nm which would be expected to be substitution labile,

Table 3
pH Dependence of $\phi_{\mathrm{Ru(III)}}$ values for the photolysis of *trans*-$[\mathrm{Ru(NH_3)_4L(NO)L}]^{3+}$ in aqueous solution

L	λ_{irr}/nm	pH	$\phi_{\mathrm{Ru(III)}}$
4-pic	330	2.0	0.08 ± 0.01
	330	3.45	0.12 ± 0.01
	330	5.0	0.26 ± 0.02
	330	6.0	0.40 ± 0.01
py	330	3.0	0.11 ± 0.01
	330	4.4	0.13 ± 0.01
	330	6.4	0.18 ± 0.01
pz	313	2.13	0.13 ± 0.03
	313	3.45	0.17 ± 0.03
	313	4.32	0.23 ± 0.03
isn	330	3.02	0.05 ± 0.01
	330	4.63	0.05 ± 0.01
	330	4.95	0.07 ± 0.01
4-acpy	313	2.13	0.10 ± 0.02
	313	3.45	0.13 ± 0.03
	313	4.32	0.19 ± 0.03
L-Hist	313	2.13	0.045 ± 0.003
	313	3.45	0.067 ± 0.004
	313	4.32	0.086 ± 0.004
imN	313	2.13	0.042 ± 0.002
	313	3.45	0.063 ± 0.003
	313	4.32	0.079 ± 0.003

the formation of a Ru(III) might be expected to result from a charge transfer of the type given in Eq. (3). However, the

$$\mathrm{L\text{-}Ru^{II}(NO^{+})} \xrightarrow{h\nu} [\mathrm{L\text{-}Ru^{III}(NO^{0})}]^{*} \qquad (3)$$

photochemistry depicted in Eq. (1) is only observed for photoexcitation at $\lambda_{\mathrm{irr}} < 370$ nm, so, if such ($\mathrm{d}_\pi \rightarrow \mathrm{NO}^+$) is responsible, then it is only that at higher energy which serves this purpose. In this context, the calculations [24] show that the higher energy ($\mathrm{d}_\pi \rightarrow \mathrm{NO}^+$) MLCT ES is the result of a transition from the Ru–NO p-bonding Ru $\mathrm{d}_{xz,yz}$ orbitals to the π^* NO orbitals. The lower energy ($\mathrm{d}_\pi \rightarrow \mathrm{NO}^+$) MLCT ES involves transition from the nonbonding $\mathrm{d}_{x^2-y^2}$ to the π^* NO orbitals. [2] Thus, the former might be expected to be more dissociative than the latter as observed. The higher energy excitation might also provide more impetus to the trajectory for NO dissociation.

It has been reported that lower energy irradiation ($\lambda_{\mathrm{irr}} > 400$ nm) of certain Ru nitrosyls leads to the observation (at $T < 0$ °C) of metastable linkage isomers with O- or η^2-bonded NO, which decayed back to the η^1-N-bonded complex upon warming [26]. While this might have occurred under longer wavelength excitation of the *trans*-$[\mathrm{Ru(NH_3)_4L(NO)}]^{3+}$ ions, such a process would have likely gone undetected under the present experimental conditions (25 °C) if it did not lead to ligand labilization products.

A particularly interesting observation is the pH dependence of the $\Phi_{\mathrm{Ru(III)}}$ values recorded for the *trans*-$[\mathrm{Ru(NH_3)_4L(NO)}]^{3+}$ photolyses, where higher solution pH results in larger quantum yields. We attribute this to the dissociation of H^+ from the product aqua ion according to Eq. (2). Except for *trans*-$[\mathrm{Ru^{III}(NH_3)_4(P(OEt)_3)(OH_2)}]^{3+}$, the p$K_\mathrm{a}$'s of various *trans*-$[\mathrm{Ru^{III}(NH_3)_4L(OH_2)}]^{3+}$ complexes fall in the range 4–5, and are reasonably independent of L [11,27]. For example, the pK_as of *trans*-$[\mathrm{Ru^{III}(NH_3)_5(OH_2)}]^{3+}$ (4.1) and *trans*-$[\mathrm{Ru^{III}(NH_3)_4(4\text{-}pic)(OH_2)}]^{3+}$ (~4.5) are quite similar. As the pH increases, a larger fraction of the product is in the hydroxo form and this is likely to be much less reactive toward the back reaction with NO than the corresponding aqua product. Thus, the net quantum yield for NO should increase with pH, as was observed.

4. Summary

The present study has shown that near-UV irradiation of *trans*-$[\mathrm{Ru(NH_3)_4L(NO)}]^{3+}$ solutions at λ_{irr}, corresponding to a Ru d_π-NO MLCT transition of these complexes, leads to NO photoaquation and formation of the Ru(III) ion *trans*-$[\mathrm{Ru(NH_3)_4L(H_2O)}]^{3+}$. Interestingly, this photochemistry is not observed when the lowest energy MLCT band(s) are excited. The quantum yields for this process is somewhat dependent on the nature of L and on the solution pH. Higher NO photolabilization quantum yields were seen for the π-acceptor ligand $\mathrm{P(OEt)_3}$ than for more strongly donating ligands but the trend, if any, among the other L was not obvious. The pH dependence of ϕ_{NO} is consistent with a mechanism where the initially formed photoproducts *trans*-$[\mathrm{Ru(NH_3)_4L(H_2O)}]^{3+}$ and NO undergo back reactions to the initial nitrosyl complex in competition terms with dissociation apart. The effect of higher pH may be to trap the aqua complex to give a less labile hydroxo complex, hence facilitating the separation of the products.

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[2] Reported calculations of reference 24 for the *py* and *pz* complexes used the following axes orientation: the L–Ru–NO axes is the *z* axis and the two $\mathrm{NH_3\text{-}Ru\text{-}NH_3}$ bond axes in the equatorial plane are bisected by the *x* and *y* axes, with the *L* plane in the *yz* plane. As a result, in this orientation, the d_{xy} and d_{xz} orbitals are bonding and the $\mathrm{d}_{x^2-y^2}$ orbital is non-bonding.

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