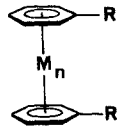
ring ^1H and ^{13}C signals of the bridging arene relative to the corresponding resonances of the terminal arenes in **2** or bis(mesitylene)chromium.[21] These shifts may arise from the electronic effects of two chromium atoms coordinated to a single bridging mesitylene[21] or anisotropic shielding by the two terminal arene rings.

In order to probe the mechanism of triple-decker sandwich formation, a matrix isolation study of the reaction of chromium vapor with mesitylene was undertaken. Microscale reactions were conducted in a Torromis matrix isolation unit[22a] by evaporation of chromium into a 5% methylcyclohexane solution of mesitylene cooled to 140 K on a sodium chloride window. The progress of the reaction was followed by monitoring changes in the UV–vis spectrum as a function of metal loading. At low Cr concentrations a single band centered at 331 nm is observed. This peak is identical with the high-energy absorption arising from a genuine sample of **1** and is thus assigned to the charge-transfer band of the bis(arene) complex.[23] At higher Cr loadings the 331-nm band increases in intensity and two new red-shifted bands centered at ca. 438 and 518 nm begin to appear. The 438-nm transition is attributed to the formation of the triple-decker sandwich complex. An authentic sample of **2** exhibits a single intense band at this wavelength. The appearance of **2** at the latter stages of the metal atom reaction suggests that the triple-decker sandwich complex is formed by competitive trapping of Cr atoms by mesitylene and **1**. The identity of the complex that gives rise to the 518-nm absorption is still in question. It is tempting to speculate that this band results from formation of the tetradecker sandwich, (mesitylene)$_4Cr_3$, via trapping of Cr^0 by 2 equiv of **1** or 1 equiv each of mesitylene and **2**. Attempts to isolate the tetradecker from preparative-scale reactions have thus far been unsuccessful.

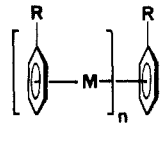
It is interesting to note that Ozin and co-workers have conducted similar matrix isolation studies of the reactions of Cr, Mo, Ti, and V vapor with a number of monomeric and polymer-supported arene substrates and with bis(arene)metal complexes. Qualitatively, the changes observed in the UV–vis spectra as a function of metal loading are identical with those reported herein. In numerous accounts of this work,[22] the appearance of a series of bands, red-shifted from the original bis(arene)metal absorption, is interpreted as evidence for the formation of "arene-stabilized metal clusters" of general structure **3**. The authors propose that the clusters are produced by stepwise addition of metal atoms to the central metal of the initially formed bis(arene)metal complex **3** (n = 1). Nuclearities as high as n = 5 have been reported.

The structure and stoichiometry represented by **3** are clearly inconsistent with our analytical and NMR data for the bimetallic mesitylene complex **2**. Based on this work, a reformulation of the purported "arene-stabilized metal clusters" as multiple-decker sandwich oligomers of general structure **4** would appear to be in



(n≥1)

3



(n≥1)

4

order, at least in the case of chromium. The likelihood that Ti, V, and Mo react in a similar fashion must be strongly considered and is currently under investigation in our lab.

Theoretical support for the existence of *extended* multiple-decker sandwich complexes comprised of long chains of alternating arene and metal units was recently established by the calculations of Burdett and Canadell[17] which indicate that the benzene–chromium multiple-decker sandwich polymer should be thermally stable. The band structure associated with such polymers and the proximity of adjacent metal centers are expected to lead to anisotropic electrical, magnetic, and optical properties. Of particular interest is the potential for one-dimensional conductivity in the mixed-valence form. The chemical and physical properties of **2** should serve as a valuable model for the more extended polymeric systems and may provide clues to the efficient synthesis of higher oligomers.

Acknowledgment. I thank Dr. R. Newmark and J. Hill (3M Analytical) for their assistance in obtaining NMR data and my colleagues Dr. F. B. McCormick and Dr. R. Wright for helpful discussions.

Supplementary Material Available: Analytical data, NMR, and UV–vis spectra for **2** and series of absorption spectra from matrix isolation study (5 pages). Ordering information is given on any current masthead page.

(20) Jonas, K.; Wiskamp, V.; Tsay, Y.-H.; Kruger, C. *J. Am. Chem. Soc.* **1983**, *105*, 5480.

(21) (a) Lagowski, J. J.; Graves, V. *J. Organomet. Chem.* **1976**, *120*, 397. (b) Lagowski, J. J.; Graves, V. *Inorg. Chem.* **1976**, *15*, 577.

(22) (a) Ozin, G. A.; Francis, C. G.; Andrews, M. *Inorg. Synth.* **1983**, *22*, 116. (b) Ozin, G. A.; Huber, H.; Francis, C. G. *Angew. Chem, Int. Ed. Engl.* **1980**, *19*, 402. (c) Ozin, G. A; Huber, H.; Francis, C. G. *Inorg. Chem.* **1980**, *19*, 219. (d) Ozin, G. A.; Francis, C. G.; Huber, H. X.; Andrews, M.; Nazar, L. *J. Am. Chem. Soc.* **1981**, *103*, 2453. (e) Ozin, G. A.; Huber, H.; Francis, C. G. *J. Am. Chem. Soc.* **1979**, *101*, 6250. (f) Ozin, G. A.; Andrews, M. P. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 212. (g) Ozin, G. A. *CHEMTECH* **1985**, Aug, 488.

(23) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979; p 219.

Excited Triplet State Resonance Raman Spectra of Magnesium, Zinc, and Palladium Tetraphenylporphine

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There is wide interest in the electronic states of metalloporphyrins because of their rich and varied spectroscopy, their utility as electron-transfer and photoactive agents, and the multifaceted roles of heme and chlorophyll groups in biology.[1] Resonance Raman (RR) spectroscopy has produced much useful information about the structures of metalloporphyrins in their ground states[2] and can be expected to help elucidate excited states. Down shifts and broadening in the picosecond RR spectrum of the oxyhemoglobin photoproduct[3] have been interpreted as arising from unrelaxed electronic excitation of the deoxy-heme. We now report RR spectra of the lowest triplet excited states of magnesium, zinc, and palladium tetraphenylporphine (TPP).

Figure 1 shows RR spectra of ZnTPP in dichloromethane, obtained with 476.5 Ar^+ CW laser excitation. ZnTPP fluoresces strongly, but the emission is from the low-energy Q-band (λ_{max} = 589 nm)[4] and does not interfere with RR spectra obtained with blue excitation. The bottom spectrum was obtained with the sample in an ordinary spinning cell and is the RR spectrum of ground-state ZnTPP;[5] frequencies and assignments[6] are listed in

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(1) *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. III.

(2) (a) Spiro, T. G. In *Iron Porphyrins*; Lever, A. B. P., Gray, H. B., Eds.; Addison-Wesley: Reading, MA, 1983; Part Two, pp 89–159. (b) Asher, S. A. *Methods Enzymol.* **1981**, *76*, 371–413. (c) Felton, R. H.; Yu, N.-T. In ref 1, Vol. III, pp 347–393. (d) Kitagawa, T., Ozaki, Y., Kajogoku, Y. *Adv. Biophys.* **1978**, *11*, 153. (e) Shelnutt, J. A.; O'Shea, D. C.; Yu, N.-T.; Cheung, L. D.; Felton, R. H. *J. Chem. Phys.* **1976**, *64*, 1156. (f) Shelnutt, J. A.; Cheung, L. D.; Chang, R. C. C.; Yu, N.-T.; Felton, R. H. *Ibid.* **1979**, *66*, 3387.

(3) Terner, J.; Voss, D. S.; Paddock, C.; Miles, R. B.; Spiro, T. G. *J. Phys. Chem.* **1982**, *86*, 859.

(4) Gouterman, M. In ref. 1, Vol. III, Chapter 1.

(5) (a) Yamaguchi, H.; Nakano, M.; Itoh, K. *Chem. Lett.* **1982**, 1397. (b) Yamaguchi, H.; Soeta, A.; Toeda, H.; Itoh, K. *J. Electroanal. Chem.* **1983**, *159*, 347.

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Table I. RR Frequencies and Shifts (cm^{-1}) for MTPP Triplets and Radical Cations and Anions

assignment	ZnTPP	Δ^{*a}	Δ^{+b}	Δ^{-c}	MgTPP	Δ^{*a}	Δ^{+b}	Δ^{-c}	PdTPP	Δ^{*}
A[d] phenyl[e]	1600	−2	−2	−1	1602		−2		1595	−2
ν_2 C_bC_b	1549	−3	−7	+3	1550	−4	−11	+5	1557	−7
ν_{12} C_bC_b	1494	−4	−19	+2	1496	−3	−9	+3		
ν_4 C_aN	1355	−3	−12	−6	1353	0	−20	+4	1364	−1
C C_mPh	1244	−5	0	−6	1239	−3	0	−4	1235	−1
ν_5 δ C_bH	1081	−5	+8	−15	1080	−5	−22	−9	1080	−3
E phenyl	1038				1033					
F phenyl	1005	−4	0	−2	1005	−2	0	−1	1013	0
ν_6 C_aC_m	1005	−4	−22	−18	1005		−20	−13		

[a] Δ^i frequency shift relative to MTPP for $MTPP^+$, $MTPP^-$, MTPP* (i = +, −, *). [b] From ref 5a. [c] From ref 5b. [d] Mode labels from ref 6a. [e] Principal internal coordinate contributor to the mode, from ref 6b.

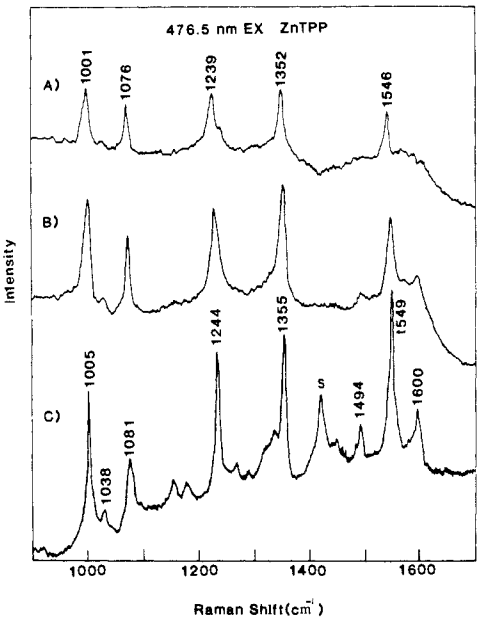

Figure 1. (A) Difference spectrum, (B) − (C), attributed to ZnTPP*. (B) Stationary sample in a NMR tube, excited at 135 °C with a 476.5-nm Ar^+ laser beam (250 mW, focused); the sample was cooled in a cold N_2 stream. The spectrum is the sum of five scans, each of a fresh sample from which O_2 was removed by freeze pumping and recorded with a computer-controlled Spex 1401 scanning monochromator, with a cooled photomultiplier tube and photon-counting electronics; 0.5 cm^{-1}/s scan rate, 1-s time constant, 5-cm^{-1} slit width. (C) As in (B), but the NMR tube was spun, and the laser power was lowered to 30 mW; seven scans were added.

Table I. The middle spectrum was obtained in the same cell, but without spinning, and with increased laser power (250 mW). There are clear broadenings and shifts in the ZnTPP RR bands, and the solvent band at 1421 cm^{-1} is greatly diminished in relative intensity. We interpret these effects as due to pumping of the ground state to form the ZnTPP triplet state (via the excited singlet), the Raman spectrum of which is elicited by a second laser photon. Because the quantum yield for triplet formation is high (0.8) and the triplet lifetime is long (1.3 ms),[7] pumping is effective even with the relatively low-power CW laser excitation. Moreover, the excitation wavelength is in resonance with the strong triplet absorption (470 nm, $\epsilon \sim 71\,000$ M^{-1} cm^{-1}).[8] The disappearance of the solvent band is due to the triplet–triplet absorption at this wavelength and is strong evidence for triplet formation in relatively large abundance (which, however, has not been quantitated). The Soret band of the ground state is at higher energy ($\epsilon = 2.5 \times 10^5$ at 416 nm) but is close enough to provide both resonance enhancement of the ground state and sufficient absorption ($\epsilon \cong 4600$ at 476.5 nm) for pumping. The top spectrum of Figure 1 is that of the triplet state, obtained by subtracting the bottom spectrum (ground state) from the middle spectrum (mixture); the weighting factor was gradually increased to the point where negative peaks began to be seen due to oversubtraction. Similar spectra are observed for MgTPP and PdTPP, with excitation at 488.0 and 457.9 nm, respectively, for resonance with the triplet absorption bands, 485 nm ($\epsilon \sim 72000$) for MgTPP, and 450 nm ($\epsilon \sim 47000$) for PdTPP.[8] Triplet quantum yields (0.8 and 1.0) and lifetimes (1.3 and 0.4 ms) are likewise suitably large for MgTPP and PdTPP.[7]

The porphyrin skeletal mode frequencies are all slightly lower for the triplet than for the ground states. Table I lists the triplet down shifts, 1–7 cm^{-1}, along with the shifts observed for the radical cations[5a] and anions[5b] of MgTPP and ZnTPP reported by Itoh and co-workers. Since the triplet excited states are formed by promoting an electron from the highest filled orbital to the lowest unoccupied orbital, the structural effects might be expected to be a superposition of those observed for radical cation and radical anion formation. Indeed, the opposing vibrational shifts which tend to be seen for electron addition and removal (Table I) help to explain the very small shifts seen for the triplet states. For example, the triplet shift for the 1550-cm^{-1} mode, −3 and −4 cm^{-1} for ZnTPP and MgTPP, is close to the resultant of the cation and anion shifts (−7 + 3 = −4; −11 + 5 = −6). For other modes, the resultant deviates more widely from the observed triplet shift. All of these shifts are relatively small; however, and it is not surprising that the simple superposition approximation would fail to account for their details.

A particularly interesting question is the fate of the phenyl modes, several of which have been identified in ground-state RR spectra of TPP's.[6b] Although relatively weak, they are clearly resonance-enhanced, although the phenyl substituents are known to be oriented at nearly right angles to the porphyrin ring,[9] and conjugation is not significant in the ground state.[10] It was suggested[6b] that resonance enhancement reflected an increase in conjugation in the excited state. If conjugation were increased in the excited state, one might expect the phenyl mode frequencies to decrease appreciably. The clearest phenyl mode in the ground-state spectra is the one at ~1600 cm^{-1}. No distinct band is seen in the triplet spectra, but in each case there seems to be a broad underlying envelope near this frequency (see Figure 1). While this envelope could have a number of explanations, an interesting possibility is that it reflects an inhomogeneous distribution of phenyl orientations with a broad range of vibrational frequencies. Such a distribution has a plausible physical basis, since the driving force for phenyl rotation into the porphyrin plane which is provided by the electronic excitation (the e_g orbital has particularly large coefficients at the meso carbon atoms[4]) encounters steric resistance from the nonbonded interactions between the protons at the ortho positions of the phenyl groups and those on the outer pyrrole carbon atoms.[9] Consequently the phenyl torsion potential in the excited state may be relatively flat. Nevertheless, the vibrational frequencies are expected to be sensitive to the torsion angle for orientations close to coplanar

(6) (a) Stein, P.; Ulman, A.; Spiro, T. G. *J. Phys. Chem.* **1984**, *88*, 369–374. (b) Burke, J. M.; Kincaid, J. R.; Spiro, T. G. *J. Am. Chem. Soc.* **1978**, *100*, 6077.
(7) Darwent, J. R.; Douglas, P.; Harriman, A.; Porter, G.; Richoux, M.-C. *Coord. Chem. Rev.* **1982**, *44*, 83.
(8) Harriman, A. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 1281.
(9) Eaton, S. S.; Eaton, G. R. *J. Am. Chem. Soc.* **1975**, *97*, 3660.
(10) LaMar, G. N.; Eaton, G. R.; Holm, R. H.; Walker, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 63.

because of the effect of conjugation. It is notable that the bandwidths for the skeletal modes are somewhat larger in the triplet than in the ground state spectra (~15 vs. 12 cm^{-1} FWHM). The skeletal mode frequencies are expected to be less sensitive to phenyl conjugation because the electronic influence is spread over a larger ring, but their increased width may nevertheless be a reflection of the proposed inhomogeneous distribution.

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Registry No. MgTPP, 14640-21-2; ZnTPP, 14074-80-7; PdTPP, 14187-13-4.

Laser-Induced Excited-State Ligation Changes for Nickel Tetraphenylporphine Monitored by Raman Spectroscopy

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Metalloporphyrins offer the interesting possibility of undergoing changes in axial ligation associated with the pumping of excited ligand field states via intersystem crossing from initially populated porphyrin $\pi-\pi^*$ states.[1,2] One example is the extremely rapid[3] and efficient photodissociation of the CO adduct of heme proteins, which has been widely exploited in studying the heme-linked protein dynamics of these O_2-carrying and -activating macromolecules.[4] Nickel porphyrins offer an attractive system for investigation since they are 4-coordinate and low spin in noncoordinating and weakly coordinating solvents but 6-coordinate and high spin in strongly coordinating solvents.[5] Holten and coworkers have shown with transient optical spectroscopy that the accessible excited state (low spin) of the 6-coordinate species rapidly loses its axial ligands, while the excited state of 4-coordinate nickel porphyrin (high spin) becomes ligated, thanks to the hole created in the d_{z^2} orbital. It should therefore be possible to shift the equilibrium between 4- and 6-coordinate species with photons. In this report we demonstrate such pumping with CW laser excitation of stationary samples of NiTPP (nickel tetraphenylporphine) in pyridine and piperidine, using resonance Raman (RR) spectroscopy to monitor the ligation changes. The RR spectra also allow assessment of the structural change attendant upon ligation, and they permit identification of a 5-coordinate species in piperidine solution, with a ground state that is probably high spin.[6] The same spinning vs. stationary sample technique was used which has allowed us to obtain triplet-state RR spectra of TPP complexes of Mg, Zn, and Pd.[7]

Figure 1 shows 406.7-nm-excited Raman spectra, in the region of the ν_4 skeletal mode,[8] for a stationary sample of NiTPP in pyridine. Two ν_4 bands are seen, at 1369 and 1346 cm^{-1}. The former is at the frequency seen for NiTPP in noncoordinating solvents and is attributed to the low-spin 4-coordinate complex. The latter band is attributed to the 6-coordinate high-spin complex,

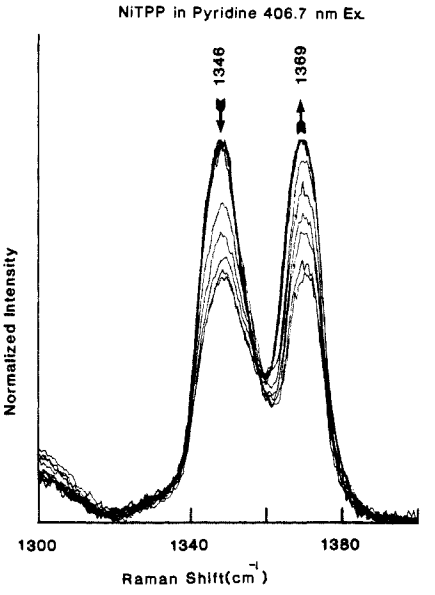

Figure 1. ν_4 Raman peaks for a stationary sample of NiTPP (purchased from Porphyrin Products and purified by chromatography on alumina A540, 0.2 mM) in pyridine, with 406.7-nm excitation. Arrows indicate the decreasing (1346 cm^{-1}) and increasing (1369 cm^{-1}) relative intensities at increasing laser power levels (1.5, 5, 10, 15, 20, 25, 50, 75, 90, 125, and 140 mW). In the absence of an internal standard (pyridine peaks are obscured by those of NiTPP) the spectra were scaled to whichever peak was stronger. (The intrinsic scattering factors are not the same for the two peaks.) Spectra were obtained via backscattering (135°) from a NMR sample tube, using a Spex 1401 double monochromator: 7-cm^{-1} slit width; 1-s time constant; 0.5 cm^{-1}/s scan rate.

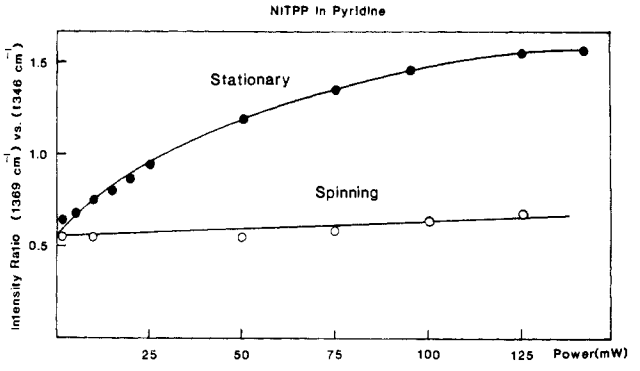

Figure 2. 1369/1346 cm^{-1} Raman peak height ratio for NiTPP in pyridine vs. 406.7-nm laser power for a stationary sample (●) (see spectra in Figure 1) and a spinning sample (○).

by comparison with the spectrum of NiTPP in piperidine (see Figure 3) in which the 6-coordinate species is dominant.[1,5] The porphyrin core is expanded in the 6-coordinate species due to electron promotion to the in-plane antibonding $d_{x^2-y^2}$ orbital; the porphyrin center-to-pyrrole nitrogen distance (C_t–N) is ~1.95 Å in 4-coordinate nickel porphyrins,[9] but 2.038 Å in the bis-imidazole adduct of nickel tetramethylpyridylporphine.[14] We attribute the ν_4 down shift upon pyridine or piperidine coordination at least in part to the core-size expansion; the porphyrin skeletal mode frequencies are known to be sensitive to the core size, as well as to electronic effects.[15]

* Author to whom correspondence should be addressed.

(1) (a) Kim, D.; Kirmaier, C.; Holten, D. *Chem. Phys.* **1983**, *75*, 305. (b) Kim, D.; Holten, D. *Chem. Phys. Lett.* **1983**, *98*, 584.

(2) (a) Kim, D.; Holten, D.; Gouterman, M. *J. Am Chem. Soc.* **1984**, *106*, 2793. (b) Tait, C. D.; Holten, D.; Gouterman, M. *Chem. Phys. Lett.* **1983**, *100*, 268. (c) Tait, C. D.; Holten, D.; Gouterman, M. *J. Am. Chem. Soc.* **1984**, *106*, 6653.

(3) Martin, J. L.; Migus, A.; Poyart, C.; Lecarpentier, Y.; Astier, R.; Antonetti, A. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 173.

(4) (a) Gibson, Q. H.; Ainsworth, S. *Nature (London)* **1957**, *180*, 1416. (b) Hofrichter, J.; Sommer, J. H.; Henry, E. R.; Eaton, W. A. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *77*, 5608. (c) Frauenfelder, H.; Wolynes, P. G. *Science (Washington, D.C.)* **1985**, *229*, 337.

(5) Walker, F. A.; Hui, E.; Walker, J. M. *J. Am. Chem. Soc.* **1975**, *97*, 2390.

(6) Ake, R. L.; Gouterman, M. *Theor. Chim. Acta* **1970**, *17*, 408.

(7) Kim, D.; Terner, J.; Spiro, T. G. *J. Am. Chem. Soc.*, preceding paper in this issue.

(8) Stein, P.; Ulman, A.; Spiro, T. G. *J. Phys. Chem.* **1984**, *88*, 369.

(9) 1.929 Å in tetragonal (D_{2d}, ruffled)[10] and 1.958 Å in triclinic (D_{4h}, planar)[11] nickel octaethylporphyrin; 1.960 Å in nickel deuterioporphyrin;[12] 1.957 Å in nickel etioporphyrin.[13]

(10) Meyer, E. F., Jr. *Acta Crystallogr., Sect. B* **1972**, *B28*, 2162.

(11) Cullen, D. L.; Meyer, E. F., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 2095.

(12) Hamor, T. A.; Caughey, W. S.; Hoard, J. L. *J. Am. Chem. Soc.* **1965**, *87*, 2305.

(13) Fleischer, E. B. *J. Am. Chem. Soc.* **1963**, *85*, 146.

(14) Kirner, J. F.; Garofalo, J., Jr.; Scheidt, W. R. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 107.

(15) Spiro, T. G. In *Iron Porphyrins*; Lever, A. B. P., Gray, H. B., Eds.; Addison-Wesley: Reading, MA, 1983; Part Two, pp 89–159.

0002-7863/86/1508-2099$01.50/0