Ruthenium Nitrosyl Complexes with N-Heterocyclic Ligands

Simone da S. S. Borges[†]

Departamento de Química Analítica e Físico-Química, Universidade Federal do Ceará,
Fortaleza-CE, Brazil

Celso U. Davanzo

Instituto de Química, Universidade Estadual de Campinas, Campinas-SP, Brazil

Eduardo E. Castellano and Julio Z-Schpector

Instituto de Física de São Carlos, Universidade de São Paulo, São Carlos-SP, Brazil

Sebastião C. Silva and Douglas W. Franco*

Instituto de Química de São Carlos, Universidade de São Paulo, Caixa Postal 780,
13560-970, São Carlos-SP, Brazil

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A new route was developed for preparing a series of trans nitrosyl complexes of general formula *trans*-$[Ru(NH_3)_4L(NO)](BF_4)_3$, where L = imidazole, L-histidine, pyridine, or nicotinamide. The complexes have been characterized by elemental analysis, molar conductance measurements, UV−visible, infrared, proton nuclear magnetic, and electron paramagnetic resonance spectroscopies, and electrochemical techniques. The compounds possess relatively high ν(NO) stretching frequencies indicating that a high degree of positive charge resides on the coordinated nitrosyl group. The nitrosyl complexes react with OH^- according to the equation *trans*-$[Ru(NH_3)_4L(NO)]^{3+} + 2OH^- \rightleftarrows$ *trans*-$[Ru(NH_3)_4L(NO_2)]^+ + H_2O$, with a K_{eq} (at 25.0 °C in 1.0 mol/L NaCl) of 2.2×10^5, 5.9×10^7, 9.7×10^{10}, and 4.6×10^{13} $L^2\ mol^{-2}$ for the py, nic, imN, and L-hist complexes, respectively. Only one redox process attributed to the reaction $[Ru^{II}(NH_3)_4L(NO^+)]^{3+} + e^- \rightleftarrows$ *trans*-$[Ru^{II}(NH_3)_4L(NO^0)]^{2+}$ was observed in the range −0.45 to 1.20 V for all the nitrosyl complexes. Linear correlations are observed in plots of ν(NO) versus $E_{1/2}$ and of $E_{1/2}$ versus $\sum E_L$ showing that the oxidizing strength of the coordinated NO increases with increase in L π-acidity. The crystal structure analysis of *trans*-$[Ru(NH_3)_4nicNO]_2(SiF_6)_3$ shows that the mean Ru−N−O angle is very close to 180° (177 ± 1°) and the mean N−O distance is 1.17 ± 0.02 Å, thus confirming the presence of the $Ru^{II}-NO^+$ moiety in the nitrosyl complexes studied.

Introduction

Nitric oxide is one of the most fascinating entities in technological and biological chemistry. The relevance of NO to environmental chemistry[1] and its behavior as a biological messenger in a wide range of physiological processes in humans and others animals[2] accounts for the renewed interest in understanding its basic chemistry.

Until now, most progress in this area has been achieved from studies using transition metal complexes.[3−5] For the design of complexes active in the catalytic decomposition[1,3,4] of NO to N_2 and O_2 or that act as a pharmaceutical agents[7−11] capable of releasing or removing NO in vivo, it is fundamental to understand how to control the nitric oxide reactivity.

In octahedral complexes the kinetic and thermodynamic reactivities of the axial ligand can be modulated[12] through the

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* To whom correspondence should be addressed.

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judicious choice of the ligand in the position trans to it. On the basis of the well-known affinity[13] of ruthenium centers for nitric oxide and taking advantage of the well-known properties of ruthenium ammines,[12a,13] a series of new complexes *trans*-$[Ru(NH_3)_4L(NO)]X_3$ have been isolated and their properties studied. The ligands L (imidazole, L-histidine, pyridine and isonicotinamide) have been selected to provide a monotonic change in the π and σ components of the Ru(II)−L and Ru(II)−NO bonds along the L−Ru(II)−NO axis.

Attempts were made to correlate the reactivity of the NO ligand with the characteristics of L.

Experimental Section

Chemicals and Reagents. Imidazole (imN), L-histidine (L-hist), nicotinamide (nic), pyridine (py), and all other chemicals were high-purity reagents (Aldrich or Merck) and were used as supplied. The solvents were purified according to the literature[14] just before use. Doubly distilled water was used throughout the experiments.

All preparations and measurements were carried out under an argon atmosphere, using standard techniques for manipulation of air-sensitive compounds.[15]

Apparatus. UV−visible spectra were recorded on a Hewlett-Packard diode array model 8452A spectrophotometer.

The IR spectra were obtained on a Bomem FTIR model MB-102 spectrometer in the 400−4000 cm^{-1}, range using solid samples pressed in KBr pellets or in aqueous solution using a silica window.

NMR spectra were recorded using a Bruker AC-200 instrument with D_2O (99.8%) as solvent and sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as internal standard.

The EPR experiments were recorded on a Bruker ESR 300E spectrometer at 25.0 and −170.0 °C.

Cyclic voltammograms were obtained with a polarographic analyzer/stripping voltammeter model 264 A from Princeton Applied Research attached to an IBM 486 microcomputer. Glassy carbon, saturated calomel (SCE), and platinum wire electrodes were used as working, reference, and auxiliary, respectively.

Differential pulse polarograms and cyclic voltammograms (between −0.50 and 1.20 V vs SCE) of deoxygenated solutions of *trans*-$[Ru(NH_3)_4L(NO)](BF_4)_3$, L = py, nic, imN, and L-hist, in 0.1 mol/L CH_3COOH/CH_3COONa and 0.1 mol/L CF_3COOH/CF_3COONa (pH 3.0−6.0) yielded only a one-electron reversible process[16] for all the nitrosyl complexes.

Syntheses of the Complexes. $[Ru(NH_3)_5Cl]Cl_2$,[17] *trans*-$[Ru(NH_3)_4SO_2Cl]Cl$,[18,19] and *trans*-$[Ru(NH_3)_4SO_4L]Cl$,[20] where L = imN or py, were prepared as described in the literature.

***trans*-[Ru(NH$_3$)$_4$SO$_4$L]Cl (L = nic, L-hist).** These new complexes were prepared by following the procedure described in ref 20.

***trans*-[Ru(NH$_3$)$_4$L(NO)](BF$_4$)$_3$ (L = imN, L-hist, or py).** *trans*-$[Ru(NH_3)_4SO_4L]Cl$ (100 mg) was dissolved in 3 mL of argon-degassed CF_3COOH pH 5.4 solution and reduced with zinc amalgam for 30 min (50 min for the pyridine complex) to generate the *trans*-$[Ru(NH_3)_4LH_2O]^{2+}$ ion. To this solution was added in the order 0.10 g of solid $NaNO_2$ and then 1.3 mL of argon-degassed 5 mol/L HBF_4. The resulting red-orange solution was allowed to stand in the argon stream for 1 h after which 100 mL of degassed ethanol was added to it. A very pale yellow product was obtained for the imidazole and L−histidine, complexes and a salmon solid, for the pyridine compound. The solid was collected by filtration, washed with ethanol, dried, and stored in a vacuum in the absence of light. The solid was purified as follows: A sample of *trans*-$[Ru(NH_3)_4L(NO)](BF_4)_3$ was dissolved in a minimum volume of 1.0 mol/L HBF_4, filtered, and reprecipitated by adding reagent grade ethanol. Yields were as high as 50%, 52%, and 38% for the imidazole, pyridine, and L-histidine complexes, respectively. Calcd for *trans*-$[Ru(NH_3)_4imN(NO)](BF_4)_3$: C, 6.82; H, 3.03; N, 18.58; Ru, 19.16. Found: C, 7.07; H, 3.07; N, 17.85; Ru, 18.88. Calcd for *trans*-$[Ru(NH_3)_4py(NO)](BF_4)_3$: C, 11.15; H, 3.18; N, 15.60; Ru 18.75. Found: C, 11.03; H, 3.19; N, 15.27; Ru, 18.39. Calcd for *trans*-$[Ru(NH_3)_4$L-hist$(NO)](BF_4)_3$: C, 11.71; H, 3.42; N, 18.22; Ru, 16.44. Found: C, 11.22; H, 3.54; N, 18.50; Ru, 16.12.

***trans*-[Ru(NH$_3$)$_4$nic(NO)](BF$_4$)$_3$.** The solid *trans*-$[Ru(NH_3)_4SO_4nic]Cl$ (100 mg) was added to 4 mL of argon-degassed CF_3COOH pH 5.4 solution and reduced with zinc amalgam for 30 min to generate the *trans*-$[Ru(NH_3)_4nicH_2O]^{2+}$ ion. The solution was transferred to a flask containing NO gas, generated by the addition of 0.10 g of $NaNO_2$ to 1.6 mL of argon-degassed 4.9 mol/L HBF_4. A pale orange color developed upon mixing the NO^+ and *trans*-$[Ru(NH_3)_4nicH_2O]^{2+}$ solutions. The solution was left in the stream of argon for 2 h and afterward in the refrigerator for 24 h. An orange crystalline solid was formed and collected by filtration, washed with ethanol, dried, and stored in a vacuum in the absence of light. The yield was as high as 42%. Anal. Calcd for *trans*-$[Ru(NH_3)_4nic(NO)](BF_4)_3$: C, 12.38; H, 3.09; N, 16.85; Ru, 17.38. Found: C, 11.96; H, 3.14; N, 16.78; Ru, 17.80.

***trans*-[Ru(NH$_3$)$_4$nic(NO$_2$)]BF$_4$.** *trans*-$[Ru(NH_3)_4nic(NO)](BF_4)_3$ (40 mg) was added to 1.0 mL of argon-degassed 1.0 mol/L NaOH. An intense red-orange color developed immediately. The solution was left in the argon stream for 5 min and afterward in a refrigerator for 30 min. A red-orange solid was formed and collected by filtration, washed with acetone, dried, and stored in a vacuum in the absence of light. The yield was as high as 52%. Anal. Calcd for *trans*-$[Ru(NH_3)_4nic(NO_2)]BF_4$: C, 16.98; H, 4.25; N, 23.11; Ru, 23.84. Found: C, 16.69; H, 4.36; N, 21.65; Ru, 24.80.

Determination of Ruthenium. This analysis was carried out by atomic absorption spectroscopy using the method of Rowston and Ottaway[21] modified by Clarke.[22]

Determination of the Equilibrium Constant. The determination of the equilibrium constant K_{eq} for the system

$$trans\text{-}[Ru(NH_3)_4L(NO)]^{3+} + 2OH^- \rightleftarrows trans\text{-}[Ru(NH_3)_4L(NO_2)]^+ + H_2O \quad (1)$$

$$L = \text{imN, nic, L-hist, py}$$

was carried out using the spectrophotometric method (absorbance measurements were performed at 360, 260, and 264 nm for the nic and py, ImN, and L-hist complexes, respectively) described by Albert and Serjeant.[23] The total ionic strength was kept at 1.0 with NaCl, according to similar studies reported for the Fe(II)[24] and Ru(II)[25] systems.

X-ray Crystallography. Crystals of *trans*-$[Ru(NH_3)_4nic(NO)]_2(SiF_6)_3{\cdot}2H_2O$ were obtained from an aqueous solution of *trans*-

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Table 1. Crystallographic and Data Collection Parameters for $C_{12}F_{18}H_{40}N_{14}O_6Ru_2Si_3$

chem formula	$C_{12}F_{18}H_{40}N_{14}O_6Ru_2Si_3$
fw	1104.93
space group	$P\bar{1}$, No. 2
a (Å)	13.074(2)
b (Å)	13.544(6)
c (Å)	22.240(7)
α (deg)	98.22(2)
β (deg)	101.04(2)
γ (deg)	105.54(2)
Z	4
V (Å^3)	3645(4)
T (K)	293
λ(Mo Kα) (Å)	0.710 73
d_{calcd} (g cm^{-3})	2.017
μ(Mo Kα) (cm^{-1})	105.03
R, wR	0.0873, 0.0984

$[Ru(NH_3)_4nic(NO)](BF_4)_3$ containing the impurity *trans*-$[Ru(NH_3)_4nic(NO)]_2(SiF_6)_3$ set aside at 25 °C for 1 month. The impurity originated in the synthesis from the reagent HBF_4, which contains SiF_6^{2-} (∼0.2%). The presence of SiF_6^{2-} as counterion in the crystals was also identified by infrared measurements. The IR spectrum showed bands at 743 and 484 cm^{-1}, assigned to SiF_6^{2-} anion,[26] and no band at 1070 cm^{-1} for the BF_4^- anion.

Crystal Data. An irregular crystal of maximum and minimum dimensions 0.65 and 0.15 mm was used for data collection. The unit cell was determined by least-squares refinement of diffraction angles obtained from 25 automatically centered reflections ($11 < \theta < 19°$). Crystal data are given in Table 1.

Data Collection and Processing. A CAD 4 diffractometer was used in the $\theta/2\theta$ scan mode with scan width = $0.8 + 0.35 \tan \theta$. Mo Kα graphite-monochromated radiation was used; 5427 reflections were measured ($0 < \theta < 30°$) of which 5404 were unique (merging R = 0.0179) and 4355 had $I > 3\sigma(I)$. Lorentz and polarization corrections were applied. At a later stage in the refinement, absorption corrections were applied[27] (maximum and minimum correction factors were 1.638 and 0.450 respectively). The intensity of one standard reflection was essentially constant throughout the experiment.

Structure Analysis and Refinement. The heavy-atom Patterson method followed by normal difference Fourier techniques were used. Blocked-matrix least-squares refinement was carried out with anisotropic thermal parameters for only the Ru and Si atoms. H atoms were not included in the model. The function minimized was $\sum w(|F_o| - |F_c|)^2$, with the weighting scheme $w = 1/[\sigma^2(F_o) + 0.0003F_o^2]$, which gave the final R $[=(|F_o|| - |F_c|)/ |F_o|]$ and w$R$$\{=[w(|F_o| - |F_c|)^2/w |F_o|^2]^{1/2}\}$ values of 0.0873 and 0.0984, respectively. Computer programs used were SHELX76[28] and ORTEP.[29] Scattering factors for non-H atoms were from Cromer and Mann[30] with corrections for anomalous dispersion from Cromer and Liberman.[31]

Results and Discussion

The nitrosyl salts, *trans*-$[Ru(NH_3)_4L(NO)](BF_4)_3$, dealt with in this study are soluble in water and insoluble in methanol, ethanol, acetone, nitromethane, acetonitrile, and dimethyl sulfoxide. Solid samples and acidic solutions (pH ≤ 4.5) of the complexes are stable in air for at least 1 month, as judged from their IR and UV−visible spectra.

The molar conductance measurements were carried out in aqueous solution at 25.0 °C ± 0.1 on the *trans*-$[Ru(NH_3)_4L(NO)](BF_4)_3$ system (L = imN, L-hist, py, and nic). The results (569, 585, 589 and 591 Ω^{-1} cm^2 mol^{-1} for the nicotinamide, imidazole, pyridine, and L-histidine complexes, respectively) are consistent with 3:1 type compounds.[32]

Electronic Spectra. Schreiner,[34] who has discussed the UV−visible bands for the *trans*-$[Ru(NH_3)_4(NO)X]^{2+}$ complexes X = NH_3, OAc^-, Cl^-, OH^-, NCO^-, N_3^-, and Br^-, observed, in general, three or four bands in this region. The first one was a broad band $^1A_1 \rightarrow {}^3\Gamma[^3T_1,{}^3T_2]$ and $t_2 \rightarrow \pi^*(NO)$ with $\epsilon < 60$ in the 420−480 nm region; also found were a band $[^1A_1 \rightarrow {}^1T_1]$ with $\epsilon < 300$ and intense charge-transfer bands assigned to $p\pi L \rightarrow (x^2 - y^2, z^2)$ Ru or $\pi L \rightarrow p^*L$ with $\epsilon > 10^3$ in the UV region.

The tentative band assignments for the nitrosyl complexes reported here were made in accordance with the Schreiner scheme[34] and are summarized in Table 2.

The higher energy bands, $\lambda_{max} < 240$ nm, cannot be unambiqously assigned since in this region of the spectrum many transitions (IL, LMCT) could occur.

On the basis of the spectrochemical series the d−d bands for *trans*-$[Ru(NH_3)_4L(NO)]^{3+}$, L = nicotinamide, pyridine, imidazole, and L-histidine, are expected to occur at higher energy than for $[Ru(NH_3)_5(NO)]^{3+}$, which shows spin−allowed d−d transition at 304 nm.[34] This was indeed observed for all the complexes studied here.

For the low-energy band, observed for all the complexes, an alternative interpretation to the mentioned Schreiner assignment[34] $^1A_1 \rightarrow {}^3\Gamma[^3\Gamma_1, {}^3\Gamma_2]$, $\pi^*(NO)$ could be considered, in which this absorption is assumed to be charge transfer in character. This last attribution would be consistent with the red shift exhibited by this band as the formal potential for the reduction of the coordinated nitric oxide becomes less negative (see Tables 2 and 4). Additional support for this assignment is provided from the light-induced excited-state studies[35] in these compounds. Upon irradiation of the *trans*-$[Ru(NH_3)_4L(NO)]X_3$ complexes in the lower energy bands, at the liquid-nitrogen temperature, the $\pi^*(NO)$ population is easily observed from the ∼120 cm^{-1} downshift in ν(NO). The above arguments suggest that this low-energy band could be assigned as a charge-transfer type transition:[58] $t_{2g} \rightarrow \pi^*(NO)$ or a ligand to ligand[36] (L →

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Table 2. UV–Visible Spectra of Ruthenium Complexes

complex	λ_{max} (nm)	ϵ (M^{-1} cm^{-1})
trans-$[Ru(NH_3)_4nicH_2O]^{2+}$ [a]	254	6.2×10^3
	426	6.6×10^3
trans-$[Ru(NH_3)_4L{-}histH_2O]^{2+}$ [a]	266	2.9×10^3
	282	2.8×10^3
trans-$[Ru(NH_3)_4nicNO](BF_4)_3$[b]	224[c]	9.4×10^3
	242, Ru(II) → L(Nic)	3.5×10^3
	272, $\pi \rightarrow \pi^*$(ligand)	2.5×10^3
	320, $^1A_1$ $^1T_1$	1.6×10^2
	485, $^1A_1$ $^3\Gamma_1$, π^*(NO), ($^1A_1$, L→ π^*(NO))[d]	2.3×10^1
trans-$[Ru(NH_3)_4pyNO](BF_4)_3$[b]	225[c]	6.7×10^3
	237, Ru(II) → L(py)	5.2×10^3
	267, $\pi \rightarrow \pi^*$(ligand)	2.3×10^3
	324, $^1A_1$ $^1T_1$	1.6×10^2
	474, $^1A_1 \rightarrow \Gamma_1$, π^*(NO), ($^1A_1$, L → π^*(NO))[d]	2.3×10^1
trans-$[Ru(NH_3)_4imNNO](BF_4)_3$[b]	221[c]	5.3×10^3
	234	4.1×10^3
	270, $^1A_1 \rightarrow {}^1T_1$	8.3×10^2
	324, $^1A_1 \rightarrow {}^1T_1$	6.6×10^2
	386, $^1A_1 - {}^3\Gamma_1$, π^*(NO), ($^1A_1$, L → π^*(NO))[d]	1.2×10^2
trans-$[Ru(NH_3)_4LhistNO](BF_4)_3$[b]	217[c]	6.6×10^3
	232	3.7×10^3
	274, $^1A_1 \rightarrow {}^1T_1$	5.9×10^2
	320, $^1A_1 - {}^1T_1$	4.1×10^2
	395, $^1A_1 \rightarrow {}^3\Gamma_1$, π^*(NO), ($^1A_1$, L → π^*(NO))[d]	8.1×10^1

[a] Spectra of the aquo ions were taken in a CF_3COOH pH 5.4 solution. [b] These spectra were taken in 0.1 mol/L CF_3COOH. [c] Doubtful values because of CF_3COOH absorbance. [d] Assuming charge-transfer character.

π^*(NO)) transition. The electronic spectra of *trans*-$[Ru(NH_3)_4L(NO)]X_3$ compounds will be discussed in detail in a forthcoming paper.[35]

X-ray Crystallography and Infrared Spectra. The *trans*-$[Ru(NH_3)_4nic(NO)]^{3+}$ cation crystallized as *trans*-$[Ru(NH_3)_4nic(NO)]_2(SiF_6)_3{\cdot}2H_2O$. A total of 4 complex ions, 12 counterions SiF_6^{2-}, and 8 molecules of water of crystallization were found in the asymmetric unit (Figure 1). The view of the isolated cation with the atom-numbering scheme is shown in Figure 2. The complex ions are nonequivalent presenting unequal distances and angles for chemically equivalent bonds. Selected interatomic distances, angles, and standard deviations are deposited as Supporting Information. For the ruthenium sites, consideration of intramolecular distances and angles shows significant deviation from idealized C_{4v} symmetry.

The four nonequivalent structures emerging from the X-ray diffration analysis have shown very interesting features, and in the subsequent discussion, we will show how carefully they must be treated.

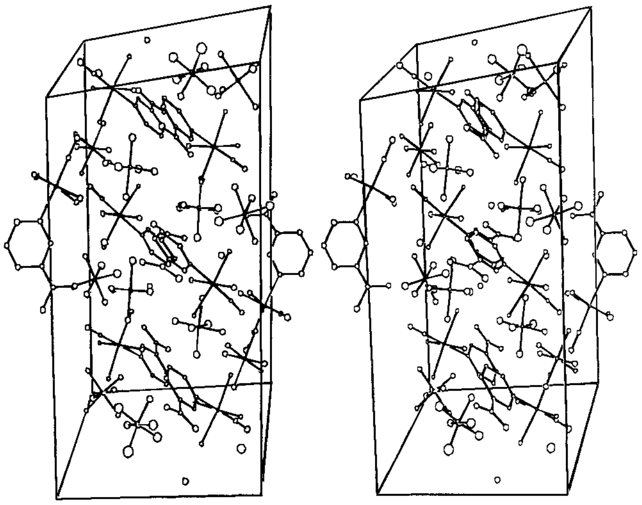

Figure 1. Stereoscopic view of the unit cell contents.

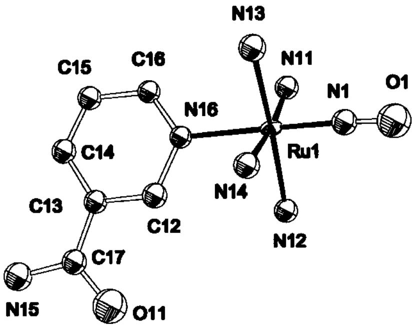

Figure 2. View of the *trans*-$[Ru(NH_3)_4nicNO]^{3+}$ cation.

The mean $Ru{-}NH_3$ distance of 2.10 ± 0.06 Å is similar to the values found for other nitrosylammineruthenium complexes such as $[Ru(NH_3)_5(NO)]Cl_3$[37] and *trans*-$[Ru(OH)(NH_3)_4(NO)]Cl_2$ (2.10 Å)[37] as well as for the ammineruthenium complexes of the type *cis*-$[Ru(NH_3)_4(isn)]ClO_4)_2$[38] and $[Ru(NH_3)_5pz](BF_4)_2$[39] (isn = isonicotinamide and pz = pyrazine). We do not attempt to comment on the differences with the literature

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Table 3. Infrared Spectra of *trans*-[Ru$(NH_3)_4$(NO)L]$(BF_4)_3$ (cm^{-1})[a]

L				
nicotinamide	pyridine	imidazole	L-histidine	assgnt
3340 s	3404 s	3230 s	3244 s	ν(NH) and ν(OH)
3240 s	3188 s	3130 s	3144 s	ν(CH)
1961 s[b]	1931 s	1923 s	1921 s	ν(NO)
1919 m				
1691 s			1734 m	ν(CO)
1609 m	1614 m, 1582 m	1610 m	1624 m	δ(NH), ring bands, δ(CH), and ν(C−N)
1396 m	1455 s		1520 w	
1364 m	1360 m	1343 s	1342 m	
1070 s	1089 s	1113 s	1113 s	$\nu(BF_4^-)$
856 m	874 w	862 m	866 w	$\rho(NH_3)$, ring bands, δ(CH), and δ(NH) out of plane
725 m	742 m	752 m	733 m	
625 w	619 m	620 m	615 m	ν(Ru−NO)
		597 m		
526 w	532 vw	522 vw		δ(Ru−NO)
482 m	484 w	484 w	480 w	$\nu(Ru-NH_3)$

[a] Abbreviations: s, strong; m, medium; vw, very weak; w, weak; sh, shoulder. [b] With the counterion SiF_6^{2-}, this complex exhibited the following ν(NO) frequencies: 1936 s, 1913 sh cm^{-1}.

Table 4. Electrochemical Data, ν(NO) Frequencies, and K_{eq} Values for Ruthenium Nitrosyl Complexes

complex	ΣE_L (V)[b]	$E_{1/2}$ (V)[a]	K_{eq}[d] (L^2 mol^{-2})	ν(NO)[a] (cm^{-1})
NO$^+$			2.3×10^{31} [e]	2220[e]
[Ru$(NH_3)_5$NO]$(PF_6)_3$[a]	0.35	−0.40		1913
trans-[Ru$(NH_3)_4$imNNO]$(BF_4)_3$	0.40	−0.36	9.7×10^{10}	1923
trans-[Ru$(NH_3)_4$L−histNO]$(BF_4)_3$[f]	0.40	−0.35	4.6×10^{13}	1921
trans-[Ru$(NH_3)_4$pyNO]$(BF_4)_3$	0.53	−0.23	2.2×10^5	1931
trans-[Ru$(NH_3)_4$isnNO]$(BF_4)_3$[f]	0.54	−0.19	2.5×10^8	1933
trans-[Ru$(NH_3)_4$nicNO]$(BF_4)_3$	0.54	−0.17	5.9×10^7	1940
trans-[Ru$(NH_3)_4$pzNO]$(BF_4)_3$[f]	0.51	−0.13	6×10^8	1942

[a] $E_{1/2}$ values are referred to the SCE in $CH_3COOH/NaCH_3COO$ or $CF_3COOH/NaCF_3COO$, pH ~ 4.0, $\mu = 0.1$ at 25.0 °C ± 0.1. The values of ν(NO) are for a KBr pellet. The estimated error in the potential measurements is ± 0.01 V and in the infrared data is ±4 cm^{-1}. [b] Calculated from ref 59. [c] The reported[53] $E_{1/2}$ value, in 0.10 M NaCl and pH 3−7 is −0.36 V. [d] Equilibrium constants for the reaction with hydroxide ion. [e] References 24 and 26. [f] Value of ref 60, connected to SCE.

values because the standard deviation of the mean value is quite large. The structures show distances from 2.16 Å (in the Ru (**1**)) to 1.91 Å (in the Ru (**4**)). We believe that very large interval (0.25 Å) reveals a difficulty inherent to the heavy metal atom method used to resolve the structure, which results in nonrealistic localization of the light atoms. We note for structures **1** and **4** mentioned above that the Ru−NH_3 distances are very different and the maximum and minimum values are found for opposite bonds. We will return to this point in the discussion of the Ru−NO bonds.

The mean Ru−NO distance is 1.71 ± 0.02 Å, which again is similar to the values found for the other nitrosyl compounds.[37] The mean N−O distance of 1.17 ± 0.02 Å is in the range of values found for other complexes. This distance and the mean Ru−NO angle of 177 ± 1°, very close to 180°, conclusively demonstrate that the compound contains a NO$^+$ ligand. These observed distances will be discussed along with the infrared results.

The IR frequencies of the trans nitrosyl complexes reported in this paper are given in Table 3 along with attempts at assignments based on the literature.[40−42] All the complexes show a strong band in the region of 1900 cm^{-1} ascribed to ν(NO). The values found, however, are higher than those observed for other trans and *cis*-nitrosylammine ruthenium complexes.[34,42] The relatively high infrared stretching frequencies for coordinated NO in these complexes indicate that a high degree of positive charge resides on the coordinated nitrosyl and therefore the complexes contain essentially ruthenium-(II).[40,43]

The free NO molecule, in the $\chi^2\ \pi_{1/2}$ fundamental state, has a ν(NO) for the $0 \rightarrow 1$ transition of 1876 cm^{-1}, and the equilibrium distance (r_e) is 1.15 Å.[44] Using an inverse relationship between ν(NO) and r_e, we can estimate the NO distance for other compounds. For the Na_2\{[Ru(NO)$(NO_2)_4$OH] complex, which had its structure established by neutron diffraction,[45] the ν(NO) frequency was observed at 1898 cm^{-1}, and using the inverse relation mentioned above, we can estimate the NO distance as 1.14 Å, which is very close to the value experimentally found (1.120−1.134 Å), especially if we consider the simplicity of our estimation.

The high ν(NO) frequency observed for our ruthenium compounds suggest that the actual NO distance is shorter than those found by X-ray diffraction. Further evidence arises from a close look at the distances in the four nonequivalent structures. We notice that the NO distances span a range of 1.14−1.20 Å, and if we apply the mentioned inverse relation, the ν(NO) frequency should occur at 1800−1890 cm^{-1} significantly below the frequency (1936−1913 cm^{-1}) observed for the nicotinamide compound.

Another intriguing observation comes from the results found for the four nonequivalent structures which show a range of NO distances of 0.06 Å. This value is about 5% of the NO distances; however, the observed distances for the Ru−NO fragment (sum of the Ru−N(O) and −NO distances) have a range of 2.86−2.89 Å, which span is only about 1%. From the 23 resolved[46] nitrosyl complexes structures, 19 show a distance for the Ru−NO fragment in the range of 2.86−2.89 Å. The values 2.82,[45] 2.94,[35] 2.97,[46] and 2.99 Å[47] were found once. The values 2.82 and 2.94 Å were admitted to be not accurate.[40,46] In contrast with this narrow range, we found in the literature[47] that the range for the NO distance is 1.07−1.18 Å, which is about 8% of the range.

The estimated NO distance from the ν(NO) frequency and the discrepancies observed for NO distances strongly suggest that the heavy metal atom method used to solve the X-ray structure does not easily localize the light nitrogen atom in the Ru−NO fragment.[48] The same difficulty applies to the N−Ru−N fragment (the angle being close 180°) as discussed earlier. In other words, when a structure is dominated by the heavy atom, the light atom positions must be treated cautiously.

The small range for the distances (2.86−2.89 Å) in the Ru−NO fragment can be explained by the largely accepted bonding model where the dominant factor is the strong back-bonding Ru → NO. Other ligands, especially equatorial and trans ligands capable of π interactions with d_{xz} and d_{yz} orbitals of ruthenium, act as a minor perturbation of the principal interaction.

The ν(NO) frequency should be a sensitive probe of the previously mentioned perturbation. However, the present work shows that the counterion is also an important factor in the determination of that frequency. The same nicotinamide complex has different frequencies (cm^{-1}) depending on the anion, BF_4^- (1961, 1919) or SiF_6^{2-} (1936, 1913). This has also been observed before for compounds of the type NO^+X^- where both anions produce a high ν(NO) frequency.[49]

The BF_4^- and SiF_6^{2-} nicotinamide complexes exhibit two ν(NO) bands in the solid state. As this splitting does not appear in water solution, the effect must be assigned to the solid state. The very complex unit cell found for the SiF_6^{2-} compound suggests a multiple site splitting for the observed IR frequencies.

Several trans-influence studies have been made in transition metal nitrosyl compounds using the NO stretching frequency as a probe.[39,42] An interpretation of the effect is that the ν(NO) decreases as the π-acceptor ability of L trans to NO decreases. According to the ν(NO) values shown in Table 4, the order of increasing π-electron donor ability is pyrazine < nicotinamide < isonicotinamide < pyridine < imidazole ∼L-histidine.

The nitrosyl complexes reported here are EPR silent even at the liquid-helium temperature.

The features of the proton NMR spectra of all complexes are consistent with the coordination of N−heterocyclic ligands to the metal center through the pyridine-type nitrogen.

The spectrum of the nicotinamide complex showed the following resonance shifts relative to the heterocyclic ligand: a singlet at 8.94 ppm assigned to the H_2 proton, a multiplet at 8.72 ppm assigned to the H_6 and H_4 protons; a double of doublets at 8.06 ppm assigned to the H_5 proton. It was observed that the H_2 and H_6 resonance peaks did not shift whereas the H_4 and H_5 exhibited both a downfield shift of $\Delta\delta = -0.48$ with respect to the free nicotinamide molecule. The pyridine complex showed a doublet at 8.53 ppm assigned to the H_2 and H_6 protons, a triplet at 8.38 ppm assigned to the H_4 proton, and a triplet at 7.93 ppm assigned to the H_3 and H_5 protons. The peak corresponding to the H_2 and H_6 protons did not shift whereas the two triplets corresponding to the H_4 and (H_3, H_5) protons suffered a downfield shift of $\Delta\delta = -0.52$ and -0.49, respectively, relative to the free pyridine spectrum. There is a proportionality between the change in the proton chemical shift and the change in electron density at the carbon atom to which it is bonded.[50] The proton chemical shifts at the *para* position correlate very well with π electron densities, while shifts at the *ortho* and *meta* positions do not appear to be simply dependent on the π electron density changes. Thus, the proton chemical shift at the *para* position has been used[50] to evaluate changes in π electron density. On this basis, the downfield or diamagnetic shift observed for the *para* position protons (also true for the *meta* protons) of the nicotinamide and pyridine complexes indicates a π electron deficiency on the rings, that is, a polarization of electron density toward the metal center.

The spectrum of the imidazole complex showed singlets at 8.36, 7.48, and 7.25 ppm assigned to the protons H_2, H_4, and H_5, respectively. All the three peaks showed a downfield shift of $\Delta\delta = -0.60$, -0.36, and -0.13 relative to the free imidazole. For the L-histidine complex, a singlet was observed at 8.32, a singlet at 7.17, a triplet at 4.13, and a doublet at 3.36 ppm assigned to the H_2, H_5, H_7, and H_6 protons, respectively; the peaks showed a downfield shift of $\Delta\delta = -0.59$, -0.14, -0.17, and -0.19 relative to the free ligand. The downfield shift observed for all the protons of the imidazole and L-histidine complexes suggests again a π electron deficiency on the rings.

A very noticeable fact is that no peak (sharp or broad) is observed for the N−H protons of the ammine ligands on *trans*-$[Ru(NH_3)_4nic(NO)]^{3+}$ and *trans*-$[Ru(NH_3)4py(NO)]^{3+}$ in D_2O in the 3.60−4.60 ppm region. The absence of the peaks for these complexes in D_2O (even in very concentrated solutions) suggests a rapid exchange of the ammine protons, as was observed[51] previously for $[Ru(NH_3)_5(NO)]^{3+}$. However, recording the NMR spectra of *trans*-$[Ru(NH_3)_4imN(NO)]^{3+}$ and *trans*-$[Ru(NH_3)_4L\text{-}hist(NO)]^{3+}$ in the same solvent, we noted a broad resonance at 4.60 ppm very close to the HOD resonance (4.80 ppm). This result suggests that, in these cases, the exchange of the ammine hydrogens is not as fast as in the former complexes.

Reactivity. According to the literature,[6] metal nitrosyl complexes exhibiting $\nu(NO) \geq 1886$ cm^{-1} are expected to undergo nucleophilic attack at the nitrosyl nitrogen. However, 1.0×10^{-3} M aqueous solutions of the complexes described here did not react with a 10-fold excess of N_3^-, N_2H_4, or $ON(CH_3)_3$ after 24 h of mixing the reagents. These tests were carried out in water, pH range 3−8, at 25 ± 2 °C, and with monitoring of the solutions using spectrophotometric and electrochemical techniques.

The nitrosyl complexes reported in this work reacted very rapidly in solution with hydroxide ion to give deep yellow solutions. The product of the reaction between *trans*-$[Ru(NH_3)_4nic(NO)]^{3+}$ and hydroxide ions, *trans*-$[Ru(NH_3)_4nic(NO_2)]BF_4$, was isolated (yield 52%) suggesting that the coordination sphere of the tetraammine complex ion remains unchanged up to 0.20 mol/L NaOH. Therefore, the deprotonation of an NH_3 ligand yielding NH_2^-, one of the strongest trans labilizing ligand known,[12c,d] producing the $[Ru(NH_2)(NH_3)_3nic(NO)]^{2+}$ species is unlikely to occur. For the other systems *trans*-$[Ru(NH_3)_4L(NO)]^{3+}$, where L = py, imN, or L-hist, we were until now unable to isolate the reaction products. Although these products have not been isolated, their UV−visible spectra are very similar to the *trans*-$[Ru(NH_3)_4nic(NO_2)]^+$ spectrum (386 nm, $\epsilon = 1.2 \times 10^4$ M^{-1} cm^{-1}; 256 nm, $\epsilon = 5.9 \times 10^3$ M^{-1} cm^{-1}) in the same medium (0.10 mol/L NaOH) suggesting also the nitro form as a result of the reaction between these nitrosyl complexes with the hydroxide ion. As judged from the electronic spectrum, reconversion to the nearly colorless nitrosyl complexes for the four systems occurs upon acidification of the solutions.

For alkaline solutions containing the $[Os(NH_3)_5(NO)]^{3+}$ or $[Ru(NH_3)_5(NO)]^{3+}$ complexes,[6] the NH_3 ligands behave as stronger acids than in the *trans*-$[Ru(NH_3)_4L(NO)]^{3+}$ complexes, and as a consequence, the formation of the amido species is facile.

It is surprising that $[Ru(NH_3)_5(NO)]^{3+}$ loses protons more readily than $[Ru(NH_3)_4L(NO)]^{3+}$, L = π acid ligand (pz, nic, and py). In these complexes there is an electron-withdrawing effect of L added to that of NO^+, and as a consequence, an enhancing on the NH_3 proton acidity is expected.

As pointed out earlier in this paper (X-ray Crystallography and Infrared Spectra section), the mean Ru−NH_3 distances for *trans*-$[Ru(NH_3)_4L(NO)]X_3$ complexes are in the 2.10 ± 0.06 Å range. Therefore the X-ray data are not so helpful in understanding the influences of L over the NH_3 ligands in the complexes described here. However, in the same complex some tendencies can be observed.

In the $[Ru(NH_3)_5(NO)]^{3+}$ complex ion,[37] the Ru−NH$_3$ distance (Å) or the axial ligand is shorter (2.047) than for the equatorial ones (2.10 ± 0.02). These data would suggest the proton in the axial NH$_3$ ligand to be more acidic than the equatorial ones. Thus it is likely that in the $[Ru(NH_3)_5(NO)]^{3+}$ ions the imido species would be formed only by the trans NH$_3$ ligand deprotonation, which does not occurs when L is a heterocyclic ligand. The NO$^+$ fragment effect over the trans ligand acidity is clearly illustrated in the case of the *trans*-$[Ru(NH_3)_4(H_2O)(NO)]^{3+}$ ion. In this last complex the aquo ligand, despite being coordinated to a formally Ru(II) center, exhibits[5e] a pK_a of 3.1 more acidic than in $[Ru(NH_3)_5(H_2O)]^{3+}$ (pK_a = 4.2).[12a,b]

The calculated values for the equilibrium constants, K_{eq}, for reaction 1 were measured spectrophotometrically at 25.0 °C ± 0.1. The measured values for K_{eq} were 2.2×10^5, 5.9×10^7, 9.7×10^{10}, and 4.6×10^{13} L^2 mol^{-2} for the pyridine, nicotinamide, imidazole, and L-histidine complexes, respectively; see Table 4. For the same equilibrium the following K_{eq} values are reported in the literature: for[24] $[Fe(CN)_5(NO)]^{2-}$, 1.5×10^6 L^2 mol^{-2}; for[25] $[Ru(bipy)Cl(NO)]^{2+}$, 1.6×10^9 L^2 mol^{-2}. Unfortunately, the comparison of the $[Ru(NH_3)_4L]^{2+}$, $[Ru(bipy)_2Cl]^+$, and $[Fe(CN)_5]^{3-}$ moieties π-donor capabilities toward NO and their influence on K_{eq} are not straightforward, being indeed questionable[12] due to the different environments for the metal centers.

Only one redox couple was observed in the voltammetric spectra of the solutions containing *trans*-$[Ru(NH_3)_4L(NO)](BF_4)_3$ salts in the range −0.45 to +1.2 V, thus suggesting the ruthenium center to be only electroactive at potentials more positive than +1.2 V. Molecular orbital analysis using the density functional theory (DFT) shows[35] that in *trans*-$[Ru(NH_3)_4L(NO)]^{2+}$, L = py and pz, the HOMO is a π orbital located mainly on the NO ligand. Therefore, in accordance with literature data for other nitrosyl complexes,[52−55] it is reasonable to assume that the site of this reduction is localized[52−55] on the nitrosyl group and the reaction can be represented as

$$\textit{trans}\text{-}[(NH_3)_4LRu^{II}(NO^+)]^{3+} + e^- \rightleftarrows \textit{trans}\text{-}[(NH_3)_4LRu^{II}(NO)]^{2+} \quad (2)$$

where L = nic, imN, py, or L-hist.

The $E_{1/2}$ for the electrochemical reduction of the NO ligand shifts to more positive potential as the π acidity of L increases. The substitution of the trans NH$_3$ molecule in $[Ru(NH_3)_5(NO)]^{3+}$ by pz destabilizes the NO$^+$ ligand with respect to the coordinate NO^0 of 0.25 V (see Table 4).

The electrochemical data at 25.0 °C indicate that *trans*-$[Ru(NH_3)_4nic(NO)]^{3+}$ and *trans*-$[Ru(NH_3)_4py(NO)]^{3+}$ can be reduced in a one-electron step and that the product has a limited stability, because at slow scan rate (0.05 V/s) the current of the anodic wave was diminished and broadened. However, the anodic wave was well defined, even at slow scan rate ($v < 0.020$ V/s) when the experiment was carried out at 3.0 °C. At 3.0 °C and scan rates ≥ 0.05 V/s the electrochemical electron-transfer process displays a reversible behavior.

trans-$[Ru(NH_3)_4LNO]^{3+}$, L = pz and nic, is chemically reduced by Eu(II) ions in 1:1 stoichiometric amounts. After the reaction the process attributed to the coordinated NO$^+$/NO^0 couple is absent in the solution voltammograms, but the Ru(III)/Ru(II) couple in the *trans*-$[Ru(NH_3)_4L(H_2O)]^{2+}$ is easily identified (L = pz, $E_{1/2} \cong 0.065$ V; L = nic, $E_{1/2} \cong -10$ V). Furthermore for the resulting solution, an electrochemical anodic wave at $E_{pa} \cong 0.76 \pm 0.03$ V can be observed, which has been attributed to the free NO oxidation.[12]

These observations are corroborated by electronic spectral data. After the reduction with Eu(II), the solutions originally containing *trans*-$[Ru(NH_3)_4L(NO)]^{3+}$ exhibit the spectral characteristics of the *trans*-$[Ru(NH_3)_4L(H_2O)]^{2+}$ ions (L = py, λ_{max} = 331 nm, $\epsilon = 3.1 \times 10^3$ M^{-1} cm^{-1}; L = nic, λ_{max} = 426 nm, $\epsilon = 6.6 \times 10^3$ M^{-1} cm^{-1}). Therefore, as far as electronic and voltammetric spectra are concerned, the ions *trans*-$[Ru(NH_3)_4L(NO)]^{3+}$ (L = py and nic) after one-electron reduction exhibited nitric oxide dissociation with the formation of the aquo species, *trans*-$[Ru(NH_3)_4L(H_2O)]^{2+}$.

A plot of ν(NO) vs $E_{1/2}$, for the series of nitrosyl complexes presented in Table 4, yields a straight line defined by the equation $\nu(NO) = 1954 + 96.1E_{1/2}$, with a correlation coefficient of 0.98. This direct relation was expected since both parameters are dependent on electronic characteristics of the nitrosyl group.[53,57,58] The oxidizing strength of NO$^+$ is related to the extent of the $d\pi \rightarrow \pi^*$(NO) interaction: as the donation increases, the electron content at NO increases, decreasing its oxidizing strength.[53] This linear correlation suggests that changes in electron density at NO (measured by $E_{1/2}$) are proportional to the $d\pi \rightarrow \pi^*$ (NO) donation. Therefore, the ν(NO) frequency could be useful as a measure[6,53] of the relative oxidizing strength of the NO group. For the series of complexes shown here, the highest oxidizing strength of the coordinated NO is observed for the pyrazine complex.

In a series of nitrosyl complexes, the net π-donor ability of ligands, except NO, can be quantified by the sum of Lever's electrochemical parameters[59] (which places each ligand ion in an electrochemical series) for the non-nitrosyl ligands. The sum of these parameters, $\sum E_L$, will correlate with the reduction potential of NO, E_{red} or $E_{1/2}$, for a given nitrosyl complex[10b,60−61]

$$E_{1/2} = S_L \sum E_L(L) + I_L$$

For the series of nitrosyl complexes presented in Table 4, we observed[61] a good linear correlation between the $E_{1/2}$ values versus $\sum_L \sum E_L$ defining the straight line[61,62] $E_{1/2} = -0.78 + 1.09\sum E_L$ with a correlation coefficient of 0.99.

Since $E_{1/2}$ for the coordinated NO$^+$/NO redox couple is a linear function of $\sum E_L$, the above correlation would express the tendency of the nitric oxide ligand to be reduced[10b] and accordingly the tendency of the metallonitrosyl complex, activated by reduction, to release NO.

According to Lever's $\sum E_L$ rules,[10b,59,60] for a series of related compounds, $\sum E_L$ would be related to the *trans*-$[Ru(NH_3)_4L]^{2+}$ moiety's ability to back-bond to NO. An increase in $\sum E_L$ would be associated with an increase in the nitrosonium character of the coordinated NO. Following the above reasoning, the extension of the Ru(II) → NO back-bonding for the complexes of Table 4 will decrease as function of L according to NH$_3$ > L-hist ~ imN > py > isn > nic > pz. This sequence is consistent with the series of π-electron donor ability of L deduced on basis of the ν(NO) data and previously discussed in this paper.

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(62) For the compounds of Table 4 plus the complexes listed in the ref 59 ($(Ru(NO)(bpy)_2(NO_2)]^{2+}$, $[Ru(NO)(bpy)_2(NH_3)]^{3+}$, $[Ru(NO)(bpy)_2(trpy)]^{3+}$, $[Ru(NO)(bpy)_2py]^{3+}$, and $[Ru(NO)(bpy)_2(CH_3CN)]^{2+}$) we obtain: $E_{1/2} = -0.72 + 0.95\sum E_L$; $R = 0.997$.

The $\sum E_L$ values have also been suggested[10b,60] as useful to predict the relative tendency of the coordinated nitric oxide to undergo nucleophilic attack. The K_{eq} data for the reaction with OH^- have been proposed as an straightforward way to compare[6] the relative electrophilicity of coordinated nitric oxide in various complexes. For the complexes of Table 4, K_{eq} decreases as L-hist < imN < pz < isn< nic < py, exhibiting a change of 2.0×10^8 orders of magnitude when L changes from L-hist to py. According to the $\sum E_L$ values and the ν(NO) data, we would expect the reverse order with the pz derivative exhibiting the highest K_{eq} value.

Probably the nitro species thermodynamic stability, which is included[6] in K_{eq}, is an important term to be considered. The remarkable stability exhibited by the *trans*-$[Ru(NH_3)_4L(NO_2)]^+$ in alkaline media is a good indicator of the nitro species relevance in the *trans*-$[Ru(NH_3)_4L(NO)]^{3+}$/*trans*-$[Ru(NH_3)_4L(NO_2)]^+$ equilibrium. This subject is now under investigation at our laboratory, and the results will be published later.

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Supporting Information Available: Tables of positional and thermal parameters and interatomic distances and angles around the Ru atoms (11 pages). Ordering information is given on any current masthead page.

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