Resonance Raman Spectrum of a $^2A_{1u}$ Ferryl Porphyrin π-Cation Radical

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Abstract: Resonance Raman spectra are reported for the iron complex of tetramethyltetramesitylporphine (TMTMP) in its ferric, ferryl, and ferryl π-cation forms. For comparison, the spectra of the copper complex and its corresponding π-cation radical are included. Vibrational assignments have been made based on depolarization ratio measurements and isotopic frequency shifts associated with methine deuteration. The observed behavior of the ν_2 and ν_{11} RR "marker bands", which shift to higher frequency upon oxidation of the macrocycle, is consistent with previously reported NMR studies wherein these radicals were shown to have predominately $^2A_{1u}$ ground states. The ν(Fe−O) stretching modes of the ferryl species (both five- and six-coordinate) and (OFeTMTMP$^{\bullet+}$)(ClO_4^-) are identified by their $^{16}O/^{18}O$ isotope shifts. This is the first observation of the ν(Fe−O) mode for a $^2A_{1u}$ type ferryl π-cation radical. Its frequency (833 cm^{-1}) is virtually identical with that of the corresponding derivative of *meso*-tetramesitylporphyrin (TMP), (O═FeTMP$^+$)(ClO_4^-), a $^2A_{2u}$ radical, which exhibits its ν(Fe−O) mode at 835 cm^{-1}. These data imply that the ν(Fe−O) modes of ferrylporphyrin π-cation radicals are rather insensitive to radical type ($^2A_{1u}$ vs $^2A_{2u}$)—behavior which is surprisingly different from the previously observed sensitivity of the ν(V−O) modes of corresponding vanadylporphyrin π-cation radicals.

Introduction

The key intermediate involved in the enzymatic cycles of a large number of oxidative heme enzymes such as peroxidases, catalases, and presumably cytochromes P450, is called compound **I**. These primary intermediates, which are two oxidizing equivalents higher than the resting state, are thought to contain an oxoiron(IV) porphyrin π-cation radical.[1] Depending on the symmetry of the highest occupied molecular orbital (HOMO), the ground electronic state of the heme π-cation radical can be assigned to one of two ($^2A_{1u}$ or $^2A_{2u}$) types[2] (*vide infra*). Their relative energies are dictated by several factors, such as position and type of substituents on the porphyrin macrocycle periphery or the nature of the axial ligand.[3]

Resonance Raman (RR) spectroscopy is a powerful tool in investigating the structure and bonding of these porphyrin π-cation radicals.[3a−d] In principle, it is potentially able to provide direct documentation for the ferryl fragment *via* observation of the Fe═O stretching mode, ν(Fe═O), and is effective in characterizing the nature of the electronic ground state of these radicals based on the frequencies of so-called RR "marker bands".

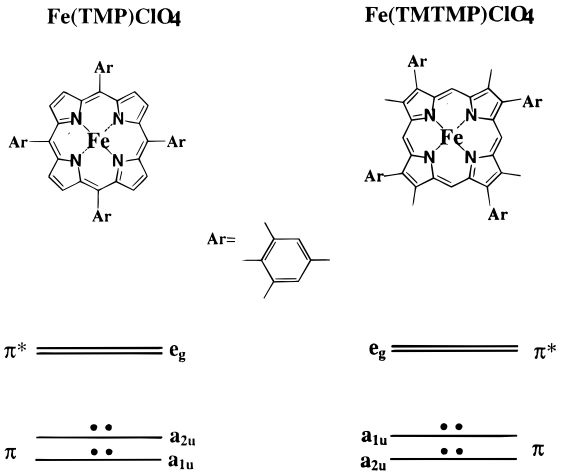

Figure 1. Structures of Fe^{III}(TMP)ClO_4 (TMP = 5,10,15,20-tetramesitylporphyrinato dianion) and Fe^{III}(TMTMP)ClO_4 (TMTMP = 2,7,12,-17-tetramethyl-3,8,13,18-tetramesitylporphyrinato dianion) and their relative molecular orbital (HOMO-LUMO) energy levels.

Fe^{III}(TMTMP)ClO_4 (TMTMP = 2,7,12,17-tetramethyl-3,8,-13,18-tetramesitylporphyrinato dianion) (Figure 1) is the only iron porphyrin reported to form a stable $^2A_{1u}$ ferryl porphyrin π-cation radical.[4] Like Fe^{III}(TMP)X (where TMP = *meso*-tetramesitylporphinato dianion), it has four bulky-aryl substituents, but in this case the substituents are at the β-pyrrole

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(1) (a) Dunford, H. B. *Adv. Inorg. Biochem.* **1982**, *4* , 41. (b) Frew, J. E.; Jones P. In *Advances in Inorganic and Bioinorganic Mechanism*; Academic Press: New York, 1984; Vol. 3, p 175. (c) Oertling W. A.; Kean, R. T.; Wever, R.; Babcock, G. T. *Inorg. Chem.* **1990**, *29*, 2633.

(2) (a) Hanson, L. K.; Chang, C. K.; Davis, M. S.; Fajer, J. *J. Am. Chem. Soc.* **1981**, *103*, 663. (b) Fujita, J.; Hanson, L. K.; Walker, F. A.; Fajer, J. *J. Am. Chem. Soc.* **1983**, *105*, 3296. (c) Du, P; Loew, G. H. *Biophys. J.* **1995**, *68*, 69.

(3) (a) Czernuszewicz, R. S.; Macor, K. A.; Li, X-Y.; Kincaid, J. R.; Spiro, G. T. *J. Am. Chem. Soc.* **1989**, *111*, 3860. (b) Oertling, W. A.; Salehi, A.; Chang, C. K.; Babcock, G. T. *J. Phys. Chem.* **1989**, *93*, 1311. (c) Macor, K. A.; Czernuszewicz, R. .S.; Spiro, G. T. *Inorg. Chem.* **1990**, *29*, 1996. (d) Kitagawa, T.; Mizutani, Y. *Coord. Chem. Rev.* **1994**, *135/136*, 685. (e) Satoh, M.; Ohba, Y.; Yamauchi, S.; Iwaizumi, M. *Inorg. Chem.* **1982**, *31*, 298. (f) Keating, K. D.; DeRopp, J. S.; LaMar, G. N.; Balch, A. L.; Shaiu, F. Y.; Smith, K. M. *Inorg. Chem.* **1991**, *30*, 3258. (g) Tan, H.; Simonis, U.; Shokhirev, N. V.; Walker, F. A. *J. Am. Chem. Soc.* **1994**, *116*, 5784.

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positions and the *meso* positions are unsubstituted. The function of these bulky substituents is to protect the active oxo ligand from the formation of the μ-oxo dimer.[5] In addition, these substituents destabilize the a_{1u} molecular orbital to the extent that it becomes the HOMO (Figure 1). Therefore, upon oxidation of the porphyrin ring the first electron will be abstracted from the a_{1u} molecular orbital.[3] Furthermore, theoretical calculations[6] indicate that the unpaired electron density in the a_{1u} molecular orbital is localized to a greater extent at the β-pyrrole positions. The above theoretical predictions were confirmed by proton NMR measurements.[4]

The essential goal of this work is thus to provide a thorough RR study of this unique oxoiron(IV) compound. In order to achieve this goal we have measured the polarized RR spectra of Fe^{III}(TMTMP)ClO_4, its *meso*-carbon-deuteriated analogue (-d_4), the nonradical ferryl complexes (penta- and hexacoordinated), as well as the π-cation ferryl radical. In addition, we report here RR spectra of Cu^{II}(TMTMP), Cu^{II}(TMTMP-d_4), and their one-electron oxidation products, i.e., Cu^{II}(TMTMP$^{\bullet+}$)($SbCl_6^-$) (-h_4 or -d_4, respectively). This rather complete data set permits assignment of the vibrational modes characteristic of the π-cation ferryl radical on the basis of -d_4 isotopic frequency shifts and depolarization ratio measurements and thereby documents the (nonradical/π-cation radical) marker band frequency shifts. The results indicate that both Cu^{II}(TMTMP) and O═Fe^{IV}(TMTMP) form $^2A_{1u}$ cation radicals upon oxidation, as previously inferred from NMR data.[4] More importantly, the present study documents, for the first time, the vibrational frequency of the Fe═O fragment of a $^2A_{1u}$ ferrylporphyrin π-cation radical.

Experimental Section

Metalloporphyrin Complexes. 2,7,12,17-Tetramethyl-3,8,13,18-tetramesitylporphyrin (H_2TMTMP) was prepared by the literature method.[7] The *meso*-carbon-deuteriated analogue (H_2TMTMP-d_4) was prepared from deuteriated 2-(hydroxymethyl)-3-mesityl-4-methylpyrrole which was obtained by the reduction of 2-(ethoxycarbonyl)-3-mesityl-4-methylpyrrole with $LiAlD_4$ and acetic acid-d_1. The deuterium NMR spectrum of the *meso*-d_4 porphyrin revealed 70% D-atom purity. Iron was inserted into the porphyrin by refluxing in a chloroform−acetic acid mixture (4:1) with ferrous chloride and sodium acetate.[4b] Copper insertion was achieved by refluxing the porphyrin in chloroform with copper acetate.[8] Copper complexes were purified by silica gel column chromatography and recrystallized from chloroform−methanol,[9] while the iron complexes were purified by column chromatography according to the following procedure. A glass column (about 30 cm × 1.5 cm), filled with toluene (Aldrich, HPLC grade), was slowly loaded (to ∼25 cm line height) with dried alumina (∼400 °C) (Aldrich, neutral, standard grade) and then with an ∼2-cm layer of dried silica gel (J. T. Baker, 40−140 mesh) and equilibrated with 150 mL of toluene. A sample of the iron porphyrin (25 mg) was dissolved in ∼2 mL of toluene and loaded onto the column. Development with toluene resulted in the elution of the metal-free ligand, H_2TMTMP (UV−vis in CH_2Cl_2: 402, 498, 530, 565, and 620 nm). Then, the heme was eluted with neat CH_2Cl_2. The main eluted heme fraction was concentrated by evaporation of solvent to ∼10 mL and converted to the chloride form by stirring overnight with a 0.1 M solution of aqueous hydrochloric acid.[10] The organic layer was separated and evaporated to dryness, and the resulting solid was recrystallized from toluene/heptane (UV−vis in CH_2Cl_2: 382, 508, 536, and 636 nm). The yield was 12 mg. The Fe^{III}(TMTMP)Cl was converted to the perchlorate form by using the following procedure. A mixture of Fe^{III}(TMTMP)Cl (12 mg, 13 μmol), $AgClO_4$ (3 mg, 13 μmol), and toluene (5 mL) was boiled gently for 10 min, then filtered hot through a 0.45-μm filter and concentrated to ∼1.5−2.0 mL. Heptane (∼5 mL) was added dropwise and solution was allowed to set overnight to induce crystallization. Fine dark-violet crystals were collected by filtration, washed with heptane and dried under vacuum for ∼5 h (UV−vis in CH_2Cl_2: 386, 500 (shoulder ∼530) and 628 nm). Fe^{II}(TMTMP)(pip)$_2$ was synthasized by a literature method[11a] and used as a starting material for the preparation of O═Fe(TMTMP) according to the procedure of Balch *et al.*[11b,c]

Solvents. Dichloromethane (CH_2Cl_2, Aldrich, spectrophotometric grade) was purified[12] by shaking approximately 500 mL of spectrophotometric grade methylene chloride with 50−60 mL portions of concentrated H_2SO_4 in a 1-L separatory funnel until the acid layer remained colorless.[12] The solvent was then washed 3 times with 100-mL portions of distilled water, passed through a K_2CO_3 column, then predried over dried $CaCl_2$, distilled over P_2O_5, and directly passed through dried (>400 °C) neutral alumina column. *N*,*N*-Dimethylformamide (DMF, Aldrich, spectrophotometric grade) was dried with $MgSO_4$ and then distilled under reduced pressure.[12] Toluene (Aldrich, spectrophotometric grade) was dried with sodium metal for 1 h and then distilled.

Oxidants. The gases $^{16}O_2$ (Monsanto Research, 98% $^{16}O_2$) and $^{18}O_2$ (ICON, 98% ^{18}O atom purity) were used without further purification. *m*-Chloroperoxybenzoic acid (*m*-CPBA(^{16}O), Aldrich, technical grade) was purified prior to use by washing its benzene solution with phosphate buffer of pH 7.5.[13] The benzene layer was dried over anhydrous $MgSO_4$, then filtered and carefully evaporated to dryness, and the solid was then recrystallized from CH_2Cl_2/EtO_2.[14] Iodometric titration[15] revealed 97% of active oxygen. Isotopically labeled *m*-CPBA(^{18}O) was synthesized using $^{18}O_2$, according to procedures described earlier.[16] Iodometric titration revealed 98% of active oxygen and Raman spectroscopy indicated 90% of ^{18}O-labeled oxygen.

Ozone was produced by an electrical discharge (Tesla coil) in pure dioxygen.

Phenoxathiinylium hexachloroantimonate (Phx-$SbCl_6$) was prepared by the published procedure.[17]

Oxidation Reactions. The ferryl porphyrin π-cation radical in CH_2Cl_2 was obtained by oxidation reactions with about a 4-fold excess of *m*-CPBA(^{16}O), and its (^{18}O) analogue, at −80 °C in a stirred, low-temperature cell according to the originally published procedure.[4] We note that use of only 4 equiv of *m*-CPBA prevents replacement of axially bound ClO_4^- and that oxidation of the ferric perchlorate species by ozone, using a procedure described elsewhere,[18] yields a spectrum identical to that obtained with 4 equiv of *m*-CPBA. The neutral ferryl porphyrin (six-coordinate, DMF adduct) was obtained by oxidation with *m*-CPBA(^{16}O) and its (^{18}O) analogue at −44 °C in a stirred, low-temperature cell according to the procedure of Gold *et al.*[19] The five-

(4) (a) Fujii, H. *J. Am. Chem. Soc.* **1993**, *115*, 4641. (b) Fujii, H.; Ichikawa, K. *Inorg. Chem.* **1992,** *31*, 1110.
(5) (a) Dunford, H. B.; Stillman, J. S. *Coord. Chem. Rev.* **1976**, *19*, 187. (b) Dunford, H. B. *Adv. Inorg. Biochem.* **1982**, *4*, 41. (c) McMurry, T. J.; Groves, J. T. In *Cytochrome P-450: Structure, Mechanism, and Biochemistry*; Ortiz de Montellano, P. R., Ed.; Plenum: New York, 1986; Chapter I.
(6) (a) Gouterman, M. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. III. (b) Spangler, D.; Maggiora, G. M.; Shipman, L. L.; Christofferson, R. E. *J. Am. Chem. Soc.* **1977**, *99*, 7478.
(7) Ono, N.; Kawamura, H.; Bougauchi, M.; Maruyama, K. *Tetrahedron* **1990**, *46*, 7483.
(8) Adler, A. D.; Longo, F. R.; Varadi, V. *Inorg. Synth.* **1976**, *16*, 213.
(9) Fujii, H. *Inorg. Chem.* **1993**, *32*, 875.
(10) Cheng, R-J.; Latos-Grazynski, L.; Balch, A. L. *Inorg. Chem.* **1982**, *21*, 2412.
(11) (a) Epstein, L. M.; Straub, D. K.; Maricondi, C. *Inorg.Chem.* **1967**, *6*, 1720. (b) Balch, A. L.; Chan, Y.-W.; Cheng, R.-J.; LaMar, G. N.; Latos-Grazynski, L.; Renner, M. W. *J. Am. Chem. Soc.* **1984**, *106*, 7779. (c) Chin, D.-H.; Balch, A. L.; LaMar, G. N. *J. Am. Chem. Soc.* **1980**, *102*, 1446.
(12) Perrin, D. P.; Armarego, W. L. F. In *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, NY, 1988.
(13) Shwartz, N. N.; Blumbergs, J. H. *J. Org. Chem.* **1964**, *29*, 1976.
(14) Bartolini, O.; Campestrini, S.; DiFuria, F.; Modena, G. *J. Org. Chem.* **1987**, *52*, 5093.
(15) Traylor, T. G.; Miksztal, A. R. *J. Am. Chem. Soc.* **1987**, *109*, 2770.
(16) (a) Braun, G. *Organic Syntheses*; Wiley: New York, 1941; Collect. I, p 4131. (b) Rosenthal, I. *J. Labeled Compd.* **1976**, *12*, 317. (c) Johnson, R. A. *Tetrahedron Lett.* **1976**, *5*, 331.
(17) Gans, P.; Buisson, G.; Duèe, E.; Marchon, J.-C.; Erler, B. S.; Scholz, W. F.; Reed, C. A. *J. Am. Chem. Soc.* **1986**, *108*, 1223.
(18) Czarnecki, K.; Nimri, S.; Gross, Z.; Proniewicz, L. M.; Kincaid, J. R. *J. Am. Chem. Soc.* in press.
(19) Gold, A.; Jayoraj, K.; Doppelt, P.; Weiss, R.; Chottard, G.; Bill, E.; Ding, X.; Trautwein, A. X. *J. Am. Chem. Soc.* **1988**, *110*, 5756.

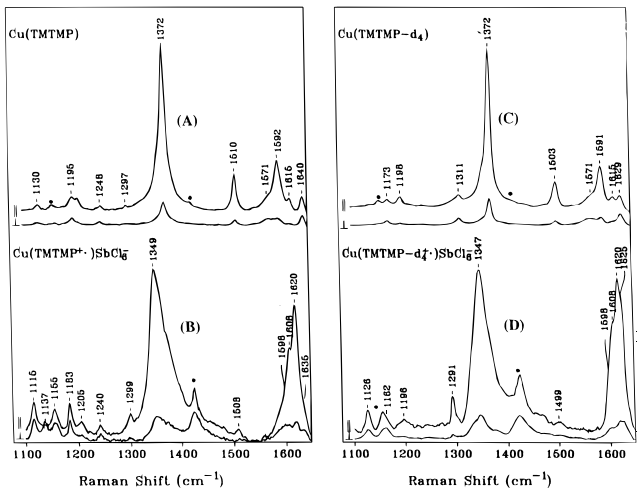

Figure 2. The high-frequency polarized resonance Raman spectra of Cu^{II}(TMTMP)ClO_4 complexes measured in CH_2Cl_2 at room temperature with excitation at 406.7 nm (spinning NMR tube, 135° scattering geometry): (A) Cu^{II}(TMTMP); (B) Cu^{II}(TMTMP$^{\bullet+}$)($SbCl_6^-$); (C) Cu^{II}-(TMTMP-d_4); (D) Cu^{II}(TMTMP-$d_4^{\bullet+}$)($SbCl_6^-$). Bands marked with asterisks are due to solvent bands.

coordinate ferryl porphyrin was obtained *via* an autoxidation reaction of the dioxygen adduct at −70 °C, using a procedure reported by Balch *et al.*[11b,c]

Cu^{II}(TMTMP) and its *meso*-d_4 analogue were oxidized with Phx-$SbCl_6$ in the following way: Cu^{II}(TMTMP) was dissolved in CH_2Cl_2 and stirred for 15 min. Then Phx-$SbCl_6$ (1.1 equiv) was added slowly and the suspension was stirred for another hour. After filtration, hexane was added dropwise to the filtrate and the solution was left overnight. The resultant crystals were filtered, washed with hexane−dichloromethane mixture (4:1), and dried under vacuum.

Spectroscopic Measurements. Low-temperature RR measurements were performed using a stirred Dewar cell with a cylindrical lens setup to minimize possible thermal or photodecomposition[20] of the observed species. Room temperature measurements were performed using a standard spinning cell technique with a 135° back-scattering geometry. Spectra were acquired with a single monochromator (SPEX Model 1269) fitted with a CCD detector (Princeton Instrument) and notch filter (Kaiser Optical System, Ann Arbor, MI). The frequencies were calibrated by using known frequencies of toluene and fenchone and are accurate to within ±1 cm^{-1}. No digital smoothing was performed on any of the spectra. The 406.7-nm line of the Coherent Model Innova 100-K3 Krypton ion laser (with the power 5 to 10 mW at the sample) was used as an excitation source. In the case of the oxidized compounds, RR spectra were acquired sequentially in separate files and summed. Those later files, which began to exhibit new features ascribable to thermal or photochemical degradation, were not included in the summation. Also, in the case of the ferryl π-cation samples (which are notoriously subject to photodegradation),[3d] RR spectra were acquired at several different incident laser powers in an attempt to ensure that none of the observed spectral features were contributed by photoproducts. Optical spectra (UV−vis) were measured in a low-temperature Dewar cell using a Hewlett-Packard 8452A diode array spectrometer.

Results and Discussion

1. Cu(II)(TMTMP) and Its Cation Radical. Figure 2 compares RR spectra of Cu^{II}(TMTMP), its -d_4 analogue, and their corresponding porphyrin π-cation radicals, all obtained with 406.7-nm excitation. The RR spectra presented in traces A and C exhibit spectral patterns quite similar to those observed for other pyrrole β-carbon-substituted metalloporphyrins, such as M(OEP) complexes (M = metal; OEP = octaethylporphyrinato dianion).[3a,b] Since the excitation line is within the Soret absorption band the most intense features observed in these spectra are associated with totally symmetric (polarized) modes; i.e., A-term scattering is responsible for their enhancement.[21] The most intense skeletal modes observed in the high-frequency region are the following: ν_2 [$\nu(C_\beta-C_\beta)$], ν_3 [$\nu(C_\alpha-C_\beta)_{sym}$], and ν_4 [ν(pyr, half ring)$_{sym}$].[3a,b,22] Also, owing to the Jahn−Teller effect,[21,23] depolarized bands assigned to ν_{10} [$\nu(C_\alpha-C_\beta)_{asym}$] and ν_{11} [$\nu(C_\beta-C_\beta)$][21,23] are observed with appreciable intensity.

Three polarized bands at 1372, 1510, and 1592 cm^{-1} are observed in trace A. In addition, the 1510-cm^{-1} band downshifts (7 cm^{-1}) upon deuteration at the *meso*-carbon positions. Thus, this band is assigned to the ν_3 mode by comparison with reported deuterium shifts for M(OEP).[3a,b] The ν_4 and ν_2 modes are observed at 1372 and 1592 cm^{-1}, respectively. Two depolarized bands, at 1571 and 1640 cm^{-1}, are assigned to the ν_{11} and ν_{10} modes, respectively, since the latter exhibits a significant deuterium isotope shift (trace B). These data agree very well with those reported in the literature for various M(OEP) complexes.[3a−c,21,23] In addition to the typical OEP-type macrocycle vibrations, a phenyl mode, located at 1615 cm^{-1} , is observed in Figure 2.

Upon oxidation of Cu^{II}(TMTMP) or its -d_4 analogue with Phx-$SbCl_6$ the porphyrin π-cation radicals are formed. The RR spectra of these species (traces B and D) are much weaker than those exhibited by the parent metalloporphyrins (traces A and C), i.e., upon comparing intensities of the vibrations of the complexes with those of the solvent, which are marked with asterisks. This intensity decrease is typically observed upon radical cation formation.[3d] The RR spectra presented in traces B and D are also dominated by polarized bands at ca. 1349 and 1620 cm^{-1}. Based on their insensitivity to deuterium isotopic substitution and depolarization ratios, these bands are readily assigned to the ν_4 and ν_2 modes, respectively. They experience 23- and 28-cm^{-1} downshifts relative to neutral Cu(TMTMP). Careful examination of traces B and D reveals the polarized ν_3 mode at 1508 cm^{-1} (trace B) which shifts to 1499 cm^{-1} in the case of the -d_4 analogue (trace D). The depolarized ν_{10} and ν_{11} bands can be seen more clearly in the spectra measured with perpendicular polarization. Thus, ν_{10} is observed at 1635 cm^{-1} (trace B) and exhibits a 10-cm^{-1} downshift upon deuterium substitution. The ν_{11} mode is seen at 1598 cm^{-1}. The RR pattern and the observed deuterium isotopic shifts of these five marker bands agree very well with those observed for other M(OEP$^{\bullet+}$) complexes.[3a−c] The observed frequencies are listed in Table 1 together with mode assignments .

The ν_2 and ν_{11} modes are the most reliable as markers to distinguish between $^2A_{1u}$ and $^2A_{2u}$ types of metalloporphyrin π-cation radicals.[3a−d] These modes involve mainly stretching vibrations of the $C_\beta-C_\beta$ bond, $\nu(C_\beta-C_\beta)$.[3a,b] The a_{1u} molecular orbital is antibonding with respect to the $C_\beta-C_\beta$ bond, while the a_{2u} is bonding.[6] Thus, oxidation of the porphyrin macrocycle in the case where the a_{1u} molecular orbital is the HOMO strengthens the $C_\beta-C_\beta$ bond and gives rise to the observed shifts to higher frequency for the ν_2 and ν_{11} modes. Conversely, formation of a $^2A_{2u}$ metalloporphyrin π-cation radical leads to the opposite result, i.e., weakening of the $C_\beta-C_\beta$ bond and concomitant downshifts of these modes. Thus, the RR data presented here confirm that Cu^{II}(TMTMP$^{\bullet+}$) has a $^2A_{1u}$ ground state, which is as expected for radicals of metalloporphyrins

(20) (a) Kincaid, J. R.; Schneider, A. J.; Paeng, K-J. *J. Am. Chem. Soc.* **1989**, *111*, 735. (b) Proniewicz, L. M.; Paeng, I. R.; Nakamoto, K. *J. Am. Chem. Soc*. **1991**, *113*, 3294.

(21) Spiro, T. G.; Czernuszewicz, R. S. *Meth. Enzymol.* **1995**, *246*, 416.

(22) (a) Li, X-Y.; Czernuszewicz, R. S.; Kincaid, J. R.; Stein, P.; Spiro, T. G. *J. Phys. Chem.* **1990**, *94*, 47. (b) Li, X. Y. Ph.D. Dissertation, Princeton University, 1988.

(23) Shelnutt, J. A.; Cheung, L. D.; Cheng, C. C.; Yu, N. T.; Felton, R. H. *J. Chem. Phys.* **1977**, *66*, 3387.

Table 1. Resonance Raman Frequencies (cm^{-1}) for $Cu^{(II)}$(TMTMP), $Cu^{(II)}$(TMTMP$^{\bullet+}$), $Fe^{(III)}$(TMTMP)ClO_4, O=$Fe^{(IV)}$(TMTMP), O=$Fe^{(IV)}$(TMTMP$^{\bullet+}$)ClO_4, and M(OEP$^{\bullet+}$) Complexes

mode	Cu(TMTMP) (Δd_4)	Cu(TMTMP$^{\bullet+}$) (Δd_4, Δox)	Fe^{III}(TMTMP)ClO_4 (Δd_4)	O=Fe^{IV}(TMTMP) (Δd_4)	M(OEP$^{\bullet+}$)[a] (Δox)	O=Fe^{IV}(TMTMP$^{\bullet+}$)ClO_4 (Δox)
ν_{10} (dp)	1640 (−11)	1635 (−10, −5)	1652 (−11)	1631 (−7)	−7 to −10	
ν_{ph} (p)	1615 (0)	1608 (0, 7)	1614 (0)	1614 (0)		
ν_2 (p)	1592 (−1)	1620 (0, 28)	1586 (0)	1593 (0)	21 to 23	1623 (30)
ν_{11} (dp)	1571 (0)	1598 (0, 27)	1567 (0)	1578 (−2)	33	1614 (36)
ν_3 (p)	1510 (−7)	1508 (−9, −2)	1521 (−7)	1511 (−7)	−2 to −8	1499 (−11)
ν_4 (p)	1372 (0)	1349 (−2, −23)	1370 (−1) 1362 (0)	1374 (0)	−5 to −17	1363 (−10)
ν(Fe=^{16}O)				845 (0)		834 (−11)
ν(Fe=^{18}O)				809 (0)		798 (−11)

[a] See refs 3a and 3b. For mode descriptions see ref 22. Δd_4 and Δox = frequency shifts (cm^{-1}) upon *meso*-d_4 isotopic substitution and π-cation porphyrin radical formation, respectively.

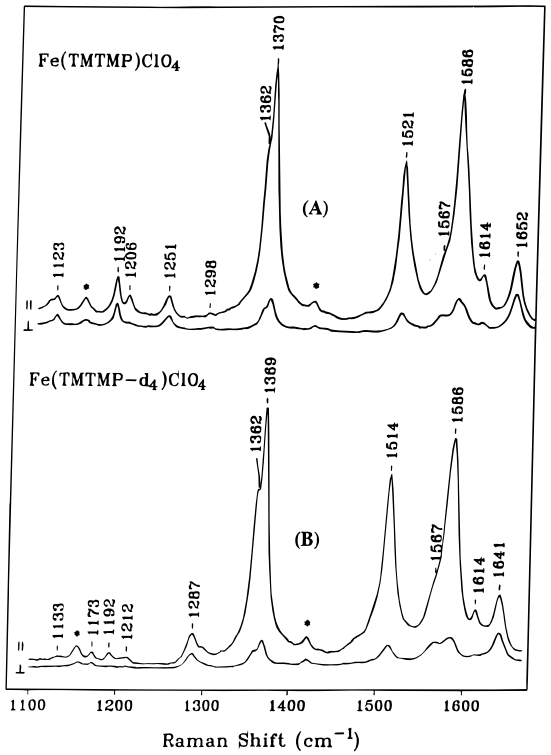

Figure 3. The high-frequency polarized resonance Raman spectra of Fe^{III}(TMTMP)ClO_4 (trace A) and Fe^{III}(TMTMP-d_4)ClO_4 (trace B) measured in CH_2Cl_2 at room temperature with excitation at 406.7 nm.

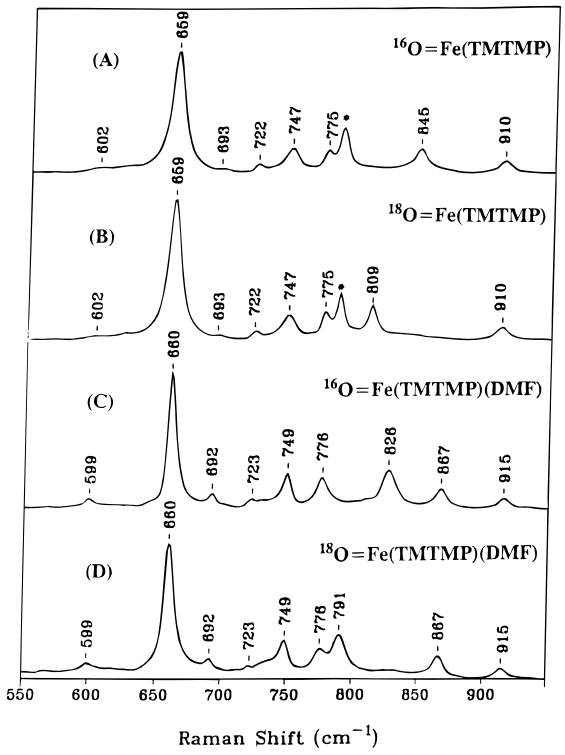

Figure 4. The low-frequency resonance Raman spectra of (A) ^{16}O=Fe^{IV}(TMTMP) and (B) ^{18}O=Fe^{IV}(TMTMP) in toluene at −70 °C and (C) ^{16}O=Fe^{IV}(TMTMP)(DMF) and (D) ^{18}O=Fe^{IV}(TMTMP)(DMF) in DMF at −44 °C with excitation at 406.7 nm. Bands marked with asterisks are due to solvent bands.

bearing eight β-pyrrole substituents (in the absence of strong donor ligands).[2,3,6]

2. Ferric and Ferryl Derivatives. Figure 3 shows the polarized RR spectra of Fe^{III}(TMTMP)ClO_4 (trace A) and Fe^{III}(TMTMP-d_4)ClO_4 (trace B) in the high-frequency region, both obtained in CH_2Cl_2 with 406.7-nm excitation. The main marker modes (ν_2, ν_3, ν_4, ν_{10}, and ν_{11}), as for the Cu^{II}(TMTMP) complex, can be assigned on the basis of deuterium shifts, observed depolarization ratios, and comparison with the literature data reported for correponding M(OEP) complexes.[3a−c,22] Assignments of these key marker bands are presented in Table 1.

Figure 4 shows the low-frequency RR spectra of five-coordinate O=Fe^{IV}(TMTMP) and six-coordinate O=Fe^{IV}-TMTMP(DMF). Trace A presents the RR spectrum of ^{16}O=Fe^{IV}-(TMTMP) measured in toluene (i.e., noncoordinating solvent) at −70 °C with excitation at 406.7 nm. Upon ^{16}O/^{18}O isotopic substitution only one RR band shifts: from 845 (trace A) to 809 cm^{-1} (trace B). These bands are therfore assigned to the ν(Fe−^{16}O) and ν(Fe−^{18}O), respectively, of ^{16}O=Fe^{IV}(TMP) and its ^{18}O analogue. The observed isotopic shift is in good agreement with that expected (38 cm^{-1}) for a harmonic diatomic Fe=O oscillator. Similar RR results have been reported by several groups[24] for other ferrylporphyrins in toluene at low temperature, where ν(Fe−O) was observed near 845 cm^{-1}.

The O^{2-} axial ligand donates both σ and π electrons (fully occupied p orbitals) to the Fe(IV) ion.[1c,3d,25] The σ bond is thus formed by interaction of the d_z (Fe) orbital with the p_z (O) orbital. Since Fe(IV) has a d^4 electronic configuration, the two valence electrons are accommodated in the d_{xy} orbital (in plane, nonbonding) and the remaining two electrons are involved in formation of π bonds. Thus, the sixth ligand, trans to the oxo atom, also donates σ and π electron density, weaking the Fe=O

(24) (a) Hashimoto, S.; Tatsuno, Y.; Kitagawa, T. *Proceedings of the 10th International Conference on Raman Spectroscopy*; Peticolas, W. L., Hudson, B., Eds.; Eugene, OR, 1986; p 1.28. (b) Su, Y. O.; Czernuszewicz, R. S.; Miller, L. A.; Spiro, T. G. *J. Am. Chem. Soc.* **1988**, *110*, 4150. (c) Paeng, I. R.; Shiwaku, H.; Nakamoto, K. *J. Am. Chem. Soc.* **1988**, *110*, 1995. (d) Mizutani, Y.; Hashimoto, S.; Tatsuno, Y.; Kitagawa, T. *J. Am. Chem. Soc.* **1990**, *112*, 6809.

(25) Proniewicz, L. M.; Bajdor, K.; Nakamoto, K. *J. Phys. Chem.* **1986**, *90*, 1760.

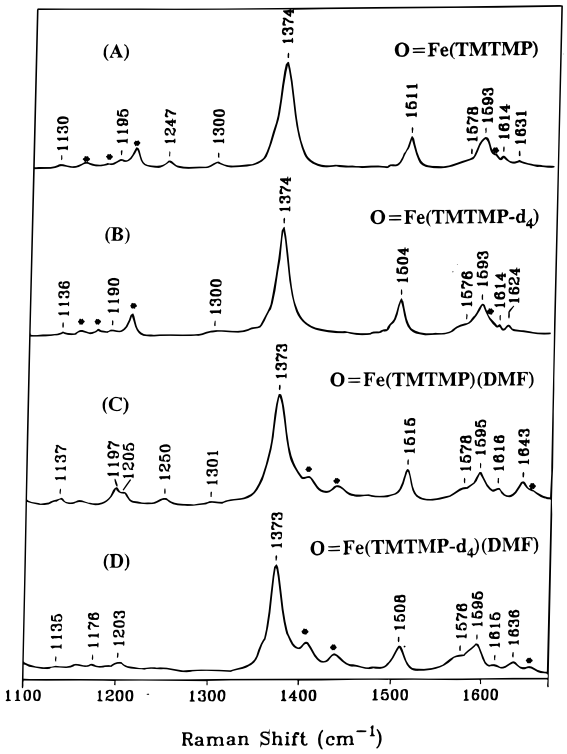

Figure 5. The high-frequency resonance Raman spectra of (A) O═Fe^{IV}-(TMTMP) and (B) O═Fe^{IV}(TMTMP-d_4) in toluene at −70 °C and (C) O═Fe^{IV}(TMTMP)(DMF) and (D) O═Fe^{IV}(TMTMP-d_4)(DMF) in DMF at −44 °C with excitation at 406.7 nm. Bands marked with asterisks are due to solvent bands.

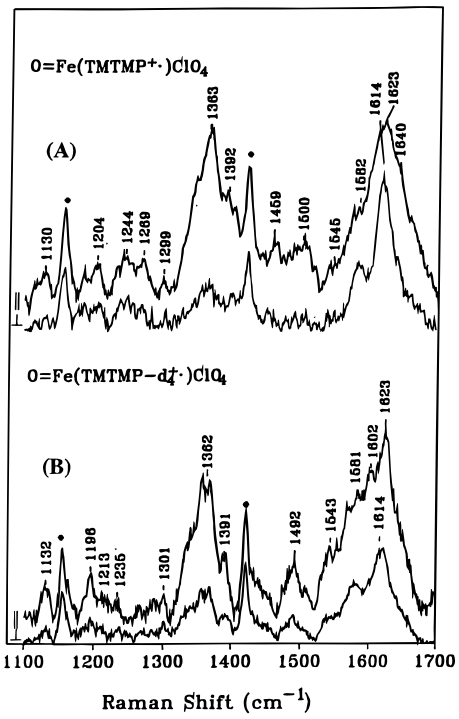

Figure 6. The high-frequency resonance Raman spectra of (A) O═Fe^{IV}-(TMTMP$^{\bullet+}$)ClO_4 and (B) O═Fe^{IV}(TMTMP-$d_4^{\bullet+}$)ClO_4 obtained with parallel and perpendicular polarization. Samples were measured in CH_2Cl_2 at −80 °C with excitation at 406.7 nm. Bands marked with asterisks are due to solvent bands.

bond. As a result the ν(Fe−O) mode will downshift. This is illustrated in traces C and D of Figure 4, where ν(Fe−^{16}O) and ν(Fe−^{18}O) are downshifted, in response to DMF ligation to 826 and 791 cm^{-1}, respectively. These observed ν(Fe−O) frequencies agree very well with those reported for other six-coordinate neutral ferryl derivatives.[17,26] Also in this case, the isotopic frequency shift is in agreement with that theoretically expected.

Comparison of the high-frequency spectra (Figure 5) of O═Fe^{IV}(TMTMP) and its -d_4 analogue reveals two deuterium isotope sensitive modes at 1511 ($\Delta\nu_{d_4} = -7$ cm^{-1}) and 1631 cm^{-1} ($\Delta\nu_{d_4} = -7$ cm^{-1}). These bands are reasonably assigned to the ν_3 and ν_{10} modes, respectively. The intense mode at 1374 cm^{-1} is not sensitive to *meso*-d_4 isotopic substitution and is assigned to the ν_4 mode. The ν_2 and ν_{11} modes are observed at 1593 and 1578 cm^{-1}. The observed frequencies are listed in Table 1 together with mode assignments.

In traces C and D of Figure 5 the high-frequency RR spectra of six-coordinate O═Fe^{IV}(TMTMP)(DMF) and its *meso*-d_4 analogue, respectively, are presented. Trace C exhibits bands at 1373, 1515, and 1595 cm^{-1}, which are polarized (omitted in the figure for clarity). The band at 1515 cm^{-1} shifts down by 7 cm^{-1} upon *meso*-d_4 deuteration, while the other two do not shift. Thus, these bands are assigned to the ν_4, ν_3, and ν_2 modes, respectively. The bands at 1578 and 1643 cm^{-1} in trace C are depolarized. While the former is not sensitive to the *meso*-d_4 isotopic substitution, the latter shows a 7-cm^{-1} downshift (trace D). These are assigned to the ν_{11} and ν_{10} modes, respectively.

3. Ferryl π-Cation Porphyrin Radical. The high-frequency polarized RR spectra of O═Fe(TMTMP$^{\bullet+}$)ClO_4 and its *meso*-d_4 analogue measured in CH_2Cl_2 at −80 °C with excitation at 406.7 nm are shown in Figure 6. Here, it is necessary to point out that, owing to the instability of the observed π-cation radical species, it was difficult to acquire polarized spectra; i.e., they are not of high quality. Nevertheless, these spectra reveal, in the region of the ν_3 mode, a polarized band at 1499 cm^{-1} (trace A), which is shifted to 1492 cm^{-1} upon *meso*-d_4 deuteration (trace B). Since the observed isotopic shift and polarization properties fit very well to the shift of the ν_3 mode observed for Fe^{III}(TMTMP)ClO_4 and the ferryl derivatives, this band is assigned to this mode. Since the high-frequency spectra of observed porphyrin π-cation radicals in regions of other marker modes consist of envelopes of several modes it is not possible to definitively identify ν_4, ν_2, ν_{11}, and ν_{10}.

However, the band at 1363 cm^{-1} is a polarized mode and thus it is a good candidate for ν_4. Note that this band is downshifted by 11 cm^{-1} from the ν_4 mode of O═Fe^{IV}(TMTMP) (see Figure 5). The spectra given in Figure 6 show that there is a strong polarized mode centered near 1623 cm^{-1} and a depolarized mode occurring at ∼1614 cm^{-1}. The polarized component can be reasonably attributed to ν_2 since it shows no d_4 shift. As is clear in the figure, the depolarized mode exibits an insignificant deuterium shift and therefore the most reasonable assignment for the 1614-cm^{-1} feature is to ν_{11}, the ν_{10} mode apparently being too weak to be observed. These assignments are summarized in Table 1. Note that data in parentheses represent shifts calculated by comparing (OFeTMTMP$^+$)(ClO_4) with the five-coordinate O═Fe^{IV}TMTMP.

Figure 7 shows the low-frequency RR spectra of O═Fe^{IV}-(TMTMP$^{\bullet+}$)ClO_4 and its *meso*-d_4 deuterated analogue in CH_2Cl_2 (temperature −80 °C, excitation at 406.7 nm), both obtained by oxidation with *m*-CPBA(^{16}O) (about four equivalences) or its (^{18}O) isotopic analogue. As can be seen, traces A and C reveal a mode at ca. 833 cm^{-1}, which is shifted to 798 cm^{-1} upon oxygen isotopic substitution (traces B and D). This mode

(26) (a) Schappacher, M.; Chottard, G.; Weiss, R. *J. Chem. Soc., Chem. Commun.* **1986**, 93. (b) Kean, R. T.; Oertling, W. A.; Babcock, G. T. *J. Am. Chem. Soc.* **1987**, *109*, 2185. (c) Chen, S. M.; Su, Y. O. *J. Chem. Soc., Chem. Commun.* **1990**, 491.

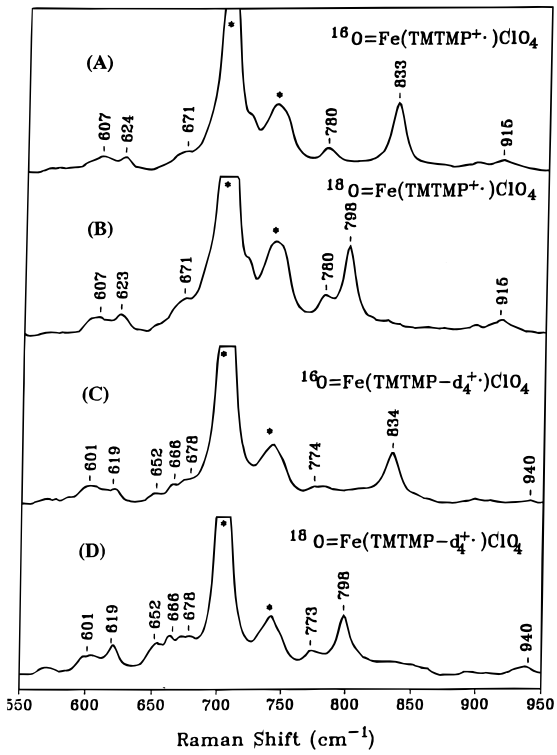

Figure 7. The low-frequency resonance Raman spectra of (A) ^{16}O═Fe^{IV}(TMTMP$^{•+}$)ClO$_4$, (B) ^{18}O═Fe^{IV}(TMTMP$^{•+}$)ClO$_4$, (C) ^{16}O═Fe^{IV}-(TMTMP-$d_4^{•+}$)ClO$_4$, and (D) ^{18}O═Fe^{IV}(TMTMP-$d_4^{•+}$)ClO$_4$. Samples were measured in CH_2Cl_2 at −80 °C with excitation at 406.7 nm. Bands marked with asterisks are due to solvent bands.

is therefore assigned to the iron(IV)−oxo stretching frequency of the O═Fe^{IV}(TMTMP$^{•+}$)ClO$_4$.

In the present study it is observed that the ν(Fe−O) of O═Fe(TMTMP$^{•+}$)(ClO_4^-) occurs at 833 cm^{-1}, while that for the five-coordinate (neutral) ferryl derivative, O═Fe(TMTMP), occurs at 845 cm^{-1}. We note here that quite similar values are observed for the corresponding derivatives of TMP; i.e., the ν(Fe−O) for OFe(TMP) occurs at around 843 cm^{-1},[24] and for OFe(TMP$^{•+}$)(ClO_4^-) it occurs at 835 cm^{-1}.[18] While the observed shift upon oxidation of either (neutral) ferryl complex reflects both an oxidation-induced component and a response to addition of an (albeit weak) axial ligand (ClO_4^-), to the extent that coordination induced shifts are presumably similar for these two iron porphyrins, the oxidation-induced shifts are also comparable. That is, apparently the oxidation-iduced shift of the Fe═O fragment is insensitive to the nature (a_{1u} vs a_{2u}) of the HOMO.

To our knowledge, this is the first observation of the ν(Fe−O) mode of an authentic $^2A_{1u}$ ferryl porphyrin π-cation radical model compound and provides the first opportunity to make a direct comparison of the influence of radical type ($^2A_{1u}$ vs $^2A_{2u}$) on the Fe═O fragment. The only previous studies relevant to the present comparison are the reports of the RR spectra of the corresponding vanadyl complexes of OEP, TPP, and TMP.[3c,27] There it was reported that the behavior of the ν(V−O) mode is dependent on the nature of the HOMO (a_{1u} vs a_{2u}). Thus, for OV(OEP), which forms an $^2A_{1u}$ radical upon oxidation of the macrocycle, ν(V−O) shifts up (to 1002 cm^{-1}) relative to its value (987 cm^{-1}) for the neutral complex.[27] On the other hand, the ν(V−O) for an $^2A_{2u}$ radical (i.e., OV(TPP$^{•+}$)) shifts down (to 982 cm^{-1}) relative to its value (998 cm^{-1}) for the neutral OV(TPP).[27]

In the present work, in attempting to compare the influence of radical type on observed ν(Fe−O) frequencies, care was taken to ensure constancy of the trans-axial ligand (i.e., ClO_4^-). To the extent that axial ligation differences did not exist in the comparison of the vanadyl analogues,[27] there appears to be a real difference in the systems (ferryl vs vanadyl) with respect to the influence of radical type on the ν(M−O) frequencies.

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(27) Macor, K. A.; Czernuszewicz, R. S.; Spiro, T. G. *Inorg. Chem.* **1990**, *29,* 1996.