(column 3) or the phase correction of ref 3 (column 4). It is evident that the phase correction expression of ref 3 is valid for the case $\Delta V = 0$, but not when $\Delta V \neq 0$.

In conclusion, therefore, we have confirmed that use of the type of WKB edge-effect correction originally proposed by Le Roy et al.³ can greatly accelerate the convergence of numerical tunneling probability calculations for potentials with long-range tails. However, for asymmetric barriers, the expression for the WKB phase correction given in ref 3 is in error and should be replaced by the present more general eq 8 and 9.

Vibrational, Electronic, and Structural Properties of Cobalt, Copper, and Zinc Octaethylporphyrin π Cation Radicals

W. Anthony Oertling, Asaad Salehi, Young C. Chung,[†] George E. Leroi, Chi K. Chang,^{*} and Gerald T. Babcock*

Department of Chemistry and Michigan State University Shared Laser Laboratory, Michigan State University, East Lansing, Michigan 48824-1322 (Received: May 26, 1987)

Optical and resonance Raman (RR) spectroscopic characterization of the oxidation products of several metallooctaethylporphyrins has been carried out. One-electron oxidation of the macrocycle yields a series of divalent metal substituted octaethylporphyrin π cation radicals, M^{II}OEP⁺⁺ClO₄⁻ (M = Ni, Co, Cu, and Zn). The porphyrin core vibrational frequencies above 1450 cm⁻ of these complexes are described by a linear function of center to pyrrole nitrogen distances. A comparison of these structural correlations and of Raman depolarization ratios with those of the parent MOEP compounds is used to establish vibrational mode assignments for the cations. The agreement between the correlation parameters of the MOEP and $MOEP^{+}ClO_{4}^{-}$ suggests similar potential energy distributions in the normal modes of both species. We find that the frequencies of the stretching modes with predominantly C_bC_b character increase, whereas those with C_aC_m and C_aN character decrease in the cation radical relative to the neutral metalloporphyrin. Similar trends in Soret band maxima for the π cation radicals and their parent compounds reflect changes in the relative energy of the $a_{2u}(\pi)$ orbital. These structural correlations seem to be essentially insensitive to ${}^{2}A_{2u}$ vs ${}^{2}A_{1u}$ radical designation. With the vibrational mode correlations as a guide to evaluation of porphyrin core geometry, we have carried out a detailed analysis of the oxidation products of Co^{II}OEP and we suggest structures for the two-electron-oxidized species $Co^{III}OEP^{*+}2ClO_4^-$ and $Co^{III}OEP^{*+}2Br^-$. Differences in the high-frequency vibrations of these two compounds are interpreted in terms of expansion or possible ruffling of the porphyrin core in the latter relative to the former compound. RR excitation in the 600-680-nm region of the Co^{III}OEP⁺²Br⁻ absorptions shows a lack of anomalously polarized scattering and produces spectra similar to those obtained with near-UV excitation. This suggests the absence of strong Herzberg-Teller coupling between the excited electronic states of this π cation radical.

Introduction

Oxidized states of metalloporphyrins (MP) participate in the redox chemistry of a variety of biological structures including light-harvesting photosynthetic systems and heme proteins. Oxidation of the MP may occur at the central metal, at the porphyrin ligand, or at both locations. The latter, doubly oxidized metalloporphyrin structures have been implicated in the catalytic cycles of heme peroxidases, P450 monooxygenases, and catalases.¹ Because of the extensive π system, oxidation at the porphyrin yields a delocalized π cation radial; indeed, in the case of the special pair bacteriochlorophyll a dimer in the photosynthetic bacterial reaction center, radical character may be shared between two porphyrin rings.² Characterization of metalloporphyrin π cation radicals is thus of interest because of their widespread occurrence in nature and because of the often unusual chemistry in which they participate.

Both chemical and electrochemical preparations of a variety of metallooctaethylporphyrin (MOEP) and metallotetraphenylporphyrin (MTPP) π cation radicals have been reported.³⁻⁶ These oxidized complexes have been characterized principally by optical absorption,⁷ EPR,⁸ MCD,⁹ NMR,^{10,11} and IR¹² spectroscopies and X-ray crystallography.¹³ Although resonance Raman (RR) spectroscopy has been applied to a few metalloporphyrin π cation radical (MP*+) systems, these studies are limited in scope for various reasons. Attempts to measure RR scattering from the oxoferrylporphyrin π cation radical of horseradish peroxidase compound I (HRP-I) are complicated by photochemistry,14,15 and special precautions are required to obtain its spectrum.¹⁶ Analysis of the RR scattering from the bacteriochlorophyll cation radical

is obscured by the complexity of the parent system.¹⁷ The work of Yamaguchi et al.¹⁸ on MTPP++ complexes is not strictly relevant

(1) (a) Frew, J. E.; Jones, P. In Advances in Inorganic and Bioinorganic Mechanism; Academic: New York, 1984; Vol. 3, pp 175–215. (b) Hewson, W. D.; Hager, L. P. In The Porphyrins; Dolphin, D., Ed.; Academic: New

W. D.; Hager, L. F. In *The* Forphyrins, Dorphin, D., Ed., Academic. 1999
York, 1979; Vol. 4, pp 295-332.
(2) (a) Norris, J. R.; Sheer, H.; Katz, J. J. in *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1979; Vol. 4, pp 159-195. (b) Lubitz, W.; Lendzian, F.; Plato, M.; Möbius, K.; Tränkle, E. Springer Ser. Chem. Phys. 1985, 42, 164-173.

(3) Fuhrhop, J. H. Struct. Bonding (Berlin) 1974, 18, 1-67.
(4) Dolphin, D.; Mulijiani, Z.; Rousseau, K.; Borg, D. C.; Fajer, J.; Felton,

 (5) Wolberg, A.; Manassen, J. J. Am. Chem. Soc. 1970, 92, 2982–2991.
 (6) Phillippi, M. A.; Goff, H. M. J. Am. Chem. Soc. 1982, 104, 6026-6034.

(7) Carnieri, N.; Harriman, A. Inorg. Chim. Acta 1982, 62, 103-107. (8) (a) Fajer, J.; Davis, M. S. in *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1979; Vol. 4, pp 197-256. (b) Fajer, J.; Borg, D. C.; Forman, A.; Felton, R. H.; Vegh, L.; Dolphin, D. *Ann. N.Y. Acad. Sci.* 1973, 206, 349-364.

(9) (a) Browett, W. R.; Stillman, M. J. Inorg. Chim. Acta 1981, 49, 69-77.

 (b) Browett, W. R.; Stillman, M. J. Biochim. Biophys. Acta 1981, 660, 1-7.
 (10) (a) Godziela, G. M.; Goff, H. M. J. Am. Chem. Soc. 1986, 108, 2237-2243. (b) Goff, H. M.; Phillippi, M. A. J. Am. Chem. Soc. 1983, 105, 7567-7571

(11) Morishima, I.; Takamuki, Y.; Shiro, Y. J. Am. Chem. Soc. 1984, 106, 7666-7672.

(12) Shimomura, E. T.; Phillippi, M. A.; Goff, H. M. Scholz, W. F.; Reed, C. A. J. Am. Chem. Soc. 1981, 103, 6778-6780.

(13) (a) Barkigia, K. M.; Spaulding, L. D.; Fajer, J. Inorg. Chem. 1983, 22, 349-351. (b) Spaulding, L. D.; Eller, P. G.; Bertrand, J. A.; Felton, R. H. J. Am. Chem. Soc. 1974, 96, 982-987.

(14) Nadezhdin, A. D.; Dunford, H. B. Photochem. Photobiol. 1979, 29, 899-903.

(15) (a) Teraoka, J.; Ogura, T.; Kitagawa, T. J. Am. Chem. Soc. 1982, 104, 7354-7356. (b) Van Wort, H. E.; Zimmer, J. J. Am. Chem. Soc. 1985, 107, 3379-3381.

[†]Present address: Department of Chemistry, Northeastern University, Boston, MA 02115.

owing to the strong vibronic coupling and altered substituent pattern of the TPP which reduces its significance as a biological model for RR studies.¹⁹ The MOEP⁺⁺ system studied by Kim et al.²⁰ is an ideal choice for systematic RR investigation; however, recent work²¹ has revealed that some of the Soret RR spectra reported by these authors were contaminated by artifacts from porphyrin diacid salt impurities produced by demetalation of their MOEP⁺⁺ samples. This led to incorrect assignments of the principal vibrational modes and to erroneous conclusions concerning the nature of metalloporphyrin π cation radical Raman scattering. This circumstance necessitates a reexamination of the **RR** spectra of these systems.

The high-symmetry (D_{4h}) and saturated C_b substituents make OEP the most simple biologically relevant porphyrin ligand for RR study, and the oxidation products of cobaltous octaethylporphyrin (CoOEP) in particular are of interest. One-electron oxidation of CoOEP in CH₂Cl₂ may occur at either the metal or the porphyrin.²² Depending on the counterion present, the CoOEP two-electron-oxidation product displays one of two distinct optical absorption spectra. These are proposed as typical of the two possible electronic ground states which result from loss of an electron from one of the two nearly degenerate HOMOs, $a_{1u}(\pi)$ or $a_{2u}(\pi)$, of the porphyrin π system.^{9,23,24} The similarity of the optical spectra of Co^{III}OEP^{•+}2ClO₄⁻ and Co^{III}OEP^{•+}2Br⁻ to those of HRP-I and catalase compound I (CAT-I) led to the early assignment of the electronic states of these enzyme transients as $^2A_{2u}$ and $^2A_{1u},$ respectively. 24 The versatility of the CoOEP system thus allows us to compare metal- vs porphyrin-centered oxidation products for the one-electron case and ${}^{2}A_{2u}$ vs ${}^{2}A_{1u}$ radicals for the two-electron case, all with the same MOEP species. Comparison of the cobaltous π cation radical, Co^{II}OEP^{•+}ClO₄⁻, with other $M^{II}OEP^{+}ClO_4^{-}$ species illustrates structural trends in both the RR frequencies and Soret absorption maxima that are consistent with recent calculations²³ and very similar to those of the parent MOEP species. Exclusion of the artifacts arising from the diacid salt impurities reveals a closer vibrational similarity of ${}^{2}A_{2u}$ and ²A_{1u} radical types than was thought previously.²⁰ RR excitation in both the Soret and visible absorption bands of cobaltic OEP^{•+} samples provide spectra that suggest the absence of strong Herzberg-Teller coupling of electronic states and a similar scattering mechanism in both spectral regions.

Experimental Section

Preparation of OEPH2 was carried out according to the recent method of Wang and Chang,25 and metal insertion was achieved by standard methods.²⁶ The metalloporphyrins were purified by recrystallization and/or chromatography to eliminate traces of free base. CH₂Cl₂ freshly distilled from CaH₂ was used as a solvent for all preparations.

Oxidations were performed chemically at room temperature by using solid anhydrous AgClO₄, solid $Fe(ClO_4)_3$, or dilute Br₂ in CH_2Cl_2 . $Co^{II}OEP^{\bullet+}ClO_4^{-}$, $Zn^{II}OEP^{\bullet+}ClO_4^{-}$, and $Cu^{II}OEP^{+}ClO_4^{-}$ were prepared by stirring dry CH_2Cl_2 solutions of CoOEP, ZnOEP, and CuOEP, respectively, with a 3-fold excess

- (18) Yamaguchi, H., Nakano, M.; Itoh, K. Chem. Lett. 1982, 1397-1400.
 (19) (a) Chottard, G.; Battioni, P.; Battioni, J.-P.; Lange, M.; Mansuy, D.
- Inorg. Chem. 1981, 20, 1718-1722. (b) Aramaki, S.; Hamaguchi, H.; Tasumi, M. Chem. Phys. Lett. 1983, 96, 555-559. (20) Kim, D.; Miller, L. A.; Rakhit, G.; Spiro, T. G. J. Phys. Chem. 1986,
- 90. 3320-3325. (21) Oertling, W. A.; Salehi, A.; Chang, C. K.; Babcock, G. T. J. Phys. Chem. 1987, 91, 3114-3116.
- (22) Salehi, A.; Oertling, W. A.; Babcock, G. T.; Chang, C. K. J. Am. Chem. Soc. 1986, 108, 5630-5631.
- (23) Edwards, W. D.; Zerner, M. C. Can. J. Chem. 1985, 63, 1763-1772.
- (24) Dolphin, D.; Forman, D. C.; Borg, J.; Felton, R. H. Proc. Natl. Acad. Sci. U.S.A. 1971, 68, 614-618.
 - (25) Wang, C. B.; Chang, C. K. Synthesis 1979, 548-549.
- (26) Falk, J. E. Porphyrins and Metalloporphyrins; Elsevier: New York, 1964; 798.

Oertling et al.

stirring excess $Fe(ClO_4)_3$ in a solution of CoOEP for ~10 min. Co^{III}OEPBr⁻ and Co^{III}OEP^{•+}2Br⁻ were prepared by dropwise addition of dilute Br₂ to CoOEP in CH₂Cl₂. Mg^{II}OEP^{•+}ClO₄⁻ and Mg^{II}OEP^{•+}Br⁻ were prepared similarly from MgOEP.

Dropwise addition of methanol (MeOH) to CH_2Cl_2 solutions of Co^{II}OEP^{•+}ClO₄⁻ and Co^{III}OEPBr⁻ resulted in the formation of species with similar absorption spectra, presumably Co^{III}-(MeOH)₂OEPClO₄⁻ and Co^{III}(MeOH)₂OEPBr⁻, respectively.²⁷ Identical samples were made by oxidation of CoOEP with HClO₄ and HBr, respectively, in 3:1 CH₂Cl₂-MeOH. All oxidations and ligand changes were monitored by optical absorption measurements with either a Cary 219 or a Perkin-Elmer $\lambda 5$ spectrophotometer.

Raman spectra excited at 351.1, 363.8, and 390 nm were measured with a Spex 1877 triple monochromator and Spex 1459 collection optics in conjunction with an EG&G PAR 1420 diode array detector and associated OMA II electronics. The 351.1and 363.8-nm laser emissions were from a Coherent 90-05 argon ion laser; the 390-nm line was the output of a Nd:YAG (Quanta Ray DCR-1A) pumped pulsed dye laser (PDL-1) in which LD390 (Exiton) laser dye was used. Instrumentation used to measure Raman scattering at 406.7, 514.5, 620, 647.1, and 676.4 nm included a Spex 1401 double monochromator with photon counting detection interfaced to a DEC LSI 11-2 computer. The lasers were powered by a Spectra Physics Model 265 Exciter; the lines at 406.7, 647.1, and 676.4 nm were from a Model 164 krypton ion laser, the 514.5-nm line was from a Model 165 argon ion laser, and the 620-nm line was the output of an argon ion pumped Spectra Physics Model 375 dye laser in which Rhodamine 590 (Exciton) laser dye was used.

Samples were spun in a cylindrical quartz cell for Raman measurements, although static samples in cuvettes gave identical spectra. Absorption spectra were checked before and after each Raman measurement. Of the oxidized species examined, only ZnOEP**ClO₄⁻ and MgOEP**Br⁻ showed any significant laserinduced change.²¹ Samples of $Co^{III}OEP^{+}2ClO_4^{-}$ and ZnOEP + ClO₄ - prepared and studied under anaerobic conditions exhibited RR scattering identical with samples that were not deoxygenated, and for this reason samples were not routinely degassed.28

Results

Effects of Oxidation on the High-Frequency Porphyrin Core Vibrations. Although the cobaltic OEP⁺⁺ system is of principal interest owing to its relevance to the compound I type enzyme intermediates, results from the Cu- and ZnOEP⁺⁺ systems are presented first. The chemistry of the cobalt system is complicated by the two easily obtainable redox states of the metal center and

^{(16) (}a) Oertling, W. A.; Babcock, G. T. J. Am. Chem. Soc. 1985, 107, 6406-6407. (b) Ogura, T.; Kitagawa, T. J. Am. Chem. Soc. 1987, 109, 2177-2179.

^{(17) (}a) Cotton, T. M.; Parks, K. D.; Van Duyne, R. P. J. Am. Chem. Soc. 1980, 102, 6399-6407. (b) Lutz, M. Adv. Infrared Raman Spectrosc. 1984, 11, 211-300.

⁽²⁷⁾ Alternative structural assignments for these compounds, particularly $Co^{III}(MeOH)_2OEPBr$, are possible. A mixed diaxial species of the type (Br-)Co^{III}(MeOH)OEP was proposed by Johnson, A. W.; Kay, I. T. J. Chem. Soc. 1960, 2979–2983 and may better explain the similar, yet distinct absorption maxima of $Co^{III}(MeOH)_2OEPCIO_4^-$ and $Co^{III}(MeOH)_2OEPBr^-$ (see Table I under Discussion). Further addition of MeOH to the latter compound produces a sample with absorption maxima identical with that of Co^{III}-(MeOH)₂OEPClO₄. For this work, however, a distinction between dimethanol ligation vs mixed axial ligation of these complexes is not necessary See also Sugimoto, H.; Ueda, N.; Mori, M. Bull. Chem. Soc. Jpn. 1981, 54, 3425-3432

⁽²⁸⁾ Under certain conditions, however, molecular oxygen (O₂) was observed to promote oxidation of metalloporphyrins. For instance, in the presence of excess ($\sim 0.1 \text{ mM}$) tertbutylammonium perchlorate, oxidation of CoOEP to Co^{III}OEP⁺⁺2ClO₄⁻ was observed, presumably via the formation of $HClO_4$ in CH_2Cl_2 solution, as discussed by Fukuzumi, S.; Ishikawa, K.; Tanaka, T. Chem. Lett. **1986**, 1-4. Upon laser irradiation in Soret resonance at 406.7 or 390 nm, CH₂Cl₂ solutions of CuOEP, ZnOEP, CoOEP, and Co^{II}OEP⁺⁺ClO₄⁻ in the presence of O₂ were observed to undergo one-electron oxidation requiring various exposure times for each species. These effects were not observed with 363.8-nm excitation. Similar photochemical oxidation of CoTPP has been discussed by Gasyna, Z.; Browett, W. R.; Stillman, M. J. Inorg. Chem. 1984, 23, 382-384; and by Yamamoto, K.; Hoshino, M.; Kohno, M.; Ohya-Nishiguchi, H. Bull. Chem. Soc. Jpn. 1986, 59, 351-354. Both MgOEP and MgOEP⁺Br⁻ were difficult to work with for RR experiments; many spectra of these compounds were collected at the outset of our study, but they are not heavily relied on in this work.



Figure 1. Electronic absorption spectra of (a) $CuOEP^{*+}ClO_4^{-}$ and (b) ZnOEP*+ClO₄- (0.2 mM) in dry CH₂Cl₂. Extinction coefficients were taken from ref 29 and 4, respectively.

by the diversity of one- and two-electron-oxidation products possible. The Cu^{II}- and Zn^{II}OEP systems are simpler in that, under the conditions utilized here, oxidation occurs exclusively at the porphyrin ligand. Since the porphyrin dication is currently of little physiological interest, we consider only the singly oxidized state here. Thus, we can establish the effects of oxidation on the porphyrin core vibrational modes before addressing the more complex cobalt system.

One-Electron Oxidation of CuOEP and ZnOEP. The optical absorption spectra of ClO₄⁻ complexes of CuOEP⁺⁺ and ZnOEP⁺⁺ are shown in Figure 1. The absorption spectrum of CuOEP*+- ClO_4^- is like that reported earlier²⁹ and has features usually attributed to the ${}^{2}A_{2u}$ state. 9,23,24 The actual electronic ground state of $CuOEP^{+}ClO_4^{-}$ is difficult to establish, however, owing to the lack of an EPR signal from this compound under most conditions.³⁰ Indeed, recent NMR measurements suggest a ²A_{1u} state for $CuOEP^{+}ClO_{4}^{-,10a}$ seemingly in contradiction with the absorption spectrum. The ground electronic configuration of the ZnOEP^{•+} species, however, is determined by EPR measurements to be ${}^{2}A_{1u}$.⁸ The absorption spectrum of ZnOEP^{•+}ClO₄⁻ presented in Figure 1b agrees well with earlier measurements.^{4,31} Although previous work indicates that ZnOEP*+ClO₄ in CH₂Cl₂ solutions is monomeric, Figure 1b shows that significant dimerization of this compound takes place at the concentrations used here (0.2-0.5)mM). The high-energy shoulder at \sim 350 nm and the absorbance at 573 nm are attributed primarily to the dimer species.³¹ Dilution of ZnOEP^{•+}ClO₄⁻ samples results in reduced intensity of these features, consistent with decreased dimerization, as shown earlier.⁴

Figure 2 shows the RR spectra (1000-1700 cm⁻¹) obtained with near-UV excitation of complexes of CuOEP ** ClO₄- and $ZnOEP^{+}ClO_4^{-}$ and their respective neutral parent compounds. RR enhancement of vibrations of ZnOEP++ClO₄- dimers was avoided by using laser excitation at 390 nm, well to the red of the dimer absorption. Under these excitation conditions, most of the resonance enhanced vibrations shown in Figure 2 correspond to totally symmetric fundamentals. The bands above 1450 cm⁻¹



Figure 2. RR spectra of Cu and ZnOEP and their corresponding π cation radicals. (a) CuOEP; (b) CuOEP*+ClO₄-; (c) ZnOEP; (d) ZnOEP^{*+}ClO₄⁻, excitation at 390 nm (1.5 mJ/pulse; [ZnOEP^{*+}] ~ 0.2 mM) selects vibrations of the monomer. CH₂Cl₂ bands are marked with an *. CW laser power 20-35 mW, at 363.8 nm for (a-c).

are known to reflect porphyrin core geometry³² and are of principal interest to this work. From the mode designations established by Abe et al.,^{33a} the ν_3 , ν_{11} , ν_2 , and ν_{10} modes of CuOEP are identified at 1502, 1563, 1591, and 1636 cm⁻¹, respectively, in Figure 2a. The intense high-frequency envelope from 1570 to 1650 cm⁻¹ is poorly resolved in the CuOEP^{•+}ClO₄⁻ spectrum in Figure 2b; however, three distinct bands with different depolarization ratios are evident from polarized scattering (spectra not shown). Thus, together with the feature at 1497 cm⁻¹, there are four bands present above 1450 cm⁻¹, and a 1:1 correlation with the modes of the parent compound is possible. We recognize the v_3 , v_{11} , v_2 , and ν_{10} frequencies of CuOEP*+ClO₄ at 1497, 1600, 1610, and 1631 cm⁻¹, respectively. While caution should be exercised in the vibrational assignment of the MOEP⁺⁺ on the basis of analogy to the parent MOEP,³⁴ our mode assignments are based on structural trends and depolarization ratio measurements discussed in detail below. The intense band at 1378 cm⁻¹ in the CuOEP spectrum in Figure 2a is v_4 , the "oxidation-state marker" of heme proteins.³⁵ This band is identified in the corresponding π cation

⁽²⁹⁾ Fuhrhop, J. H.; Mauzerall, D. J. Am. Chem. Soc. 1969, 91, 4174-4181.

⁽³⁰⁾ Konishi, S.; Hoshino, M.; Imamura, M. J. Am. Chem. Soc. 1982, 104, 2057-2059.

⁽³¹⁾ Fuhrhop, J. H.; Wasser, P.; Riesner, D.; Mauzerall, D. J. Am. Chem. Soc. 1972, 94, 7996-8001.

⁽³²⁾ Spiro, T. G. In Iron Porphyrins; Lever, A. B. P.; Gray, H. B., Eds.;

<sup>Addison-Wesley: Reading, MA, 1983; Part 2, pp 89-159.
(33) (a) Abe, M.; Kitagawa, T.; Kyogoku, Y. J. Chem. Phys. 1978, 69, 4526-4534. (b) Gladkov, L. L.; Solovyov, K. N. Spectrochim. Acta, Part A</sup> 1986, 42A, 1-10.

⁽³⁴⁾ Boldt, N. J.; Donohoe, R. J.; Birge, R. R.; Bocian, D. F. J. Am. Chem. Soc. 1987, 109, 2284-2298.



Figure 3. Resonance Raman spectra excited at 406.7 nm. (a) $Co^{II}OEP^{++}ClO_4^{-}$; (b) $Co^{III}OEP^{++}2ClO_4^{-}$ containing small amounts of porphyrin diacid impurity; (c) $H_4OEP^{2+}2ClO_4^{-}$; (d) a mixture of $H_3OEP^{+}ClO_4^{-}$ and $H_4OEP^{2+}ClO_4^{-}$ resulting from treatment of $OEPH_2$ with AgClO₄; (e) $H_4OEP^{2+}2Br^{-}$. RR bands of the solvent, dry CH_2Cl_2 , are marked with an *. Vertical dashed lines mark the vibrations of diacid, $H_4OEP^{2+}2Br^{-}$. Laser power 20 mW.

radical spectrum (Figure 2b) at 1360 cm⁻¹. Thus, in the highfrequency region, the modes involving primarily $C_a C_m$ stretching character (ν_3 and ν_{10})³³ decrease in frequency upon oxidation of the porphyrin ring, while modes involving primarily $C_b C_b$ stretching character (ν_{11} and ν_2) increase in frequency. The frequency of ν_4 , primarily a $C_a N$ stretch, decreases upon formation of the porphyrin π cation radical. These trends are common to all of the MOEP systems studied here.

The RR spectra of ZnOEP and ZnOEP^{•+}ClO₄⁻ are shown in Figure 2c,d. The vibrational mode assignments for both the parent compound and the oxidized species are analogous to those of CuOEP and CuOEP^{•+}ClO₄⁻ (see Table I, below). The ν_{10} frequency of ZnOEP^{•+}ClO₄⁻ is estimated to be 1617 cm⁻¹ from depolarization ratio measurements and spectra obtained under 363.8-nm excitation (not shown). Inspection of these vibrational frequencies reveals shifts in the Zn cation radical spectrum similar to those observed upon oxidation of CuOEP.

Porphyrin Diacid Impurities. Resonance Raman excitation of ZnOEP*+ClO₄⁻ at 406.7 nm (spectrum not shown) reproduces the features present in the 390-nm spectrum (Figure 2d). However, additional peaks are present with 406.7-nm excitation that cannot be correctly assigned to any ZnOEP*+ClO₄⁻ species. As we established earlier,²¹ these vibrations arise from trace amounts of porphyrin diacid salt impurities produced by demetalation of the ZnOEP*+ClO₄⁻ complex. Because the intensity of the diacid vibrations may totally obscure those of the metalloporphyrin π cation radical under certain excitation conditions, it is essential



Figure 4. Electronic absorption spectra of CoOEP and its oxidation products. (a) CoOEP (—); (b) $Co^{II}OEP^{+}ClO_4^{-}$ (---); (c) $Co^{III}OEP^{+}2ClO_4^{-}$ (...). Solvent, dry CH_2Cl_2 .

that these artifacts be recognized and eliminated from RR spectra of these compounds. We present here additional information on this subject.

Spectra a and b of Figure 3 show RR scattering under 406.7-nm excitation from samples of Co^{II}OEP^{•+}ClO₄⁻ prepared with AgClO₄ and of $Co^{III}OEP^{\bullet+}ClO_4^{-}$ prepared with $Fe(ClO_4)_3$, respectively. Although the RR spectra of these two samples excited at 363.8 nm are similar²² (cf. Figure 6 c,d), excitation at 406.7 nm produces additional features in the spectrum of cobaltic OEP*+ relative to the cobaltous sample (Figure 3a,b) which arise from the diacid salt impurities. Figure 3c shows the RR spectrum of the interfering species, $H_4OEP^{2+}2ClO_4^{-}$. Addition of AgClO₄ to a solution of H₂OEP in CH₂Cl₂ results in a mixture of mono- and diacid species which produces the RR spectrum shown in Figure 3d. Whereas the vertical lines identify the vibrations of the diacid, the additional peaks labeled in Figure 3d most likely arise from the monoacid species. This suggests that the mono- and diacid species have different vibrational properties, possibly owing to the lowered symmetry resulting from the inequivalence of the x and y axes in the monoacid structure. The formation of diacid in the sample of $Co^{III}OEP^{+}2ClO_4^{-}$ prepared with $Fe(ClO_4)_3$ probably results from aqueous acid (i.e., HClO₄) present in the reagent. Thus, acid demetalation of the MP followed by protonation of the resultant free base could compete with the oxidation process. The lack of artifacts in the spectrum in Figure 3a illustrates that this process does not occur when anhydrous AgClO₄ is used to oxidize CoOEP. The spectrum in Figure 3d is of interest because it suggests the possibility of both monoacid and diacid contamination of MP⁺⁺ samples. Furthermore, the absence of aqueous acid impurities in the AgClO₄ reagent suggests that porphyrin acid formation is a true byproduct of the oxidation process in certain cases and not merely the result of "wet" oxidant. Figure 3e illustrates that changing the counterion for the diacid from ClO₄⁻ to Br⁻ decreases the frequencies of the intense vibrational bands above 1300 cm⁻¹ by approximately 3 cm⁻¹. The above observations are pertinent to the interpretation of the RR spectrum of Co^{III}OEP⁺⁺2Br⁻ obtained with 406.7-nm excitation by Kim et al.,²⁰ which we suggest results from H₄OEP²⁺2Br⁻ (possibly mixed with $H_3OEP^+Br^-$) impurities present in the sample.

The frequent occurrence of these trace impurities in MP^{++} samples was not recognized until the application of the RR technique. The strong selective enhancement of the diacid vibrational modes with 406.7-nm excitation, even when the species occurs as a minor impurity (less than 3%) in MP^{++} samples, is rationalized by its optical properties.^{21,36} We find that the extent of demetalation and diacid formation in $MOEP^{++}$ samples is dependent on a number of factors, including the oxidation method, solvent, and core size of the $MOEP^{++}$. In some cases it is enhanced by laser irradiation in the Soret band region.²¹ By exciting well

^{(35) (}a) Brunner, H.; Mayer, A.; Sussner, H. J. Mol. Biol. 1972, 70, 153.
(b) Yamamota, T.; Palmer, G.; Gill, D.; Salmeen, I. T.; Rimai, L. J. Biol. Chem. 1973, 248, 5211-5213.

⁽³⁶⁾ Corwin, A. H.; Chivvis, A. B.; Poor, R. W.; Whitten, D. G.; Baker, E. W. J. Am. Chem. Soc. **1968**, *90*, 6577-6583.



Figure 5. Electronic absorption spectra of oxidation products of CoOEP. (a) $Co^{III}(MeOH)_2OEPBr^-$ (--); (b) $Co^{III}OEPBr^-$ (---); (c) $Co^{III}OEP^{*+}2Br^-$ (...), the small feature at 401 nm is due to 1% $H_4OEP^{2+}2Br^-$ contamination as discussed in the text. Solvent, dry CH_2Cl_2 , except for (a) which contains ~5% methanol (MeOH).

to the blue of the absorption maxima of these potential contaminants, we avoid the complications imposed by these species upon RR measurements.

One- and Two-Electron Oxidation of CoOEP. Figure 4 shows UV-visible absorption spectra of CoOEP and products of its oxidation in dry CH_2Cl_2 in the presence of ClO_4 . The spectra of the starting material, CoOEP, and the product of ring-centered, one-electron oxidation, $Co^{II}OEP^{+}ClO_{4}$, are shown in spectra a and b of Figure 4, respectively. Figure 4c shows the spectrum of the two-electron-oxidation product, $Co^{III}OEP^{+}2CIO_4^{-}$. As we recently demonstrated,²² cobaltous OEP^{•+} is extremely sensitive to the presence of axial ligands that coordinate more strongly than ClO_4^{-} . Such coordination promotes electron transfer from Co^{II} to the electron-depleted porphyrin. Addition of methanol (MeOH) to CH₂Cl₂ solutions of Co^{II}OEP^{•+}ClO₄⁻ produces a cobaltic species, Co^{III}(MeOH)₂OEPClO₄⁻, with an absorption spectrum similar to, but red-shifted with respect to, that of the parent CoOEP species. Because water coordinates and produces a cobaltic species similar to the dimethanol adduct (see Figure 9, below), rigorously anhydrous conditions are necessary to provide a homogeneous preparation of $Co^{II}OEP^{+}ClO_4^{-}$. The absorption spectrum of this species (Figure 4b) closely resembles that of NiOEP^{•+}ClO₄^{-,29} and has features usually attributed to the ${}^{2}A_{2u}$ state (as does Co^{III}OEP^{•+}2ClO₄⁻, Figure 4c).

Figure 5 shows absorption spectra of three species obtained by Br₂ oxidation of CoOEP in CH₂Cl₂. One-electron oxidation in this case also produces two distinct species, but both exhibit metal-centered oxidation. One-electron oxidation by Br_2 followed by dropwise addition of MeOH produces the six-coordinate Co^{III}(MeOH)₂OEPBr⁻ shown in Figure 5a. The absorption spectrum of this species is typical of six-coordinate cobaltic porphyrins³⁷ and similar, although slightly red-shifted, to that of the dimethanol adduct, Co^{III}(MeOH)₂OEPClO₄⁻, described previously²² (see Table III, below). One-electron oxidation of CoOEP by Br₂ in dry CH₂Cl₂ produces a presumably five-coordinate cobaltic porphyrin which displays the spectrum shown in Figure 5b. For this compound, Co^{III}OEPBr⁻, the Soret band (373 nm) blue-shifts with respect to that of CoOEP (391 nm), and the extinction coefficient ratio of the visible to the Soret band increases. The spectrum of the two-electron-oxidized π cation radical, Co^{III}OEP^{•+}2Br⁻, is shown in Figure 5c. The near-UV region contains three distinct bands, at 290 (not shown), 345, and 410 nm, and there are at least two bands in the visible region at ~ 600 and 670 nm. These features (split Soret with an intense red-shifted visible band) are considered typical of the ${}^{2}A_{1u}$ electronic state.^{9,23,24} The feature at 401 nm in Figure 5c is attributed to the diacid salt (H₄OEP²⁺2Br⁻), the presence of which explains the subtle variations in band shape and maximum of the 410-nm transition evident in different preparations of this compound.^{9,24} We estimate the diacid salt contamination in the preparation represented by Figure 5c to be $\sim 1\%$.³⁸

Near-UV RR Spectra of One- and Two-Electron Oxidation Products of CoOEP. Figure 6 collects RR spectra produced by 363.8-nm excitation of various products of CoOEP oxidation. The effects of metal-centered, one-electron oxidation accompanied by axial metal ligation are demonstrated by comparing the spectra of CoOEP and Co^{III}(MeOH)₂OEPClO₄⁻ depicted in Figure 6a,b. The oxidation-state marker, ν_4 , increases from 1379 to 1383 cm⁻¹, reflecting depopulation of the porphyrin π^* orbitals caused by metal oxidation.³⁹ There is little systematic change in frequency of the modes above 1450 cm⁻¹, indicating that the core size of the porphyrin ring does not change significantly upon metal oxidation and addition of axial MeOH ligands.^{32,40} The ν_2 mode, which occurs at 1599 cm⁻¹ in CoOEP, is very weak in this spectrum of Co^{III}(MeOH)₂OEPClO₄⁻, but it is seen at 1596 cm⁻¹ in spectra excited at 406.7 nm (not shown). The remaining high-frequency bands of CoOEP (Figure 6a) at 1512, 1575, and 1647 cm⁻¹ are assigned to ν_3 , ν_{11} , and ν_{10} , respectively. The weak mode at 1476 cm⁻¹ may correspond to v_{28} . Although this mode is not observed in Soret excited spectra of other MOEP complexes, it is reported for NiPP (PP = protoporphyrin IX) at 1482 cm^{-1.40} These frequencies are consistent with the CaCm stretching character of this mode. Assignments for Co^{III}(MeOH)₂OEPCIO₄are similar. Figure 6c,d shows the spectra of the cobaltous and cobaltic OEP^{•+} complexes. Neglecting differences in relative intensity produced by the differences in Soret absorption, the RR spectra of Co^{II}OEP^{•+}ClO₄⁻ and Co^{III}OEP^{•+}2ClO₄⁻ are essentially identical and (above 1300 cm⁻¹) radically different from those of the neutral ring compounds in Figure 6a,b. These observations provide a strong fingerprint basis for identifying the former species as an authentic π cation radical.²² With the exception of ν_{28} at 1466 cm⁻¹, our vibrational assignments for both $Co^{II}OEP^{+}CIO_4^{-1}$ and $Co^{III}OEP^{+}2ClO_4^{-}$ (spectra c and d of Figure 6, respectively) are similar to those of $CuOEP^{+}ClO_4^{-}$ (see Tables I and IV).

The RR spectra excited at 363.8 nm of the bromide adducts of oxidized CoOEP are shown in Figure 6e-g. The RR spectrum of Co^{III}(MeOH)₂OEPBr⁻, Figure 6e, is similar to that of CoOEP and Co^{III}(MeOH)₂OEPClO₄⁻ in Figure 6a,b. The RR spectrum of Co^{III}OEPBr⁻ is shown in Figure 6f. While ν_4 (1378 cm⁻¹) is slightly lower than in the other Co^{III} compounds, the core-sensitive bands above 1450 cm⁻¹, particularly ν_{10} (1657 cm⁻¹), have increased in frequency, suggesting a slight core contraction in this species.^{32,40} The spectrum of the π cationic radical species, Co^{III}OEP^{•+}2Br⁻ (Figure 6g), is dominated by two bands around 1600 and 1611 cm⁻¹ (presumably ν_{11} and ν_2 , respectively), similar to that of the other π cations discussed above. There is, however, no band easily assignable to v_4 . The features at 1460 and 1648 cm⁻¹ are assigned to ν_{28} and ν_{10} , respectively. The RR spectrum of this compound with laser excitation at 351.1 nm is essentially identical with the spectrum at 363.8 nm shown here. The v_3 vibration, which is enhanced in Soret RR spectra of neutral metalloporphyrins, does not appear in these spectra. We assign this mode to the polarized feature at 1497 cm⁻¹ present in the spectra obtained in resonance with the 670-nm transition of Co^{III}OEP^{•+}2Br⁻ (see Figure 8 below).

⁽³⁸⁾ We emphasize that the presence of trace amounts of diacid salts in preparations of MP⁺⁺ in CH₂Cl₂ is not always evident from absorption spectra. For example, no diacid contributions to the absorption spectrum in Figure 4c of Co^{III}OEP⁺⁺2ClO₄⁻ are apparent, yet RR excitation at 406.7 nm reveals their presence as shown by Figure 3b. Likewise, RR measurements at 406.7 nm of Co^{III}OEP⁺⁺2Br⁻ preparations invariably reflect the presence of porphyrin acid impurities. Earlier, the blue-shifted Soret absorption of metalloporphyrin diacid impurities from UV-visible absorption spectra of these samples (see ref 47a). It was not until the application of the RR technique, however, that the presence of the diacid was recognized in metalloporphyrin π cation radicals (ref 21).

⁽³⁹⁾ Spiro, T. G.; Strekas, T. C. J. Am. Chem. Soc. 1974, 96, 338-345.
(40) Choi, S.; Spiro, T. G.; Langry, K. C.; Smith, K. M.; Budd, D. L.; LaMar, G. N. J. Am. Chem. Soc. 1982, 104, 4345-4351.



Figure 6. RR spectra excited at 363.8 nm (~35 mW) of CoOEP and its oxidation products. (a) CoOEP; (b) $Co^{III}(MeOH)_2OEPCIO_4^-$; (c) $Co^{II}OEP^{++}CIO_4^-$; (d) $Co^{III}OEP^{++}2CIO_4^-$; (e) $Co^{III}(MeOH)_2OEPBr^-$; (f) $Co^{III}OEPBr^-$; (g) $Co^{III}OEP^{++}2Br^-$. Solvent, dry CH_2Cl_2 except (b and e), which contain ~5% methanol. Solvent bands are marked with an *.

Visible RR Spectra of One- and Two-Electron Oxidation Products of CoOEP. While Soret (or B band) resonance Raman excitation of neutral metalloporphyrins enhances totally symmetric modes (A_{1g} in D_{4h} symmetry) via a Franck-Condon (FC) scattering mechanism, excitation in the visible absorption (Q band) of these species enhances primarily nontotally symmetric modes (B_{1g}, B_{2g}, and A_{2g}) via a Herzberg-Teller (HT) mechanism.⁴¹ In particular, excitation in the β or Q(0-1) band strongly enhances A_{2g} modes of the MP,⁴² well-known for their inverse polarization.⁴³ Figure 7a shows both polarization components of the spectrum of CoOEP obtained in Q(0-1) resonance under 514.5-nm excitation. The A_{2g} modes are easily identified in the I_{\perp} scan at 1123, 1310, 1394, and 1598 cm⁻¹ and are assigned as ν_{22} , ν_{21} , ν_{20} , and v_{19} , respectively. Although theory predicts that the value of the depolarization ratio, $\rho \equiv I_{\perp}/I_{\parallel}$, will be ∞ for these modes, the measured values are usually finite for various reasons.^{43,44} The large ρ values obtained from Figure 7a indicate that in CH₂Cl₂ solutions CoOEP assumes a planar configuration and D_{4h} symmetry as does NiOEP in solution.⁴⁵ In agreement with Soret RR data for these ring-neutral species, Figure 7b shows that little

(41) (a) Stewart, B.; Clark, R. J. H. Struct. Bonding (Berlin) 1979, 36, 1-80.
(b) Rousseau, D. L.; Friedman, J. M.; Williams, P. F. Top. Curr. Phys. 1978, 11, 202-252.

change occurs in the spectrum as the metal center is oxidized and ligated axially by MeOH. The RR spectrum of Co^{III}OEPBr⁻ (Figure 7c), however, is different from that of other ring-neutral MOEP compounds excited at 514.5 nm, of which the previous two examples are typical. While the A_{2g} modes in the spectra of CoOEP and Co^{III}(MeOH)₂OEPBr⁻ are absent in the spectrum of Co^{III}OEPBr⁻, the appearance of ap modes at 1054, 1077, 1252, 1274, and 1572 cm⁻¹ is clear from the I_{\perp} scan in Figure 7c. The 1572-cm⁻¹ band is reported in the early study by Spaulding et al.,⁴⁵ and this frequency is noted as an exception to the trends presented in that work. This band may not be assignable to v_{19} since it is $\sim 30 \text{ cm}^{-1}$ too low. It is possible that none of the ap modes appearing in the spectrum of this compound is assignable to an A_{2g} fundamental. E_g Raman active vibrations should also exhibit anamolous polarization in D_{4h} symmetry. However, owing to their relatively high frequencies, it is improbable that these modes correspond to E_e vibrations. Furthermore, activation of E_e modes (out of plane) would presumably require electronic transition moments normal to the in-plane porphyrin transitions.⁴³ The appearance of these modes thus indicates a change in symmetry from D_{4h} , resulting in anamolous polarization of other vibrational species.41

In contrast to the cobaltic derivatives obtained by one-electron oxidation of CoOEP with Br_2 , the two-electron-oxidized cobaltic π cation radical, $Co^{III}OEP^{*+}2Br^{-}$, fails to exhibit ap modes when excited in the intense visible transition at 670 nm. Figure 8 shows RR spectra of $Co^{III}OEP^{*+}2Br^{-}$ excited at 620, 647.1, and 676.4 nm. The high-frequency spectrum from 1000 to 1700 cm⁻¹ produced with 620-nm excitation (Figure 8a) is similar to the 363.8-nm spectrum (Figure 6g), except that the 1611-cm⁻¹ (ν_2)

⁽⁴²⁾ Shelnutt, J. A. J. Chem. Phys. 1981, 74, 6644-6657.

⁽⁴³⁾ Spiro, T. G.; Strekas, T. C. Proc. Natl. Acad. Sci. U.S.A. 1972, 69, 2622-2626.

⁽⁴⁴⁾ Verma, A. L.; Mendelsohn, R.; Bernstein, H. J. J. Chem. Phys. 1974, 61, 383-390.

⁽⁴⁵⁾ Spaulding, L. D.; Chang, C. C.; Yu, N. T.; Felton, R. H. J. Am. Chem. Soc. 1975, 97, 2517-2524.



Figure 7. RR spectra excited at 514.5 nm (100 mW). (a) CoOEP; (b) $Co^{III}(MeOH)_2OEPBr^-$; (c) $Co^{III}OEPBr^-$. CH_2Cl_2 bands marked with an *.

band observed with near-UV excitation is absent from the 620-nm spectrum. The similarity of these spectra suggests that the same scattering mechanism(s) is (are) effective in both Soret and visible RR spectra of this compound. As the excitation frequency is moved into 0-0 resonance with the 670-nm electronic transition, the enhancement of polarized modes at 160, 343, 355, 1126, and 1497 cm⁻¹ (tentatively assigned to ν_3) is apparent in the spectra presented in Figure 8b-d. Figure 8d shows both parallel and perpendicular components to the scattering at 676.4 nm. Clearly there are no ap modes present in these spectra. The ρ values obtained at 647.1 nm are the same as those measured from scattering at 676.4 nm in Figure 8d. These observations suggest an absence of strong H-T coupling of the excited states of Co^{III}OEP^{•+}2Br⁻. We believe the band at 160 cm⁻¹ to be a mode involving the metal and the Br⁻ ligand, although no experiments to confirm this suggestion have been attempted. This mode is also present in spectra excited at 406.7 nm (not shown).

For the ${}^{2}A_{1u}$ radical, Co^{III}OEP*+2Br⁻, RR excitation within the intense, strongly red-shifted electronic transition at 670 nm produces RR spectra of reasonable quality that are free of contributions from other absorbing species. RR excitation within the much weaker, diffuse visible absorption bands of ${}^{2}A_{2u}$ -type radicals is much more difficult owing to the smaller RR scattering cross section. Room temperature scattering from Co^{II}OEP*+ClO₄⁻ and



Figure 8. RR spectra of Co^{III}OEP*+2Br⁻. $\lambda_{ex} = (a)$ 620 nm, 300 mW; (b) 647.1 nm, 250 mW; (c and d) 676.4 nm, 100 mW. CH₂Cl₂ bands marked with an *. Spike (**) in (b) is Rayleigh scattering at 676.4 nm.

Co^{III}OEP⁺⁺2ClO₄⁻ with 514.5-nm excitation (not shown) is similar, and consists of weak, poorly resolved Raman bands on a high fluorescence background, and it is obtained only at high laser power. Our data for Co^{II}OEP⁺⁺ClO₄⁻ show anomalously polarized features at 1312 and 1597 cm⁻¹ and a polarized feature at 1383 cm⁻¹. However, these are all attributed to the ring-neutral cobaltic species, Co^{III}(H₂O)₂OEPClO₄⁻. Other weak features which we attribute to the cobaltous π cation radical seem to correspond to modes present in the spectrum of this sample excited at 363.8 nm (Figure 6c). There is possibly an ap feature between 1560 and 1570 cm⁻¹ arising from the π cation radical; however, further experiments are required to reach firm conclusions concerning the scattering mechanisms operative in visible-region RR spectra of this and other ²A_{2u}-type π cation radicals.

Low-Temperature Effects. The results of our room temperature visible excitation RR work described above are in contrast to those obtained by Kim et al.²⁰ at low temperatures (77 K). While our work suggests a lack of anomalously polarized scattering from the π cations (at least for Co^{III}OEP^{•+}2Br⁻), the earlier study assigns A_{2g} modes of the π cations only slightly changed in frequency from those of the parent compounds. We suggest that these features most likely arise from ring-neutral contaminants in the preparations. This is particularly feasible for visible Raman measurements on ${}^{2}A_{2u}$ -type radicals, which must be excited in the diffuse 500-600-nm absorption, near the Q bands of the ringneutral compounds, in order to obtain resonance conditions. (Raman excitation in the 500–570-nm region of the ${}^{2}A_{1u}$ radicals, e.g., Co^{III}OEP + 2Br-, will not achieve resonance conditions owing to the absence of absorption in this range by the π cation radical.) The technical difficulties in obtaining scattering from these ${}^{2}A_{2u}$ -type π cation radicals is magnified at low temperatures. Figure 9 shows optical spectra that document the formation of increased amounts of Co^{III}(H₂O)₂OEPClO₄⁻ in a sample of



Figure 9. Electronic absorption spectra showing conversion of $Co^{II}OEP^{*+}ClO_4^{-}$ to $Co^{III}(H_2O)_2OEPClO_4^{-}$ as the temperature is lowered. Solvent, dry CH_2Cl_2 ; path length ~ 2 mm (EPR tube).

 $Co^{II}OEP^{+}ClO_4^{-}$ as the temperature is lowered. As the 376-nm Soret band of the cobaltous π cation decreases in intensity, absorptions characteristic of the cobaltic complex at 409, 523, and 556 nm become apparent. Thus, simply lowering the temperature of this sample has much the same effect on the absorption spectrum as the addition of methanol,²² presumably due to increased diaxial ligation by H_2O with decreasing temperature. Freeze-pump-thawing to remove water vapor over the sample prior to cooling results in minimized conversion to Co^{III}- $(H_2O)_2OEPClO_4^-$, consistent with diaquo ligation. Several other examples of the formation of ring-neutral species in preparations of metalloporphyrin π cation radicals have been observed. Addition of methanol at room temperature to CH₂Cl₂ solutions of the cobaltic π cation Co^{III}OEP⁺⁺2ClO₄⁻ will also produce $Co^{III}(MeOH)_2OEPClO_4^-$, although much more methanol is required than in the previous case. The redox chemistry involved here is unknown, although it may be similar to the room temperature reduction of $Fe^{III}(Cl^{-})TPP^{+}ClO_4^{-}$ by imidazole (Im) which produces $Fe^{III}(Im)_2TPPCl^{-,10b}$ Thus, strong axial ligation of the metal center may destabilize the porphyrin π cation radical. Similarly, Soret RR measurements at 406.7 nm on frozen samples of $Co^{III}OEP^{+}2ClO_4^{-}$ (not shown) show increased contributions from a $Co^{III}(H_2O)_2OEPCIO_4^{-}$ -type species with repeated scanning. Subsequent warming of these samples causes conversion back to cobaltic π cation radicals, as evidenced by the room temperature absorption spectrum, indicating reversible reduction in the lowtemperature case. Reversible conversion of Ni^{II}TPP++ to Ni^{III}TPP at low temperatures has also been reported; however, no axial ligation was implicated.^{5,46} In general, low-temperature RR studies are limited by elevated fluorescence levels and by the inability to measure depolarization ratios of frozen samples. Further complications are imposed by the increased aggregation of MOEP⁺⁺ compounds that occurs upon cooling.^{4,29,31,47} We note that under anhydrous conditions at room temperature both Co^{II}OEP⁺⁺ClO₄⁻ and Co^{III}OEP⁺⁺2ClO₄⁻ exhibit striking stability to relatively high power laser irradiation at 514.5 nm. Thus, in view of the above, attempts to utilize cryogenic RR techniques to stabilize these compounds is of questionable expediency and will not easily produce reliable spectra. Room temperature visible excitation RR studies of these ${}^{2}A_{2u}$ -type cation radicals will be limited, not by sample instability, but by the weak scattering cross section offered by the samples.

Discussion

In this section the four-orbital model of the neutral metalloporphyrin electronic states is introduced briefly in order to provide a framework for our analysis of the RR and UV-visible absorption spectra of the oxidized MP species. Next, spectra of the oneelectron, ring-oxidized, $M^{II}OEP^{*+}ClO_4^{-}$ systems are shown to exhibit structural trends in both the vibrational frequencies and electronic transition energies which are similar to those of the parent MOEP systems. The one-electron, metal-oxidized cobaltic OEP system is then discussed in order to establish the electronic and structural effects of metal oxidation accompanied by axial ligation. Finally, the above correlations and analysis are used to examine structural and electronic properties of the two-electron-oxidized $Co^{III}OEP^{*+}2X^{-}$ species.

In the four-orbital model of Gouterman⁴⁸ the optical absorption bands of the MP originate from transitions involving the nearly degenerate HOMOs of the porphyrin π system, $a_{1u}(\pi)$ and $a_{2u}(\pi)$, and the degenerate LUMOs, $e_g(\pi^*)$. Transitions to the CI (configuration interaction) mixed excited states, Q and B, produce the α and Soret bands, respectively. The red-shifts in the Soret and α band maxima produced by metal variation in the series Ni, Co, Cu, Zn, MgOEP are explained by variations in metal electronegativity producing a totally symmetric perturbation to the electronic states of the porphyrin. Red-shifts accompanying axial coordination are explained similarly, as an effective variation in electronegativity of the metal resulting in charge donation into the $a_{2u}(\pi)$ orbital of the ring system.⁴⁸

Structural Correlations. The frequencies of many of the vibrations of the porphyrin macrocycle are linear functions of the center to pyrrole nitrogen distance d or the core size.^{32,45} This dependency is described by the expression $\nu = K(A - d)$ where K and A are parameters characteristic of the porphyrin macrocycle.⁴⁹ For a given vibrational mode, the K value, i.e., the slope of the line, is indicative of the PED (potential energy distribution) and increases with the percentage of $C_a C_m$ stretching character.^{32,50} Correlations of vibrational frequency to core size for a series of metal-substituted porphyrins can be used to establish normal mode assignments. This approach has been used to assign vibrations of metallochlorophyll a complexes⁵¹ and is particularly useful when combined with vibrational data from isotopically substituted porphyrins.⁵² In the following, we use depolarization ratios and core size correlations from RR measurements to assign vibrational modes in MOEP** species. Similar analysis has been applied to establish RR band assignments of iron octaethylchlorin complexes.53

Table I collects RR frequencies from 1300 to 1700 cm⁻¹ obtained with Soret excitation of divalent metal OEP*+ complexes with ClO_4^- counterions and juxtaposes them with known frequencies of the corresponding starting materials. Depolarization ratios measured with 363.8-nm excitation and wavelengths of the Soret band maxima are included. For MOEP^{•+}ClO₄⁻ complexes with core sizes of 2.00 Å or less (i.e., M = Ni, Co, and Cu), our Soret RR results ($\lambda_{ex} = 363.8$ nm) agree well with those of Kim et al.²⁰ ($\lambda_{ex} = 406.7$ nm). This is because, for oxidation by AgClO₄ or electrochemical techniques, diacid impurities occur only for complexes with core sizes larger than 2.00 Å (i.e., M = Zn and Mg).²¹ Here we use RR frequencies for NiOEP^{•+}ClO₄⁻ taken from Kim et al.²⁰; however, we employ alternative vibrational mode assignments consistent with those we have made for other MOEP*+ species. Figure 10 shows plots of these vibrational frequencies as a function of core size, assuming that there is no appreciable change in d upon oxidation of the porphyrin ring. The core size measurements are those used by Spaulding et al.45 Given the

⁽⁴⁶⁾ Johnson, E. C.; Niem, T.; Dolphin, D. Can. J. Chem. 1978, 56, 1381-1388.

^{(47) (}a) Fajer, J.; Borg, D. C.; Forman, A.; Dolphin, D.; Felton, R. H. J. Am. Chem. Soc. 1970, 92, 3451-3459. (b) Mengersen, C.; Subramanian, J.; Fuhrhop, J. H. Mol. Phys. 1976, 32, 893-897.

^{(48) (}a) Gouterman, M. J. Chem. Phys. 1959, 30, 1139-1161. (b)
Gouterman, M. J. Mol. Spectrosc. 1961, 6, 138-163.
(49) Huong, P. V.; Pommier, J. C. C. R. Acad. Sci., Ser. C 1977, 285,

 ⁽⁴⁹⁾ Huong, P. V.; Pommer, J. C. C. R. Acaa. Sci., Ser. C 1977, 285,
 519-522.
 (50) (a) Warshel A. Rev. Biorhys. Biorny 1077, 6, 273. (b) Collaboration (Science) 1077, 6, 273.

 ^{(50) (}a) Warshel, A. Rev. Biophys. Bioeng. 1977, 6, 273. (b) Callahan,
 P. M.; Babcock, G. T. Biochemistry 1981, 20, 952-958.

^{(51) (}a) Fujiwara, M.; Tasumi, M. J. Phys. Chem. 1986, 90, 5646-5650.
(b) Fonda, H. N.; Babcock, G. T. In Progress in Photosynthesis Research;

Biggins, J., Ed.; Martinus Nijhof: The Hague, 1987; Vol. 1, pp 449-452. (52) Kincaid, J. R.; Urban, M. W.; Watanabe, T.; Nakamoto, K. J. Phys. Chem. 1986, 90, 5646-5650.

Chem. 1986, 90, 5646-5650. (53) Ozaki, Y.; Iriyama, K.; Ogoshi, H.; Ochiai, T.; Kitagawa, T. J. Phys. Chem. 1986, 90, 6105-6112.

TABLE I: Resonance Raman Frequencies (cm⁻¹), Depolarization Ratios, and Optical Absorption Maxima (nm) for Parent MOEP Compounds and Their Corresponding π Cation Radicals, MOEP+ClO₄-

	NiOEP ^a	NiOEP***	CoOEP	CoOEP*+	CuOEP	CuOEP**	ZnOEP	ZnOEP*+	K, cm ⁻¹ /Å	<i>A</i> , Å
ν ₄	1383		1379 (0.2) ^c		1378 (0.3)		1376 (0.3)			
C_aN		1370		1363 (0.3)		1360 (0.3)		1342 (0.3)		
ν_3	1519		1512 (0.3)		1502 (0.3)		1485 (0.4)		383 (386) ^d	5.93 (5.89)
$C_a C_m$		1511		1505 (0.4)		1497 (0.4)		1477 (0.4)	384	5.90
ν_{11}	1576		1574 (0.6)		1563 (0.8)		1559 (0.8)		197 (227)	9.95 (8.90)
CbCb		1605		1604 (0.7)		1600 (0.6)		1587 (0.8)	210	9.61
V2	1602		1599 (0.3)		1591 (0.4)		1581 (0.5)		243 (266)	8.56 (7.98)
C _b C _b		1623		1620 (0.4)		1610 (0.4)		1600 (0.5)	268	8.02
¥10	1655		1647 (0.7)		1636 (0.8)	• •	1618 (0.8)		415 (403)	5.94 (6.06)
$C_{a}C_{m}$		1651		1642 (0.8)		1631 (0.6)		1617 (0.7)	377	6.33
Soret, nm	391	377	391	376	397	383	400	387 ` ´		
α , nm	551		551		561		566			

^aReference 33a. ^bReference 20. ^cDepolarization ratios, given in parentheses, were measured with 363.8-nm excitation. ^dThe values of K and A in parentheses were calculated from frequencies reported in ref 57a.



d Ct-N(Å)

Figure 10. Porphyrin core vibrational mode frequencies (for Raman allowed bands, 1450–1700 cm⁻¹) vs porphyrin core size for the indicated MOEP complexes and their corresponding π cation radicals, MOEP⁺⁺-ClO₄⁻. Mode assignments are according to ref 33a. ∇ , ν_3 ; \square , ν_{11} ; O, ν_2 ; Δ , ν_{10} . Open symbols correspond to parent MOEP frequencies; filled symbols correspond to MOEP⁺⁺ClO₄⁻ frequencies. The regression analysis does not include the Ni (D_{2d}) points. Ct–N distances are from ref 45.

assumptions inherent in the plot (see below), Figure 10 indicates that the high-frequency RR bands of the MOEP^{•+} in the 1450– 1700-cm⁻¹ range are metal dependent and correlate to core size in the same manner as the analogous bands of the neutral parent species. The close agreement between the K values obtained for the neutral MOEP and the MOEP^{•+} for each mode suggests that little change occurs in the percentage of C_aC_m stretching character of the normal modes upon oxidation of the porphyrin ring.⁵⁴ It is thus of interest that the frequency shifts in the predominantly C_aC_m stretching modes are substantially smaller than the shifts



Figure 11. Electronic transition energies vs porphyrin core size for the indicated MOEP and MOEP^{*+}ClO₄⁻ complexes. Symbols: O, α band of MOEP; \Box and \blacksquare , Soret band of MOEP and MOEP^{*+}ClO₄⁻, respectively.

in the C_aN and C_bC_b stretching modes upon oxidation. Together with the relative agreement of the depolarization ratio measurements for modes of the MOEP and MOEP⁺⁺, these core size correlations provide support for our band assignments in the MOEP⁺⁺ spectra. Further confirmation is provided by RR measurements on MOEP⁺⁺ incorporated with isotopic substitutions, which are in progress. Our results suggest that, in general, normal mode calculations for the parent MP will remain useful for interpreting the vibrations of the MP⁺⁺ species.

Additional evidence of the correlation of vibrational frequencies of the porphyrin core stretching modes above 1450 cm⁻¹ to core size is provided by IR studies of MOEP⁺⁺ compounds.¹² If we use complexes that presumably exhibit D_{4h} solution geometries,^{55,56} i.e., Co^{III}OEP⁺⁺2ClO₄⁻, Fe^{III}OEP⁺⁺2ClO₄⁻, and Fe^{III}OEP⁺⁺-2CF₃SO₃⁻, we can correlate their diagnostic IR band frequencies¹² to the core sizes provided by Spaulding et al.⁴⁵ Although the number of points is too few to establish a reliable correlation, we can estimate K and A from these data to be 420 cm⁻¹/Å and 5.67 Å, respectively. They compare remarkably well to K and A values calculated for ν_{38} from IR measurements of MOEP complexes obtained at 15 K in argon matrices.⁵² While there is some controversy as to the normal mode composition of ν_{38} ,^{32,33,52} these IR frequencies yield K and A values of 421.3 cm⁻¹/Å and 5.69 Å, and imply predominantly C_aC_m stretching character for this mode.

⁽⁵⁴⁾ The decrease in K value upon oxidation for ν_{10} is not considered significant owing to the uncertainty in the ν_{10} measurement of $ZnOEP^{*+}ClO_4^{-}$ by Soret excitation RR. Visible excitation of this compound at 647.1 nm, which should more clearly show the ν_{10} band, was not possible owing to intense fluorescence emission centered around 675 nm. Thus it is possible that the relatively high ν_{10} value measured for $ZnOEP^{*+}ClO_4^{-}$ anomalously lowers the K value (for ν_{10}) of the MOEP^{*+} series.

^{(55) (}a) Scholz, W. F.; Reed, C. A.; Lee, Y. J.; Scheidt, W. R.; Lang, G. J. Am. Chem. Soc. **1982**, 104, 6791-6793. (b) Buisson, G.; Deronzier, A.; Duée, E.; Gans, P.; Marchon, J.-C.; Regnard, J.-R. J. Am. Chem. Soc. **1982**, 104, 6793-6796.

⁽⁵⁶⁾ Gans, P.; Buisson, G.; Duče, E.; Marchon, J.-C.; Erler, B. S.; Scholz, W. F.; Reed, C. A. J. Am. Chem. Soc. **1986**, 108, 1223-1234.

TABLE II: Core Size Parameters from Crystal Structures of Metalloporphyrin π Cation Radicals and Related Compounds

		Ct-N,	Ct-M,	core
	ref	Å	Å	ruffle, Å
MP*+				
Mg(ClO ₄ ⁻)TPP ^{•+}	13	2.051	0.43	±0.4
$Zn(ClO_4^{-})TPP^{++}$	13	2.047	0.347	±0.4
Fe ^{III} (Cl ⁻)TPP ^{•+} S _b Cl _b ⁻	55	2.01	0.5 ^a	"saddle shaped"
$Fe^{III}(ClO_4^-)_2TPP^{*+}$	55	2.045	0	"planar"
CuTPP**SbCl ₆ -	55	1.988 ^b	?	"unusually large"
MP				
Mg(H ₂ O)TPP	60	2.054	0.273	?
$Zn(Py)TPyP^{c}$	61	2.047	0.33	±0.17
Fe ^{III} (X ⁻)TPP ^d	62	2.001	0.51	±0.14
$Fe^{III}(H_2O)_2TPP$	63	2.045	0	±0.034
CuTPP ^e	64	1.981		
Fe ^{III} (ClO ₄ ⁻)OEP	65	1.977	0.26	± 0.04
Fe ^{III} (ClO ₄ ⁻)TPP	66	1.978	0.3	±0.3

"This value is assumed in order to calculate Ct-N distance from Fe-N distances. ^bCu-N distance. If the Cu is displaced from the macrocycle plane, the Ct-N distance will be less than this value. ^cTPyP = tetrapyridylporphyrin. ^dThis represents an average from available X^- = halide structures. ^cCopper porphyrins seem to exhibit two distinct crystal structures, one with a Ct-N distance of 2.00 Å and another with d = 1.98 Å (see ref 45).

For CoOEP, ν_{38} is reported⁵² at 1565 cm⁻¹, whereas the diagnostic IR band of $Co^{III}OEP^{+}2ClO_4^{-}$ is reported at 1554 cm⁻¹. The ~ 10 -cm⁻¹ difference in these frequencies is in good agreement with the frequency decreases in C_aC_m stretching modes resulting from porphyrin ring oxidation observed in our Raman work. This, and the agreement between K and A values, suggest that the diagnostic band of MOEP⁺⁺ complexes corresponds to ν_{38} of the parent MOEP.

In addition to RR frequencies, Table I also lists Soret maxima for MOEP and MOEP⁺⁺ compounds. These values, along with α -band energies for the parent MOEP, are plotted as a function of core size in Figure 11. Absorption data for MgOEP (408-nm Soret; 580-nm α band) and MgOEP⁺⁺ClO₄⁻ (392-nm Soret) in CH_2Cl_2 have been added. Our spectrum of the MgOEP⁺⁺ClO₄⁻⁻ resembles the previous measurement by Dolphin et al.⁴ The Soret maximum for MgOEP⁺⁺ClO₄⁻ in Figure 11 represents the lowest energy transition in the near-UV envelope of the absorption spectrum. The qualitative similarity of the trends for all transition energies is striking and can be explained by the dominance of the $a_{2u}(\pi) \rightarrow e_g(\pi^*)$ character of the transitions in determining the core size dependencies of these values. For neutral MOEP the $a_{2u}(\pi)$ orbital energy may be considered to vary linearly with core size while the $e_g(\pi^*)$ and $a_{1u}(\pi)$ orbitals remain relatively constant.^{48,57-59} Thus, the $a_{2u}(\pi) \rightarrow e_g(\pi^*)$ character of the excited state determines the core size dependency of the α and Soret band

energies. Calculations by Edwards and Zerner²³ predict that, in the case of the ${}^{2}A_{2u}$ cobaltic porphyrin radical, the dominant transition in the Soret region has 30% $a_{2u}(\pi) \rightarrow e_g(\pi^*)$ character, while for the ${}^{2}A_{1u}$ cobaltic species the least energetic transition in the Soret envelope has 70% $a_{2u}(\pi) \rightarrow e_g(\pi^*)$ character. Thus the correlations in Figure 11 suggests that the $a_{2u}(\pi) \rightarrow e_g(\pi^*)$ character of these transitions is responsible for the core size dependency of the Soret band energies in both the MOEP and MOEP⁺⁺ compounds.

Porphyrin Core Geometry. The key assumption made in establishing the parameters K and A in the relation v = K(A - d)for the MOEP⁺⁺ series is the invariability of the core size (d) upon oxidation of the parent MOEP. Table II summarizes the relevant parameters that describe the four X-ray crystal structures of metalloporphyrin π cation radicals determined to date and compares them to the structures of the analogous parent compounds. The table also compares perchlorate ligated ferric TPP and OEP as a control to establish possible steric effects limited to TPP complexes. In each case the agreement between the structures of MP and MP*+ is good in terms of the Ct-N distances and the metal displacements from the plane of the pyrrole nitrogens. However, the porphyrin core structures of MgTPP⁺⁺ and ZnTPP⁺⁺ display larger deviations from planarity than do the model parent structures. This is not considered to represent a significant general structural deviation between MP and MP*+ and is explained rather as a result of steric interaction of the bulky ClO₄⁻ counterions and the mesophenyl groups resulting from crystal packing forces.¹³ Two other examples support this idea: (1) While crystalline CuTPP^{•+}SbCl₆⁻ exhibits "unusually large ruffling of the porphyrin core", the CH_2Cl_2 solution structure is planar.⁵⁵ (2) Crystalline $Fe^{III}(ClO_4)TPP$ exhibits core ruffling almost as large as the perchlorate ligated MTPP⁺⁺ examples, whereas Fe^{III}(ClO₄⁻)OEP has a planar core (see Table II). Thus, we speculate that CH₂Cl₂ solution structures of the type $MOEP^{+}ClO_4^{-}$ do not exhibit significant ruffling of the porphyrin core, and the lines described by Figures 10 and 11 are useful references, uncomplicated by the effects of macrocycle distortion. The success of the correlation attests to this and suggests that in general we can assume that in solution the Ct-N distance of the MP^{•+} and probably other aspects of core geometry are comparable to those of the parent MP. Thus, it is assumed that no significant changes in geometric structure of the porphyrin ring accompany the abstraction of an electron from the $a_{2u}(\pi)$ or $a_{1u}(\pi)$ orbital of the metalloporphyrin in solution.

Ring Buckling Effects. Distortions of the porphyrin core are known to weaken the bonding in the macrocycle, thus lowering the frequencies of stretching vibrations of the core and causing negative deviations from the relation $\nu = K(A - d)$.⁶⁷ The classic example is shown in Figure 10 by the vibrational frequencies of the D_{2d} form of NiOEP,⁴⁵ which displays deviations from planarity in the macrocycle of ±0.5 Å.⁶⁸ Spiro et al.⁶⁷ conclude that the effects of core distortions on vibrational frequencies, although significant, are minor in comparison to changes in Ct-N distance, demonstrating that core size is the main determinant of the vibrational frequencies of the porphyrin macrocycle. Our results indicate that the relationship of core size to vibrational frequency is similar for the oxidized porphyrin ring. It is expected that the effects of core distortions, such as S_4 ruffling, will be manifest also in the vibrational frequencies of the MP*+, producing negative deviations from the correlations of Figure 10.

Cobaltic Octaethylporphyrin π Cation Radicals. The Co^{III}OEP^{•+}2X⁻ system is particularly interesting owing to the variety of spectrally distinct two-electron-oxidation products possible as a function of counterions X^{-.69} In order to compare the electronic spectra of Co^{III}OEP^{•+}2X⁻ to the parent system, Co^{II}OEP, it is necessary to determine how oxidation of the metal

^{(57) (}a) Kitagawa, T.; Ogoshi, H.; Watanabe, E. Yoshida, Z. J. Phys. Chem. 1975, 79, 2629-2635. (b) Shelnutt, J. A.; Ondrias, M. R. Inorg. Chem. 1984, 23, 1175-1177

^{(58) (}a) Shelnutt, J. A.; Straub, K. D.; Rentzepis, P. M.; Gouterman, M.; Davidson, E. R. *Biochemistry* **1984**, *23*, 3946-3954. (b) Shelnutt, J. A.; Alston, K.; Ho, J.-Y.; Yu, N.-T.; Yamamoto, T.; Rifkind, J. M. *Biochemistry* 1986. 25. 620-628

⁽⁵⁹⁾ The model presented here is an oversimplification. Similar trends in *) orbital energy levels (LUMO) are revealed by reduction potentials the e. for MOEP complexes. Comparative measurements of the first oxidation potential reflect trends in the HOMO energies. The results show that both the HOMO and the LUMO rise in energy in the series Ni \approx Cu, Zn, MgOEP; however, the HOMO levels increase more, thus producing the spectral redshift. See ref 29 and Fuhrhop, J.-H.; Kadish, K. M.; Davis, D. G. J. Am. Chem. Soc. 1973, 95, 5140-5147.

 ⁽⁶⁰⁾ Timkovich, R.; Tulinsky, A. J. Am. Chem. Soc. 1969, 91, 4430–4432.
 (61) Collins, D. M.; Hoard, J. L. J. Am. Chem. Soc. 1968, 92, 3761–3771.

⁽⁶²⁾ Mitra, S. In *Iron Porphyrins*; Lever, A. B. P.; Gray, H. B., Eds.;
Addison-Wesley: Reading, MA, 1982; Part II, pp 3-42.
(63) Scheidt, W. R.; Cohen, I. A.; Kastner, M. E. *Biochemistry* 1979, 18,

³⁵⁴⁶⁻³⁵⁵²

⁽⁶⁴⁾ Fleischer, E. B.; Miller, C.; Webb, L. J. Am. Chem. Soc. 1964, 86, 2342-2343.

⁽⁶⁵⁾ Masuda, H.; Taga, T.; Osaki, K.; Sugimoto, H.; Yoshida, Z.-I.;
Ogoshi, H. Inorg. Chem. 1980, 19, 950–955.
(66) Reed, C. A.; Mashiko, T.; Bentley, S. P.; Kastner, M. E.; Sheidt, W. R.; Spartalian, K.; Lang, G. J. Am. Chem. Soc. 1979, 101, 2948–2958.

⁽⁶⁷⁾ Spiro, T. G.; Strong, J. D.; Stein, P. J. Am. Chem. Soc. 1979, 101, 2648-2655.

⁽⁶⁸⁾ Meyer, E. F. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst.

Chem. 1972, B28, 2162-2167. (69) Setsume, J.; Ikeda, M.; Kishimoto, Y.; Kitao, T. J. Am. Chem. Soc. 1986, 108, 1309-1311.

TABLE III: Resonance Raman Frequencies and Optical Absorption Maxima for Axially Ligated Cu^{II}-, Ni^{II}-, and Co^{III}OEP Complexes

	frequency, cm ⁻¹							
	ν ₄	ν ₃	<i>v</i> ₁₁	<i>v</i> ₁₉	ν2	ν_{10}	α , nm	Soret, nm
CuOEP/hexane ^a	1378	1503	1568	1582		1637	562	398
Cu(pyr)OEP ^a	1376	1503 ^c	1566	1580		1629	570	414
NiOEP/CH ₂ Cl ₂ ^b	1382	1519		1602	1601	1656	551	391
Ni(pip) ₂ OEP ^b	1370	1481		1559	1587	1615		421
Co ^{ll} OÉP	1379	1512	1575	1598	1598	1647	551	391
Co ^{III} (MeOH),OEPClO ₄ ⁻	1382	1515	1575	1597	1598	1647	556	409
Co ^{III} (MeOH) ₂ OEPBr ⁻	1382	1515	1575	1596	1599	1648	558	411
Co ^{III} (Im) ₂ OEPX ⁻	1383	1514	1575		1598	1646	559	417

^aReference 58a. ^bReferences 58b and 70. ^c ν_3 frequency for Cu(pip)OEP (ref 58a). Abbreviations: pyr, pyrrolidine; pip, piperidine; Im, 1methylimidazole.

and addition of axial ligands influence the electronic states of the OEP⁺⁺ system. For example, the agreement between the Soret maxima of Co^{II}OEP (391 nm) and its two-electron-oxidation product Co^{III}OEP^{•+}2ClO₄⁻ (393 nm) would be misleading without acknowledging the counterbalancing effects present. Recognition of the blue-shifted Soret maximum of the cobaltous species $Co^{II}OEP^{+}ClO_4^{-}$ (376 nm) isolates the effect of ring oxidation upon the Soret absorption maximum and reveals a blue-shifted band of diminished intensity compared to the parent CoOEP. Axial ligation by the ClO₄⁻ ion is unlikely in the cobaltous OEP^{•+} because of the presence of an electron in the metal d_{z^2} orbital. Thus, we consider this and the other M^{II}OEP^{•+}ClO₄⁻ complexes discussed here to contain four-coordinate metal centers, devoid of the effects of metal oxidation and axial ligation. Empirically we see that oxidation of the ring causes a 1000-cm⁻¹ blue-shift in the Soret maximum with respect to the parent CoOEP. This is compensated for in Co^{III}OEP^{•+}2ClO₄⁻ by a 1150-cm⁻¹ red-shift produced by oxidation at the metal center accompanied by weak axial ligation by the ClO_4^- ions. Compared to the cobaltous case noted above, weak ligation of the cobaltic center by both ClO₄ions in the latter complex is more likely because the d⁶ configuration of Co^{III} leaves the d_{z^2} orbital empty. Thus, we consider $Co^{III}OEP^{+}2ClO_4^{-}$ to represent a six-coordinate complex, albeit with weak axial ligands. This example illustrates the importance of recognizing the combined effects of metal oxidation and axial ligation on the electronic states of the OEP⁺⁺ systems in order to interpret the absorption spectra correctly.

Effects of One-Electron, Metal-Centered Oxidation and Axial Ligation. In order to assess these effects on the electronic transitions of the OEP^{*+} system, a good starting point is to consider the effects of metal oxidation and ligation in the parent OEP system. For this analysis we utilize the ring-neutral Co^{III}-(MeOH)₂OEPX⁻ as an example of a weakly ligated, six-coordinate cobaltic complex. Comparison of the spectra of this species to those of CoOEP will establish the effects of ligation and oxidation of the metal. These effects will be compared to the effects of axial ligation alone on Cu- and NiOEP.

Shelnutt et al.⁵⁸ have shown that the red-shifts in the α and Soret bands of copper and nickel porphyrins upon axial ligation are accompanied by expansion of the porphyrin ring as revealed by decreases in RR frequencies of the core size sensitive modes. The core expansion accompanying axial ligation in nickel porphyrins, confirmed by similar RR measurements by Kim et al.⁷⁰ is much greater than in copper porphyrins and involves a change in spin state and subsequent occupancy of the $d_{x^2-y^2}$ orbital of the Ni.⁷⁰ These spectroscopic results are explained by a relative increase in the porphyrin $a_{2u}(\pi)$ orbital energy level caused by the interaction of the metal atom with its axial ligands and are thus in agreement with the model for axial ligation proposed by Gouterman.48 Table III collects RR frequencies and absorption maxima for Cu-, Ni-, and CoOEP and their axially ligated systems. We emphasize that with these examples we consider the effects of ligation alone for Cu- and NiOEP and ligation accompanied by metal oxidation for CoOEP. Inspection of Table III reveals that the red-shifts in the optical absorptions of Co^{III}- $(L)_{2}OEPX^{-}$ (where L = methanol or 1-methylimidazole) with respect to those of CoOEP are similar to those encountered upon ligation of CuOEP or NiOEP. However, the RR data clearly show that axial ligation and autoxidation of CoOEP is not accompanied by core expansion, as there is no decrease in the vibrational frequencies of $Co^{III}(L)_2 OEPX^-$ compared to CoOEP. The slight increases in ν_4 frequencies reflect a decrease in the $e_p(\pi^*)$ orbital occupancy upon oxidation of CoII to CoIII and are not related to core size. (The Cu- and NiOEP systems show the opposite behavior and exhibit decreases in the ν_4 frequencies.) RR wavenumbers reflect the structure of the ground state of the scattering species. Thus, red-shifts in the absorption spectra without concomitant decreases in RR frequencies suggest stabilization of the excited state, i.e., a decrease in the $e_g(\pi^*)$ rather than an increase in the $a_{2u}(\pi)$ orbital energies upon axial ligation and metal oxidation of these species. These considerations indicate that the spectral red-shifts observed upon metal oxidation and ligation of CoOEP are not simply comparable to those caused by ligation alone of Cu and NiOEP. Whether these conclusions apply to ligation alone of cobaltous porphyrins under anaerobic conditions cannot be determined from this analysis.

 $Co^{III}OEP^{*+}2ClO_4^{-}$. Having established the combined effects of metal oxidation and weak axial ligation on the electronic transitions and RR vibrations of Co^{II}OEP, we can consider like effects in the analogous π cation radical system, Co^{II}OEP⁺⁺. Comparison of Soret maxima and RR frequencies (Figure 6c,d) of Co^{III}OEP⁺⁺2ClO₄⁻ to those of Co^{II}OEP⁺⁺ClO₄⁻ reveals optical red-shifts without porphyrin cation radical core expansion. The spectral differences between these two species are analogous to those observed when comparing Co^{II}OEP to Co^{III}- $(MeOH)_2OEPCIO_4^-$. In the former (π cation) case the Soret maximum shifts 1150 cm⁻¹, or from 376 to 393 nm, while in the later (ring-neutral) case, the shift is from 391 to 409 nm or 1180 cm⁻¹. In both cases, RR results imply no change in the porphyrin core size. The similarity of these examples suggests that in both instances we are comparing a four-coordinate cobaltous species to a six-coordinate cobaltic one and that ring planarity and D_{4h} symmetry are maintained throughout. Furthermore, the absorption spectra imply that the behavior of the Soret absorption in these π cations is little changed from that of the ring-neutral analogues.

As discussed above, a key assumption in our analysis concerns the effects of ring oxidation per se on macrocycle geometry. On the basis of X-ray studies of crystalline compounds,¹³ we assume that in general the core geometries of porphyrin π cations, MP⁺⁺, are not significantly different from those of the parent compound MP. By "parent" we specifically refer to a complex that exhibits the same oxidation state and coordination geometry of the central metal. For example, the "parent" compound for Co^{II}OEP⁺⁺ClO₄⁻⁻ is Co^{II}OEP, and the "parent" for Co^{III}(ClO₄⁻⁻)₂OEP⁺⁺ is Co^{III}. (MeOH)₂OEPClO₄⁻⁻. (The cobaltic π cation radical complex is now written in a manner as to imply axial ligation by the perchlorate anions.) Thus, our analysis suggests that the core sizes of all four of these complexes are the same, approximately 1.97 Å.

 $Co^{III}OEP^{+2}Br^{-}$. To date, EPR and ENDOR measurements are the most reliable criteria to establish the MP^+ electronic ground state (${}^{2}A_{2u}$ or ${}^{2}A_{1u}$).⁸ EPR measurements of Co^{III}OEP^+2ClO₄⁻ and Co^{III}OEP^+2Br⁻ are consistent with the

⁽⁷⁰⁾ Kim, D.; Su, Y. O.; Spiro, T. G. Inorg. Chem. 1986, 25, 3988-3993.

TABLE IV: Comparison of Resonance Raman Frequencies (cm⁻¹) and of Depolarization Ratios for Cobaltic OEP+ Complexes

	Co ^{III} OEP++2ClO ₄ -	Co ^{III} OEP ^{•+} 2Br ⁻
ν ₄	1361 (0.2)	?
ν_3	1505 (0.5)	1498 (0.3)
v_{11}	1605 (0.7)	1598 (0.5)
ν_2	1617 (0.5)	1611 (0.4)
ν_{10}	1642 (0.7)	1649 (0.7)

 ${}^{2}A_{2u}$ and ${}^{2}A_{1u}$ states, respectively.²⁴ Perhaps the most interesting aspect of the correlations presented in Figures 10 and 11 is the apparent insensitivity of the RR frequencies and Soret transition energies of the $M^{II}OEP^{+}ClO_{4}^{-}$ complexes to radical electronic state. This implies that we can use these correlations for structural analysis of OEP++ compounds of either radical type, and we can extend our discussion to include Co^{III}OEP*+2Br⁻.

Aside from differences in relative intensities, the RR spectra of Co^{III}OEP⁺⁺2ClO₄⁻ and Co^{III}OEP⁺⁺2Br⁻ are similar (see Figure 6d,g; Figure 8). Table IV compares the RR frequencies of these two complexes. The vibrational frequencies of the latter (presumably a ${}^{2}A_{1u}$ complex), however, are 6-7 cm⁻¹ lower than those of the former (presumably a ${}^{2}A_{2u}$ complex), with the as yet unexplained exception of v_{10} . Because the core size correlations seem independent of radical electronic state, and because the frequency differences between these two complexes are small, we speculate that they can be attributed to differences in porphyrin core geometry caused by the different axial ligation of these two species. Decreases in frequency of the macrocycle vibrations (above 1450 cm⁻¹) may result from either expansion or buckling of the porphyrin core. It is reasonable to assume that Co^{III}OEP⁺⁺2Br⁻ is a six-coordinate complex with a planar porphyrin core. The ν_3 , ν_{11} , ν_2 , and ν_{10} frequencies (Table IV) can then be used, along with K and A values from Table I, to predict a core size of 1.99 ± 0.02 Å for this complex. This is to be compared to 1.974 ± 0.008 Å predicted similarly for the core size $Co^{11}OEP^{+}2ClO_4^{-}$. However, the possibility that the vibrational frequencies of Co^{III}OEP⁺2Br⁻ are lowered from those of $Co^{III}OEP^{+}2ClO_4^{-}$ as a result of porphyrin core distortions, rather than core expansion, cannot be ruled out by this analysis.⁷²

Conclusions

While the interpretation of the spectra described in this paper essentially ignores radical designation as ${}^{2}A_{2u}$ or ${}^{2}A_{1u}$, other researchers have emphasized the species symmetry of MP*+ compounds. Characterization of the MP^{+} as ${}^{2}A_{2u}$ or ${}^{2}A_{1u}$, as revealed by spin-density profiles, has been based primarily on MO calculations, $^{47a,73-75}$ as well as on EPR and ENDOR studies.^{4,8,24,47a,73,75-77} These studies have established many useful

generalizations concerning radical type. For instance, the porphyrin ring substituents have a profound influence, and structures of the type MTAP^{•+} (where A is an alkyl or aryl group in the meso position) exhibit ²A_{2u} characteristics,⁸ while MHP*+ (where HP = hydroporphyrin) tend to be classified as ${}^{2}A_{1u}$ radicals. 73,76,77 Structures of the type MOAP⁺⁺ (octaalkylporphyrin where the C_b substituents are not necessarily identical) may exhibit either state depending primarily on the metal center and the axial ligands.^{8,24,73} Examples of the latter type include the high-valent catalytic intermediates of heme peroxidases and catalases. The compound I structures of these enzymes are usually described as oxoferrylprotoporphyrin IX π cation radicals, $O = Fe^{IV}(X)PP^{\bullet+,2}$ The electronic state is considered to be mediated by the identity of the sixth ligand X, and MO calculations predict that ligation by tyrosine or thiolates promotes the ${}^{2}A_{1u}$ configuration (e.g., CAT-I and CPO-I, respectively)^{73,76} while imidazole ligation generally favors a predominantly ²A_{2u} state (e.g., HRP-I).^{73,74} ESR and ENDOR studies, however, are interpreted to suggest a ²A_{2n} configuration for both HRP-I and CPO-I.⁷⁸ The EPR measurement of CPO-I (chloroperoxidase compound I) was judged inconsistent with a ²A_{1u} configuration owing to the relatively strong antiferromagnetic coupling between the S = 1 oxoferryl structure and the $S = 1/2 \pi$ cation radical suggested by the spectra. The authors reason that such magnetic coupling is more likely in the ${}^{2}A_{2u}$ configuration where relatively large spin densities are placed on the pyrrole nitrogens.73

Distortion of the porphyrin ring may provide an orbital overlap pathway for the strong, $|J| \sim 250 \text{ cm}^{-1}$, antiferromagnetic coupling displayed by Fe^{III}(Cl⁻)TPP⁺⁺SbCl₆^{-, 55,56} While such magnetic coupling was previously thought to occur only in ²A_{2u} radicals,⁸ more recent interpretations⁷⁶ suggest magnetic coupling between the paramagnetic metal center and porphyrin π cation radical can occur in either radical type, with the radical type influencing the magnitude of the interaction.^{55a} While the weak coupling, $|J| \sim$ 2 cm⁻¹, displayed by HRP-I⁷⁸ has been attributed to possibly a planar configuration of the porphyrin ring,⁵⁶ the stronger, $|J| \sim$ 37 cm⁻¹, coupling for CPO-I⁷⁸ may reflect a more buckled configuration (other explanations are also possible^{11,76,78,79}). Recent work clearly indicates that evaluation of porphyrin core geometry must be addressed in order to interpret results from magneticbased techniques.

The similarity of the vibrational frequencies in the 1450-1700-cm⁻¹ range of the proposed ${}^{2}A_{2u}$ and ${}^{2}A_{1u} \pi$ cation radicals, Co^{III}OEP*+2ClO₄⁻ and Co^{III}OEP*+2Br⁻, respectively, suggests that these frequencies are insensitive to radical type. There are, however, small wavenumber differences which can be attributed to relatively minor differences in porphyrin core geometry of these two compounds. Because these geometric differences are as yet speculative, other interpretations are plausible. Although these vibrations of the porphyrin macrocycle may well be insensitive to radical electronic state, the abnormally high values of the $\nu(C_bC_b)$ modes provide a clear basis to identify ring-centered oxidations, particularly in MOEP^{•+} species.²²

Acknowledgment. W.A.O. thanks Dwight Lillie and Bob Kean for their computer programming and Harold Fonda for discussion. This work was supported by NIH Grants GM25480 (G.T.B.) and GM36520 (C.K.C.) and NSF Grant CHE86-10421 (G.E.L.).

Registry No. CuOEP, 14409-63-3; CuOEp⁺⁺ClO₄⁻, 78520-99-7; ZnOEP, 17632-18-7; ZnOEP⁺⁺ClO₄⁻, 103904-51-4; Co^{II}OEP⁺⁺ClO₄⁻, 55845-55-1; Co^{III}OEP+2ClO₄⁻, 33058-44-5; H₄OEP²⁺2ClO₄⁻, 51319-02-9; H₃OEP+ClO₄⁻, 110354-21-7; H₄OEP²⁺2Br⁻, 110372-41-3; CoOEP, 61226-34-4; Co^{III}(MeOH)₂OEPBr⁻, 110354-22-8; Co^{III}OEPBr⁻, 55845-53-9; Co^{III}OEP+2Br-, 78521-00-3; NiOEP, 24803-99-4; NiOEP++, 74876-13-4.

⁽⁷¹⁾ Actually the question of radical ground state for these compounds is not completely clear-cut. Of the ClO_4^- complexes used in the correlations, only MgOEP^{*+} and ZnOEP^{*+} have been firmly assigned a ground electronic state (²A_{1u}) on the basis of EPR studies (ref 8). Coupling between the paramagnetic metal centers and the porphyrin radical of CollOEP++ClO4- and $CuOEP^{*+}$ render these complexes EPR silent. Although the UV-visible absorption spectra of Cu, Co^{II}, and NiOEP^{*+} imply ${}^{2}A_{2u}$ character for their ClO₄⁻ complexes, the electronic state of CuOEP^{*+}ClO₄⁻ is assigned as ${}^{2}A_{1u}$ on the basis of NMR spectra (ref 10a). To our knowledge, the EPR spectrum of NiOEP⁺⁺ClO₄⁻ (ref 29) has never been discussed in terms of ${}^{2}A_{2u}$ or ${}^{2}A_{1u}$ ground-state symmetry.

⁽⁷²⁾ On the basis of RR frequencies, the precursor compound, $Co^{III}OEPBr$, is predicted to have a contracted core, ~1.957 ± 0.009 Å. We also note that this one-electron-oxidized compound displays certain Raman and absorption spectroscopic features analogous to a structure known to possess a buckled porphyrin core, namely the μ -nitrido dimer (FeOEP)₂N. See (a) Hoffman, J. A.; Bocian, D. F. J. Phys. Chem. **1984**, 88, 1472–1479. (b) Scheidt, W. R.; Summerville, D. A.; Cohen, I. A. J. Am. Chem. Soc. 1976, 98, 6623-6628 for spectra and crystal structure of µ-nitrido dimers, respectively. However, it is not yet clear if the geometry of this precursor (not "parent" as defined above) is relevant to the structure of the two-electron-oxidized product, Co^{III}OEP*2Br⁻.

⁽⁷³⁾ Hanson, L. K.; Chang, C. K.; Davis, M. S.; Fajer, J. J. Am. Chem. Soc. 1981, 103, 663-670.

⁽⁷⁴⁾ Loew, G. H.; Herman, Z. S. J. Am. Chem. Soc. 1980, 102, 6174-6175.

⁽⁷⁵⁾ Fujita, I.; Hanson, L. K.; Walker, F. A.; Fajer, J. J. Am. Chem. Soc. 1983, 105, 3296-3300.

⁽⁷⁶⁾ Fujita, E.; Chang, C. K.; Fajer, J. J. Am. Chem. Soc. 1985, 107, 7665-7669.

⁽⁷⁷⁾ Chang, C. K.; Hanson, L. K.; Richardson, P. F.; Young, R.; Fajer, J. Proc. Natl. Acad. Sci. U.S.A. 1981, 78, 2652-2656. (78) (a) Roberts, J. E.; Hoffman, B. M.; Rutter, R.; Hager, L. P. J. Biol.

Chem. 1981, 256, 2118-2121. (b) Rutter, R.; Hager, L. P. J. Biol. Chem.
 1982, 257, 7958-7961. (c) Schultz, C. E.; Rutter, R.; Sage, S. T.; Debrunner,
 P. G.; Hager, L. P. Biochemistry 1984, 23, 4743-4754.
 (79) Sontum, S. F.; Case, D. A. J. Am. Chem. Soc. 1985, 107, 4013-4015.