ligands (i.e. tyrosine or histidine imidazole). The presence of non-sulfur terminal ligands already has been suggested for the Rieske protein from *T. thermophilus*, where two of the coordination sites on the $Fe_2S_2$ centers are thought to be occupied by the nitrogen atoms of two histidine imidazole residues.[16] The possible involvement of non-sulfur terminal ligands on the iron atoms of the Fe/Mo/S aggregate in nitrogenase has been suggested by the small number of cysteinyl residues in the Fe-Mo protein of nitrogenase[36] and by recent Fe EXAFS studies. In the latter, performed on the Fe-Mo cofactor of nitrogenase, each of the iron atoms shows (on the average) approximately one light atom (O or N) at a distance of 1.81 (7) Å.[37]

The availability of a preformed hexanuclear Fe/S cluster in the form of the $Fe_6S_6$ prismanes presents a unique opportunity for the assembly of heterometallic Fe/Mo/S clusters of possible structural relevance to the Fe/Mo/S center of nitrogenase. The assembly of such clusters is possible by virtue of the stereochemical position of the sulfur atoms in the $Fe_3S_3$ hexagonal units of $Fe_6S_6$ clusters. The latter can serve as tridentate ligands for coordinatively unsaturated $M(L)_n$ fragments. In our quest for at least a structural analogue for the active site in nitrogenase we have synthesized and characterized the $[(Fe_6S_6L_6)(M(CO)_3)_2]^{n-}$ octanuclear clusters ($L = ArO^-$, $M = Mo$, $n = 3$;[38] $L = Cl$, $M = Mo$, $n = 3, 4$;[39] $L = ArO^-$, $M = W$, $n = 3$[40]). The adduct-forming properties of the $[Fe_6S_6L_6]^{n-}$ clusters and the characterization of the polymetallic products are presently under investigation in our laboratory.

**Acknowledgment.** This research was supported by a grant from the National Institutes of Health (GM-26671).

**Registry No.** I, 94499-96-4; II, 94499-92-0; $[Et_4N]_3[Fe_6S_6(O\text{-}p\text{-}C_2H_5C_6H_4)_6]$, 102538-68-1; $[Et_4N]_3[Fe_6S_6(O\text{-}2,4,6\text{-}(CH_3)_3C_6H_2)_6]$, 102538-70-5; $[Et_4N]_3[Fe_6S_6(OC_6H_5)_6]$, 102538-72-7; $[Et_4N]_3[Fe_6S_6Cl_6]$, 91294-19-8; $[Et_3MeN]_3[Fe_6S_6Br_6]$, 102538-73-8; $[Et_4N]_3[Fe_6S_6(p\text{-}CH_3C_6H_4S)_6]$, 94499-98-6; $[Et_4N]_3[Fe_6S_6(m\text{-}CH_3C_6H_4S)_6]$, 102538-75-0; $[Fe_6S_6Cl_6]^{2-}$, 93530-53-1; $[Fe_6S_6Br_6]^{2-}$, 93530-57-5; $[Fe_6S_6(p\text{-}CH_3C_6H_4O)_6]^{2-}$, 94499-99-7; $[Fe_6S_6(p\text{-}C_2H_5C_6H_4O)_6]^{2-}$, 102538-78-3; $[Fe_6S_6(p\text{-}CH_3C_6H_4S)_6]^{2-}$, 94500-00-2; $[Fe_6S_6(SCH_2Ph)_6]^{2-}$, 102538-79-4; $[Et_4N]_3[Fe_6S_6(SCH_2Ph)_6]$, 102538-77-2; $[Fe_6S_6Cl_6]^{4-}$, 94500-01-3; $[Fe_6S_6Br_6]^{4-}$, 102538-80-7; $[Fe_6S_6(p\text{-}C_2H_5C_6H_4O)_6]^{4-}$, 102538-81-8; $[Fe_6S_6(SCH_2Ph)_6]^{4-}$, 102538-82-9.

**Supplementary Material Available:** Tables of positional and thermal parameters and bond distances and angles for the cations of I and II and figures showing the temperature dependence of the isotropically shifted phenyl ring proton resonances of $[Et_4N]_3[Fe_6S_6(p\text{-}CH_3C_6H_4X)]$ (X = S, O) (11 pages). Ordering information is given on any current masthead page.

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# Notes

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## Intramolecular Electron Transfer in the One-Electron Oxidation Product of (Tetraphenylporphinato)nickel(II), As Studied by Resonance Raman Spectroscopy

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*Received December 9, 1985*

There is much current interest in porphyrin radical cations because of their involvement in photoinduced electron transfer in natural and synthetic systems[1] and because of the occurrence of a $Fe^{IV}$ porphyrin radical as an identifiable intermediate in peroxidase enzymes.[2] A point of considerable interest is the competition between electron removal from the porphyrin ring vs. the central metal ion of metalloporphyrins. It is known that iron(III) porphyrin radicals are stable when the axial ligands are chloride or perchlorate,[3] but oxidation to the iron(IV) porphyrin is favored when there is an oxo ligand, e.g. in compound II of horseradish peroxidase,[4] while removal of a second electron (compound I) is from the porphyrin ring.[5] The metal vs. porphyrin based oxidation products are in general valence tautomers rather than resonance forms, because the valence porphyrin orbitals, $a_{1u}$ or $a_{2u}$, are of odd parity and are orthogonal to the even-parity valence d orbitals of the redox-active transition metals.

An early example of this valence tautomerism was discovered by Dolphin and co-workers,[6] who noted that oxidation of nickel tetraphenylporphine ($Ni^{II}TPP$) gave a green solution, with an absorption spectrum characteristic of $TPP^{\bullet +}$. Freezing the solution to 77 K led to an orange product when the oxidation had been carried out electrolytically in hexafluorophosphate electrolyte, although no spectral change was observed when bromine oxidation was used. The orange product was established to be a nickel(III) porphyrin via its anisotropic ESR spectrum ($g_\perp = 2.286$, $g_\parallel = 2.086$) as well as its optical spectrum. Apparently, $PF_6^-$ stabilizes the $Ni^{III}$ product at low temperature, whereas $Br^-$ does not.

We have reexamined this system using resonance Raman (RR) spectroscopy, which provides a sensitive probe of the porphyrin structure via the porphyrin vibrational mode frequencies. The results are fully consistent with the interpretation from optical and ESR spectra. The green product shows large frequency shifts, associated with porphyrin cation radical formation, whereas the orange product shows essentially the same frequencies as $Ni^{II}TPP$, because electron removal from the $Ni^{II}$ $d_{z^2}$ orbital has a negligible effect on porphyrin structure. Because of this sensitivity to the ligand structure, resonance Raman spectroscopy is expected to be a useful probe of valence tautomerism.

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**Table I.** RR Frequencies of $Ni^{II}TPP$, $[Ni^{III}TPP]^+$ and $Ni^{II}TPP^{\bullet+}$

| assignment[a] | room temp $Ni^{II}TPP$ | 77 K $Ni^{II}TPP$ | 77 K $[Ni^{III}TPP]^+$ | 77 K $Ni^{II}TPP^{\bullet+}$ | $\Delta$[b] |
|---|---|---|---|---|---|
| A $A_{1g}$ phenyl | 1596 | 1596 | 1594 | 1595 | −1 |
| $\nu_2$ $A_{1g}$ $\nu(C_b - C_b) + \delta(C_b - H)$ | 1568 | 1569 | 1568 | 1552 | −16 |
| $\nu_{20}$ $A_{2g}$ $\nu(C_a - C_m) + \nu(C_b - C_b)$ | 1546 | 1546 | 1545 | 1541 | −5 |
| $\nu_{11}$ $B_{1g}$ $\nu(C_b - C_b) + \delta(C_b - H)$ | 1505 | 1505 | 1505 | 1473 | −32 |
| $\nu_4$ $A_{1g}$ $\nu(C_a - N)$ | 1369 | 1371 | 1369 | 1362 | −7 |
| C $A_{1g}$ $\nu(C_m - C_\phi)$ | 1233 | 1235 | 1232 | 1231 | −2 |

[a] References 7 and 8. [b] $\nu_{Ni^{II}TPP^{\cdot+}} - \nu_{Ni^{II}TPP}$.

## Experimental Section

$Ni^{II}TPP$ was obtained from Mid-Century Chemical and purified by chromatography on alumina (A540) to remove fluorescent impurities. It was oxidized with equimolar bromine in $CH_2Cl_2$ or by controlled-potential electrolysis (1.15 V vs. SCE) in $CH_2Cl_2$ containing 0.1 M tetrabutylammonium hexafluorophosphate (TBHP). A standard electrochemical cell was modified to permit circulation of the solution through a glass capillary through Viton tubing connected to the cell. The capillary served as a flowing Raman cell. The bromine oxidation product was contained in a spinning NMR cell for Raman spectroscopy via backscattering. Chemical integrity was checked via absorption spectrophotometry. Low-temperature spectra were obtained by 135° backscattering from the surface of anaerobically transferred solution frozen in a small glass cup (~1-cm diameter). The glass cup was attached to the liquid-$N_2$ cold finger with copper grease.[7]

Raman spectra were obtained with a Spex 1401 double monochromator equipped with a cooled photomultiplier and photon-counting electronics. The data were collected digitally with a MINC (DEC) computer. Excitation lines at 406.7, 413.1, and 568.2 nm were provided by a Spectra-Physics 171 $Kr^+$ laser.

## Results and Discussion

Figure 1 (bottom) shows the RR spectrum of $Ni^{II}TPP$ obtained with 406.7-nm excitation, in resonance with the Soret absorption band. The strong RR bands are the totally symmetric porphyrin skeletal modes $\nu_2$ and $\nu_4$ at 1568 and 1369 $cm^{-1}$ and the porphyrin phenyl stretch at 1233 $cm^{-1}$.[8a] Also seen with moderate intensity are the $\nu_{12}$ mode at 1298 $cm^{-1}$ and a phenyl mode at 1596 $cm^{-1}$, whose enhancement is believed to reflect phenyl conjugation in the excited state.[8b] The top spectrum is that of the one-electron oxidation product prepared electrochemically; bromine oxidation produced an identical spectrum. Large downshifts, of 16 and 7 $cm^{-1}$, are seen for $\nu_2$ and $\nu_4$, respectively; neither the phenyl mode nor the porphyrin phenyl stretch shift significantly. This is the same pattern observed by Yamaguchi et al.[9] for the radical cations of MgTPP and ZnTPP, and there is little doubt that the species produced by $Ni^{II}TPP$ oxidation is the $Ni^{II}$ porphyrin radical cation, as was inferred from the absorption spectrum.[6] The vibrational frequency shifts reflect bonding changes associated with the extraction of an electron from the porphyrin $a_{2u}$ orbital, although the pattern is not as expected from orbital symmetry consideration.[9,10]

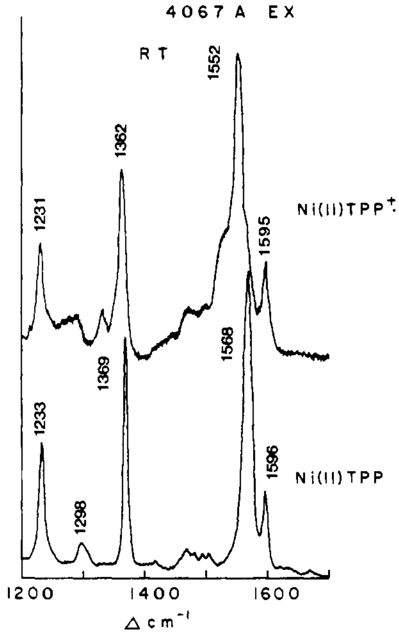

**Figure 1.** RR spectra at room temperature with 406.7-nm excitation for (bottom) $Ni^{II}TPP$ (0.2 mM) in $CH_2Cl_2$ (50-mW incident laser power) and for (top) $Ni^{II}TPP^{\bullet+}$ formed by electrolysis in 0.1 M TBHP/$CH_2Cl_2$ at 1.15 V vs. SCE (5 mW).

Figure 2 presents the same spectral comparison for frozen solutions at 77 K, when the oxidation was carried out electrochemically in the presence of hexafluorophosphate; in this case the green color of the solution changed to orange upon freezing, as observed by Dolphin and co-workers.[6] The spectra of NiTPP and the orange oxidation product are seen to be essentially the same, frequency shifts amounting to no more than 2 $cm^{-1}$. This is consistent with formulation of the oxidized species as $[Ni^{III}TPP]^+$ because the electron is removed from the Ni $d_{z^2}$ orbital, which does not interact significantly with the porphyrin orbitals. The situation is quite similar to the spectral comparison between cobalt(II) and cobalt(III) porphyrins[11a] or between iron(II) and iron(I) porphyrins;[11b] in each case, the molecules differ by one electron in the metal $d_{z^2}$ orbital and the frequency shifts are likewise very small. When the NiTPP solution prepared by bromine oxidation was frozen, the color remained green and the RR spectrum remained the same as that shown in Figure 1.

Figure 3 shows RR spectra obtained with Q-band excitation at 568.2 nm for solution species at 77 K. At this wavelength, which is in resonance with the porphyrin Q-band, nontotally symmetric modes are enhanced, $\nu_{20}$ and $\nu_{11}$ at 1546 and 1505 $cm^{-1}$, respectively, for $Ni^{II}TPP$.[8] Oxidation of the nickel to $Ni^{III}$ has very little effect on the frequencies, while radical cation formation induces appreciable frequency shifts, especially for $\nu_{11}$, which shifts down by 32 $cm^{-1}$. At this wavelength some laser-induced reduction can be seen for the radical cation, whose spectrum contains shoulders at the frequencies of the $Ni^{II}TPP$ bands. These are the first TPP radical cation frequencies reported with Q-band excitation, the previous studies having been limited to Soret excitation.[9] Table I lists the observed frequencies for $Ni^{II}TPP$, $[Ni^{III}TPP]^+$, and $Ni^{II}TPP^{\bullet+}$. Several of the frequencies are quite sensitive to cation radical formation.

In summary, RR spectroscopy can readily distinguish between oxidation of the porphyrin ring or of the metal. Porphyrin radical cation formation is accompanied by a specific pattern of skeletal mode frequency shifts. For physiological-type porphyrins, with substituents at the pyrrole instead of the methine carbon atoms, the shift pattern is even more distinctive.[11a] Consequently, the technique should be generally useful in evaluating valence tau-

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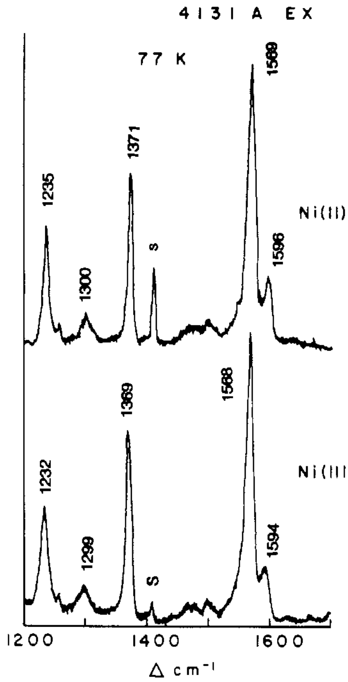

**Figure 2.** RR spectra at 77 K with 413.1-nm excitation for (top) $Ni^{II}TPP$ (0.2 mM) in $CH_2Cl_2$ (50-mW incident laser power) and for (bottom) frozen solutions containing $[Ni^{III}TPP]^+$ formed by freezing after electrolysis as in Figure 1 (10 mW).

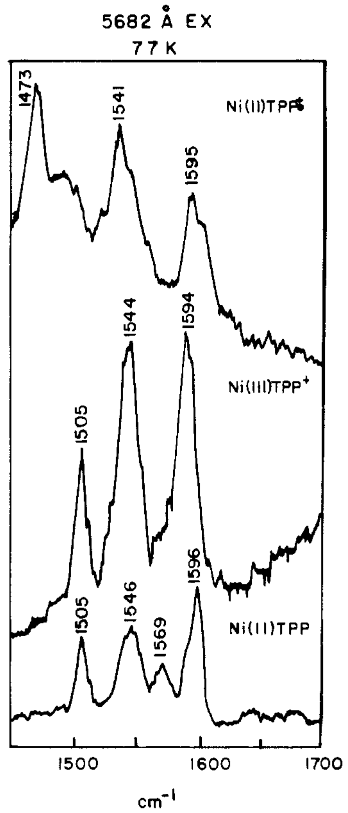

**Figure 3.** RR spectra at 77 K with 568.2-nm excitation for (bottom) $Ni^{II}TPP$ (0.4 mM) in $CH_2Cl_2$, (middle) $[Ni^{III}TPP]^+$ frozen after electrolysis as in Figure 1 (40 mW), and (top) $Ni^{II}TPP^{\bullet+}$ frozen after $Br_2$ oxidation in $CH_2Cl_2$ (20 mW).

tomerism in oxidized metalloporphyrins.

**Acknowledgment.** This work was supported by Grant DE-AC02-81ER10861 from the U.S. Department of Energy.

**Registry No.** $Ni^{III}TPP^+$, 29484-62-6; $Ni^{II}TPP$, 14172-92-0.

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## Visible-Light Production of Molecular Hydrogen by Sensitization of a Cobalt Dihydride Complex

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*Received June 26, 1985*

Visible-light-absorbing, transition-metal complexes have been of interest as a potential catalysts for solar energy conversion by the photodissociation of water. Balzani and co-workers,[1] in developing a two-photon catalytic system for water splitting, have proposed a potential cycle as follows:

$$ML_4H_2^{n+} \xrightarrow{h\nu} ML_4^{n+} + H_2 \qquad (1)$$

$$X + H_2O \xrightarrow{h\nu'} X^{2-} + 2H^+ + {}^1/_2O_2 \qquad (2)$$

$$ML_4^{n+} + X^{2-} + 2H^+ \rightarrow ML_4H_2^{n+} + X \qquad (3)$$

Equation 1, which describes the photoelimination of molecular hydrogen from a metal dihydride, has literature precedence;[2] however, the examples reported require ultraviolet rather than visible light.

Recently, we have been interested in developing photochemical systems in which a bimetallic complex contains a visible-light-absorbing (antenna) fragment covalently coupled to a visible-light-transparent, but photochemically useful reactive metal center. With these systems, absorption of visible light at the antenna fragment can be followed by intramolecular energy (or electron) transfer to the reactive fragment and subsequent reaction. While these bimetallic systems have the advantage that they avoid the inherent inefficiencies of bimolecular sensitization processes, an important criterion in the system is that the energy transfer must be competitive with electronic relaxation at the antenna fragment.

We have studied the bimolecular systems $Fe(bpy)_2(CN)_2$ and $Co(bpy)(PEt_2Ph)_2H_2^+$ (where bpy = 2,2′-bipyridine and $PEt_2Ph$ = diethylphenylphosphine) to probe the thermodynamic and kinetic constraints of the energy transfer process. The cobalt complex was chosen as a potential metal dihydride complex (eq 1) because of a preliminary report[3] indicating that broad-band irradiation produced a spectral change consistent with $H_2$ loss. The results of this study are reported herein.

### Experimental Section

**Materials.** Water used for synthesis and photochemical studies was deionized and then distilled from alkaline permanganate in an all-glass apparatus. Argon for deoxygenating solutions was purified by passing through two gas-washing bottles equipped with coarse air stones containing a Cr(II) solution over amalgamated Zn to remove $O_2$, one gas-washing bottle filled with unactivated R3-11 catalyst (Chemalog) to remove any residual $H_2$, and one gas-washing bottle filled with methanol to saturate the gas. All other materials were of reagent grade and used without further purification.

**Syntheses.** $[Co(bpy)(PEt_2Ph)_2(H_2)](ClO_4)$ was prepared by the method of Camus et al.[3] Recrystallization was achieved in a minimum volume of acetone by adding water until the first evidence of precipitation was observed. The mixture was allowed to stand in the dark for 1 h while some of the acetone evaporated. The resulting crystals were collected by filtration and dried by washing with anhydrous diethyl ether. The complex was stored in a desiccator in the dark, but slow decomposition occurred over a period of months.

$Fe(bpy)_2(CN)_2$ was prepared by a previously published procedure.[4]

**Instrumentation.** The electronic spectra of the complexes and the spectroscopic changes observed during the photochemical reaction were measured on a Bausch & Lomb Spectronic 2000 spectrophotometer using

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