Detection of the EPR Spectra of NO$^\bullet$ in Ruthenium(II) Complexes

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The EPR of NO$^\bullet$ can be detected in the liquid and solid states when crystal fields are sufficient to remove the axial symmetry and separate the $(\pi^*)_x$ and $(\pi^*)_y$ orbitals by a few hundred reciprocal centimeters. The theory of the EPR spin Hamiltonian of bound NO$^\bullet$ is reviewed, further developed, and then applied to the observed frozen-liquid spectra of NO$^\bullet$ bound to Ru(II) obtained from Ru^{II}NO$^+$ complexes by reduction. Comparisons to earlier reports on the observation of the EPR spectra of NO$^\bullet$ are made.

Introduction

In a recent paper,[1] we reported the EPR detection of NO$^\bullet$ in *trans*-[Ru^{II}Cl(cyclam)(NO$^\bullet$)]$^+$, after reduction of *trans*-[Ru^{II}Cl(NO$^+$)(cyclam)]$^{2+}$ by Eu(II), in a frozen liquid. In this paper, we report the detection of the EPR spectra of coordinated NO$^\bullet$ in several ruthenium(II) complexes. We will give the theory and analysis of the EPR spectra of bound NO$^\bullet$ and compare them with those given in other reports of the spectra of NO$^\bullet$.

Although the spectrum of NO$^\bullet$ was detected early in the gas state,[2] there are few reliable reports on the EPR spectra of NO$^\bullet$ in the liquid or solid state. In most metal nitroxide compounds, NO is better represented as NO$^+$ with the unpaired electron residing more in the metal ion d orbitals than in any nitrogen p orbitals. For example, the biological Fe^{II}NO$^\bullet$ complexes are considered to have the unpaired electron primarily in the d_{z^2} orbital on the basis of the g value and ^{14}N hyperfine coupling[3−5] of the NO$^+$ ligand. The observation of a ^{14}N hyperfine interaction[3] for nitrogen bases bonded trans to the NO group provides further evidence that the unpaired electron resides in the d_{z^2} orbital of Fe. Ruthenium complexes strongly coordinate NO as Ru^{II}NO$^+$ but readily release NO$^\bullet$ after a one-electron reduction. Reports of the EPR of bonded NO$^\bullet$ with the unpaired electron located mainly on NO$^\bullet$ are rare. NO$^\bullet$ in an axial environment will have a nonmagnetic ground state due to the spin−orbit coupling between the orbital angular momentum for the π state and the electron spin. However, since the spin−orbit interaction is only about 100 cm^{-1} in NO$^\bullet$, any crystal field interaction of a few thousand reciprocal centimeters that removes the axial symmetry will lock the unpaired electron in one of the two antibonding π molecular orbitals of NO$^\bullet$, making the ground state nonsilent in EPR spectra. This will be discussed in the theoretical part of our paper.

One of the earliest reports of the EPR spectrum of trapped NO$^\bullet$ was that of Mergerian and Marshall,[6] who identified one of the signals of irradiated KN$_3$ as NO$^\bullet$ but this assignment has been disputed. They did derive an equation for g values of trapped NO$^\bullet$, that has been used in later studies, but their experimental g values did not fit their own theory. Later Owens[7] pointed out that one of the signals would fit NO$^\bullet$ if one assumed that the molecule was rotating about an axis perpendicular to the NO bond and that the $g_{\|}$ reported was along the rotation axis. Owens[7] attempted to analyze the spin Hamiltonian to extract spin densities in the $(\pi^*)_x$ orbital, but this attempt was flawed by the use of an incorrect equation for g_z. Wylie et al.,[8] in another irradiation study of KN$_3$, reported the EPR spectrum of the isoelectronic N$_2^-$. They reported that $g_x = g_y = 2.001$, $g_z = 1.984$, $A_x = 6.4$ G, $A_y = 4.0$ G, and $A_z = 4.0$ G. The g values are consistent with the theory of Mergerian and Marshall,[6] and the larger value of A_x is consistent with a spin in the $(\pi^*)_x$ orbital but, as will be seen later, is rather small in magnitude.

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The first authentic report on an EPR spectrum of bound NO$^{\bullet}$ was that of Lunsford[9] for NO$^{\bullet}$ condensed on the surface of MgO at 77 K. This was followed by a series of papers for NO$^{\bullet}$ condensed on other surfaces.[10,11] On these surfaces, $g_x \sim g_y \sim 1.99$, $g_z \sim 1.89$, $A_x \sim 33$ G, and $A_y \sim A_x < 10$ G. Kasai and Bishop[12] showed that more highly resolved spectra could be obtained by allowing samples to stand for several days at room temperature before cooling to 77 K to observe the spectra. Others[13−18] have also reported detecting EPR spectra of NO$^{\bullet}$ adsorbed on other surfaces.

Ohigashi and Kurita[19] reported detecting NO$^{\bullet}$ trapped in a single crystal of NH_3OHCl by growing the single crystal in an NO$^{\bullet}$ atmosphere. After bleaching out other defect centers, they were left with a signal at 77 K with the spin Hamiltonian parameters

$$g_x = 1.998 \qquad g_y = 1.999 \qquad g_z = 1.886$$
$$A_x = 36.4\ \mathrm{G} \qquad A_y = 5.4\ \mathrm{G} \qquad A_z = 11.5\ \mathrm{G}$$

which they attributed to NO$^{\bullet}$. The signal disappeared at 120 K. Since these parameters are similar to those found by Lunsford,[9] it seems likely that their assignment was correct.

Couture et al.[20] reported what they consider to be a case of NO$^{\bullet}$ in the irradiation of a single crystal of $\mathrm{Fe(CO)_2(NO)_2}$ to form $[\mathrm{Fe(CO)_2(NO)_2}]^-$ with the parameters

$$g_x = 1.9993 \qquad g_y = 1.9982 \qquad g_z = 1.9606$$
$$A_x^{\mathrm{N1}} = 2.3\ \mathrm{G} \qquad A_y^{\mathrm{N1}} = 6.0\ \mathrm{G} \qquad A_z^{\mathrm{N1}} = 21.1\ \mathrm{G}$$
$$A_x^{\mathrm{N2}} = 2.6\ \mathrm{G} \qquad A_y^{\mathrm{N2}} = 5.4\ \mathrm{G} \qquad A_z^{\mathrm{N2}} = 21.1\ \mathrm{G}$$

Since the single electron sees both nitrogen atoms, the large anisotropy in both hyperfine values certainly indicates that the unpaired electron occupies the two nitrogen p orbitals from 59% to 85%, depending on the signs of the hyperfine parameters, but the g_z value and the fact that the largest hyperfine splitting is in the axis of the NO$^{\bullet}$ ligand argue against it being simply a bound NO$^{\bullet}$. Also the large positive Fermi contact term is not reasonable if the electron is in a predominantly π orbital.

Symons et al.[21] identified a species observed in γ-irradiated pentacyanonitrosylferrate(II) salts as NO$^{\bullet}$ attached to Fe^{2+} at a bent angle such that the added electron was located on NO$^{\bullet}$. Its average spin Hamiltonian parameters were reported to be

$$g_x = 2.008\ g_y = 1.997\ g_z = 1.93$$
$$A_x = 26\ \mathrm{G}\ A_y = 30\ \mathrm{G}\ A_z = 8{-}10\ \mathrm{G}$$

Except for the large magnitude of A_x, the parameters are similar to those reported for NO$^{\bullet}$ by Lunsford.[9] Perhaps these powder spectra should be reexamined, as they do not agree with the NO$^{\bullet}$ spectra found by Lunsford.

There is a report of the EPR spectrum of NO$^{\bullet}$ bound to a metal ion in a paper by Callahan and Meyer.[22] These authors give EPR spectra for frozen solutions of *trans*-$[\mathrm{Ru^{II}Cl(NO^{\bullet})(bpy)_2}]^+$ and $[\mathrm{Fe^{II}(CN)_5(NO^{\bullet})}]^{3-}$ but give no analysis or interpretation of the spectra obtained and, also, insufficient detail to allow a complete analysis of the published spectra. The spectrum of the Ru(II) complex is similar to the one we report below, and we estimate from their figure that $A_x \sim 30$ G and $g_z \sim 1.92$, if $g_{x,y} \sim 2.00$, for this spectrum. For the Fe(II) complex, we estimate $A_x \sim 24$ G and $g_z \sim 1.97$, if $g_{x,y} \sim 2.00$.

Theory of the EPR Spin Hamiltonian of Bound NO•

We have found no complete development of the theory of the spin Hamiltonian for NO$^{\bullet}$ in the literature and, therefore, include it here. The theory of the spin Hamiltonian of the related O_2^- has been developed.[23,24] In this radical, we have a single hole in the $(\pi^*)_x(\pi^*)_y$ shell rather than a single electron so the equations should be related by a change in sign for certain spin−orbit terms.

In the gaseous NO$^{\bullet}$ molecule, the ground state is $\sigma^2\pi^4\pi^{*1}$, which places the unpaired electron in the 4-fold degenerate π^* orbital. The π^* orbital can be written as $(\pi^*)^{\pm}_{\pm 1}$, where the upper ± refers to the two orientations of the electron spin and the lower ±1 refers to the two orientations of the orbital angular momentum of the π^* orbital.

$$s_z(\pi^*)^{\pm}_{\pm 1} = \pm\frac{1}{2}(\pi^*)^{\pm}_{\pm 1} \qquad l_z(\pi^*)^{\pm}_{\pm 1} = \pm 1(\pi^*)^{\pm}_{\pm 1} \tag{1}$$

The spin−orbit $\xi l{\cdot}s$ interaction creates two states

$$^2\Pi_{1/2} \qquad E = -\frac{1}{2}\xi \qquad \psi = (\pi^*)^{+}_{-1}, (\pi^*)^{-}_{+1}$$
$$^2\Pi_{3/2} \qquad E = \frac{1}{2}\xi \qquad \psi = (\pi^*)^{+}_{+1}, (\pi^*)^{-}_{-1}$$

and since $\xi \approx 100\ \mathrm{cm^{-1}}$, the two states are separated by 100 $\mathrm{cm^{-1}}$. The g_z value is given by $(l_z + 2s_z)$, so for both states

$$^2\Pi_{1/2} \qquad g_z = 0 \qquad\qquad ^2\Pi_{3/2} \qquad g_z = 4.0$$

Thus the ground state is essentially nonmagnetic in the gaseous state but the excited state will be thermally occupied at room temperature and is easily detected in the gas.

If NO$^{\bullet}$ is tied down as a ligand or trapped in the solid state or frozen solution state, the axial symmetry is likely to be removed and the orbital angular momentum quenched, thus giving rise to a $(\pi^*)_x$ or $(\pi^*)_y$ orbital as the ground state, which will be EPR active.

$$(\pi^*)_x = \frac{1}{\sqrt{2}}[-(\pi^*)_{+1} + (\pi^*)_{-1}]$$
$$(\pi^*)_y = \frac{\mathrm{i}}{\sqrt{2}}[(\pi^*)_{+1} + (\pi^*)_{-1}] \tag{2}$$

If V_{L} is the portion of the crystal field operator that removes the axial symmetry, we define a lattice potential distortion parameter V as

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$$V = \langle \pi_y | V_L | \pi_y \rangle - \langle \pi_x | V_L | \pi_x \rangle \tag{3}$$

and apply the spin−orbit interaction to the four degenerate π^* orbitals, obtaining two Kramers' doublet states with the energies

$$E = \pm \frac{1}{2}\xi\sqrt{1+\omega^2} \qquad \omega = V/\xi \tag{4}$$

and the ground-state wave functions

$$\psi_+ = A(\pi^*)^+_{+1} + B(\pi^*)^+_{-1} \qquad \psi_- = -B(\pi^*)^-_{+1} - A(\pi^*)^-_{-1} \tag{5}$$

$$A = -\frac{1}{\sqrt{2}}\left[1 - \frac{1}{\sqrt{1+\omega^2}}\right] \qquad B = \frac{1}{\sqrt{2}}\left[1 + \frac{1}{\sqrt{1+\omega^2}}\right] \tag{6}$$

g Matrix of NO$^\bullet$. This ground state gives the following g values:

$$g_z = 2\left[1 - \frac{1}{\sqrt{1+\omega^2}}\right] \qquad g_x, g_y = \frac{2\omega}{\sqrt{1+\omega^2}} \tag{7}$$

The g_z expression in eq 7 was first derived by Mergerian and Marshall.[6] In eq 6, the value of A goes from zero to $-1/\sqrt{2}$ as ω increases from zero and B goes from 1 to $1/\sqrt{2}$. Thus, for large V, the ground state becomes the $(\pi^*)_x$ orbital. The g values are plotted in Figure 1. Note that it only takes a $V > 300-400$ cm^{-1} to bring $g_{x,y}$ close to 2 from zero, while g_z requires values of >1000 cm^{-1}. Thus, it takes only a small distortion interaction to convert the ground state to an active state in EPR.

That the **g** matrix appears to have axial symmetry when the molecule does not is due to the fact that our calculation involves a system of only four functions and two energy states. If we include the existence of other excited states, the low symmetry will appear in the **g** matrix. The most likely state to contribute would arise from promoting an electron from the σ-bonding orbital to the π^* orbital. This would give rise to second-order contributions to g_x and g_y of

$$\Delta g_x = \frac{a^2 d^2 (A+B)^2 \xi}{\Delta E_\sigma} \tag{8}$$

$$\Delta g_y = \frac{a^2 d^2 (A-B)^2 \xi}{\Delta E_\sigma} \tag{9}$$

where d is the MO coefficient for the p_σ orbital in the σ-bonding MO. The addition to g is positive because we are dealing with a hole in a filled orbital situation in this case. In the limit of large V, the g_x term goes to zero and the g_y term to

$$\Delta g_y = \frac{2a^2 d^2 \xi}{\Delta E_\sigma}$$

Thus, when ω is large, we would expect g_x to be near 2.0, g_y to be greater than 2.0, and g_z to be smaller than 2.0.

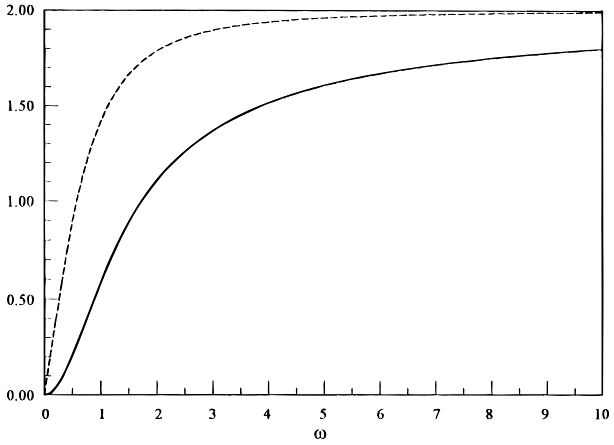

Figure 1. $g_\parallel$ (solid line) and $g_\perp$ (dotted line) for bound NO$^\bullet$ versus ω calculated using eq 7.

Hyperfine Matrix for ^{14}N in NO$^\bullet$. Using the ground-state functions in eq 5 and taking the antibonding MO of NO$^\bullet$ to have the form $(\pi^*)_{\pm 1} = a\mathrm{p}_{\pm 1}(\mathrm{N}) - b\mathrm{p}_{\pm 1}(\mathrm{O})$, the hyperfine parameters are given by

$$A_z = A_F + a^2 P\left[-\frac{2}{5} + 2(A^2 - B^2)\right] \rightarrow A_F - \frac{2}{5}a^2 P$$

$$A_x = A_F + a^2 P\left[\frac{2}{5}(-AB + 3B^2)\right] \rightarrow A_F + \frac{4}{5}a^2 P \quad \text{when } V \rightarrow \infty \tag{10}$$

$$A_y = A_F + a^2 P\left[\frac{2}{5}(-AB - 3B^2)\right] \rightarrow A_F - \frac{2}{5}a^2 P$$

$$P = 2g_N \beta_e \beta_N \langle 1/r^3 \rangle_{2p} \tag{11}$$

where A_F is the Fermi contact contribution either from the unpaired spin density in the 2s orbital of nitrogen or from the polarization of spin in the filled 1s shell. The P term has been estimated[25] to be 49.53 G for ^{14}N. The limiting value for eq 10 is what would be expected for a ground state of $(\pi^*)_x$. If $V \rightarrow -\infty$, the ground state will be $(\pi^*)_y$ and the x and y expressions in eq 10 will be interchanged. The A_F parameter should be positive if there is a sizable population of unpaired spin in the nitrogen 2s orbital and negative if only the polarization mechanism from spin in the 2p orbital is operative.

Experimental Section

All preparations and measurements were carried out under an inert atmosphere (argon or nitrogen), using standard techniques.[26]

Reagents and Materials. All chemicals were of reagent grade (Aldrich or Merck) and were used without further purification. The ligand 1,4,8,11-tetraazacyclotetradecane (cyclam) was recrystallized from chlorobenzene. The solvents were purified as described in the literature.[27] Doubly distilled or 18 MΩ Milli-Q 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 Bio-Rad AG-50WX8 (200−400 mesh), in the sodium ion form, was used for purification of the complexes. Sodium trifluoroacetate (Aldrich) was used as the background electrolyte for ionic strength control.

Syntheses. The complexes $[RuCl(NH_3)_5]Cl_2$,[28] *trans*-$[RuCl(NH_3)_4(SO_2)]Cl$,[29,30] *trans*-$[Ru(SO_3)(NH_3)_4(NO)]Cl$,[31] *trans*-$[\{Ru(NH_3)_4NO\}_2$-

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(μ-S_2)]Cl_6·H_2O,[32] *trans*-[$RuCl_2$(cyclam)]Cl,[33] *trans*-[RuCl(tfms)(cyclam)]-(tfms)[34] (tfms = trifluoromethanesulfonate), and Ru(NO)Cl_3·$5H_2O$[35] used in the syntheses below were prepared and characterized by following published procedures.

Although recently described[1] elsewhere, the syntheses of *trans*-[RuCl(NO)(cyclam)]$(PF_6)_2$ and *trans*-[Ru(NO)$(NH_3)_4$(H_2O)]Cl_3 are not yet generally known and are, therefore, presented here.

***trans*-[RuCl(NO)(cyclam)]$(PF_6)_2$.** This complex was synthesized as described elsewhere.[1] *trans*-[Cl(CF_3SO_3)(cyclam)Ru](CF_3SO_3) (0.5 g; 0.78 mmol) was dissolved in 50 mL of deaerated water. Nitric oxide, which was generated by dripping concentrated sulfuric acid onto $NaNO_2$ and passing it through a saturated aqueous solution of NaOH, was bubbled through the solution, causing the dark green solution to slowly become light yellow. After 3 h, 1 mL of a saturated aqueous solution of NH_4PF_6 was added, and the mixture was left in a refrigerator for 6 h. The resulting yellow precipitate was collected by filtration, washed with diethyl ether, and stored under vacuum in the dark. The compound was characterized by UV–vis, infrared, and electrochemical measurements as previously described.[1]

***trans*-[Ru(NO)$(NH_3)_4$(H_2O)]Cl_3.** This compound was synthesized as described elsewhere,[36] by isolation during the preparation of [(NO)-$(NH_3)_4$RuSSRu$(NH_3)_4$(NO)]Cl_6·H_2O.[32] 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 an 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 the filtrate was charged onto a cation exchange column (Bio-Rad AG-50WX8, 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 elute a yellow solution was then collected and concentrated by rotary evaporation to one-tenth of the original volume. The resulting solution was left to cool in the refrigerator for 24 h. A solid precipitated, which was isolated by filtration and washed with ethyl alcohol. The compound was characterized by UV–vis, infrared, and electrochemical measurements as previously described.[36]

***trans*-[Ru(NO){$(CH_3CH_2)_2PCH_2CH_3)_2$}$_2$Cl]$(PF_6)_2$** was synthesized[37] as follows. A 0.100 g (0.306 mmol) sample of Ru(NO)Cl_3·$5H_2O$ was dissolved in 20 mL of ethanol, 0.132 g (0.642 mmol) of 1,2-bis(diethylphosphino)ethane was added, and the solution was stirred for 1 h. The initially dark red solution became orange. The yellow solid that precipitated upon NH_4PF_6 addition was collected by filtration, washed successively with ethanol/ether (2:1), and dried under vacuum. The product was then stored under vacuum in a desiccator with $CaCl_2$.

Instrumentation. The elemental analyses were carried out at the Instituto de Química da Universidade de São Paulo. The ruthenium analyses were performed according to the method of Rowston and Ottaway,[38] modified by Clarke,[39] 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 8452A diode array spectrophotometer. IR spectra were recorded on Bomem MB-102 FT-IR, Nicolet 210 FT-IR, Nicolet 510 FT-IR, and Hewlett-Packard 5890 FT-IR spectrophotometers in the 300–4000 cm^{-1} range, in KBr pellets and/or Nujol mulls and by diffuse reflectance.

EPR spectra were obtained on a Bruker ESP300E X-band spectrometer at 77 K. The spectra were recorded after the reduction of *trans*-[RuCl(NO)(cyclam)]$^{2+}$ and *trans*-[Ru(NO)$(NH_3)_4$(H_2O)]Cl_3 by Eu(II) in an ethylene glycol + 30% H_2O solution. The solution was frozen by liquid N_2 immediately after mixing both components. The EPR data were recorded at 9.43 GHz, 1 mW power, and 3.9 G modulation amplitude.

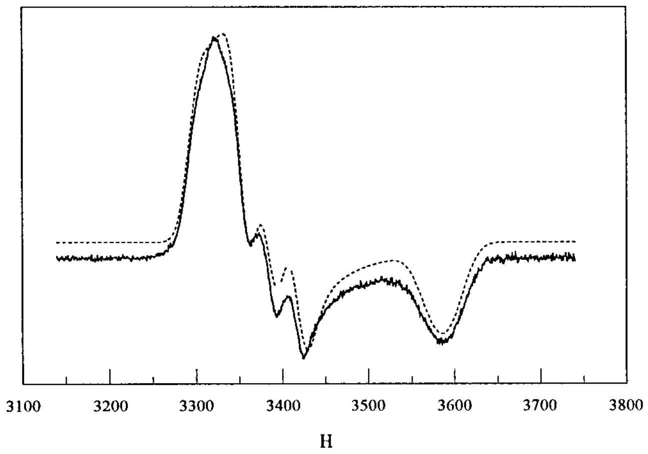

Figure 2. EPR spectrum of a frozen solution of *trans*-[RuCl(NO)-(cyclam)]$^{2+}$ in an ethylene glycol + 30% H_2O solution which was frozen after the addition of Eu^{2+}. The dashed line is the simulated spectrum.

Results

At this writing, we have found three compounds of an Ru^{II}-NO^+ complex that appears to give the EPR spectrum of $NO^•$ after reduction to the $Ru^{II}NO^•$ form. They are *trans*-[Ru^{II}Cl-(NO^+)(cyclam)]$^{2+}$, *trans*-[Ru^{II}(NO^+)$(NH_3)_4$(H_2O)]$^{2+}$, and *trans*-[Ru^{II}(NO^+){$(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$}$_2$Cl]$(PF_6)_2$). In Figure 2 is shown the EPR spectrum obtained after the reduction of *trans*-[Ru^{II}Cl(NO^+)(cyclam)]$^{2+}$ by Eu(II) in the ethylene-glycol + 30% H_2O solution. The solution was frozen by liquid N_2 shortly after its preparation. Figure 6 also shows a simulation of the frozen-solution spectrum using the parameters

$$g_x = 1.995 \qquad g_y = 2.035 \qquad g_z = 1.883$$

$$A_x = 32.1\ \text{G} \qquad A_y = 17\ \text{G} \qquad A_z = 15\ \text{G}$$

A similar spectrum was obtained when *trans*-[Ru^{II}(NO^+)$(NH_3)_4$-(H_2O)]$^{2+}$ was reduced by Eu(II). A study of *trans*-[Ru(NO)-{$(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$}$_2$Cl]$(PF_6)_2$ was found to give a similar, but less resolved, spectrum using the parameters

$$g_x = 1.984 \qquad g_y = 2.010 \qquad g_z = 1.888$$

$$A_x = 35\ \text{G} \qquad A_y = 18\ \text{G} \qquad A_z = 19\ \text{G}$$

Reduction of coordinated NO^+ in *trans*-[Ru^{II}Cl(NO^+)-(cyclam)]$^{2+}$ results in *trans*-[Ru^{II}Cl(cyclam)($NO^•$)]$^+$, which has been found[1] to undergo a relatively fast chloride labilization (k = 2.0 s^{-1} at 8 °C) resulting in *trans*-[Ru^{II}(H_2O)(cyclam)-($NO^•$)]$^{2+}$, which in turn releases $NO^•$ slowly ($k = 6.4 \times 10^{-4}$ s^{-1} at 25 °C). Thus, we believe that we are observing the EPR spectrum of *trans*-[Ru^{II}(H_2O)(cyclam)($NO^•$)]$^{2+}$ rather than that of a solvated $NO^•$. This is also the case for the other two complexes, *trans*-[Ru^{II}(NO^+)$(NH_3)_4$(H_2O)]$^{2+}$ and *trans*-[Ru-(NO){$(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$}$_2$Cl]$(PF_6)_2$, which release $NO^•$ slowly after reduction ($k = 4.0 \times 10^{-2}$ and $<1 \times 10^{-1}$ s^{-1} at 25 °C, respectively). This is also supported by the fact that we were unable to detect a spectrum for complexes known to release $NO^•$ rapidly and, also, for a saturated solution of NO gas.

An analysis of the spin Hamiltonian parameters obtained using eqs 6, 7, and 10 requires a knowledge of the signs for the

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hyperfine parameters, which are not known experimentally. Realistically, we have two choices: (1) $A_x = +$, $A_{y,z} = -$; (2) $A_x = +$, $A_{y,z} = +$. From the g_z value and eq 7, we obtain a value of $\omega = 17$, which gives a value of $V = 1700$ cm^{-1}, if $\xi = 100$ cm^{-1}. For sign choice 1, eq 10 gives $a^2 = 0.72$ and $A_F = -1$ G, which are reasonable values for the model developed above for a bound NO$^\bullet$ with the electron in a π orbital, although the density of the unpaired spin on the nitrogen atom is somewhat higher than the expected 0.5. For sign choice 2, eq 10 gives $a^2 = 0.27$ and $A_F = 20$ G, but these parameters are unreasonable because they require the unpaired spin to be mostly in a nitrogen 2s orbital and therefore not in a π orbital. Also, the g values are not what one would expect for an electron in a hybrid sp orbital. Thus we conclude that only choice 1 is reasonable for the signs of the hyperfine parameters.

Conclusions

The satisfactory agreement with the experimental spin Hamiltonian parameters found here and those found for NO$^\bullet$ condensed on surfaces and with the theory developed for a bound NO$^\bullet$ molecule makes a strong case for the species we find after reduction of the Ru^{II}(NO$^+$) species being, in fact, the Ru^{II}NO$^\bullet$ that is formed by the reduction of the coordinated NO$^+$ before the release of NO gas.

A comparison of the FeNO and RuNO systems is in order at this point. Both Fe(III) and Ru(III) react with NO$^\bullet$ to form Fe^{II}-NO$^+$ and Ru^{II}NO$^+$. Reduction of the two give very different EPR results. For Fe, g_z is about 2.00 and $g_{x,y} \approx 2.07$, indicating that the unpaired electron is in a d_{z^2} orbital. The ^{14}N hyperfine matrix has its largest splitting in the z direction and is axial about the z axis, although there is a report[4] that the principal z axis is bent about 15° from the z axis of **g** matrix. All of these findings suggest that Fe^{I}NO$^+$ best represents the ferrous NO complex. Calculations on the heme system[6] suggest that the Fe^{II}-NO$^\bullet$ excited state is close in energy, and certain EPR spectral features have been attributed to this state.

The reduction of Ru^{II}NO$^+$ gives an EPR spectrum for which $g_z \approx 1.9$ and $g_{x,y} \approx 2.0$ and the nearly axial ^{14}N hyperfine matrix is perpendicular to the z axis of the **g** matrix. Also, the hyperfine splitting in the principal direction is double that found in the Fe system. We have shown in this work that all of this is what would be expected for Ru^{II}NO$^\bullet$. It should be noted that calculations[36,40] have predicted that the reduction of Ru^{II}NO$^+$ should produce Ru^{II}NO$^\bullet$. The requirement of a large anisotropy perpendicular to the NO bond axis further tells us that Ru−N−O is very much a bent moiety.

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