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# Oxidation of Nickel(II) Tetraphenylporphyrin Revisited. Characterization of Stable Nickel(III) Complexes at Room Temperature

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The absorption, resonance Raman, and EPR spectra of the one-electron oxidation products of Ni$^{\mathrm{II}}$TPP (TPP = tetraphenylporphyrin) are examined in detail. The data indicate that the $\pi$-cation radical, Ni$^{\mathrm{II}}$(TPP$^{\bullet}$)$^{+}$, which is the oxidation product obtained in solution at ambient temperature, is converted to Ni(III) complexes of the general form [(L)$_2$Ni$^{\mathrm{III}}$TPP]$^{+}$ upon addition of coordinating ligands such as tetrahydrofuran (THF), pyridine (py), and CH$_3$CN. Contrary to previous reports, the Ni(III) complexes of TPP are readily formed at ambient temperature and are stable for extended periods (up to 24 h) when maintained under inert atmosphere. The electronic ground states of the [(L)$_2$Ni$^{\mathrm{III}}$TPP]$^{+}$ complexes (L = THF, py, CH$_3$CN) are low-spin ($S = {}^1/_2$), and the unpaired electron resides in the d$_{z^2}$ orbital of the Ni(III) ion. The addition of coordinating ligands such as (C$_6$H$_5$)$_3$P and CO to solutions containing Ni$^{\mathrm{II}}$(TPP$^{\bullet}$)$^{+}$ immediately reduces the complex back to the neutral starting material. The CN$^{-}$ ion also reduces Ni$^{\mathrm{II}}$(TPP$^{\bullet}$)$^{+}$ to Ni$^{\mathrm{II}}$TPP; however, an unstable complex of the form [(CN)$_2$Ni$^{\mathrm{III}}$TPP]$^{-}$ is produced as a minority species. The ground state of this latter complex is $S = {}^1/_2$; however, the unpaired electron resides in the d$_{x^2-y^2}$ rather than the d$_{z^2}$ orbital. The spectroscopic data obtained for Ni$^{\mathrm{II}}$(TPP$^{\bullet}$)$^{+}$ and the [(L)$_2$Ni$^{\mathrm{III}}$TPP]$^{-}$ complexes (L = THF, py, CH$_3$CN) indicate that the conversion to Ni(III) species is facilitated by mixing of the d orbitals of the metal ion with the a$_{2u}$ orbital of the porphyrin ring, the latter of which contains the hole in the $\pi$-cation radical form. This mixing also introduces some metal ion character into the wave function for Ni$^{\mathrm{II}}$(TPP$^{\bullet}$)$^{+}$. Collectively, the studies indicate that the limiting case descriptors "Ni(III) complex" and "porphyrin $\pi$-cation radical" do not accurately describe the ground states of the oxidation products of Ni$^{\mathrm{II}}$TPP.

## Introduction

The cation radicals of metalloporphyrins have been extensively investigated because these species serve as model systems for biological redox intermediates.[1] The formation of a ring- versus a metal-centered cation is determined by various factors including the intrinsic redox potentials of the porphyrin ring and metal center, the number and type of ligands on the metal ion, and the properties of the solvent.[1a,b] A number of years ago, Dolphin and co-workers showed that the one-electron oxidation product of Ni$^{\mathrm{II}}$TPP (TPP = tetraphenylporphyrin) undergoes a novel valence tautomerism.[2] At room temperature, oxidation of the Ni(II) complex (orange solution) yields a $\pi$-cation radical Ni$^{\mathrm{II}}$(TPP$^{\bullet}$)$^{+}$ (green solution).[3] As expected, this species exhibits an EPR signal near $g = 2.00$. However, the signal is extremely broad (48 G) and atypical of porphyrin $\pi$-cation radicals. Upon freezing at 77 K, the green solution becomes orange and an anisotropic EPR spectrum is observed ($g_{\perp} = 2.286$, $g_{\parallel} = 2.086$).[2] These spectral changes are consistent with conversion to a low-spin ($S = {}^1/_2$) Ni(III) complex, [Ni$^{\mathrm{III}}$TPP]$^{+}$, in which the unpaired electron resides in the d$_{z^2}$ orbital.[4] The resonance Raman (RR) signatures of the oxidation products of Ni$^{\mathrm{II}}$TPP are also consistent with the Ni$^{\mathrm{II}}$(TPP$^{\bullet}$)$^{+}$ and [Ni$^{\mathrm{III}}$TPP]$^{+}$ formulations for the species obtained at ambient and low temperatures, respectively.[5] Kadish and co-workers have shown that the one-electron oxidation products of the Ni(II) complexes of other types of tetraarylporphyrins also exhibit a temperature-dependent valence tautomerism.[6]

Although the valence tautomerism exhibited by the oxidation products of Ni(II) tetraarylporphyrins is well established, the factors affecting the interconversion process have not been fully elucidated. Dolphin and co-workers suggested that axial ligation of the nickel ion plays a significant role in mediating the tautomerism.[2] This suggestion was based on the observation that conversion to the Ni(III) complex at low temperature occurs in the presence of PF$_6^{-}$ and ClO$_4^{-}$ but not in the presence of H$_2$O or Br$^{-}$. If axial ligation is a key factor in mediating the valence tautomerism, it seems reasonable to expect that more strongly coordinating ligands should stabilize [Ni$^{\mathrm{III}}$TPP]$^{+}$ to such an extent that this tautomer would be preferred at ambient temperature. Indeed, Connick and Macor have shown that the Ni(III) complexes of $\beta$-oxoporphyrins can be formed at ambient temperature in the presence of coordinating solvents.[7] Regardless, the formation of stable Ni(III) complexes of TPP or other tetraarylporphyrins at ambient temperature has not been reported. Wolberg and Manassen reported that [Ni$^{\mathrm{III}}$TPP]$^{+}$ does form at ambient temperature in the presence of coordinating solvents; however, it rapidly decomposes.[3] Consistent with this report, Ni(III) complexes of TPP and certain other porphyrins have been tentatively identified as a short-lived (seconds or less) transient species formed during pulse radiolysis at ambient

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temperature.[8] Nickel(III) species have also been proposed as intermediates in the acid-induced cleavage of Ni(II) complexes of tetraarylporphyrin *N*-oxides at −25 °C.[9]

Recently, Fajer and co-workers have taken a different tack in attempts to obtain stable Ni(III) porphyrin complexes.[10] These workers examined the one-electron-oxidation products of $Ni^{II}$OETPP (OETPP = octaethyltetraphenylporphyrin). The OETPP macrocycle is highly distorted from planarity and exhibits a lower oxidation potential than TPP.[10a] In $CH_2Cl_2$ solutions at ambient temperature, $Ni^{II}$OETPP is oxidized to a $\pi$-cation radical, $Ni^{II}(OETPP^{\bullet})^+$, as expected. Upon freezing at 77 K, the $\pi$-cation form is maintained; there is no evidence for the $[Ni^{III}OETPP]^+$ tautomer. On the other hand, addition of coordinating ligands, such as pyridine (py), tetrahydrofuran (THF), imidazole, and $CN^-$, to solutions of $Ni^{II}(OETPP^{\bullet})^+$ at ambient temperature converts the $\pi$-cation radical to species whose EPR signatures are consistent with those of low-spin Ni(III) complexes of the general form $[(L)_2Ni^{III}OETPP]^+$.[10b] Unexpectedly, these "Ni(III)" complexes exhibit unusually long $Ni-N_{por}$ bonds. This observation led Fajer and co-workers to speculate that a more appropriate description might be a high-spin Ni(II) ion ($S = 1$) antiferromagnetically coupled to the $S = {}^1/_2$ porphyrin $\pi$-cation radical, yielding an $S = {}^1/_2$ ground state for the three-hole system.

The valence tautomerism exhibited by the oxidation products of $Ni^{II}$TPP along with the unusual electronic structure proposed for the cations of $Ni^{II}$OETPP suggest there is more diversity in the electronic properties of oxidized Ni(II) porphyrins than was previously suspected. These observations prompted us to carefully reexamine the cations of the prototypical $Ni^{II}$TPP system. In the course of this work, absorption, RR, and EPR spectra were recorded for the cations in the presence of a variety of coordinating ligands. The temperature dependences of the EPR signals were also examined in detail. Collectively, these studies provide new insight into the factors controlling the electronic ground state of the cations of Ni(II) porphyrins.

## Experimental Section

$H_2$TPP (chlorin free) was obtained from Midcentury and used as received. Nickel(II) was inserted via the DMF method using nickel acetate.[11] The spectroscopic and electrochemical studies were performed on samples prepared in $CH_2Cl_2$ (Aldrich, HPLC grade). $CH_2Cl_2$ was purified by vacuum distillation from $P_2O_5$ followed by another distillation from $CaH_2$. The effects of coordinating ligands were investigated by adding an ~100-fold excess of the ligand (L = THF, py, $CH_3CN$, $(C_6H_5)_3P$, CO, and $CN^-$) to the solution containing electrochemically generated $Ni^{II}(TPP^{\bullet})^+$ (vide infra). THF (Aldrich, HPLC grade) was stirred over sodium metal and distilled under vacuum; py and py-$d_5$ (Aldrich) were dried for 3 weeks over molecular sieves; $CH_3CN$ (Burdick and Jackson) was refluxed over $CaH_2$ and distilled under vacuum; $(C_6H_5)_3P$ (Aldrich), KCN (Aldrich), tetrabutylammonium cyanide ((TBA)CN) (Aldrich), and LiCN (Alpha) were dried under vacuum for 24 h; CO (Matheson) was used as received. All solvents were degassed thoroughly by several freeze−pump−thaw cycles prior to use. Tetrabutylammonium hexafluorophosphate (TBAH; Aldrich, recrystallized three times from methanol and dried under vacuum at 110 °C) was used as the supporting electrolyte in the electrochemical experiments.

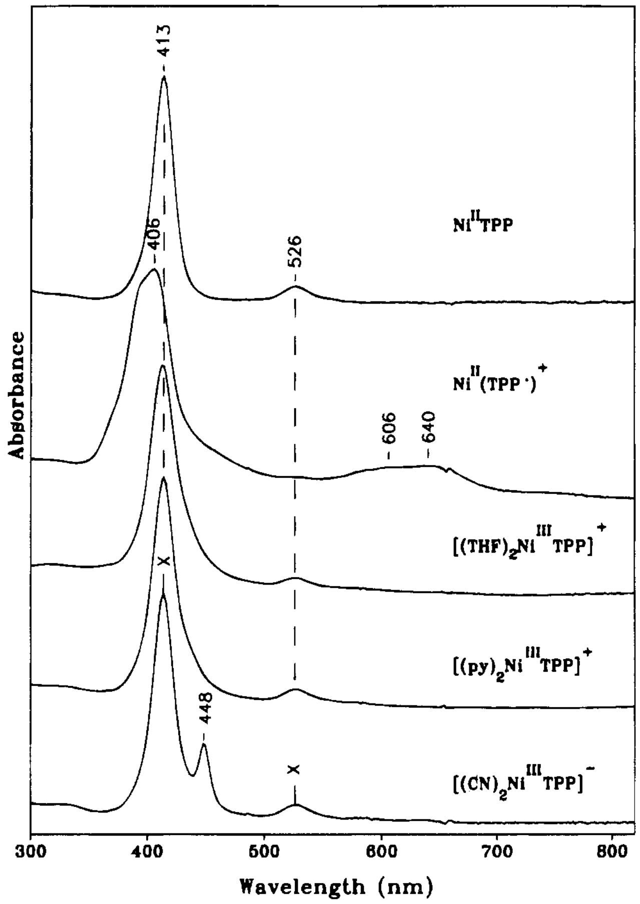

**Figure 1.** Ambient-temperature absorption spectra of $Ni^{II}$TPP, $Ni^{II}(TPP^{\bullet})^+$, $[(THF)_2Ni^{III}TPP]^+$, $[(py)_2Ni^{III}TPP]^+$, and $[(CN)_2Ni^{III}TPP]^-$. All spectra were recorded in $CH_2Cl_2$ solutions containing 0.1 M TBAH. The bands marked by an × in the spectrum of $[(CN)_2Ni^{III}TPP]^-$ are due to $Ni^{II}$TPP (see text).

$Ni^{II}$TPP was oxidized to $Ni^{II}(TPP^{\bullet})^+$ using standard electrochemical instrumentation. The electrochemical cell was housed in a glovebox under inert atmosphere. All subsequent manipulations of the oxidized samples were also conducted in the glovebox. The integrity of $Ni^{II}(TPP^{\bullet})^+$ was checked by cyclic voltammetry after the termination of electrolysis. The $Ni^{II}(TPP^{\bullet})^+$ sample was then transferred into an optical cuvette (absorption), quartz capillary (RR), quartz tube (EPR), or small vial. The ligands were added to the samples in the vials and these solutions were immediately transferred to a cuvette, tube, or capillary. In the case of CO, the gas was bubbled through the solution for ~5 min. In all cases, the samples were carefully sealed prior to their removal from the glovebox. The spectroscopic studies were performed immediately after removal from the glovebox using procedures and instrumentation previously described.[12] The absorption and RR spectra of the complexes were obtained at ambient temperature. The EPR spectra were obtained at both ambient and low temperatures.

## Results and Discussion

Oxidation of $Ni^{II}$TPP in $CH_2Cl_2$/0.1 M TBAH changes the color of the solution from orange to green. The ambient-temperature absorption, RR, and EPR spectra of the green product are consistent with those previously reported for $Ni^{II}(TPP^{\bullet})^+$.[2,3,5] These spectra are shown in Figures 1−3, respectively. For comparison, the ambient-temperature absorption and RR spectra of $Ni^{II}$TPP are included in Figures 1 and 2 (top traces). Upon freezing of the solution containing $Ni^{II}(TPP^{\bullet})^+$, the color changes from green to orange and an anisotropic EPR spectrum characteristic of the $[Ni^{III}TPP]^+$ valence tautomer

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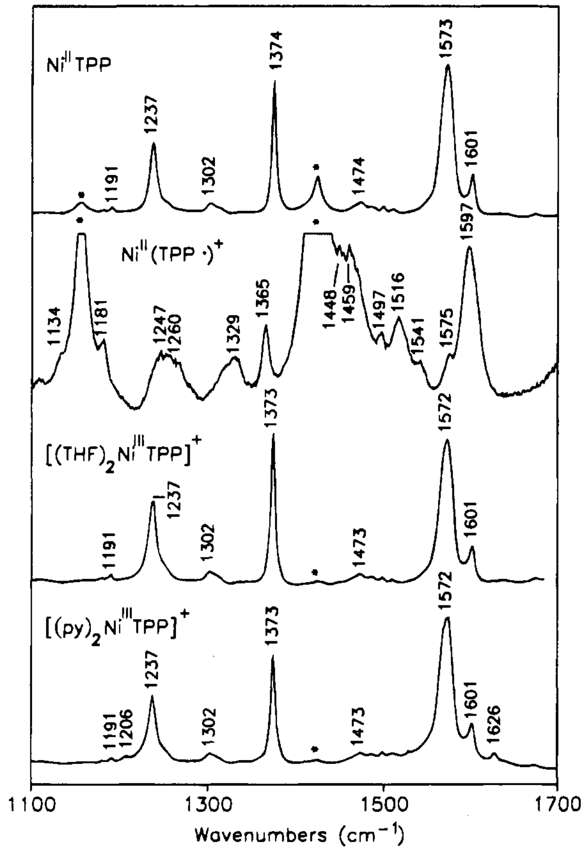

**Figure 2.** High-frequency regions of the ambient-temperature, B-state-excitation RR spectra of $Ni^{II}TPP$, $Ni^{II}(TPP^{\bullet})^+$, $[(THF)_2Ni^{III}TPP]^+$, and $[(py)_2Ni^{III}TPP]^+$ recorded in $CH_2Cl_2$ solutions containing 0.1 M TBAH. The bands marked by the asterisk are due to solvent. The spectra of all the complexes were recorded with $\lambda_{ex} = 413.1$ nm with the exception of $Ni^{II}(TPP^{\bullet})^+$, for which $\lambda_{ex} = 457.9$ nm. The laser power at the sample was typically 5 mW; the spectral resolution was ~2 $cm^{-1}$.

appears.[2] The low-temperature (77 K) EPR spectrum observed for this species is included in Figure 3 (second trace). For reasons discussed below, the low-temperature valence tautomer is designated as $[(PF_6)_2Ni^{III}TPP]^-$ in the figure and in all subsequent discussion. The fact that the low-temperature EPR spectrum also exhibits a signal characteristic of $Ni^{II}(TPP^{\bullet})^+$ ($g \sim 2.00$) indicates that the conversion to $[(PF_6)_2Ni^{III}TPP]^-$ is not quantitative.

**A. Effects of Coordinating Ligands.** The addition of coordinating ligands (THF, py, $CH_3CN$, $(C_6H_5)_3P$, CO, and $CN^-$) to the solution containing $Ni^{II}(TPP^{\bullet})^+$ results in an immediate change in all the spectral properties of the complex. In all cases, the color of the solution changes from green to orange and the absorption, RR, and EPR signatures characteristic of the $\pi$-cation radical completely disappear. The detailed features of the spectra indicate that certain ligands react with the $Ni^{II}(TPP^{\bullet})^+$ yielding the neutral starting material, $Ni^{II}TPP$, whereas others form Ni(III) complexes of the general form $[(L)_2Ni^{III}TPP]^+$. The rationale for these conclusions is discussed in more detail below.

**1. THF, py, and $CH_3CN$.** The ambient-temperature absorption spectra observed upon addition of THF and py to the solution containing $Ni^{II}(TPP^{\bullet})^+$ are shown in Figure 1 (third and fourth traces). The spectra observed in the presence of THF, py, and $CH_3CN$ (not shown) are similar to one another and similar to those previously reported for the $[(PF_6)_2Ni^{III}TPP]^-$ valence tautomer formed by freezing solutions of $Ni^{II}(TPP^{\bullet})^+$.[2,5a] The absorption spectra of these species are also qualitatively similar to those of $Ni^{II}TPP$; however, there are discernible differences. In particular, the Soret band of the oxidized complexes is broader and a weak shoulder appears on the red side of the band contour. Collectively, these observations suggest that the addition of THF, py, and $CH_3CN$ converts $Ni^{II}(TPP^{\bullet})^+$ to Ni(III) species which have an electronic ground state similar to that of the $[(PF_6)_2Ni^{III}TPP]^-$ valence tautomer (low-spin Ni(III) with the unpaired electron in the $d_{z^2}$ orbital[2,5a]). This is confirmed by the RR and EPR signatures observed for the oxidized complexes (vide infra).

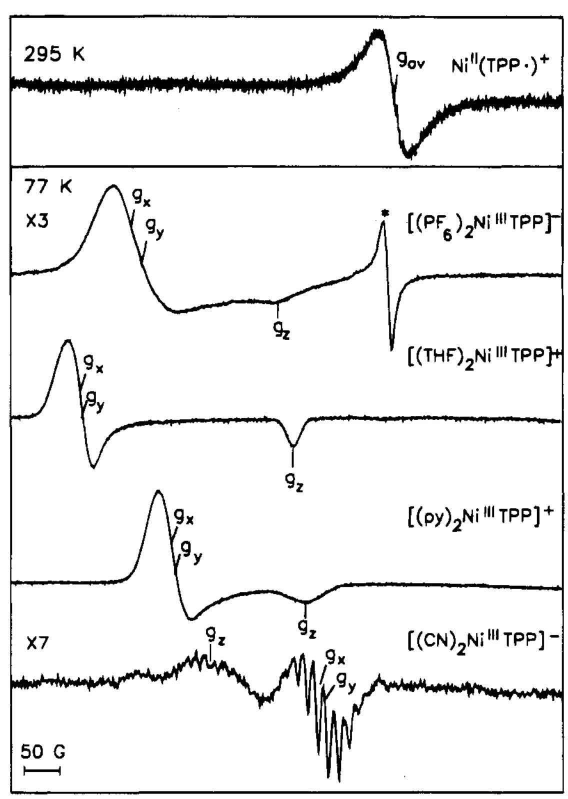

**Figure 3.** EPR spectra of the oxidized complexes. The spectrum of $Ni^{II}(TPP^{\bullet})^+$ (top trace) was recorded at 295 K. All other spectra were recorded at 77 K. The Ni(III) valence tautomer formed at low temperature (second trace) is designated as $[(PF_6)_2Ni^{III}TPP]^-$ (see text). The signal marked by the asterisk in the spectrum of this complex is due to residual $Ni^{II}(TPP^{\bullet})^+$ (see text). All spectra were recorded in $CH_2Cl_2$ solutions containing 0.1 M TBAH. The microwave power and modulation amplitude were typically 5 mW and 5 G, respectively.

The ambient-temperature RR spectra observed after addition of THF and py to the solution containing $Ni^{II}(TPP^{\bullet})^+$ are shown in Figure 2 (third and fourth traces). As is the case for the absorption spectra, the ambient-temperature RR spectra observed in the presence of these ligands (and $CH_3CN$) are similar to one another and similar to that previously reported for the $[(PF_6)_2Ni^{III}TPP]^-$ valence tautomer at low temperature.[5a] The RR spectra observed after addition of the coordinating ligands are also qualitatively indistinguishable from those of $Ni^{II}TPP$. This similarity of the RR spectra of the Ni(II) and Ni(III) complexes is consistent with the removal of an electron from the $d_{z^2}$ orbital of the metal ion yielding a low-spin species.[5a] The general appearance of the RR spectra of the orange oxidation products rules out the possibility that they are high-spin Ni(II) complexes antiferromagnetically coupled to a porphyrin $\pi$-cation radical. The RR spectra of both the $\pi$-cation radical (Figure 2, second trace) and high-spin Ni(II) porphyrins[13]

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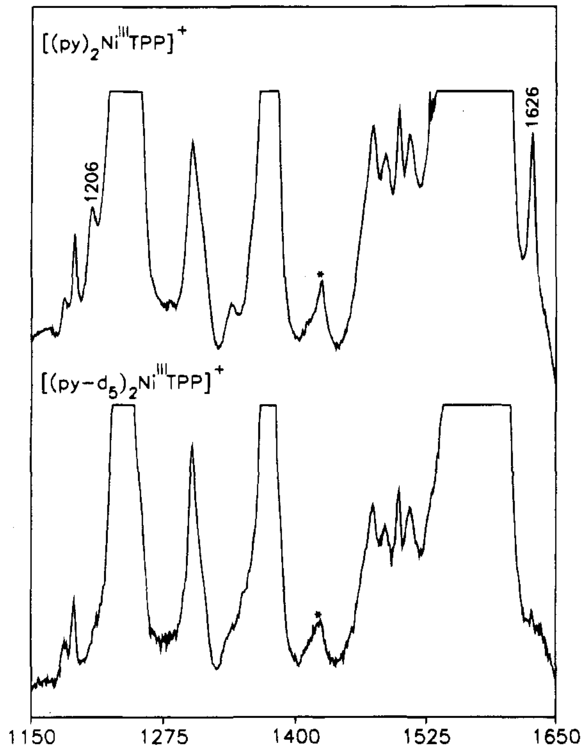

**Figure 4.** Expanded view of the high-frequency regions of the ambient temperature, B-state-excitation RR spectra of [(py)$_2$Ni$^{III}$TPP]$^+$ and [(py-$d_5$)$_2$Ni$^{III}$TPP]$^+$ recorded in $CH_2Cl_2$ solutions containing 0.1 M TBAH. The band marked by the asterisk is due to solvent. The conditions are the same as those listed for Figure 2.

are quantitatively different from those of low-spin Ni(II) and Ni(III) porphyrins.[5]

The fact that the RR spectra of the orange oxidized complexes are nearly indistinguishable from that of Ni$^{II}$TPP prompted us to carefully examine the spectra for bands due to bound axial ligands. In the case of complexes formed in the presence of THF (Figure 2, third trace) and $CH_3CN$ (not shown), no features could be found that are assignable to bound ligands. This is not surprising, given that there is no obvious mechanism for resonance enhancement of axial-ligand vibrations. Nevertheless, RR bands assignable to axial-ligand modes are observed for the complex obtained upon addition of py. An expanded view of the RR spectrum of the py complex is shown in Figure 4 (top trace). The spectrum obtained upon substitution of py-$d_5$ is also shown in the figure (bottom trace). Close inspection of the data obtained for the py complex reveals weak bands at 1626 and 1206 cm$^{-1}$ bands that are not present in the spectrum of Ni$^{II}$TPP. Both of these bands are identified as py modes by the fact that they undergo an isotope shift upon substitution of py-$d_5$. The analogs of the 1626- and 1206-cm$^{-1}$ are not readily identified in the spectrum of the complex formed with py-$d_5$. The 1626- and 1206-cm$^{-1}$ RR bands cannot be attributed to either free py, which exhibits bands at 1580 and 1214 cm$^{-1}$,[14] or py adducts of Ni$^{II}$TPP, which cannot be formed at the low concentrations of py used in the experiments. The assignment of the 1626- and 1206-cm$^{-1}$ bands as vibrations of bound py has precedent in RR studies of (py)$_2$M$^{II}$(octaethylporphyrin) complexes (M = Fe(II), Ru(II), Os(II)).[15] These studies have shown that complexation of py results in a significant upshift (~20 cm$^{-1}$) of the 1580-cm$^{-1}$ band and a small downshift (~4 cm$^{-1}$) of the 1214-cm$^{-1}$ band. These trends parallel those observed here for the nickel species. The absence of the RR bands from the spectrum of the complex formed with py-$d_5$ can be rationalized by the magnitudes of the expected deuteriation shifts of the 1626- and 1206-cm$^{-1}$ bands (~40 and 300 cm$^{-1}$, respectively[14,15]). A 40-cm$^{-1}$ shift would place the analog of the 1626-cm$^{-1}$ band under the strong porphyrin modes in the 1580−1600-cm$^{-1}$ region. Similarly, a 300-cm$^{-1}$ shift would place the analog of the 1206-cm$^{-1}$ band under porphyrin bands in the 900-cm$^{-1}$ region (not shown).

The final confirmation that the addition of THF, py, and $CH_3CN$ converts Ni$^{II}$(TPP$^{\bullet}$)$^+$ to Ni(III) complexes comes from the EPR signatures. In the presence of all three ligands, no EPR signals are observed at ambient temperature. As the sample is cooled, the optical signatures of the solutions are retained (orange color) and EPR signals characteristic of square planar Ni(III) complexes[4] begin to appear. These signals are only clearly observed below 180 K. Similar behavior is observed for the Ni(III) complexes of the $\beta$-oxoporphyrins.[7] We attribute the absence of EPR signals at ambient temperature to fast electron-spin relaxation of the Ni(III) ion. At 77 K, strong EPR signals are observed from all three complexes. This is illustrated for the THF and py complexes in Figure 3 (third and fourth traces). These signals are significantly stronger than those observed for the [(PF$_6$)$_2$Ni$^{III}$TPP]$^-$ valence tautomer (second trace). The stronger signals observed for the THF and py complexes is attributed to quantitative conversion to the Ni(III) species as is evidenced by the absence of an EPR signal due to residual Ni$^{II}$(TPP$^{\bullet}$)$^+$.

The EPR spectra of the THF, py, and $CH_3CN$ (not shown) complexes are qualitatively similar to one another and similar to those of the [(PF$_6$)$_2$Ni$^{III}$TPP]$^-$ valence tautomer. Consistent with the optical and RR data, the EPR signatures are characteristic of an axially symmetric $S = {}^1/_2$ spin system with the unpaired electron in the $d_{z^2}$ orbital ($g_{\perp} > g_{\parallel}$).[4] The $g_{\perp}$ values vary among the complexes, indicative of different ligand-field strengths for the different axial ligands. In order to obtain a better understanding of the EPR data, the spectra of the various complexes were simulated. These simulations revealed that the signals from all the complexes are rhombic rather than axial (for convenience, we have retained the designations $g_{\parallel}$ and $g_{\perp}$ in the text). The $g$ values and hyperfine parameters (vide infra) obtained from the simulations are summarized in Table 1.

Comparison of the EPR spectra of the various Ni(III) species reveals that the $g_{\parallel}$ signal of the complex with THF (Figure 3, third trace) is relatively narrow whereas the $g_{\parallel}$ signals of the complexes with py (fourth trace) and $CH_3CN$ (not shown) are much broader. The broad $g_{\parallel}$ signals observed for the latter two complexes are qualitatively similar to that observed for the [(PF$_6$)$_2$Ni$^{III}$TPP]$^-$ valence tautomer (second trace). Simulations of the EPR spectra of the py and $CH_3CN$ complexes indicate that the broadening can be accounted for if superhyperfine interactions from two equivalent $^{14}$N nuclei are included. Inclusion of a single $^{14}$N nucleus gives much poorer fits to the spectra. This result establishes the Ni(III) species as complexes of the general form [(L)$_2$Ni$^{III}$TPP]$^+$. The broadening observed for the EPR signals of the [(PF$_6$)$_2$Ni$^{III}$TPP]$^-$ valence tautomer can also be accounted for in terms of superhyperfine interactions due to axial ligands. The width of the EPR signals observed for the valence tautomer suggests that the hyperfine interactions are large and that more than two nuclei contribute. Simulations which include interactions with two $^{19}$F and two $^{31}$P nuclei give the best fit to the spectrum. This result confirms that conversion to the Ni(III) species is induced by complexation with PF$_6^-$ at

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**Table 1.** EPR Parameters for the Oxidized Complexes[a]

| | $g_{av}$ | $g_x$ | $g_y$ | $g_z$ | $A_x$ (G) | $A_y$ (G) | $A_z$ (G) |
|---|---|---|---|---|---|---|---|
| $Ni^{II}(TPP^{\bullet})^+$ | 2.005 | 2.012 | ~2.004 | ~2.002 | 1.44($^{14}N_{por}$) | 1.44($^{14}N_{por}$) | 1.44($^{14}N_{por}$) |
| $[(PF_6)_2Ni^{III}TPP]^-$ | 2.227[b] | 2.272 | 2.230 | 2.110 | 0.0 | 0.0 | 70.4($^{19}F_{ax}$) 17.6($^{31}P_{ax}$) |
| $[(THF)_2Ni^{III}TPP]^+$ | 2.242[b] | 2.328 | 2.305 | 2.093 | 0.0 | 0.0 | 0.0 |
| $[(CH_3CN)_2Ni^{III}TPP]^+$ | 2.217[b] | 2.286 | 2.256 | 2.108 | 0.0 | 0.0 | 15.8($^{14}N_{ax}$) |
| $[(py)_2Ni^{III}TPP]^+$ | 2.173[b] | 2.228 | 2.207 | 2.083 | 0.0 | 0.0 | 15.8($^{14}N_{ax}$) |
| $[(CN)_2Ni^{III}TPP]^-$ | 2.096[b] | 2.065 | 2.045 | 2.178 | 14.1($^{14}N_{por}$) | 14.1($^{14}N_{por}$) | 12.3($^{14}N_{por}$) |

[a] All values were obtained from the low-temperature (77 K) spectra with the exception of $g_{av}$ for $Ni^{II}(TPP^{\bullet})^+$, which was obtained from the ambient-temperature spectrum. All values are ±0.001. [b] Calculated value.

low temperatures, as was originally suggested by Dolphin and co-workers.[2]

In order to explore further the properties of the $[(L)_2Ni^{III}TPP]^+$ complexes (L = THF, py, $CH_3CN$) a number of other studies were conducted. In one study, the complexes were maintained at ambient temperature, under an inert atmosphere, and their spectral features were periodically examined. In the case of $[(THF)_2Ni^{III}TPP]^+$ and $[(CH_3CN)_2Ni^{III}TPP]^+$, the complexes were stable for at least a day. $[(py)_2Ni^{III}TPP]^+$ was somewhat less stable but typically maintained its integrity for periods of 6–10 h. With time, all the complexes reduced back to $Ni^{II}TPP$. This was evidenced by the gradual loss of both the characteristic Ni(III) EPR signature observed at low-temperature and the optical features which distinguish the Ni(III) from Ni(II) species at ambient temperature. Reduction to the neutral species most likely occurs due to the presence of small amounts of impurities in the solvents and, in the case of $[(py)_2Ni^{III}TPP]^+$, reaction with the excess py in solution.[16] When stored at low temperature, all the complexes appear to be stable indefinitely. In other studies, electrochemical oxidations were conducted in THF, py, and $CH_3CN$ solutions. These experiments did not afford one-electron-oxidized species that were sufficiently stable for characterization. These results explain why certain previous studies on the oxidation products of $Ni^{II}TPP$ have failed to identify stable Ni(III) species.[3,8] Finally, efforts were made to isolate the $[(L)_2Ni^{III}TPP]^+$ complexes. However, these attempts have been unsuccessful thus far, largely due to the presence of excess supporting electrolyte.

**2. $(C_6H_5)_3P$ and CO.** The ambient-temperature absorption and RR spectra observed upon addition of $(C_6H_5)_3P$ and CO to the solution containing $Ni^{II}(TPP^{\bullet})^+$ (not shown) are identical to those of $Ni^{II}TPP$ (Figure 1, top trace). No EPR signals are observed from the solutions at either ambient or low temperatures. Together, these results indicate that both $(C_6H_5)_3P$ and CO reduce $Ni^{II}(TPP^{\bullet})^+$ back to $Ni^{II}TPP$. In the case of $(C_6H_5)_3P$, this result is not surprising, considering the reducing capability of the compound.[17] On the other hand, the reactivity of CO is somewhat unexpected and merits additional investigation.

**3. KCN, (TBA)CN, and LiCN.** The addition of $CN^-$ to solutions containing $Ni^{II}(TPP^{\bullet})^+$ results in more complicated behavior than is observed upon addition of the other ligands. Initially, $CN^-$ was introduced by adding KCN to the solution. The absorption spectrum observed in the presence of KCN is characterized by two Soret features, one near that observed for the other Ni(III) complexes (413 nm) and the other significantly to the red (448 nm). This spectrum is included in Figure 1 (bottom trace). Over the course of ~30 min, the 448 nm feature disappears and only the 413 nm band remains. The general appearance of the absorption spectrum observed in the presence of KCN is suggestive of a mixture containing at least two species. We anticipated that a mixture might arise because KCN has very low solubility in $CH_2Cl_2$, thus impeding complex formation. In attempts to address this issue, experiments were also conducted with (TBA)CN and LiCN, both of which are soluble in organic solvents. Unexpectedly, addition of these salts results only in the formation of a complex which exhibits a 413 nm Soret band.

RR and EPR studies were also conducted on the oxidized complexes obtained upon addition of the various $CN^-$ salts. Excitation into the 413 nm absorption band yielded RR spectra (not shown) identical to those of $Ni^{II}TPP$. Attempts to obtain RR spectra of the complex exhibiting both 413 and 448 nm Soret bands were unsuccessful due to the instability of this species. At ambient temperature, no EPR signals are observed for any of the complexes formed upon addition of $CN^-$. The solutions exhibiting a single Soret band at 413 nm also fail to yield signals at low temperature. In contrast, weak EPR signals are observed at low temperature for the solution exhibiting two Soret bands. A representative EPR spectrum is included in Figure 3 (bottom trace). This spectrum is characteristic of an approximately axially symmetric $S = {}^1/_2$ system with the unpaired electron in the $d_{x^2-y^2}$ orbital ($g_{\parallel} > g_{\perp}$).[4] The $g_{\perp}$ EPR signal also displays a well-resolved nine-line superhyperfine pattern which can be attributed to interaction of the unpaired electron with the four pyrrole $^{14}N$ nuclei (Table 1). Collectively, these observations suggest that the 413 nm absorbing species is $Ni^{II}TPP$, which is formed via reduction of the $\pi$-cation radical by $CN^-$. Reduction back to the neutral starting material appears to be quantitative when large amounts of $CN^-$ are present in solution, as is the case for the soluble $CN^-$ salts ((TBA)CN and LiCN). On the other hand, the sparing solubility of KCN appears to allow formation of a Ni(III) complex (albeit unstable), most likely formulated as $[(CN)_2Ni^{III}TPP]^-$. The Soret band of this complex occurs at 448 nm. The red shift of the Soret band is consistent with the occupation of the $d_{x^2-y^2}$ orbital.[13]

Both the EPR and optical data obtained for $[(CN)_2Ni^{III}TPP]^-$ indicate that the electronic ground state of this complex is different from that of the other $[(L)_2Ni^{III}TPP]^+$ complexes (L = THF, py, $CH_3CN$) ($^2B_{2g}$ vs $^2A_{1g}$, $D_{4h}$ symmetry). The change in electronic ground state is attributed to the very strong ligand field of the $CN^-$ ion, which raises the energy of the $d_{z^2}$ orbital above that of $d_{x^2-y^2}$. The fact that an unpaired electron of $[(CN)_2Ni^{III}TPP]^-$ resides in the $d_{x^2-y^2}$ orbital raises the possibility that this complex is not actually a Ni(III) species but rather contains a high-spin Ni(II) ion antiferromagnetically coupled to a porphyrin $\pi$-cation radical. As was previously noted, this formulation has been proposed for the ground states of the oxidation products of $Ni^{II}OETPP$ obtained in the presence of coordinating ligands.[10b] The spectroscopic data reported here for $[(CN)_2Ni^{III}TPP]^-$ do not definitively distinguish between these two formulations for the electronic ground state. Nevertheless, the features observed in both the absorption and EPR spectra appear to be qualitatively more consistent with a metal-oxidized species.

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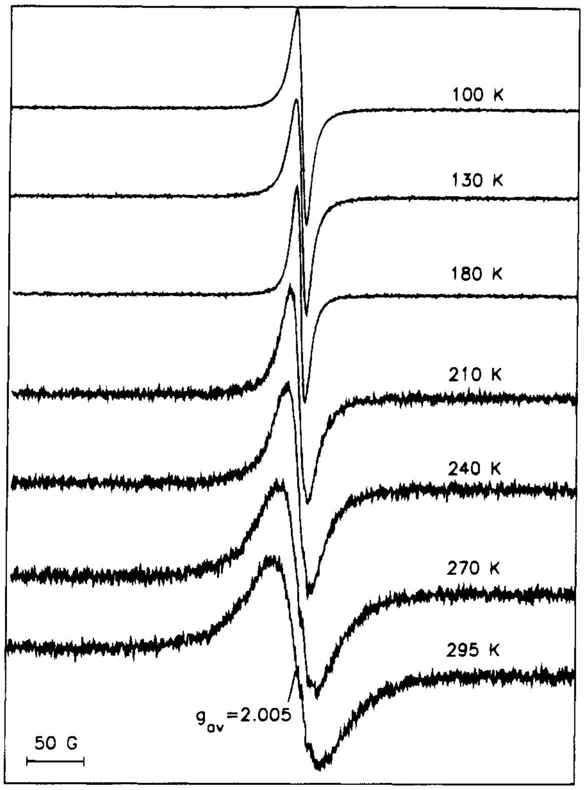

**Figure 5.** Temperature dependence (100–300 K) of the EPR spectra of $Ni^{II}(TPP^{\bullet})^+$. All spectra were recorded in $CH_2Cl_2$ solutions containing 0.1 M TBAH and trace amounts of $H_2O$ (see text). The microwave power and modulation amplitude were typically 5 mW and 5 G, respectively.

**B. Effects of Metal–Porphyrin Orbital Mixing.** The detailed characteristics of the EPR signals observed for the $Ni^{II}(TPP^{\bullet})^+$ valence tautomer provide additional insight into the properties of the electronic ground states of all the oxidized species. The temperature dependence of the EPR signal observed for the $\pi$-cation radical is shown in Figure 5. The spectra shown in the figure were obtained for the oxidized species formed in the presence of trace amounts of $H_2O$. The EPR line shapes observed for $Ni^{II}(TPP^{\bullet})^+$ in the presence and absence of $H_2O$ are identical. However, in the presence of $H_2O$ (or $Br^-$), $Ni^{II}(TPP^{\bullet})^+$ does not convert to a Ni(III) complex at low temperature.[2] This allows for a more quantitative analysis of the EPR signal of the $\pi$-cation radical than is possible when both this species and the Ni(III) complex are present at low temperature. In the latter case, the low-field side of the EPR signal of the $\pi$-cation radical is perturbed by the $g_{\parallel}$ signal of the Ni(III) complex (Figure 3).

At ambient temperature, the EPR signal of $Ni^{II}(TPP^{\bullet})^+$ is isotropic and very broad (48 G) (Figure 5). Upon cooling, the signal narrows and appears to remain isotropic. However, simulations of the frozen solution EPR spectrum of $Ni^{II}(TPP^{\bullet})^+$ indicate that the signal is actually anisotropic and slightly rhombic (Table 1). The anisotropy (~0.01) is much larger than expected for a species nominally classified as a porphyrin $\pi$-cation radical[1b] and is indicative of nonnegligible nickel ion character in the wave function for $Ni^{II}(TPP^{\bullet})^+$. Accordingly, it is fortuitous that the average $g$ value observed for $Ni^{II}(TPP^{\bullet})^+$ in liquid solution is near the free electron value. The rhombicity observed for the EPR signals of $Ni^{II}(TPP^{\bullet})^+$ further indicates that there are no symmetry restrictions on the mixing between the d orbitals of the metal and the $a_{2u}$-like porphyrin orbital, the latter of which formally contains the hole in the $\pi$-cation radical.[1b,5b] However, the principal mixing channel is most likely through the $d_{z^2}$ orbital of the metal ion. The overlap of this metal orbital with the $a_{2u}$-like porphyrin orbital in the low-symmetry environment provides a direct pathway for transferring hole density between the metal and ligand. The mixing of metal character into the wave function for $Ni^{II}(TPP^{\bullet})^+$ would also be expected to shorten the electron-spin relaxation time and could account for the unusually broad EPR signal observed at ambient temperature. Recall that the ambient-temperature relaxation rates for the $[(L)_2Ni^{III}TPP]^+$ complexes are sufficiently fast that no EPR signals are observed. Collectively, these results indicate that the limiting-case descriptors "Ni(III) complex" and "porphyrin $\pi$-cation radical" do not accurately describe the ground states of the oxidation products of $Ni^{II}TPP$.

## Summary and Conclusions

The spectroscopic data reported herein indicate that relatively stable Ni(III) complexes of TPP can be obtained at ambient temperature when coordinating ligands, such as THF, py, and $CH_3CN$, are present. The formation of these complexes is facilitated by mixing of the metal and porphyrin orbitals. On the basis of the ease of obtaining the $[(L)_2Ni^{III}TPP]^+$ complexes, it is not obvious why these species have not been identified in previous studies of the oxidized complexes of $Ni^{II}TPP$. The most plausible explanation lies in the purity of the solvents and/or the type of solvent system used to obtain the oxidized species. The relative stability of the $[(L)_2Ni^{III}TPP]^+$ complexes suggests that these species can be isolated. Efforts to obtain these complexes in pure solid or crystalline form are currently in progress.

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