

# Direct Resonance Raman Evidence for a Trans Influence on the Ferryl Fragment in Models of Compound I Intermediates of Heme Enzymes

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Received July 3, 1995. Revised Manuscript Received December 21, 1995<sup>®</sup>

**Abstract:** Resonance Raman (RR) spectra are reported for a series of ferric complexes of *meso*-tetramesitylporphyrin  $\text{XFe}^{\text{III}}(\text{TMP})$  (where  $\text{X} = \text{F}^-$ ,  $\text{Cl}^-$ , *m*-chlorobenzoate ( $\text{mCB}^-$ ),  $\text{CF}_3\text{O}_2\text{SO}^-$  ( $\text{trif}^-$ ) and  $\text{ClO}_4^-$ ) and their oxidized derivatives,  $\text{OFe}^{\text{IV}}(\text{TMP}^{*+})(\text{X})$ . Mode assignments are made by RR studies of the  $\beta$ -pyrrole-deuterated and  $^{18}\text{O}$ -labeled analogues. The results demonstrate that the oxo–iron bond strength is sensitive to the nature of the trans-axial ligand (X), the  $\nu(\text{Fe}=\text{O})$  stretching mode appearing near  $800\text{ cm}^{-1}$  for the  $\text{F}^-$ ,  $\text{Cl}^-$ , and  $\text{mCB}^-$  complexes and near  $835\text{ cm}^{-1}$  for the  $\text{trif}^-$  and  $\text{ClO}_4^-$  complexes. The high-frequency marker modes and the  $^1\text{H}$  chemical shifts are consistent with stronger electron donation by the former three anions. An explanation for the apparent absence of a correlation between the  $\nu(\text{Fe}=\text{O})$  stretching frequencies and the previously reported rate constants for substrate epoxidation is also suggested.

## Introduction

In the past decade extensive studies of oxidation reactions catalyzed by synthetic metalloporphyrins have been reported.<sup>1</sup> Among all porphyrin complexes of transition metals, particular importance is attached to iron porphyrins, because of their biological relevance. It has been shown<sup>2</sup> that the high-valent ferryl porphyrin  $\pi$ -cation radicals and their one-electron-reduced analogues, ferryl porphyrins, are the active species in the epoxidation of olefins and hydroxylation of alkanes. In these reactions they mimic the behavior of biologically important intermediates of the heme-containing enzymes such as peroxidases, catalases, and cytochrome P450, which selectively catalyze various oxidation reactions.<sup>1</sup>

In the last 15 years there have been many successful attempts to characterize these two important species by various methods: EPR,<sup>3</sup> Mössbauer,<sup>3</sup> EXAFS,<sup>4</sup> and NMR.<sup>2a,5</sup> Fortunately, resonance Raman (RR) spectroscopy offers the possibility of directly observing the iron–oxygen stretching mode. Bajdor

and Nakamoto<sup>6</sup> first succeeded in observing the  $\nu(\text{Fe}=\text{O})$  of  $\text{OFe}(\text{TPP})$  (where TPP is tetraphenylporphinato dianion) obtained in low-temperature matrices by laser photolysis of  $\text{Fe}(\text{TPP})\text{O}_2$ . Later, Nakamoto and co-workers<sup>7</sup> extended their work for other porphyrins and observed two  $\nu(\text{Fe}=\text{O})$  modes in the ranges of  $852\text{--}861\text{ cm}^{-1}$ <sup>7a–c</sup> and  $809\text{--}815\text{ cm}^{-1}$ .<sup>7c</sup> The former one was associated with the neutral ferryl porphyrin, whereas the latter one was assigned to the  $a_{2u}$  ferryl porphyrin  $\pi$ -cation radical. Several other groups reported the  $\nu(\text{Fe}=\text{O})$  mode of five- and six-coordinate ferryl porphyrins obtained in solutions.<sup>8</sup> Among all these compounds,  $\text{O}=\text{Fe}^{\text{IV}}(\text{TMP}^{*+})$  and  $\text{O}=\text{Fe}^{\text{IV}}(\text{TMP})$  have been studied the most frequently since they form fairly stable complexes at low temperatures. Kitagawa and co-workers<sup>8a</sup> were the first to document the frequencies of the less reactive,  $\text{O}=\text{Fe}^{\text{IV}}(\text{TMP})$ , i.e.,  $\nu(\text{Fe}=\text{O})$  at  $843\text{ cm}^{-1}$ ,  $\nu_4$  at  $1368\text{ cm}^{-1}$ , and  $\nu_2$  at  $1570\text{ cm}^{-1}$  (in toluene). Later studies by Czernuszewicz and Macor,<sup>8d</sup> Paeng et al.,<sup>8e</sup> and Mizutani et al.<sup>8g</sup> confirmed these assignments. The RR characterization of the more reactive and unstable counterpart,  $\text{O}=\text{Fe}^{\text{IV}}(\text{TMP}^{*+})$ , has been reported by Hashimoto et al.<sup>9</sup> for the species observed in the presence of methanol. In a subsequent study, Kincaid et al.<sup>10</sup> suggested that the earlier reported spectra<sup>9</sup> were associated

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<sup>®</sup> Abstract published in *Advance ACS Abstracts*, March 15, 1996.

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with a photoproduct and unambiguously assigned the  $802\text{ cm}^{-1}$  to the  $\nu(\text{Fe}=\text{O})$  of  $\text{O}=\text{Fe}^{\text{IV}}(\text{TMP}^+)$ , generated in the absence of methanol. Later Kitagawa et al.<sup>11</sup> confirmed the result obtained by Kincaid et al.<sup>10</sup> in the absence of methanol, but disputed results obtained in the presence of methanol. They argued that the differences in the observed frequencies of the  $\nu(\text{Fe}=\text{O})$  in the absence and presence of methanol are attributable to the effect of the trans ligand, i.e., excess of oxidant in the absence of methanol, but methanol when it is present.

Very recently, Gross and Nimri<sup>12</sup> have demonstrated remarkable differences in reactivity toward styrene for the series of oxidized species  $\text{O}=\text{Fe}^{\text{IV}}(\text{TMP}^+)\text{X}$  ( $\text{X} = \text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{MeOH}$ ,  $^-\text{OAc}$ ,  $^-\text{OSO}_2\text{CF}_3$  ( $\text{trif}^-$ ),  $^-\text{ClO}_3$ ). In this series the complexes differ only in the nature of their axial ligands trans to the oxo-iron fragment. There was, however, no obvious correlation between the second-order rate constants and the NMR and ESR spectroscopic features of the complexes. This suggests an apparent discrepancy between the *trans effect*—the kinetic phenomena—and the *trans influence*—the static phenomena—of the axial ligands. Since RR is the most direct spectroscopic probe for examination of oxo-metal bond strengths,<sup>6–11</sup> the present work is undertaken to document the *trans influence* of the sixth ligands on the  $\nu(\text{Fe}=\text{O})$  stretching vibrations of oxo-iron(IV) porphyrin cation radical complexes.

In this study we report RR spectra of the series  $\text{O}=\text{Fe}^{\text{IV}}(\text{TMP}^+)\text{X}$  ( $\text{X} = \text{F}^-$ ,  $\text{Cl}^-$ , *m*-chlorobenzoate ( $\text{mCB}^-$ ),  $^-\text{OSO}_2\text{CF}_3$  ( $\text{trif}^-$ ),  $^-\text{ClO}_3$ ). The species were generated by oxidation of the corresponding ferric complexes with ozone in order to preserve the identity of the trans-axial ligand. The results show that two distinct spectral patterns are observed. The first set (involving complexes with halides and  $\text{mCB}^-$ ) yield a  $\nu(\text{Fe}=\text{O})$  at  $\sim 800\text{ cm}^{-1}$  and virtually identical high-frequency RR spectra. The second set (including the triflate and  $\text{ClO}_4^-$  anions) exhibits a  $\nu(\text{Fe}=\text{O})$  at  $\sim 835\text{ cm}^{-1}$  along with a common high-frequency RR spectrum, which is distinctly different from that observed for the first set of complexes. Resonance Raman characterization of the ferric porphyrin complexes is also presented.

## Experimental Section

**Materials and Methods.** Methylene chloride (Aldrich, spectrophotometric grade) was purified by a procedure described previously,<sup>13</sup> which consists of shaking approximately 500 mL of the solvent with 50–60 mL portions of concentrated  $\text{H}_2\text{SO}_4$  in a 1 L separatory funnel until the acid layer remained colorless. The solvent was then washed with 100 mL portions of distilled water, passed through a  $\text{K}_2\text{CO}_3$  column, predried over dried  $\text{CaCl}_2$ , distilled over  $\text{P}_2\text{O}_5$ , and directly passed through a dried ( $>400^\circ\text{C}$ ) neutral alumina column. The gases

$^{16}\text{O}_2$  (Monsanto Research, 98%  $^{16}\text{O}_2$ ) and  $^{18}\text{O}_2$  (ICON, 98%  $^{18}\text{O}_2$ ) were used without further purification. Ozone was prepared from  $\text{O}_2$  gases as described by Andrews and Spiker<sup>14</sup> by electrical discharge (for 6 h) using a Tesla coil. The extent of the reaction was monitored by Raman spectroscopy.

The  $\text{Fe}^{\text{III}}(\text{TMP})\text{Cl}$  was purchased from Midcentury Chemicals (Posen, IL), and an additional purification was done in order to obtain a fluorescence-free product by using the following procedure:  $\text{Fe}^{\text{III}}(\text{TMP})\text{Cl}$  (25 mg) was dissolved in a minimum amount of chloroform (3–5 mL) and loaded onto a column of neutral alumina (deactivated with 10% (w/w)  $\text{H}_2\text{O}$ ). Development with toluene resulted in the elution of a fluorescent band (metal-free ligand). After the fluorescent band had eluted completely, the heme was eluted with neat  $\text{CH}_2\text{Cl}_2$ . The collected heme fractions were pooled and concentrated by evaporation of solvent and converted to the chloride form by stirring overnight with a 0.1 M solution of hydrochloric acid. The  $\text{CH}_2\text{Cl}_2$  layer was separated and evaporated to dryness. Upon recrystallization from toluene/heptane, violet crystals were obtained, which were dried under vacuum at  $50^\circ\text{C}$ . The final product gave a single spot on silica gel TLC plates developed in toluene, and the UV/vis spectrum matched that reported in the literature.<sup>15</sup> Portions of eluted heme were converted to the fluoride<sup>12</sup> and *m*-chlorobenzoate<sup>2b</sup> forms by literature methods. The  $\text{Fe}^{\text{III}}(\text{TMP})(\text{trif})$  was prepared according to the method of Gross and Nimri.<sup>12</sup> The  $\text{Fe}^{\text{III}}(\text{TMP})\text{ClO}_4$  (Porphyrins Product) was used as received. All compounds were recrystallized prior to use and examined by  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ) to confirm their purity.  $\text{Fe}^{\text{III}}(\text{TMP})\text{F}$ :  $\delta$  81.5 (pyr-H, 8H), 12.8 and 11.7 (*m*-H, 8H), 3.4 (*p*-CH<sub>3</sub>, 12H).  $\text{Fe}^{\text{III}}(\text{TMP})\text{Cl}$ :  $\delta$  80.3 (pyr-H, 8H), 15.4 and 13.9 (*m*-H, 8H), 3.9 (*p*-CH<sub>3</sub>, 12H).  $\text{Fe}^{\text{III}}(\text{TMP})\text{OAc}$ :  $\delta$  79.6 (pyr-H, 8H), 13.9 and 12.7 (*m*-H, 8H), 3.6 (*p*-CH<sub>3</sub>, 12H).  $\text{Fe}^{\text{III}}(\text{TMP})(\text{trif})$ :  $\delta$  52.6 (pyr-H, 8H), 15.3 and 14.2 (*m*-H, 8H), 4.4 (*p*-CH<sub>3</sub>, 12H).  $\text{Fe}^{\text{III}}(\text{TMP})\text{ClO}_4$ :  $\delta$  29.2 (pyr-H, 8H), 14.1 and 13.4 (*m*-H, 8H), 4.2 (*p*-CH<sub>3</sub>, 12H).

$\text{H}_2(\text{TMP}-d_8)$  was initially synthesized according to Lindsey and Wagner<sup>16</sup> using pyrrole- $d_5$ <sup>17</sup> and purified by the method of Kihn and Meunier,<sup>18a</sup> while in later studies the modification introduced by Gross and Kaustov<sup>18b</sup> was used. Metalation with  $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$  in DMF followed by the earlier described workup afforded violet crystals of  $\text{Fe}^{\text{III}}(\text{TMP}-d_8)\text{Cl}$ . The  $\text{Fe}^{\text{III}}(\text{TMP}-d_8)\text{ClO}_4$  was obtained by a method described previously.<sup>19</sup>

Oxidation reactions were performed in  $\text{CH}_2\text{Cl}_2$  at  $-80^\circ\text{C}$  in a stirred Dewar cell specially designed for Raman measurements at low temperature.<sup>20</sup> Ozone was purged through solutions of iron(III) porphyrin complex by using a gas-tight syringe, followed by purging of the reaction cell with  $\text{N}_2$ .

**Spectroscopic Measurements.** Low-temperature Raman measurements were performed using a stirred Dewar cell (temperature  $-80^\circ\text{C}$ ) with a cylindrical lens setup in order to minimize thermal decomposition or photodecomposition of the samples.<sup>10</sup> Resonance Raman spectra were acquired with a CCD detector (Princeton Instrument) and notch filter (Kaiser Optical System, Ann Arbor, MI) attached to a single monochromator (SPEX Model 1269). The frequencies were calibrated by using known frequencies of toluene and fenchone and are accurate to  $\pm 1\text{ cm}^{-1}$ . No smoothing was performed on any of the spectra. The 406.7 nm line (with 5 mW power at the sample) of a Coherent Model Innova 100-K3 krypton ion laser was used as the excitation source. Optical spectra were measured in a low-temperature Dewar cell using a Hewlett-Packard 8452A diode array spectrometer.

## Results and Discussion

**1. Characterization of  $\text{Fe}^{\text{III}}(\text{TMP})\text{X}$  ( $\text{X} = \text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{mCB}^-$ ,  $\text{trif}^-$ ,  $\text{ClO}_4^-$ ).** Representative RR spectra of the parent (ferric) complexes are given in Figure 1 along with those of their  $\beta$ -pyrrole-deuterated analogues. The assignment of the observed

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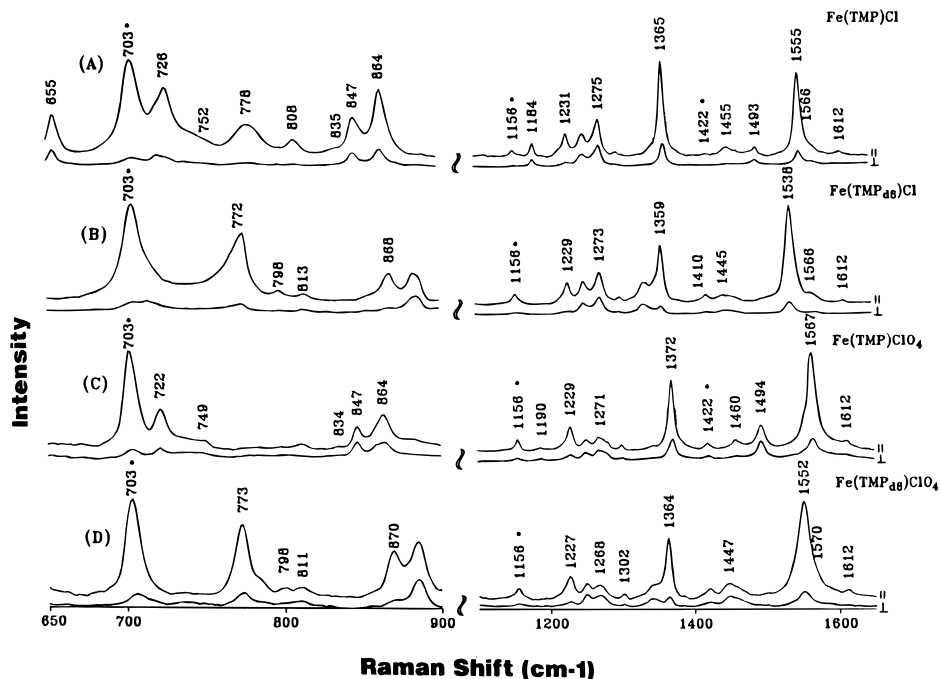
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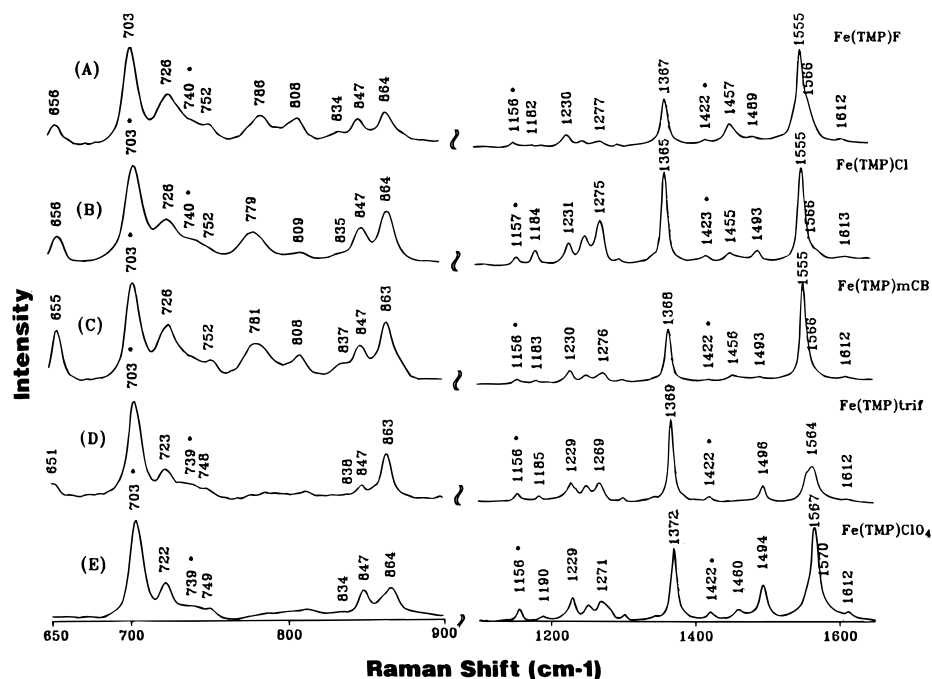
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**Figure 1.** Low- and high-frequency RR spectra of  $\text{Fe}^{\text{III}}(\text{TMP})\text{Cl}$  and  $\text{Fe}^{\text{III}}(\text{TMP})\text{ClO}_4$  and their pyrrole-substituted analogues ( $-\text{d}_8$ ) measured at  $-80^\circ\text{C}$  in  $\text{CH}_2\text{Cl}_2$  with excitation at 406.7 nm. Asterisks denote solvent bands.



**Figure 2.** Low- and high-frequency RR spectra of  $\text{Fe}^{\text{III}}(\text{TMP})\text{X}$  complexes ( $\text{X} = \text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{mCB}^-$ ,  $\text{trif}^-$ ,  $\text{ClO}_4^-$ ) measured at  $-80^\circ\text{C}$  in  $\text{CH}_2\text{Cl}_2$  with excitation at 406.7 nm. Asterisks denote solvent bands.

RR modes for  $\text{Fe}^{\text{III}}(\text{TMP})\text{Cl}$  has been proposed by Kitagawa and co-workers.<sup>11</sup> These assignments we extend for  $\text{Fe}^{\text{III}}(\text{TMP})\text{ClO}_4$  by using data for the  $\beta$ -pyrrole-deuterated analogues and the observed depolarization ratios of the modes, as well as with reference to a complete vibrational analysis of NiTPP.<sup>21</sup> These results, taken together with the observed depolarization ratios of the modes, allow us to assign the modes observed for the other three analogues of  $\text{Fe}^{\text{III}}(\text{TMP})\text{X}$  (Figure 2 and Table 1).

The high-frequency RR spectra of  $\text{Fe}^{\text{III}}(\text{TMP})\text{Cl}$  (Figure 1, trace A) show features characteristic for high-spin complexes.<sup>11</sup> Its key modes,  $\nu_4(\text{p})$ ,  $\nu_2(\text{p})$ ,  $\nu_3(\text{p})$ , and  $\nu_{11}(\text{dp})$ , are observed at 1365, 1555, 1455, and 1493  $\text{cm}^{-1}$ , respectively. Upon  $\beta$ -pyrrole deuteration (trace B), these marker modes are shifted

down by 6, 17, 45, and 48  $\text{cm}^{-1}$ , respectively. The corresponding marker modes of the perchlorate complex (Figure 1, trace C) occur at different frequencies, i.e.,  $\nu_4(\text{p})$  at 1372,  $\nu_2(\text{p})$  at 1567,  $\nu_3(\text{p})$  at 1460, and  $\nu_{11}(\text{dp})$  at 1494  $\text{cm}^{-1}$ . Their  $\beta$ -pyrrole deuteration shifts (Figure 1, trace D, and Table 1) match those observed for the chloride derivative. Furthermore, for both complexes, the shifts observed upon  $\beta$ -pyrrole deuteration are in good agreement with the corresponding shifts observed for NiTPP.<sup>21</sup> The most noticeable difference in the low-frequency spectra of the  $\text{Fe}^{\text{III}}(\text{TMP})\text{Cl}$  and  $\text{Fe}^{\text{III}}(\text{TMP})\text{ClO}_4$  complexes is the appearance of the two bands observed at 778 and 808  $\text{cm}^{-1}$

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**Table 1.** Summary of Mode Assignment for Series of Fe<sup>III</sup>(TMP)X Complexes (X = F<sup>-</sup>, Cl<sup>-</sup>, mCB<sup>-</sup>, trif<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>)<sup>a</sup>

assignment	P	$\nu_i$ ( $\Delta\nu_i d_8$ )				
		Fe(TMP)Cl	Fe(TMP)F	Fe(TMP)mCB	Fe(TMP)trif	Fe(TMP)ClO <sub>4</sub>
N(phenyl-8a)	p	1612 (0)	1612	1612	1612	1612 (0)
$\nu_{10}$	dp	1566 (0)	1566	1566		1570 (0)
$\nu_2$	p	1555 (-17)	1555	1555	1564	1567 (-15)
$\nu_{11}$	dp	1493 (-48)	1489	1493	1496	1494 (-47)
$\nu_{28}$	dp	1468 (-9)	1469	1468	1466	1474 (-8)
$\nu_3$	p	1455 (-45)	1457	1456		1460 (-44)
$\nu_{29}$	dp	1377 (-41)	1377	1378	1383	1384 (-41)
$\nu_4$	p	1365 (-6)	1367	1368	1369	1372 (-8)
$\nu_{20}$	dp	1347 (-454)	1347	1348	1346	1347 (-454)
N(phenyl)	dp	1301 (+1)	1301	1302	1301	1301 (+1)
$\nu_{12}$	dp	1275 (-2)	1277	1276	1269	1271 (-3)
$\nu_{27}$	dp	1253 (-3)	1251	1253	1250	1250 (-2)
$\nu_1$	p	1231 (-2)	1230	1230	1229	1229 (-2)
$\nu_{34}$	dp	1184 (-)	1182	1183	1185	1190 (-)
$\nu_7$	p	864 (+4)	864	863	863	864 (+6)
$\nu_{32}$	dp	864 (-51)	864	863	863	864 (-53)
$\nu_{16}$	dp	847 (+38)	847	847	847	847 (+38)
$\nu_{24}$	dp	835 (-37)	834	837	838	834 (-36)
	p	809 (-)	808	808		
	p	779 (-)	786	781		
	p	752 (-)	752	752	748	749 (-)
	p	726 (-108)	726	726	723	722 (-108)
	dp	656 (-95)	656	655	651	638 (-85)

<sup>a</sup> Abbreviations: p, polarized mode; dp, depolarized mode;  $\nu_i$ , observed frequencies;  $\Delta\nu_i d_8$ , isotopic frequency shifts upon deuteration at the pyrrole  $\beta$ -carbon positions.

in the spectrum of the former which are very weak or missing in the case of the latter complex.

On the basis of the similarity of the spectra of the Fe<sup>III</sup>(TMP)F and Fe<sup>III</sup>(TMP)(mCB) complexes to that of the Fe<sup>III</sup>(TMP)Cl complex (Figure 2) and the general similarity of the spectrum of the triflate analogue to that of the Fe<sup>III</sup>(TMP)ClO<sub>4</sub> spectrum, the series can be considered to fall into two sets, those for the halide and mCB<sup>-</sup> complexes being distinctly different from those for the triflate and ClO<sub>4</sub><sup>-</sup> analogues. The spectral assignments for all of the complexes are given in Table 1.

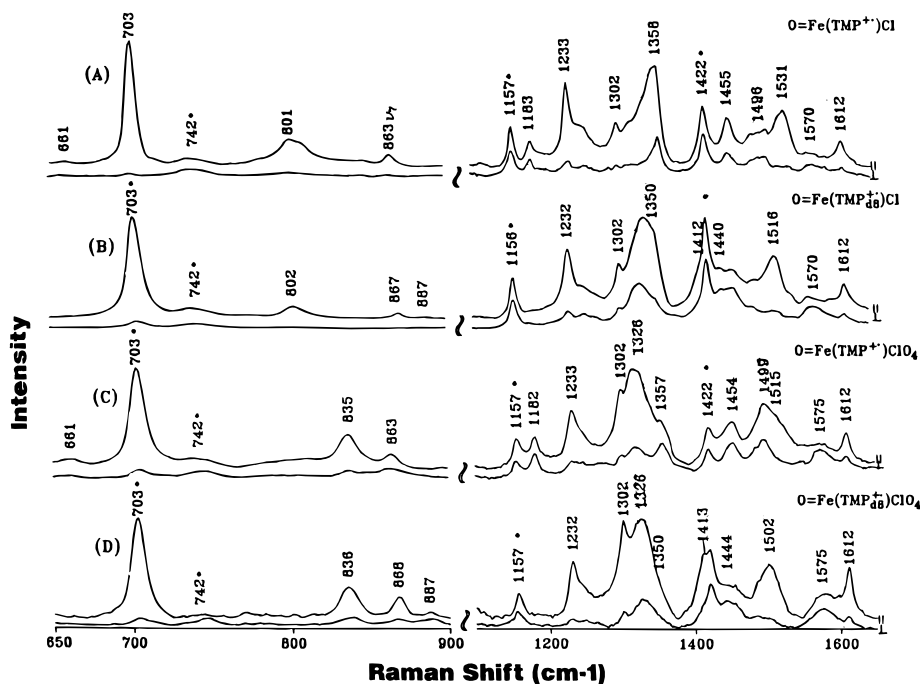
It is known that many Fe<sup>III</sup>(P)ClO<sub>4</sub> complexes adopt the spin-admixed or intermediate spin<sup>22</sup> electronic configuration ( $S = 3/2$ ). For intermediate-spin complexes, the <sup>1</sup>H NMR spectra show the pyr-H resonance near -30 ppm and an ESR signal at  $g = 4.2$ .<sup>22a,b</sup> We have, however, examined the ESR spectrum of Fe<sup>III</sup>(TMP)ClO<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> at 110 K, which reveals that it is predominantly high spin, since it exhibits a typical signal at  $g = 6$ .<sup>22b,c</sup> It has been suggested<sup>22d</sup> that the isotropic shifts of the pyr-H resonances in the <sup>1</sup>H NMR spectra of Fe<sup>III</sup>(P)L complexes are due to M  $\rightarrow$  L  $\sigma$ -spin transfer. The observed signals for the pyr-H of this series of complexes show a monotonic shift, implying the following order of ligand  $\sigma$ -donor strength: F<sup>-</sup> > Cl<sup>-</sup> > AcO<sup>-</sup> > trif<sup>-</sup> > ClO<sub>4</sub><sup>-</sup> (i.e.,  $\delta_{\text{pyr}} = 81.5, 80.3, 79.6, 52.6,$  and  $29.2$  ppm, respectively). The same explanation probably holds for the changes in the  $\nu_2$  frequencies of the complexes, which is the C $\beta$ -C $\beta$  stretching mode. The monotonic shift to higher frequencies (1555 cm<sup>-1</sup> for X = F<sup>-</sup>, Cl<sup>-</sup>, and mCB<sup>-</sup> and 1564 and 1567 cm<sup>-1</sup> for X = trif<sup>-</sup> and ClO<sub>4</sub><sup>-</sup>, respectively) indicates that the C $\beta$ -C $\beta$  bond is stronger for the weaker axial ligands. Since the Fe-axial ligand bond has the proper symmetry to interact with the filled porphyrin a<sub>2u</sub> orbital, electron donation by axial ligands is reflected in a weaker C $\beta$ -C $\beta$  bond. The same behavior was recently observed

for magnesium porphyrin; i.e., the  $\nu_2$  mode was downshifted by 6 cm<sup>-1</sup> upon coordination of THF or MeOH.<sup>23</sup>

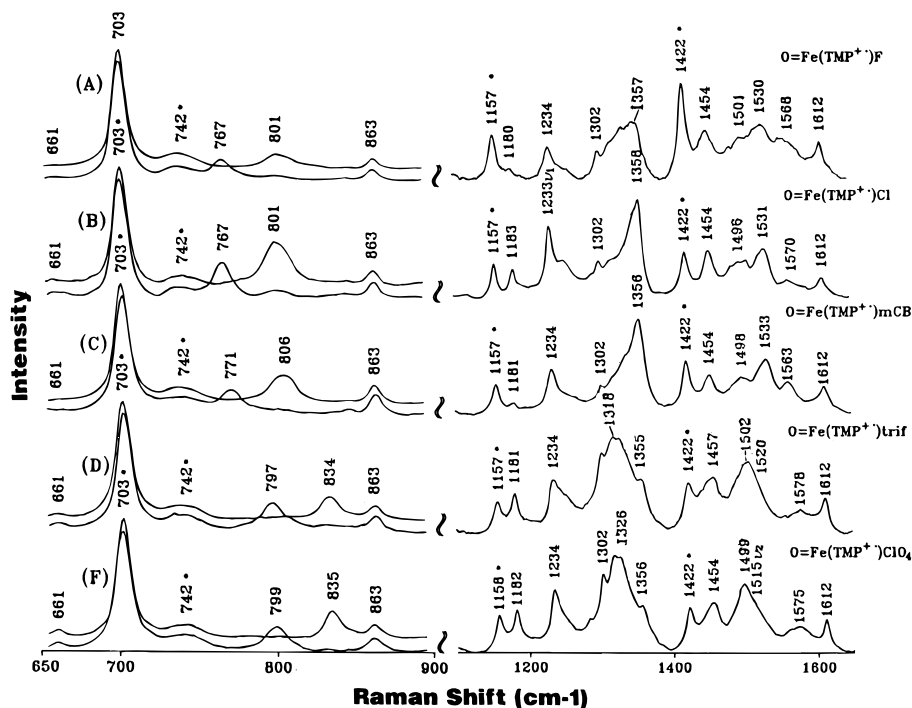
**2. Characterization of O=Fe<sup>IV</sup>(TMP<sup>+</sup>)X.** The O=Fe<sup>IV</sup>-(TMP<sup>+</sup>)X complexes were characterized by ESR and <sup>1</sup>H NMR in our previous studies.<sup>12a</sup> The ESR spectra of all complexes were very similar, showing two signals at around  $g = 4$  and one at  $g = 2$  characteristic of such complexes<sup>3</sup> (Fe<sup>IV</sup> cation ( $S = 1$ ) is ferromagnetically coupled to the porphyrin radical ( $S = 1/2$ )), while differences in their NMR spectra confirmed the presence of the different axial ligands (*vide infra*). In Figure 3 are shown representative RR spectra of O=Fe<sup>IV</sup>(TMP<sup>+</sup>)Cl and O=Fe<sup>IV</sup>(TMP<sup>+</sup>)ClO<sub>4</sub> and their  $\beta$ -pyrrole-deuterated analogues. In both cases, dramatic decreases are observed in the intensities of the modes, compared to the corresponding parent (ferric) complexes (the 1157 and 1422 cm<sup>-1</sup> solvent bands, marked with asterisks, serve as internal intensity standards). This behavior has previously been noted as characteristic of porphyrin  $\pi$ -cation formation.<sup>3b,9-11</sup> In Figure 4 the RR spectra of the above complexes are shown together with the spectra of the other three complexes investigated, i.e., O=Fe<sup>IV</sup>(TMP<sup>+</sup>)F, O=Fe<sup>IV</sup>(TMP<sup>+</sup>)-(mCB), and O=Fe<sup>IV</sup>(TMP<sup>+</sup>)(trif). Here, it can be pointed out that, as was observed for the ferric complexes, the RR spectra of the O=Fe<sup>IV</sup>(TMP<sup>+</sup>)X series can also be grouped into two sets. The first set consists of complexes ligated with Cl<sup>-</sup>, F<sup>-</sup>, and mCB<sup>-</sup>, while the second set has ClO<sub>4</sub><sup>-</sup> and trif<sup>-</sup> as axial ligands. The low-frequency RR spectra shown in Figure 4 were obtained by oxidation with <sup>16</sup>O<sub>3</sub> and <sup>18</sup>O<sub>3</sub>, respectively. As has been previously reported,<sup>10,11</sup> the low-frequency spectrum of O=Fe<sup>IV</sup>(TMP<sup>+</sup>)Cl exhibits a polarized  $\nu(\text{Fe}=\text{O})$  mode at 801 cm<sup>-1</sup>, which is downshifted to 767 cm<sup>-1</sup> upon <sup>18</sup>O isotropic substitution (Figure 4, traces A). In the case of O=Fe<sup>IV</sup>-(TMP<sup>+</sup>)ClO<sub>4</sub> this mode is observed at 835 cm<sup>-1</sup> (shifting to 799 cm<sup>-1</sup> upon <sup>18</sup>O isotropic substitution) (Figure 4, traces F). The high-frequency spectra also show noteworthy differences. The mode observed at 1531 cm<sup>-1</sup> for O=Fe<sup>IV</sup>(TMP<sup>+</sup>)Cl is polarized and shows a 15 cm<sup>-1</sup> downshift upon  $\beta$ -pyrrole deuteration: a deuterium shift similar to that of the  $\nu_2$  mode of

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**Figure 3.** Low- and high-frequency RR spectra of  $\text{O}=\text{Fe}^{\text{IV}}(\text{TMP}^{\bullet+})\text{Cl}$  and  $\text{O}=\text{Fe}^{\text{IV}}(\text{TMP}^{\bullet+})\text{ClO}_4$  and their pyrrole-substituted analogues ( $-d_8$ ) measured at  $-80^\circ\text{C}$  in  $\text{CH}_2\text{Cl}_2$  at 406.7 nm. Asterisks denote solvent bands.



**Figure 4.** Low- and high-frequency RR spectra of  $\text{O}=\text{Fe}^{\text{IV}}(\text{TMP}^{\bullet+})\text{X}$  complexes ( $\text{X} = \text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{mCB}^-$ ,  $\text{trif}^-$ ,  $\text{ClO}_4^-$ ) and their  $^{18}\text{O}$  analogues measured at  $-80^\circ\text{C}$  in  $\text{CH}_2\text{Cl}_2$  at 406.7 nm excitation. Asterisks denote solvent bands.

$\text{Fe}^{\text{III}}(\text{TMP})\text{Cl}$ . In the spectrum of  $\text{O}=\text{Fe}^{\text{IV}}(\text{TMP}^{\bullet+})\text{ClO}_4$  this polarized mode is observed at  $1515\text{ cm}^{-1}$  and is downshifted by  $13\text{ cm}^{-1}$  upon  $\beta$ -pyrrole deuteration. This is assigned to the  $\nu_2$  stretching vibration. Consideration of the observed shifts upon  $\beta$ -pyrrole deuteration and the depolarization ratios of the features for  $\text{O}=\text{Fe}^{\text{IV}}(\text{TMP}^{\bullet+})\text{X}$  series, along with those observed in the spectra of the ferric analogues, permits assignment of the modes for the three remaining  $\text{O}=\text{Fe}^{\text{IV}}(\text{TMP}^{\bullet+})\text{X}$  complexes ( $\text{X} = \text{F}^-$ ,  $\text{mCB}^-$ , and  $\text{trif}^-$ ), and a summary is provided in Table 2.

The  $\nu_2$  mode is observed at  $1531\text{ cm}^{-1}$  for  $\text{O}=\text{Fe}^{\text{IV}}(\text{TMP}^{\bullet+})\text{Cl}$  and exhibits a  $15\text{ cm}^{-1}$  downshift upon  $\beta$ -pyrrole deuteration.

This frequency is virtually identical with those observed for the  $\text{F}^-$  and  $\text{mCB}^-$  complexes (Figure 4, trace A, band C). However, the  $\nu_2$  mode is observed at  $1520\text{ cm}^{-1}$  for  $\text{O}=\text{Fe}^{\text{IV}}(\text{TMP}^{\bullet+})\text{trif}$  and at  $1515\text{ cm}^{-1}$  for  $\text{O}=\text{Fe}^{\text{IV}}(\text{TMP}^{\bullet+})\text{ClO}_4$ . The region of the  $\nu_4$  mode consists of an envelope of several unresolved bands in the spectra of all of the complexes, though definitive location of the position of  $\nu_4$  is not possible.

Recently it has been shown<sup>24</sup> that a decrease in the isotropic shift of the pyr-H resonances in  $^1\text{H}$  NMR spectra of  $\text{Mn}^{\text{III}}(\text{P})\text{L}$  complexes (isoelectronic with  $\text{Fe}^{\text{IV}}$  porphyrin complexes) reflects the  $\pi$ -donor strength of the ligand, L. Accordingly, on the basis

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**Table 2.** Summary of Observed Modes and Their Oxidation Shifts ( $\Delta\nu_{ox}$ ) for  $O=Fe^{IV}(TMP^{+})X$  ( $X = Cl^{-}, F^{-}, mCB^{-}, trif^{-}, ClO_4^{-}$ ),  $O=Fe^{IV}(TMP)$ , and  $O=V^{V}(TPP^{+})^a$ 

assignment	P	$O=Fe^{IV}(TMP^{+})Cl$ $\nu_i (\Delta\nu_{d8}, \Delta\nu_{ox})$	$O=Fe^{IV}(TMP^{+})F$ $\nu_i (\Delta\nu_{ox})$	$O=Fe^{IV}(TMP^{+})mCB$ $\nu_i (\Delta\nu_{ox})$	$O=Fe^{IV}(TMP^{+})trif$ $\nu_i (\Delta\nu_{ox})$	$O=Fe^{IV}(TMP^{+})ClO_4$ $\nu_i (\Delta\nu_{d8}, \Delta\nu_{ox})$	$O=Fe^{IV}(TMP)^b$ $\nu_i$	$O=V^{V}(TPP^{+})^c$ $\nu_i (\Delta\nu_{ox})$
$\nu(\text{phenyl-8a})$	p	1612 (0, -)	1612 (-)	1612 (-)	1612 (-)	1612 (0, -)		1598 (-3)
$\nu_{10}$	dp	1570 (0, -)	1568 (-)	1563 (-)	1578 (-)	1575 (0, -)		
$\nu_2$	p	1531 (-15, -39)	1530 (-40)	1533 (-37)	1520 (-50)	1515 (-13, -55)	1570	1517 (-41)
$\nu_{11}$	dp	1496 (-56, -)	1501 (-)	1498 (-)	1506 (-)	1499 (-55, -)		1491 (-8)
$\nu_3$	p	1454 (-42, -)	1454 (-)	1454 (-)	1457 (-)	1454 (-41, -)		
$\nu_4$	p						1370	1366 (-2)
$\nu(\text{phenyl})$	p	1302 (0, -)	1302 (-)	1302 (-)	1302 (-)	1302 (0, -)		
$\nu_{27}$	dp	1256 (-3, -)	1258 (-)	1255 (-)	1252 (-)	1248 (-3, -)		
$\nu_1$	p	1233 (-1, +4)	1234 (+5)	1234 (+5)	1234 (+5)	1233 (-1, +5)	1229	
$\nu_7$	p	863 (+4, +1)	863 (+1)	863 (+1)	863 (+1)	863 (+5, +1)	862	
$\nu(M=O)$	p	801 (0, -42)	801 (-42)	806 (-37)	834 (-9)	835 (+1, -8)	843	982 (-16)

<sup>a</sup> Abbreviations:  $\nu_i$ , observed frequencies;  $\Delta\nu_{d8}$ , isotropic frequency shifts upon deuteration at the pyrrole  $\beta$ -carbon positions;  $\Delta\nu_{ox}$ , difference in frequencies between ( $O=Fe(TMP)$  and  $\pi$ -cation radical. <sup>b</sup> Mizutani, Y.; Hashimoto, S.; Tatsuno, Y.; Kitagawa, T. *J. Am. Chem. Soc.* **1990**, *112*, 6809–6814. <sup>c</sup> Macor, K. M.; Czernuszewicz, R. S.; Spiro, T. G. *Inorg. Chem.* **1990**, *29*, 1996–2000.

**Table 3.** RR and  $^1H$  NMR<sup>b</sup> Data for the Various Complexes and the Second-Order Rate Constants ( $\pm 5\%$ ) for Their Reaction with Styrene<sup>a</sup>

	$F^{-}$	$Cl^{-}$	$mCB^{-}$	$CH_3OH$	$^{-}OSO_2CF_3$	$^{-}OClO_3$
$\nu(Fe=O)$	801	801	806	831	834	835
$\nu_2$	1530	1531	1533	1517	1520	1515
pyr-H	-13.0	-6.7	-8.3 <sup>c</sup>	-26.7	-26.2	-26.9
$k^d$	706	149	114 <sup>c</sup>	196	46	<sup>e</sup>

<sup>a</sup> Reference 12a. <sup>b</sup>  $\delta$ , ppm in  $CD_2Cl_2$  at  $-80$  °C. <sup>c</sup> Data for  $^{-}OAc$  (ref 12). <sup>d</sup>  $10^{-3} M^{-1}$ . <sup>e</sup> No reaction.

of the results of the earlier  $^1H$  NMR study<sup>12a</sup> of the series,  $O=Fe^{IV}(TMP^{+})X$ , the order in the  $\pi$ -donor strength of the ligand,  $X^{-}$ , is apparently  $Cl^{-} > F^{-} \gg trif^{-} > ClO_4^{-}$ . This provides an explanation for the variation of  $\nu_2$  in the RR spectral data. Removal of an electron from the macrocycle's  $\pi$  system upon forming the  $\pi$ -cation causes a dramatic downshift of  $\nu_2$ . The reason is that the reduced bond order is mostly reflected in the  $C_{\beta}-C_{\beta}$  bonds, which have large coefficients in the  $a_{2u}$  orbital, the HOMO in all TMP metal complexes.<sup>25</sup> While the  $Cl^{-}$ ,  $F^{-}$ , and  $mCB^{-}$  partially compensate for this via  $\pi$ -donation, the complexes with weaker  $\pi$ -donors ( $ClO_4^{-}$  and triflate) yield lower frequencies for  $\nu_2$ . Interestingly, because of the opposite effect of electron donors on the  $C_{\beta}-C_{\beta}$  bond strength in  $Fe^{III}(TMP)X$  (decrease) and  $O=Fe^{IV}(TMP^{+})X$  (increase), the difference in the  $\nu_2$  frequencies of the two complexes is only  $24\text{ cm}^{-1}$  for  $X = Cl^{-}$ , but  $52\text{ cm}^{-1}$  for  $X = ClO_4^{-}$ .

The difference between the  $\nu(Fe=O)$  frequencies for the two subsets of ferryl porphyrin  $\pi$ -cation radicals is consistent with the relative donor strength of the ligands, i.e.,  $Cl^{-}$ ,  $F^{-}$ , and  $mCB^{-} \gg ClO_4^{-}$  and triflate. Furthermore, as is shown in Table 3, there is good agreement among a number of spectroscopic parameters for this series of complexes. Thus,  $\nu(Fe=O)$ ,  $\nu_2$ , and the  $^1H$ -NMR resonances fall into two distinct sets, the values for the  $F^{-}$ ,  $Cl^{-}$ , and  $mCB^{-}$  (or  $OAc^{-}$ ) complexes being consistent, while the corresponding values for the  $trif^{-}$  and  $ClO_4^{-}$  are similar (but distinctly different from the first set). We have included data for the case where methanol was present and presumably serves as the trans-axial ligand. While there is some disagreement<sup>10,11</sup> regarding the validity of the assignment of  $\nu(Fe=O)$  for this species, it is noted that the  $831\text{ cm}^{-1}$  frequency reported by Kitagawa and co-workers,<sup>9,11</sup> taken together with the reported  $\nu_2$  frequency and  $\delta(\text{pyr-H})$  resonance, is consistent with the other data in Table 3.

Thus, it can be concluded that the stronger axial donor ligands destabilize the oxo-iron bond [ $\nu(Fe=O) = 801\text{--}806\text{ cm}^{-1}$ ],

while that bond is significantly stronger for  $X = trif^{-}$ ,  $ClO_4^{-}$ , and MeOH. A further noteworthy point is that the value of  $831\text{ cm}^{-1}$  for the weak donors is quite close to that of the compound II analogue ( $O=Fe^{IV}(TMP)$ , no axial ligand,  $\nu(Fe=O) = 843\text{ cm}^{-1}$ ). Interestingly, that complex was indeed recently shown to be much more reactive toward olefins than previously thought.<sup>19</sup> A direct comparison of the reactivity of  $O=Fe^{IV}(TMP)$  with that of the  $O=Fe^{IV}(TMP^{+})$  cannot be made, however, because the former complex is a one-electron oxidant, thus lacking a mechanism for formation of epoxides from olefins.

The modified Badger's rule<sup>26</sup> that describes the relationship between the equilibrium bond length ( $r_e$ ) and stretching force constant ( $K$ ) for the  $Fe=O$  fragment is given by the simple equation  $r_e = 0.74 + 1.54(K)^{-1/3}$ . For example, assuming that the  $Fe=O$  fragment behaves as a diatomic harmonic oscillator with reduced mass  $\mu$  of  $2.05 \times 10^{-23}$  au, the observed frequencies of  $835\text{ cm}^{-1}$  for  $O=Fe(TMP^{+})ClO_4$  and  $801\text{ cm}^{-1}$  for  $O=Fe(TMP^{+})Cl$  and  $O=Fe(TMP^{+})F$  yield corresponding force constants of 5.04 and 4.68 mdyne/Å. Substituting these " $K$ " values into the above equation, the calculated  $Fe=O$  bond lengths of the  $\pi$ -cation radicals investigated in this work are in the range of 1.64–1.66 Å. For comparison we calculated the  $Fe=O$  distances of  $O=Fe(TPP)$  formed in low-temperature matrices<sup>7</sup> ( $\nu(Fe=O) = 852\text{ cm}^{-1}$ ;  $K = 5.30$  mdyne/Å;  $r_e = 1.63$  Å), horseradish peroxidase (HRP) compound I<sup>27</sup> ( $\nu(Fe=O) = 790\text{ cm}^{-1}$  at pH 7.0;  $K = 4.56$  mdyne/Å;  $r_e = 1.67$  Å), and compound II<sup>27</sup> ( $\nu(Fe=O) = 776\text{ cm}^{-1}$  at pH 7.0;  $K = 4.40$  mdyne/Å;  $r_e = 1.68$  Å). We note that the value of 1.63 Å obtained here for  $O=Fe(TPP)$  corrects the value calculated previously.<sup>7a</sup> These distances (1.63–1.68 Å) for the  $Fe=O$  fragment calculated here from RR data are in excellent agreement with EXAFS data<sup>4</sup> reported for HRP compounds I and II and their model complexes (there an average  $Fe=O$  bond distance was reported as  $1.64 \pm 0.03$  Å). However, it is emphasized here that, while clearly resolvable frequency differences (e.g., 801 and  $835\text{ cm}^{-1}$ ) are observed in the RR spectra, the corresponding bond length changes ( $0.02$  Å) are within the experimental uncertainty of the EXAFS technique (estimated at  $\pm 0.02$  Å<sup>4</sup>). Thus, the RR technique is a more sensitive probe of the  $Fe=O$  bond strength, as expected.<sup>28</sup>

Finally, there still remains an apparent discrepancy between the *trans* influence—the spectroscopic results for the  $O=Fe^{IV}(TMP^{+})X$  complexes—and the *trans* effect—the reactivity of the same complexes in the epoxidation of styrene. The

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$\text{O}=\text{Fe}^{\text{IV}}(\text{TMP}^+)\text{F}$  and  $\text{O}=\text{Fe}^{\text{IV}}(\text{TMP}^+)\text{Cl}$  complexes have identical  $\text{Fe}=\text{O}$  stretching frequencies, but the former is almost 5 times as reactive as the latter. Similarly, despite the almost identical value of  $\nu(\text{Fe}=\text{O})$  for  $\text{X} = \text{MeOH}$ ,  $\text{trif}^-$ , and  $\text{ClO}_4^-$ , their reactivity is very different. A plausible explanation is based on many other examples of *nonlinear* free energy relationships in organic chemistry, such as curvature in Hammett plots or deviation from the Bronsted relation.<sup>29</sup> This behavior is caused by changes either in reaction mechanism (Hammett) or in the identity of the rate-limiting step (Hammett and Bronsted). In the present case, the simplest explanation for the different effect of the axial ligand on the thermodynamic and kinetic properties of the complexes relies on well-documented evidence that the epoxidation reaction consists of two steps, both partially rate limiting.<sup>30</sup> Furthermore, we have recently found conditions to trap the intermediate of the first step; i.e., under specific conditions the second step is fully rate limiting.<sup>12b</sup> In addition, we have provided new evidence for its characterization as a complex formed by electron transfer from the olefin

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to the ferryl fragment.<sup>12b</sup> Thus, if it is assumed that only the first step is sensitive to the strength of the oxo-iron bond, the apparent discrepancy between the *trans effect* and the *trans influence* is resolved.

**Acknowledgment.** This work was supported by National Institutes of Health DK35153 (to J.R.K.). J.R.K. also gratefully acknowledges the Wehr Foundation for partial support of this work. Partial support of L.M.P. by Grant 2P 303 060 05 from the Polish Committee for Scientific Research is gratefully acknowledged. Z.G. acknowledges the Energy Research Endowment Fund and the United States-Israel Binational Science Foundation for partial support of this work.

JA952177C

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