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# Water $\pi$-Donation in *trans*-Tetraammineruthenium(II): Effect on Coordinated-Water Properties Induced by a Trans NO Ligand

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The complex *trans*-$[Ru(NH_3)_4NO(H_2O)]Cl_3{\cdot}H_2O$ has been isolated as a decomposition product of the dimeric cation $[\{Ru(NH_3)_4NO\}_2(\mu\text{-}S_2)]^{6+}$. The elemental analysis and electronic, infrared, X-ray, and ESR spectroscopies fit well with the formulation *trans*-$[Ru(NH_3)_4NO(H_2O)]Cl_3{\cdot}H_2O$. The $\nu_{NO}$ (1912 cm$^{-1}$) observed and the $\angle(Ru{-}N{-}O) = 178.1°(5)$ are consistent with the nitrosonium character of the NO ligand. Cyclic voltammetry showed only one redox process in the range $-0.5$ to $+1.2$ V, which was attributed to the reaction *trans*-$[(H_2O)(NH_3)_4Ru^{II}(NO^+)]^{3+} + e^- \leftrightarrow$ *trans*-$[(H_2O)(NH_3)_4Ru^{II}(NO^0)]^{2+}$. The p$K_a$ values $3.1 \pm 0.1$ and $7.7 \pm 0.1$ ($\mu = 0.10$ M, NaCl) have been measured for the reaction *trans*-$[Ru(NH_3)_4L(H_2O)]^{n+} + H_2O \leftrightarrow$ *trans*-$[Ru(NH_3)_4L(OH)]^{(n-1)+} + H_3O^+$, where L = $NO^+$ and CO, respectively. The substitution of the coordinated water molecule in *trans*-$[Ru(NH_3)_4(H_2O)NO]^{3+}$ by chloride ions proceeds about 30-fold times slower than in $[Ru(NH_3)_5(H_2O)]^{3+}$ ($k_{Cl^-} = 8.7 \times 10^{-5}$ M$^{-1}$ s$^{-1}$ and $3.7 \times 10^{-6}$ M$^{-1}$ s$^{-1}$, respectively; 40 °C, $\mu = 2.0$ NaCl, $[H^+] = 1.0 \times 10^{-2}$ mol L$^{-1}$). Quantum mechanical DFT calculations show that the mixing between the lone pair of the oxygen, $\pi$ in character, and the $d_{xz}$ orbital of the metal is linearly related to the p$K_a$ of the water ligand and to the water lability. The calculations have also shown that the $\pi{-}d$ mixing is strongly dependent on the trans ligand L. The electronic spectra of the *trans*-$[Ru(NH_3)_4(H_2O)L]^{n+}$ (L = CO and $NO^+$) species are discussed on the basis of DFT and ZINDO/S calculations.

## Introduction

It is well-known that the presence of the NO ligand strongly affects the metal center and the coordination sphere ligand's properties. Then, there is a growing concern over our understanding of how the NO and the ligand in the position trans to it influence one another in their chemical behavior. This knowledge would help us to understand how to control the properties of coordination compounds and therefore tailor complex ions to a desired target.

For such a purpose, the *trans*-$[Ru(NH_3)_4(H_2O)(NO)]^{3+}$ complex is of particular interest. This complex[1] has not been isolated and properly characterized as a solid before, despite the fact that its conjugate base, *trans*-$[Ru(OH)(NH_3)_4(NO)]^{2+}$, has been adequately described in the literature.[2,3]

This paper describes the synthesis, characterization, and properties of the *trans*-$[Ru(NH_3)_4(H_2O)(NO)]Cl_3{\cdot}H_2O$ compound. A comparison is made with the isoelectronic complex *trans*-$[Ru(NH_3)_4(H_2O)(CO)]^{2+}$. The analysis of the $L{-}Ru{-}OH_2$ bonds and their influence on the water molecule acidity and chemical behavior in the *trans*-$[Ru(NH_3)_4(H_2O)(NO)]^{3+}$, $[Ru(NH_3)_4(H_2O)(CO)]^{2+}$, and related complexes was also done on the basis of quantum chemical DFT (density functional theory) calculations. Electronic spectra for these complexes were also analyzed on the basis of ZINDO/S calculations performed on optimized DFT structures.

## Experimental Section

All preparations and measurements were carried out under an inert atmosphere (argon or nitrogen), using standard techniques.[4] During the experiments the temperature was controlled within ±0.2 °C using a Superhom thermostat.

**Reagents and Materials.** All chemicals were reagent grade (Aldrich or Merck) and were used without further purification. The solvents were purified as described in the literature;[5] 18 MΩ Milli-Q or doubly

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[†] This paper dedicated in memorian to our master, colleague and friend Waldemar Saffioti and is the main part of the Ph.D. Thesis of this author to be presented at the Instituto de Química de São Carlos, Universidade de São Paulo. Permanent address: Departamento de Química, Universidade Federal do Maranhão.

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distilled water was used throughout the experiments. Ruthenium trichloride ($RuCl_3 \cdot 3H_2O$) was the starting material for the syntheses of the ruthenium complexes. The ion exchange resin employed was Bio Rad AG-50W X8 (200−400 mesh), in the sodium ion form. Sodium trifluoroacetate (Aldrich) was used as the background electrolyte for the ionic strength control.

**Syntheses.** The complexes $[RuCl(NH_3)_5]Cl_2$,[6] *trans*-$[RuCl(NH_3)_4(SO_2)]Cl$,[7,8] *trans*-$[RuCl_2(NH_3)_4]Cl$,[9] *trans*-$[Ru(NH_3)_4(H_2O)(CO)]Br_2$,[10] $[Ru(NH_3)_5NO]Cl_3$,[11] *trans*-$[Ru(OH)(NH_3)_4(NO)]Cl_2$,[11] *trans*-$[Ru(SO_3)(NH_3)_4(NO)]Cl$,[12] and *trans*-$[\{Ru(NH_3)_4NO\}_2(\mu\text{-}S_2)]Cl_6 \cdot H_2O$[13] were synthesized and characterized following published procedures.

***trans*-$[Ru(NH_3)_4(H_2O)(NO)]Cl_3$.** This compound was isolated during the preparation of $[(NO)(NH_3)_4RuSSRu(NH_3)_4(NO)]Cl_6 \cdot H_2O$.[13] The latter compound was obtained by reduction of *trans*-$[Ru(SO)_3(NH_3)_4(NO)]Cl$ (0.3 g) (∼1 mmol) with zinc amalgam, in acidic medium (10 mL of 0.05 mol $L^{-1}$ HCl) and under an argon atmosphere. After 10 min, the mixture was filtered in a glovebag and charged onto a cation exchange column (Bio Rad AG-50W X8, sodium ion form). The resin was successively eluted with 0.2, 0.8, 1.5, 2.5, 4.0, and 6.0 mol $L^{-1}$ HCl. From the 1.5 to 6.0 mol $L^{-1}$ HCl eluate a yellow solution was then collected and concentrated by rotary evaporation to $^1/_{10}$ of the original volume. The resulting solution was left to cool in a refrigerator for 24 h. A solid precipitated, which was separated by filtration and washed with ethyl alcohol. Yield = 40%. Anal. Calcd for *trans*-$[Ru(NH_3)_4(H_2O)(NO)]Cl_3 \cdot H_2O$: H, 4.7; N, 20.5; Ru, 29.6; Cl, 31.1. Found: H, 4.4; N, 19.8; Ru, 28.8; Cl, 30.9. Relevant infrared absorption bands,[14] $cm^{-1}$: 3240 br s [$\nu_{NH}$, $\nu_{OH}$], 1912 s [$\nu_{NO}$], 1637 m [$\delta_{OH}$, $\delta_{dNH}$], 1325 m [$\delta_{sNH}$], 959 w [$\nu_{Ru-OH2}$], 845 m [$\rho(NH_3)$, $\delta(NH)_{\text{out of plane}}$], 614 w [$\nu_{M-NO}$], 570 w [$\delta_{Ru-NO}$], and 481 w [$\nu_{M-NH3}$], where br = broad, s = strong, m = medium, and w = weak.

The *trans*-$[Ru(NH_3)_4(H_2O)NO]^{3+}$ can also be obtained from the treatment of *trans*-$[Ru(HO)(NH_3)_4NO]^{2+}$ with concentrated $CF_3SO_3H$ (8 mol $L^{-1}$).

**Instrumentation.** The elemental analyses were carried out at the Instituto de Química da Universidade de São Paulo. The ruthenium analysis was performed according to the method of Rowston and Ottaway,[15] modified by Clarke,[16] using a Polarized Zeeman atomic absorption spectrophotometer, Hitachi (model Z-8100).

UV−visible measurements were performed in a 1.0 cm quartz cell on a Hewlett-Packard diode array model 8452A spectrophotometer. IR spectra were recorded on a Bomem FTIR, model MB-102, spectrophotometer in the 300−4000 $cm^{-1}$ range, in KBr pellets and by diffuse reflectance. ESR experiments were carried out on a Bruker ESR 300E spectrometer, at the liquid $N_2$ temperature.

A polarographic analyzer/stripping voltammeter model 264A from Princeton Applied Research attached to a microcomputer employing Microquímica eletrochemical software was used for the electrochemical measurements. The electrochemical cell used was a conventional three-electrode type with an aqueous saturated calomel electrode (SCE) as a reference electrode and glassy-carbon and platinum wire as working and auxiliary electrodes, respectively.

**Table 1.** Crystallographic Data for *trans*-$[Ru(NH_3)_4(H_2O)NO]Cl_3 \cdot H_2O$

| | |
|---|---|
| formula | $[Ru(NH_3)_4(H_2O)NO]Cl_3 \cdot H_2O$ |
| fw | 341.59 |
| space group | monoclinic, $P2_1/c$ |
| $a$ (Å) | 6.6293(6) |
| $b$ (Å) | 14.982(1) |
| $c$ (Å) | 11.526 (1) |
| $\beta$ (deg) | 99.904(8) |
| $Z$ | 4 |
| $V$ (Å$^3$) | 1127.7(2) |
| $\lambda$(Mo Kα) (Å) | 0.710 73 |
| $\rho$ (g·cm$^{-3}$) | 2.012 |
| $R$; $R_w$ | 0.039; 0.047 |

The acidity of the coordinated water molecule in *trans*-$[Ru(NH_3)_4(H_2O)L]^{n+}$ ($L = NO^+$, CO) was determined by potentiometric titration[17] with (0.01 M) NaOH solution. For $L = NO^+$, a potentiometric titration of *trans*-$[Ru(OH)(NH_3)_4(NO)]^{2+}$ with (0.01 M) HCl solution, $\mu = 0.10$ mol $L^{-1}$, was also performed. All measurements were run in triplicate using compounds from different preparations.

All of the kinetic anations were followed using a Hewlett-Packard diode array model 8452A recording spectrophotometer. Temperatures of the experiments were fixed to 40.5 ± 0.5 °C and controlled by a thermostated Tecnal TE 184 temperature bath. *trans*-$[Ru(NH_3)_4NO(H_2O)]^{3+}$ and $[Ru(NH_3)_5(H_2O)]^{3+}$ solutions were prepared by dissolving the respective solids in degassed 2.0 mol $L^{-1}$ chloride solutions (1.0 $\times 10^{-2}$ mol $L^{-1}$ $CF_3COOH$, $\mu = 2.0$) and quickly transferred to a quartz 1 cm spectrophotometric cell which was glass-sealed.

Crystals of *trans*-$[Ru(NH_3)_4(H_2O)(NO)]Cl_3 \cdot H_2O$ for X-ray diffraction were obtained from an aqueous solution of 6.0 mol $L^{-1}$ HCl kept in a refrigerator for 48 h. A crystal of this compound was mounted in the Enraf-Nonius CAD4 diffractometer, at 243 K, and, using 25 reflections automatically centered, the cell parameters were obtained and refined. Table 1 shows the data collection and refinement conditions. The intensity data were reduced to $F_o$ and corrected by absorption factors $\mu$ (KαMo = 20.7 $cm^{-1}$) by the PSISCAN method.[18]

The structure was solved by Patterson function and difference Fourier synthesis and refined by full-matrix least squares.[18] The hydrogen water atoms were found in the DF map, and the others are located in their ideal positions and not refined, using $d(N-H) = 0.960$ Å and thermal vibration equal to 4.0 Å$^2$. All non-hydrogen atoms were refined anisotropically, and the atomic scattering factors were those from Cromer and Mann[19] with anomalous dispersion from Cromer and Liberman,[20] and for the hydrogen atoms from Stewart et al.[21]

The quantum chemical calculations were carried out at the ab initio level, using the B3LYP DFT method and 3-21G as the basis set, both standard in the quantum chemistry computational package GAUSSIAN-94.[22] The simulated electronic spectra were obtained by configuration interaction (CI) at the semiempirical level and at the DFT optimized geometry, using the ZINDO/S method from the HyperChem4.5 package.[23]

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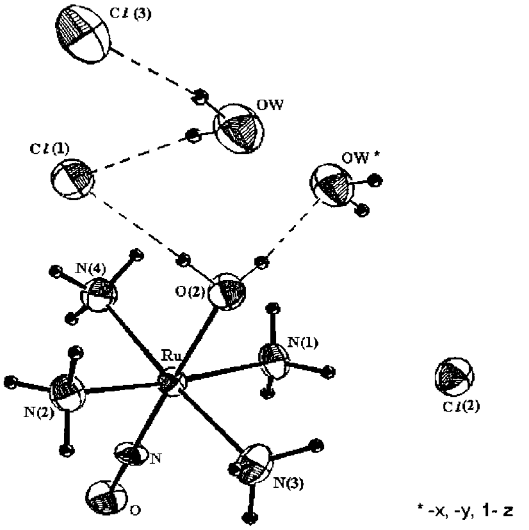

**Figure 1.** ORTEP representation with 50% of probability for $[Ru(NH_3)_4(H_2O)NO]Cl_3{\cdot}H_2O$.

**Table 2.** Observed and Calculated Interatomic Distances (Å) for Some *trans*-$[M(NH_3)_4(L)(L')]^{n+}$ Ions

| L′ | L | M | M−L′ | M−L | O−H | ref |
|---|---|---|---|---|---|---|
| $H_2O$ | $NH_3$ | Ru(II) | 2.189 | 2.172 | 0.990 | this work |
| $H_2O$ | $NH_3$ | Ru(III) | 2.096 | 2.158 | 0.997 | this work |
| $H_2O$ | CO | Ru(II) | 2.214 | 1.859 | 0.991 | this work |
| $H_2O$ | $NO^+$ | Ru(II) | 2.112 | 1.793 | 0.997 | this work |
| $H_2O$ | $NO^+$ | Tc(I) | 2.209 | 1.756 | 0.991 | this work |
| $H_2O$ | $NO^+$ | Tc(II) | 2.159 | 1.811 | 0.997 | this work |
| $H_2O$ | $NO^{+\,a}$ | Ru(II) | 2.035(5) | 1.715(5) | | this work |
| $NH_3$ | pz | Ru(II) | | 2.006(6) | | 25h |
| $NH_3$ | pz | Ru(III) | | 2.076(8) | | 25h |
| $NH_3$ | Mepz | Ru(II) | | 1.95(1) | | 25k |
| $NH_3$ | Mepz | Ru(III) | | 2.08(1) | | 25k |

[a] Values of structural data; pz = pyrazine; Mepz = 1-methylpyrazinium.

## Results and Discussion

**Molecular and Crystal Structure.** Table 1 shows some of the X-ray data for *trans*-$[Ru(NH_3)_4(H_2O)(NO)]Cl_3$, and Figure 1 displays the ORTEP[24] view with the atom labeling scheme. Table 2 shows relevant observed and calculated interatomic distances for this and related complexes.

The X-ray data for *trans*-$[Ru(NH_3)_4(H_2O)(NO)]Cl_3{\cdot}H_2O$ indicate only a minor distortion from an idealized $C_{4v}$ symmetry. This distortion is smaller than those seen for the *trans*-$[Ru(OH)(NH_3)_4(NO)]Cl_2$ and $[Ru(NH_3)_5(NO)]Cl_3$ complexes.[3b] The Ru−N−O angle in the aqua complex is 178.1(5)°, very close to the reported values for *trans*-$[Ru(OH)(NH_3)_4(NO)]Cl_2$ (173.8(3)°)[3b] and $[Ru(NH_3)_5(NO)]Cl_3$ (172.8 (9)°)[3b]. These data are in agreement with the observed $\nu_{NO}$ (1912 $cm^{-1}$) and the fact that the *trans*-$[Ru(NH_3)_4(H_2O)(NO)]Cl_3{\cdot}H_2O$ is ESR silent, thus, strongly suggesting the nitrosonium character of the NO ligand in this complex. The X-ray bond lengths for $Ru-NH_3$ are 2.093(5), 2.093(6), 2.099(5), and 2.107(5) Å, respectively, for N(1), N(2), N(3), and N(4).

The Ru−NO bond length in *trans*-$[Ru(NH_3)_4(H_2O)(NO)]Cl_3{\cdot}H_2O$ is quite short, 1.715(5) Å, and is close to the reported values for the similar bond in *trans*-$[Ru(OH)(NH_3)_4(NO)]Cl_2$ (1.735(3) Å)[3b] and $Ru(NH_3)_5NO]Cl_3$ (1.770(9) Å),[3b] but much smaller than the $Ru-NH_3$ distance in several Ru(II) and Ru(III) ammine complexes, which is in the 2.1 ± 0.1 Å range.[3b,7,25a−p] This short distance in the nitrosyl complexes is consistent with the strong Ru(II)−NO $d_\pi \rightarrow \pi^*$NO back-bonding. The shorter Ru−N(azine or diazine) interatomic distances for the Ru(II) compared with the respective Ru(III) complexes in ruthenium ammines with such $\pi$-acceptor ligands is explained as a result of this back-bonding in Ru(II), such as illustrated by the $[Ru^{II}(NH_3)_5(pz)](BF_4)_2/[Ru^{III}(NH_3)_5(pz)](CF_3SO_3)_3{\cdot}H_2O$ (2.006 Å for Ru(II) and 2.076 Å for Ru(III))[25h] and $[Ru^{II}(NH_3)_5(mpz)]I_3/[Ru^{III}(NH_3)_5(mpz)](tos)_4{\cdot}5H_2O$ (mpz = 1-methylpyrazinium; tos = tosylate (*p*-toluenesulfonate) (1.95 Å for Ru(II) and 2.08 Å for Ru(III)) complexes.[25k] It is noteworthy that in the 1-methylpyrazinium−Ru(II) complex a Ru(mpz) double bond was suggested to occur.[25g] Thus, on the basis of interatomic distances, the Ru−NO bonds in the above nitrosyl complexes is shorter than expected for a double bond. The N−O distance in *trans*-$[Ru(NH_3)_4(H_2O)(NO)]Cl_3{\cdot}H_2O$ is 1.142(7) Å, similar to the distance reported for *trans*-$[Ru(OH)(NH_3)_4(NO)]Cl_2$ (1.159(5) Å)[3b] and $[Ru(NH_3)_5(NO)]Cl_3$ (1.172(14) Å)[3b]. These short NO interatomic distances are consistent with a $NO^+$ fragment with an unfilled $\pi^*$ MO and also consistent with the observed NO stretching frequency values ($\nu_{NO}$) of 1912 and 1850[2b] $cm^{-1}$ for the aqua and hydroxo compounds, respectively.

As expected, the ruthenium−oxygen distance in the Ru−OH fragment of the hydroxotetraammine species, 1.961(3) Å,[3b] is shorter than that observed for the ruthenium−oxygen distance $Ru-OH_2$ in *trans*-$[Ru(NH_3)_4(H_2O)(NO)]Cl_3$ (2.035(5) Å).

**Electrochemical Properties.** Only one monoelectronic redox process was observed in the range −0.5 to +1.2 V vs SCE for *trans*-$[Ru(NH_3)_4(H_2O)(NO)]^{3+}$, which has been attributed to the electron transfer process at the NO ligand. The observed $E_{1/2}$ value ($(E_{1/2})_{NO^+/NO^0} = -0.39 \pm 0.01$ V vs SCE) is in good agreement with the expected one (−0.43 V)[25a] on the basis of the empirical correlation $\nu_{NO}$ versus $E_{1/2}$ observed for the tetraamminenitrosylruthenium analogues.[26a] As observed for other nitrosyl ruthenium−ammine complexes,[12,26] the ruthenium(II) center is not electroactive in the potential range mentioned above. The $NO^+ + e^- \rightarrow NO^0$ electron transfer is reversible, followed by a chemical reaction in which the $NO^0$ ligand undergoes an aquation reaction to yield *trans*-$[Ru(NH_3)_4(H_2O)_2]^{2+}$. The formation of this latter species was confirmed by the spectrophotometric detection of *trans*-$[Ru(NH_3)_4(pz)_2]^{2+}$

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**Table 3.** p$K_a$ Values at 25 °C for the *trans*-$[M(NH_3)_4L(L'H)]^{n+}$ + $H_2O$ ↔ *trans*-$[M(NH_3)_4L(L')]^{(n-1)+}$ + $H_3O^+$ Reaction and Metal−Oxygen π-Interaction Percentage

| L′H | L($M^{n+}$) | p$K_a$ | % interaction ($d_{xz}$ and $p_x$ orbitals) |
|---|---|---|---|
| $H_2O$ | $NH_3(Ru^{III})$ | $4.1 \pm 0.1^{a-c}$ | $11.8^d$ |
| $H_2O$ | $NH_3(Ru^{II})$ | $13.1 \pm 0.1^{a,b}$ | $>1.5^d$ |
| $H_2O$ | $NH_3(Os^{III})$ | $5.2^e$ | |
| $H_2O$ | $NH_3(Os^{II})$ | $\approx 12^f$ | |
| $H_2O$ | $isn(Ru^{II})$ | $11.7 \pm 0.1^g$ | |
| $H_2O$ | $CO(Ru^{II})$ | $7.7 \pm 0.1^d$ | $5.7^d$ |
| $H_2O$ | $NO(Ru^{II})$ | $3.1 \pm 0.1^d$ | $11.7^d$ |
| $H_2O$ | $NO(Tc^{II})$ | $2.0^h$ | $12.1^d$ |
| $H_2O$ | $NO(Tc^{I})$ | $7.3^h$ | $4.6^d$ |
| pzH | $NH_3(Ru^{II})$ | $2.5^a$ | |
| pzH | $NH_3(Ru^{III})$ | $-0.8\ (-2.5)^{a,i}$ | |
| pzH | $(py)(Ru^{II})$ | $2.0^j$ | |
| pzH | $(pz)(Ru^{II})$ | $1.5^j$ | |
| pzH | $(pzH)(Ru^{II})$ | $-0.6\ (-1.4)^{i,j}$ | |

[a] Reference 27. [b] Reference 31. [c] Also reported as 3.7 ± 0.1. (Eliades, T.; Harris, R.; Reinsalu, P. *Can. J. Chem.* **1969**, *47*, 3823.) [d] Present work. [e] Gulens, J.; Gage, J. A. *Elec. Anal. Chem. Int. Elec.* **1974**, *55*, 239. Recently the p$K_a$ value for $[Os(NH_3)_5(H_2O)]^{3+}$ was revised and the value found was 4.85 (Shi, A. A.; Anson, F. C. *Inorg. Chem.* **1997**, *36*, 2682). [f] Estimated value due to instability of the solution of the Os(II) aquo pentaamine. [g] Reference 27. [h] Reference 14. [i] Corrected p$K_a$ value using $H_0$ rather than $-\log$ [HX]. [j] Reference 27b.

upon reduction of ($1.0 \times 10^{-3}$ M) *trans*-$[Ru(NH_3)_4(H_2O)(NO)]^{3+}$ with Cd(Hg) followed by addition of pyrazine (1 M).

The observed electrochemical behavior for the aqua nitrosyl ion is consistent with that described for other *trans*-$[Ru(NH_3)_4(NO)L]^{3+}$ complexes[12,26] and can be explained by the scheme

$$trans\text{-}[Ru(NH_3)_4(H_2O)(NO)]^{3+} + e^- \xrightarrow{\text{fast}} trans\text{-}[Ru(NH_3)_4(H_2O)(NO)]^{2+} \quad (1)$$

$$trans\text{-}[Ru(NH_3)_4(H_2O)(NO)]^{2+} + H_2O \xrightarrow{\text{slow}} trans\text{-}[Ru(NH_3)_4(H_2O)_2]^{2+} + NO \quad (2)$$

**Protonation Equilibria.** The p$K_a$'s for the reaction

$$trans\text{-}[Ru(NH_3)_4(H_2O)L]^{3+} + H_2O \leftrightarrow trans\text{-}[Ru(OH)(NH_3)_4L]^{2+} + H_3O^+ \quad (3)$$

was calculated from potentiometric titrations, as 3.1 ± 0.1 (L = $NO^+$) and 7.7 ± 0.1 (L = CO), respectively.

The acidity of a ligand in a complex is influenced by the nature of the trans ligand. This is illustrated by the p$K_a$ changes of the coordinated pyrazine in the *trans*-tetraammine(pyrazinium)ruthenium complexes with different *trans*-L ligands ($NH_3$, py, pz, $pzH^+$)[27] (see Table 3). In these complexes, the p$K_a$ order decreases as increases the acidity of the trans ligand L, $NH_3$ > py > pz > $pzH^+$. This order is consistent with both the increasing π-acceptor and decreasing σ-donor strengths of the ligand, which did not allow a proper evaluation of the individual contribution of each factor.[27b,c] Examination of Table 3 shows that the p$K_a$ of *trans*-$[Ru(NH_3)_4(H_2O)(CO)]^{2+}$ (7.7) is smaller than those of the isonicotinamide derivative, *trans*-$[Ru(NH_3)_4(H_2O)(isn)]^{2+}$ (11.7),[28] and $[Ru(NH_3)_5(H_2O)]^{2+}$ (13.1).[28] This decrease is consistent with the higher π-acceptor and smaller σ-donor strength of CO compared with those of ammonia and isonicotinamide. Changing the trans ammonia ligand to $NO^+$, in $[Ru(NH_3)_5(H_2O)]^{2+}$, results in a dramatic decrease in the $H_2O$ ligand p$K_a$ of 10 orders of magnitude (13.1 for $NH_3$ and 3.1 for $NO^+$). The nitrosyl is considered to have a lower σ-donor and a higher π-acceptor strength than the isoelectronic CO,[29] resulting in, as an overall effect, a higher electron acceptor strength for nitrosyl.[29] This effect is such that the p$K_a$ for the water ligand in the Ru(II) complex *trans*-$[Ru(NH_3)_4(H_2O)(NO)]^{3+}$ (3.1) is even lower than that in the Ru(III) complex $[Ru(NH_3)_5(H_2O)]^{3+}$ (4.1),[30] which in turn is 9 orders of magnitude lower than that in its Ru(II) homologue $[Ru(NH_3)_5(H_2O)]^{2+}$ (p$K_a$ of the 13.1).[28] Thus, replacing $NH_3$ for $NO^+$ would turn the Ru(II) fragment even harder than Ru(III) in $[Ru(NH_3)_5(H_2O)]^{3+}$. As a matter of fact, this high water acidity had been anticipated earlier for these NO and CO complexes by Taube.[31]

In addition, the strong influence of the NO on the acidity of the trans ligand is also observed in the *trans*-$[Ru(NH_3)_4(pz)(NO)]^{3+}$ complex. While the p$K_a$ value for $[Ru(NH_3)_5(pzH)]^{3+}$ is 2.5,[27a] the *trans*-$[Ru(NH_3)_4(pz)(NO)]^{3+}$ species, as far as the electronic spectrum is concerned, does not undergo protonation[13] even in 2.0 mol $L^{-1}$ HCl. This observation suggests that pz in *trans*-$[Ru(NH_3)_4NO(pz)]^{3+}$ exhibits an acidity higher than that for *trans*-$[Ru(NH_3)_4(pz)(py)]^{2+}$, *trans*-$[Ru(NH_3)_4(pz)(pzH)]^{3+}$, *trans*-$[Ru(NH_3)_4(pzH)(pzH)]^{4+}$, and $[Ru(NH_3)_5(pzH)]^{4+}$ (see Table 3).

The presence of the nitrosyl ligand seems also to exercise a large effect upon the coordinated water lability and the affinity of the Ru(II) center to π-acid ligands. Indeed, as far as the voltammetric and electronic spectra are concerned, no formation of *trans*-$[Ru(NH_3)_4(NO)(pz)]^{3+}$ was observed when the *trans*-$[Ru(NH_3)_4(H_2O)(NO)]^{3+}$ complex was left in the presence of 1.0 M pz (100 times the stoichiometric amount), after 48 h of standing (40 °C, pH 1.5 KCl/HCl). This observation is quite interesting considering that pz substitutes $H_2O$ in $[Ru(NH_3)_5(H_2O)]^{2+}$ at the specific second-order rate constant of $5.6 \times 10^{-2}$ $M^{-1}$ $s^{-1}$ and the affinity of pz for the *trans*-$[Ru(NH_3)_5(H_2O)]^{2+}$ moiety was calculated[31] as $10^{12}$ $M^{-1}$.

Another example of the remarkable reduction of the water ligand lability comes from the experiments using $Cl^-$ as an entering ligand on $[Ru(NH_3)_5(H_2O)]^{3+}$ and on *trans*-$[Ru(NH_3)_4(H_2O)(NO)]^{3+}$. The replacement of the water molecule by $Cl^-$ in the pentaammine species ($k_{Cl^-} = 8.7 \times 10^{-5}$ $M^{-1}$ $s^{-1}$) takes place 30-fold times faster (2.0 $mol^{-1}$ L NaCl, 0.01 $mol^{-1}$ L $CF_3COOH$ and at 40.0 ± 0.5 °C) than in *trans*-$[Ru(NH_3)_4(H_2O)(NO)]^{3+}$ ($k_{Cl^-} = 3.7 \times 10^{-6}$ M $s^{-1}$), for the same experimental conditions. Similar to what was observed in the comparison of p$K_a$ values, the delabilizing effect of NO upon the trans water ligand and on the affinity of the Ru(II) for π-acid ligands is dramatic and higher than expected on the basis of the one unit increase in the metal center charge.

The above observations are also consistent with the reported relative substitution inertness of chloride in acidic medium in *trans*-$[RuCl(NH_3)_4(NO)]^{2+}$ [2k] and with our results[32] from a related study on the dimer *trans*-$[\{Ru(NH_3)_4(NO)\}_2(\mu\text{-}Cl)]^{5+}$. Despite the well-known low affinity[1d] of the $[Ru(NH_3)_5]^{2+}$ center for $Cl^-$, the chloride bridge in this complex is quite strong, indicative of the high Ru(II) center σ acidic character in such compounds. Aqueous solutions (pH ∼3) of *trans*-$[\{Ru(NH_3)_4$-

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**Table 4.** DFT Energy Levels ($cm^{-1}$) and Symbolic Representation for Some *trans*-$[M(NH_3)_4(L)(L')]^{n+}$ Ions

| orbitals | symbol | energy |
|---|---|---|
| $[Ru(NH_3)_5(H_2O)]^{2+}$ | | |
| $d_{x^2-y^2}$ | $\psi_{10}$ | −50 555.2 |
| $d_{z^2}$ | $\psi_9$ | −53 072.7 |
| 5p | $\psi_8$ | −54 558.6 |
| 5p | $\psi_7$ | −55 759.1 |
| 5p | $\psi_6$ | −57 021.2 |
| 5s (LUMO) | $\psi_5$ | −64 569.1 |
| $d_{xz}$ (HOMO) | $\psi_4$ | −94 605.1 |
| $d_{xy}$ | $\psi_3$ | −95 368.9 |
| $d_{yz}$ | $\psi_2$ | −96 069.0 |
| $p_x(H_2O)$ | $\psi_1$ | −135 727.1 |
| $[Ru(NH_3)_5(H_2O)]^{3+}$ α | | |
| 5s | $\psi_7$ | −99 047.4 |
| $d_{x^2-y^2}$ | $\psi_6$ | −111 467.8 |
| $d_{z^2}$ (LUMO) | $\psi_5$ | −115 938.6 |
| $d_{xy}$ (HOMO) | $\psi_4$ | −160 120.1 |
| $d_{yz}$ | $\psi_3$ | −161 151.7 |
| $d_{xz} - p_x(H_2O)$ | $\psi_2$ | −166 226.1 |
| $d_{xz} + p_x(H_2O)$ | $\psi_1$ | −184 368.4 |
| $[Ru(NH_3)_5(H_2O)]^{3+}$ $\beta$ | | |
| 5s | $\psi_7$ | −98 988.1 |
| $d_{x^2-y^2}$ | $\psi_6$ | −108 046.1 |
| $d_{z^2}$ | $\psi_5$ | −113 263.2 |
| $d_{xz}$ (LUMO) | $\psi_4$ | −131 945.4 |
| $d_{xy}$ (HOMO) | $\psi_3$ | −156 525.1 |
| $d_{yz}$ | $\psi_2$ | −157 547.8 |
| $p_x(H_2O)$ | $\psi_1$ | −181 278.1 |
| *trans*-$[Ru(NH_3)_4CO(H_2O)]^{2+}$ | | |
| $\pi_{py}$*CO | $\psi_9$ | −62 135.1 |
| $\pi_{px}$*CO | $\psi_8$ | −63 043.7 |
| $d_{x^2-y^2}$ | $\psi_7$ | −64 751.3 |
| $d_{z^2}$ | $\psi_6$ | −66 735.4 |
| 5s (LUMO) | $\psi_5$ | −67 417.9 |
| $d_{xy}$ (HOMO) | $\psi_4$ | −111 412.9 |
| $d_{xz} + \pi_{px}{*}CO - p_x(H_2O)$ | $\psi_3$ | −114 812.7 |
| $d_{yz} + \pi_{py}{*}CO$ | $\psi_2$ | −116 070.3 |
| $d_{xz} + \pi_{px}{*}CO + p_x(H_2O)$ | $\psi_1$ | −142 329.0 |
| *tert*-$[Ru(NH_3)_4NO(H_2O)]^{3+}$ | | |
| 5s | $\psi_9$ | −100 498.2 |
| $d_{x^2-y^2}$ | $\psi_8$ | −117 488.2 |
| $d_{z^2}$ | $\psi_7$ | −120 697.0 |
| $d_{yz} - \pi_{py}{*}NO$ | $\psi_6$ | −130 951.1 |
| $d_{xz} - \pi_{px}{*}NO$ (LUMO) | $\psi_5$ | −131 554.7 |
| $d_{xy}$ (HOMO) | $\psi_4$ | −166 362.2 |
| $d_{xz} + \pi_{px}{*}NO - p_x(H_2O)$ | $\psi_3$ | −171 146.9 |
| $d_{yz} + \pi_{py}{*}NO$ | $\psi_2$ | −174 030.9 |
| $d_{xz} + \pi_{px}{*}NO + p_x(OH_2)$ | $\psi_1$ | −186 220.9 |

$(NO)\}_2(\mu\text{-}Cl)]Cl_5$ are stable for more than 48 h, but, with the addition of Eu(II), the $NO^+$ ligand is reduced to $NO^0$ and the dimer readily decomposes, according to

$$[\{Ru(NH_3)_4(NO)\}_2(\mu\text{-}Cl)]^{5+} + 2Eu^{II} + 2H_2O \rightarrow 2\ trans\text{-}[Ru(NH_3)_4(H_2O)_2]^{2+} + Cl^- + 2Eu^{III} + 2NO \quad (4)$$

as indicated by UV−vis, cyclic voltammetry, and conductometric chloride ion titration experiments.[32]

**Molecular Orbital Calculations and Electronic Spectra.** Table 4 shows the calculated DFT MO energy levels for the *trans*-$[Ru(NH_3)_4(H_2O)(NO)]^{3+}$, *trans*-$[Ru(NH_3)_4(H_2O)(CO)]^{2+}$, $[Ru(NH_3)_5(H_2O)]^{2+}$, and $[Ru(NH_3)_5(H_2O)]^{3+}$ complexes. Figure 2 shows schematic MO diagrams for the $NO^+$ and CO complexes, under $C_{2v}$ symmetry. The $z$ axis is coincident with the $C_2$ symmetry axis in these complexes. The CO and the nitrosyl species each have two $\pi$* orbitals of appropriate energies and symmetry to combine with two $d_\pi$ Ru(II) orbitals, $d_{xz}$ and $d_{yz}$. For the hydroxo complexes with these two trans ligands, the oxygen center has also two $\pi$* orbitals, parallel to the $x$ and $y$ axes, available for combination with the $d_{xz}$ and $d_{yz}$ Ru orbitals and with the $\pi$* CO and nitrosyl orbitals, forming in this case six MO's involving L−Ru−OH. In its turn, the trans $\pi$-donor $H_2O$ has a lone pair of $\pi$ symmetry (assumed parallel to the $x$ axis), which is able to combine with the $d_{xz}$ metal orbital. The combination of these orbitals leads, for the aqua complexes, to a five molecular orbital set rather than six as for the hydroxo. Also a $d_\pi$ orbital splitting is observed.

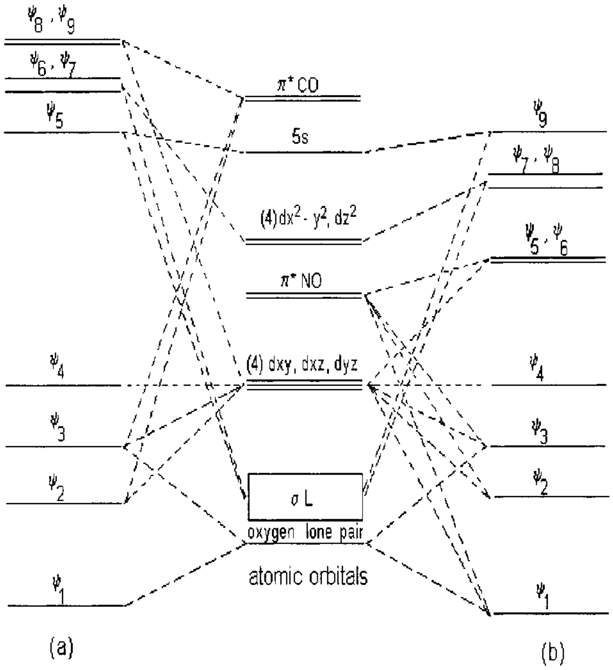

**Figure 2.** Relevant molecular orbitals and qualitative energy level scheme for (a) *trans*-$[Ru(NH_3)_4CO(H_2O)]Cl_2$ and (b) *trans*-$[Ru(NH_3)_4NO(H_2O)]Cl_3$.

The sets of five MO's in the CO and $NO^+$ aqua complexes comprise the $\psi_1$, $\psi_2$, $\psi_3$, $\psi_8$, and $\psi_9$ orbitals for CO and the $\psi_1$, $\psi_2$, $\psi_3$, $\psi_5$, and $\psi_6$ orbitals for $NO^+$. For both complexes, as can be seen in Figure 2, the HOMO orbital, $\psi_4$ (Ru $d_{xy}$), is nonbonding in character. All other five remaining orbitals ($\psi_1$, $\psi_2$, $\psi_3$, $\psi_8$, and $\psi_9$ orbitals for CO and $\psi_1$, $\psi_2$, $\psi_3$, $\psi_5$, and $\psi_6$ orbitals for $NO^+$) have a contribution from either $p_y-\pi^*$ or $p_x-\pi^*$ CO or NO orbitals, while only $\psi_1$, $\psi_3$, and $\psi_8$ (for the CO complex) and $\psi_1$, $\psi_3$, and $\psi_5$ (for the NO complex) have a contribution from the water oxygen $p_x\pi$ orbital, since the MO involving the $yz$ components would be nonbonding with respect to Ru−O. So, this set of five orbitals involves a combination of the Ru $d_{yz}$ orbital with the CO or NO $p_y-\pi^*$ orbital, resulting in one bonding and one antibonding molecular orbital ($\psi_2$ and $\psi_9$ for CO, and $\psi_2$ and $\psi_6$ for $NO^+$), the first one ($\psi_2$) giving rise to the back-bonding stabilization energy (bbse). The $d_{xz}$ orbital would give rise to a similar orthogonal set of orbitals with the same energies if there were not a water trans to NO or CO. The presence of the water oxygen $\pi$ orbital results in three extended three-centered molecular orbitals ($\psi_1$, $\psi_3$, and $\psi_8$ for CO; $\psi_1$, $\psi_3$, and $\psi_5$ for $NO^+$), derived from the combination of the following orbitals: Ru $d_{xz}$, CO or NO $p_x-\pi^*$, and the water O orbital of $\pi$ symmetry oriented through the $x$ axis. The completely bonding, lowest energy MO ($\psi_1$), for both complexes, would be close in energy to the water O orbital, from which it has the major contribution (52%). The next one, $\psi_2$, for both complexes has a contribution from the $d_{yz}$ orbital and the CO or NO $p_y-\pi^*$ orbitals. The bonding $\psi_3$ orbitals have a greater contribution from the $d_{xz}$ orbital (65%). In the absence

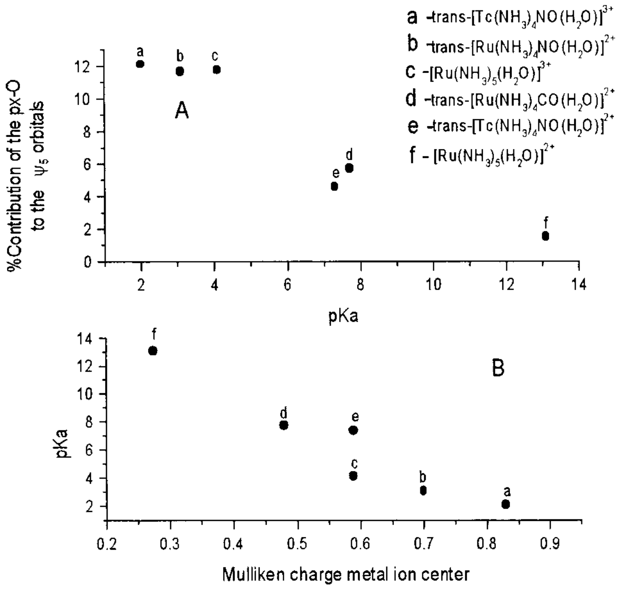

**Figure 3.** Correlation between p$K_a$ and (a) percentage of the $\pi$-oxygen orbital to the $\psi_3$ orbital and (b) calculated Mulliken charge on the metal centers.

of the O orbital, the $d_{xz}$ orbital would have the same energy as the above-described bonding orbital with the $d_{yz}$ orbital, $\psi_2$; the $\psi_3$ orbitals are higher in energy given the O orbital contribution (5.7% and 11.7% for CO and $NO^+$, respectively). In fact, considering that $H_2O$ is not a $\pi$-acceptor (and, thus, does not contribute to a higher back-bonding), but rather a $\pi$-donor,[33] although poor, its presence would lead to an increase in the energy. Actually, the strong trans L $\pi$-acceptor ability, which "hardens" the Ru(II) core, would favor the $H_2O$ $\pi$-donation. The third orbital ($\psi_8$ for CO and $\psi_5$ for $NO^+$) is antibonding with respect to Ru−L and Ru−O and has a higher contribution from the L $p_z$−$\pi^*$ orbital. For $[Ru(NH_3)_5(H_2O)]^{2+}$ and $[Ru(NH_3)_5(H_2O)]^{3+}$, the presence of the saturated trans $NH_3$ ligands results in a set of two MO's derived from the combination of a $d_{xz}$ orbital with the water O $\pi$-donor orbital, with a much lower $d_{xz}$ contribution to the bonding orbital in the Ru(II) complex, and a higher one in Ru(III), as a result of the charge and increased $\pi$-acceptor ability of the metal center. Removal of one electron from $[Ru(NH_3)_5(H_2O)]^{2+}$ results in $[Ru(NH_3)_5(H_2O)]^{3+}$, with the $d_{xy}$ orbital as the monoelectronic HOMO orbital. This removal breaks up the degeneracy of the $\alpha$ (spin up) and $\beta$ (spin down) forms, as shown in Table 4. The empty $\beta$-form $d_{xz}$ orbital is moved to high energy, and the mixing between the O $p_x$ orbital and the metal $d_{xz}$ orbital occurs only for the $\alpha$-form $d_{xz}$ orbital.

The contributions of the water oxygen orbital of $\pi$ symmetry to the $\psi_3$ orbital are 1.5%, 5.7%, and 11.7%, for *trans*-L = $NH_3$, CO, and $NO^+$, respectively, and 11.8% for $[Ru(NH_3)_5(H_2O)]^{3+}$. Noteworthy also is a close correlation between these values and the p$K_a$ values of these complexes (see Table 3). In fact, this means that, as the water O orbital contribution increases, the charge density on the water O decreases, resulting in a lower p$K_a$. This can be easily seen by plotting the p$K_a$ values vs the calculated charge on the metal center (Figure 3). This can be regarded as a rather reasonable correlation if we consider the experimental uncertainties and peculiarities of the theoretical model.[34] It should be noted that, although displaying close values, the p$K_a$'s and the calculated Mulliken charge on the metal center of $[Ru(NH_3)_5(H_2O)]^{3+}$ and *trans*-$[Ru(NH_3)_4(H_2O)(NO)]^{3+}$ also follow that trend. In addition to the above considerations, in the aqua complexes the lowest energy orbital, $\psi_1$, involving the metal $d_{xz}$ and the oxygen orbital of $\pi$ symmetry strengthens the Ru−O bond and, consequently, weakens the O−H bonds, thus decreasing the p$K_a$.

Important differences between the molecular orbital levels of the *trans*-$[Ru(NH_3)_4(H_2O)(NO)]^{3+}$ and *trans*-$[Ru(NH_3)_4(H_2O)(CO)]^{2+}$ complexes are found for the MO's from $\psi_5$ to $\psi_9$. The CO complex $\psi_8$ and $\psi_9$ orbitals correspond to the NO complex $\psi_5$ and $\psi_6$ orbitals, respectively. The energies of the NO $\psi_7$ and $\psi_8$ orbitals are closer in energy to the Ru(II) $d_{xy}$ nonbonding orbital, $\psi_6$, whereas the CO $\psi_8$ and $\psi_9$ orbitals are higher. The energies of $\psi_8$ and $\psi_9$ for the CO complex are, respectively, $\sim -63\,000$ and $\cong -62\,100$ $cm^{-1}$, respectively differing by $\sim 48\,400$ and $\sim 49\,300$ $cm^{-1}$ from the energy of the LUMO $\psi_7$ orbital. The energies of $\psi_7$ and $\psi_8$ for the NO complex are, respectively, $\sim -131\,500$ and $\sim -131\,000$ $cm^{-1}$, and their respective gaps $\psi_7 - \psi_6$ and $\psi_7 - \psi_8$ are respectively $\sim 34\,800$ and $\cong 35\,400$ $cm^{-1}$. The NO complex $\psi_7$ and $\psi_8$ orbitals are lower in energy than the $d_\pi$ orbitals of $t_{2g}$ parentage, namely, $\psi_9$ and $\psi_{10}$. For the CO complex it should be pointed out that $\psi_{10}$ and $\psi_{11}$ are the highest in energy, and, noteworthily, the LUMO orbital, $\psi_7$, is essentially 5s (more than 90%) in character, while the LUMO for the nitrosyl complex, $\psi_7$, would have a contribution from the NO ligand $p_x$−$\pi^*$ orbital (~73%). These features should be reflected in some of the complexes' properties.

The nature of the combinations results in some interesting features. The NO complex $\psi_5$ and $\psi_6$ orbitals have a rather large $d_\pi$ contribution (~27%), while the corresponding $\psi_8$ and $\psi_9$ orbitals for the CO complex have 13.9% of $d_\pi$ contribution. Accordingly, transitions to these levels would have more metal to ligand charge transfer (MLCT) character in the carbonyl than in the nitrosyl complex.

**Electronic Spectra.** The electronic spectrum of the *trans*-$[Ru(NH_3)_4(H_2O)(NO)]^{3+}$ ion in solution is shown in Figure 4. This spectrum shows some similarities to the spectra of other *trans*-tetraamminenitrosyl complexes (*trans*-$[Ru(NH_3)_4(NO)L]^{n+}$ (L = $NH_3$, $OAc^-$ (acetate), $Cl^-$, $OH^-$, $NCO^-$, $N_3$- or $Br^-$;[2k] L = isn, pz, $SO_3{}^{2-}$, or $NO_2{}^-$;[12] L = imN (imidazole), L-hist (L-hystidine), py (pyridine), or nic (nicotinamide);[26a] and L = $P(OEt)_3$) (triethyl phosphite)). These complexes usually display at least three or four absorption bands in the UV−vis range, depending on the nature of the ligand trans to NO. The spectral assignments for these complexes (L = isn, pz, $SO_3{}^{2-}$, or $NO_2{}^-$;[12] L = $P(OEt)_3$);[26b] and L = imN, L-hist, py, or nic[26a]) were made using Schreiner's assignments[2k] for L = $NH_3$, $OAc^-$, $Cl^-$, $OH^-$, $NCO^-$, $N_3{}^-$, or $Br^-$. These complexes display a very weak and broad absorption band in the 400−500 nm range. A very weak and broad absorption band ($\lambda_{max} = 426$, $\epsilon = 45$ $mol^{-1}$ L $cm^{-1}$) is also observed in the electronic spectrum of the *trans*-$[Ru(NH_3)_4(H_2O)(NO)]^{3+}$ ion. These low-energy bands for the former complexes were assigned[2k] as a mixture of two transitions: one ligand-field (LF) spin-forbidden (${}^1A_1 \rightarrow {}^3\Gamma_1$) and one charge transfer process [$t_{2g} \rightarrow \pi^*(NO)$], which would be a metal to ligand charge transfer (MLCT). The assignment of the absorption band at 426 nm in the spectrum of *trans*-$[Ru(NH_3)_4(H_2O)(NO)]^{3+}$ as a one charge transfer process [$t_{2g} \rightarrow \pi^*(NO)$], regardless of spin considerations, does not agree with the MO's described above for the *trans*-$[Ru(NH_3)_4(H_2O)(NO)]^{3+}$ complex. According to our calculations, for this aqua complex, both $\psi_5$

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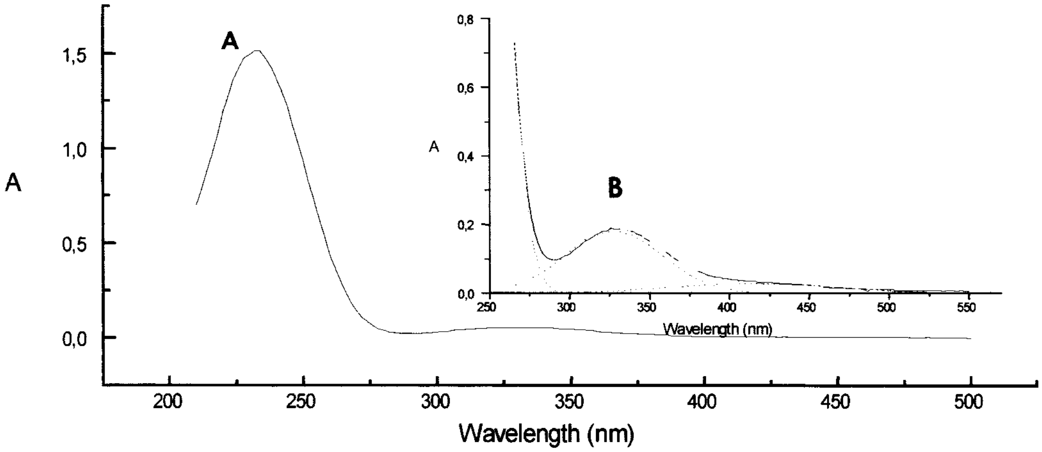

**Figure 4.** Electronic spectra of *trans*-$[Ru(NH_3)_4NO(H_2O)]Cl_3$ in 0.1 mol $L^{-1}$ $CF_3COOH$: (A) 6.5 × $10^{-4}$ mol $L^{-1}$ and (B) 9.6 × $10^{-4}$ mol $L^{-1}$.

and $\psi_6$ have a metal orbital contribution. As a matter of fact, in these species, all orbitals that have an NO orbital contribution would have also a metal orbital contribution. Thus, transitions involving exclusively these orbitals, for *trans*-$[Ru(NH_3)_4(H_2O)(NO)]^{3+}$, although displaying some CT character, could not be described as purely MLCT in character. A spin-forbidden ligand-field (LF) transition contributing to the 426 nm absorption in *trans*-$[Ru(NH_3)_4(H_2O)(NO)]^{3+}$ cannot be completely ruled out. For similar systems, such as the isolectronic *trans*-$[Ru(NH_3)_4(H_2O)(CO)]^{2+}$,[35] the lowest energy bands are singlet and mostly LF in character, as also occurs[35,36] for *trans*-$[Ru(NH_3)_4(P(OR)_3)(CO)]^{2+}$, *trans*-$[Ru(NH_3)_4(P(OR)_3)_2]^{2+}$, and *trans*-$[Ru(NH_3)_4(H_2O)(P(OR)_3)]^{2+}$. These bands occur in the 300−400 nm range, and no triplet bands were observed in these systems. Furthermore, the spectroscopically nonobserved lowest energy triplet LF bands of $[Ru(NH_3)_5(py)]^{2+}$ and $[Ru(NH_3)_6]^{2+}$ were determined to occur at $\cong 1.7 \times 10^4$ $cm^{-1}$ (588 nm).[37] In the ammineruthenium(II)−nitrosyl complexes these levels could be expected to lie at higher energy, given the very strong LF character of NO. In addition there would be a larger splitting of the d orbitals. Accordingly, the $d_{z^2}$ and $d_{x^2-y^2}$ orbitals would split, with one higher and the other lower in energy, which would result in the splitting of the bands toward higher and lower energies, respectively. However, a definite statement would be hard to make given the different nature of the molecular orbitals involved in the complexes, with NO, CO, and the other unsaturated ligands, despite their apparent similarity. This can be illustrated by the MO diagrams of the NO and CO complexes where the energetic order of the unoccupied orbitals is different in both complexes (see below).

The absorption bands of *trans*-$[Ru(NH_3)_4(H_2O)(NO)]^{3+}$ were assigned using semiempirical CI ZINDO/S calculations (Table 5). Seven transitions comprise the band at 426 nm, involving transitions from $\psi_2$ or $\psi_3$ to $\psi_5$ or $\psi_6$ and from $\psi_4$ to $\psi_5$ or $\psi_6$. These latter two have some MLCT character, since the nonbonding $\psi_4$ is purely metal in character. The second absorption band ($\lambda_{max} = 322$, $\epsilon = 280$ $mol^{-1}$ L $cm^{-1}$) of *trans*-$[Ru(NH_3)_4(H_2O)(NO)]^{3+}$ can be assigned to a spin-allowed d−d transition: $d_{xy} \rightarrow d_{x^2-y^2}$ ($^1A_1 \rightarrow {}^1A_2$) ($\psi_4 \rightarrow \psi_8$). The third band ($\lambda_{max}$ = 235, $\epsilon = 2.5 \times 10^3$ $mol^{-1}$ L $cm^{-1}$) can be assigned to a combination of seven transitions from $\psi_3$ or $\psi_5$ to $\psi_7$ or $\psi_8$ (Table 5). Transitions involving $\psi_7$ and $\psi_8$ are essentially LF in character. These assignments are in agreement with those of Gray and Manoharan[38] for the nitroprusside ion.

**Table 5.** Electronic Spectrum of *trans*-$[Ru(NH_3)_4NO(H_2O)]Cl_3$

| exptl[a] $\lambda$ (nm) | $\epsilon$ ($mol^{-1}$ L $cm^{-1}$) | calcd $\lambda$ (nm) | assignments |
|---|---|---|---|
| 426 | 45 | 433.1 | $^1A_1 \rightarrow {}^1A_1$ ($\psi_3 \rightarrow \psi_5$) |
| | | | $^1A_1 \rightarrow {}^1B_2$ ($\psi_2 \rightarrow \psi_5$) |
| | | | $^1A_1 \rightarrow {}^1A_1$ ($\psi_2 \rightarrow \psi_6$) |
| | | 427.8 | $^1A_1 \rightarrow {}^1A_1$ ($\psi_2 \rightarrow \psi_6$) |
| | | | $^1A_1 \rightarrow {}^1B_2$ ($\psi_2 \rightarrow \psi_5$) |
| | | 396.6 | $^1A_1 \rightarrow {}^1B_2$ ($\psi_4 \rightarrow \psi_5$) |
| | | 391.9 | $^1A_1 \rightarrow {}^1B_1$ ($\psi_4 \rightarrow \psi_6$) |
| 322 | 280 | 337 | $^1A_1 \rightarrow {}^1A_2$ ($\psi_4 \rightarrow \psi_8$) |
| 235 | 2500 | 259.0 | $^1A_1 \rightarrow {}^1A_2$ ($\psi_4 \rightarrow \psi_7$) |
| | | 253.2 | $^1A_1 \rightarrow {}^1B_1$ ($\psi_3 \rightarrow \psi_7$) |
| | | | $^1A_1 \rightarrow {}^1A_2$ ($\psi_4 \rightarrow \psi_8$) |
| | | | $^1A_1 \rightarrow {}^1A_2$ ($\psi_4 \rightarrow \psi_7$) |
| | | 251.6 | $^1A_1 \rightarrow {}^1B_1$ ($\psi_3 \rightarrow \psi_8$) |
| | | | $^1A_1 \rightarrow {}^1B_1$ ($\psi_3 \rightarrow \psi_7$) |
| | | 235.1 | $^1A_1 \rightarrow {}^1B_1$ ($\psi_3 \rightarrow \psi_8$) |

[a] After Gaussian deconvolution.

**Table 6.** Electronic Spectrum of *trans*-$[Ru(NH_3)_4CO(H_2O)]Br_2$

| exptl[a] $\lambda$ (nm) | $\epsilon$ ($mol^{-1}$ L $cm^{-1}$) | calcd $\lambda$ (nm) | assignments |
|---|---|---|---|
| 358 (sh) | 54 | 291.8 | $^1A_1 \rightarrow {}^1A_2$ ($\psi_4 \rightarrow \psi_7$) |
| 282 | 267 | 284.5 | $^1A_1 \rightarrow {}^1B_1$ ($\psi_3 \rightarrow \psi_6$) |
| | | 283.8 | $^1A_1 \rightarrow {}^1A_2$ ($\psi_4 \rightarrow \psi_6$) |
| | | 277.8 | $^1A_1 \rightarrow {}^1B_2$ ($\psi_2 \rightarrow \psi_6$) |
| 240 | 420 | 269.2 | $^1A_1 \rightarrow {}^1A_1$ ($\psi_3 \rightarrow \psi_8$) |
| | | | $^1A_1 \rightarrow {}^1A_1$ ($\psi_2 \rightarrow \psi_9$) |
| | | 261.6 | $^1A_1 \rightarrow {}^1B_1$ ($\psi_4 \rightarrow \psi_8$) |
| | | 261.3 | $^1A_1 \rightarrow {}^1B_1$ ($\psi_4 \rightarrow \psi_9$) |
| | | 260.6 | $^1A_1 \rightarrow {}^{1A}{}_2$ ($\psi_3 \rightarrow \psi_9$) |
| | | | $^1A_1 \rightarrow {}^1A_2$ ($\psi_4 \rightarrow \psi_{10}$) |

[a] After Gaussian deconvolution.

The electronic spectrum of the ion *trans*-$[Ru(NH_3)_4(H_2O)(CO)]^{2+}$ (Table 6) shows some different features, compared to that of *trans*-$[Ru(NH_3)_4(H_2O)(NO)]^{3+}$. In the carbonyl species spectrum, there is an absorption band at 240 nm ($\epsilon = 420$ $mol^{-1}$ L $cm^{-1}$), and there is another at 282 nm ($\epsilon = 440$ $mol^{-1}$ L $cm^{-1}$), with one shoulder on the lower energy side. A Gaussian deconvolution of the spectrum shows an absorption component

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at 358 nm ($\epsilon = 54$ mol$^{-1}$ L cm$^{-1}$), as occurs with the spectrum of *trans*-$[Ru(NH_3)_4(P(OR)_3)(CO)]^{2+}$,[35] which displays two bands. The higher energy band in this latter complex was assigned, under $C_{4v}$ symmetry, to a $^1A_1 \rightarrow {}^1E$ transition, and the lower energy band to a $^1A_1 \rightarrow {}^1A_2$ transition.[35] The photochemical behavior of *trans*-$[Ru(NH_3)_4(P(OR)_3)(CO)]^{2+}$ [34] is consistent with the spectral assignment.[35] However, for *trans*-$[Ru(NH_3)_4(H_2O)(CO)]^{2+}$, the assignment of the bands[35] following the same model above (282 nm, $^1A_1 \rightarrow {}^1E$; 358 nm, $^1A_1 \rightarrow {}^1A_2$) leads to some discrepancies regarding the expected and the observed photochemical behavior of the complex.[35] Using semiempirical CI ZINDO/S calculations, although appoximate for electronic spectra, the band at 282 nm can be assigned to three transitions (from $\psi_2$, $\psi_3$, or $\psi_4$ to $\psi_6$), LF in character. The shoulder at 358 nm can be assigned to a $^1A_1 \rightarrow {}^1A_2$ ($\psi_4$ to $\psi_7$ or $d_{xy}$ to $d_{x^2-y^2}$) transition. These assignments, using $C_{2v}$ symmetry, are not dramatically different from the former,[35] using $C_{4v}$ symmetry, but are not consistent with the photochemical behavior of the complex. The band at 240 nm can be assigned to a combination of six transitions, two of them ($\psi_4 \rightarrow \psi_8$ and $\psi_4 \rightarrow \psi_9$) being MLCT in character. These two assignments imply that the lowest energy band would not have a contribution from the $d_{z^2}$ orbital. However, the photochemical results indicate photolabilization of the CO ligand, therefore suggesting that the $d_{z^2}$ orbital should contribute to some extent to the lowest energy excited state.[35]

## Conclusions

The substitution of the trans $NH_3$ ligand in the Ru coordination sphere by the NO ligand makes the ruthenium(II) center a stronger Lewis acid than the formally Ru(III) center in $[Ru(NH_3)_5(H_2O)]^{3+}$ and at the same time markedly decreases the lability of the coordinated water and the affinity of the Ru(II) center for $\pi$-acid ligands. The experimental data show that the presence of the nitrosyl ligand affects the metal center properties more than expected by increasing its charge by one unit. Thus, the explanations for the acidic character of the water and its kinetic delabilization go beyond only the metal's formal charge. Molecular orbital analyses performed at the quantum chemical DFT level show that the lone pair of the water, $\pi$ in character, plays an important role in the metal−water bond properties. The involvement of $d_\pi$ orbitals in the metal−water bond results in a depletion of electronic density on the oxygen, increasing the water acidity. The p$K_a$'s of the coordinated water in a series of complexes are linearly related to the calculated mixing between the water oxygen $p_x$ orbital of $\pi$ symmetry and the metal $d_{xz}$ orbital.

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**Supporting Information Available:** Tables listing detailed crystallographic data, interatomic distances, atomic positional and thermal parameters, and short interactions involving hydrogen and a stereoscopic view of the molecular packing for *trans*-$[Ru(NH_3)_4(H_2O)NO]Cl_3 \cdot H_2O$. This material is available free of charge via the Internet at http://pubs.acs.org.

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