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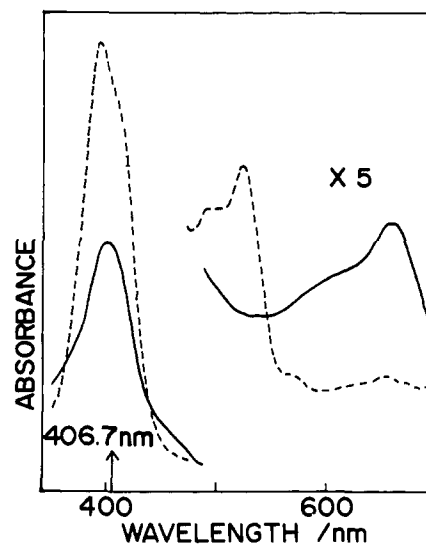
**Supplementary Material Available:** Tables of atomic coordinates, thermal parameters, and a full listing of bond lengths and angles for both the X-ray and neutron diffraction studies of  $\text{Ti}(\text{BH}_4)_2(\text{dmpe})_2$  and  $\text{Ti}(\text{CH}_3)_2(\text{dmpe})_2$  (10 pages); tables of observed and calculated structure factors for  $\text{Ti}(\text{BH}_4)_2(\text{dmpe})_2$  and  $\text{Ti}(\text{CH}_3)_2(\text{dmpe})_2$  (22 pages). Ordering information is given on any current masthead page.

### Observation of the $\text{Fe}^{\text{IV}}=\text{O}$ Stretching Raman Band for a Ferryl Porphyrin $\pi$ Cation Radical

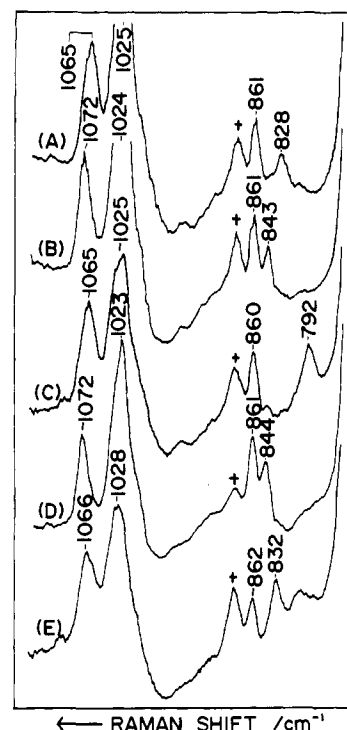
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High valent oxo-metalloporphyrins have attracted chemists' attention<sup>1-5</sup> since the first demonstration by Groves et al.<sup>6</sup> that an oxo-iron(IV) porphyrin exhibits the monooxygenation activity to olefins like cytochrome P-450. Originally, the presence of the ferryl heme was pointed out for the catalytic intermediates of peroxidases called compound I and II,<sup>7,8</sup> which have the oxidation states higher than the ferric state by 2 and 1 equiv, respectively. On the basis of the close similarity in their visible spectra, Dolphin et al.<sup>9</sup> suggested that compound I had the ferryl porphyrin  $\pi$  cation radical, and subsequent studies with ESR,<sup>10</sup> NMR,<sup>11</sup> and ENDOR<sup>12</sup> confirmed this conclusion. Since then the physicochemical properties of the ferryl porphyrin complexes have been investigated with various techniques.<sup>13-16</sup> While the  $\text{Fe}^{\text{IV}}=\text{O}$  stretching



**Figure 1.** Visible absorption spectra of  $(\text{TMP})\text{Fe}^{\text{III}}\text{Cl}$  (broken line) and its green complex (solid line) in the  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  mixed solvent at  $-80^\circ\text{C}$ . An arrow indicates the excitation wavelength for Raman scattering.



**Figure 2.** Resonance Raman spectra of the green complex observed at  $-80^\circ\text{C}$ : (A) the  $^{16}\text{O}$ -derivative under the spinning condition; (B) the  $^{16}\text{O}$ -derivative without spinning; (C) the  $^{18}\text{O}$ -derivative under the spinning condition; (D) the  $^{18}\text{O}$ -derivative without spinning; (E) the green complex derived from  $(\text{TMP})^{54}\text{Fe}^{\text{III}}\text{Cl}$  and  $^{16}\text{O}$ -*m*-CPBA. Excitation, 406.7 nm, 5 mW at sample point. Accumulation time, 320 s.

( $\nu_{\text{Fe}=\text{O}}$ ) Raman band has been identified for compound II of peroxidases<sup>17,18</sup> and the ferryl porphyrin complexes,<sup>19-22</sup> the

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corresponding band of compound I and its model compound has never been observed so far partly due to photolability of the sample. Recently we succeeded in observing the  $\nu_{\text{Fe}=\text{O}}$  Raman band of the ferryl porphyrin  $\pi$  cation radical for the first time by using the spinning cell at  $-80^\circ\text{C}$  and the OMA detection system. Here we discuss the nature of the  $\text{Fe}^{\text{IV}}=\text{O}$  bond of the ferryl porphyrin  $\pi$  cation radical.

The so called green complex,<sup>5a</sup> which was characterized as the oxo-iron(IV) porphyrin  $\pi$  cation radical,<sup>13</sup> was derived in the Raman or absorption cell by the reaction of (5,10,15,20-tetramethylporphyrinato)iron(III) chloride [(TMP)Fe<sup>III</sup>Cl] with *m*-chloroperoxybenzoic acid (*m*-CPBA) in a  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  (5:1 in volume) mixed solvent at  $-80^\circ\text{C}$  according to Groves et al.<sup>5a</sup> The  $^{18}\text{O}$  labeled *m*-CPBA was synthesized from *m*-chlorobenzoyl chloride and  $\text{H}_2^{18}\text{O}_2$  in the presence of NaOH.<sup>23</sup> Raman scattering was excited at 406.7 nm with the power as low as possible (5 mW) and detected with a diode array detector (PAR 1420) attached to a Spex 1404 double monochromator. The sample was spun (1800 rpm) at  $-80^\circ\text{C}$ , and the measurements were finished within a few minutes after exposure of the sample to the laser beam.

Figure 1 shows the visible absorption spectra of (TMP)Fe<sup>III</sup>Cl and the green complex observed at  $-80^\circ\text{C}$ . These are in reasonable agreement with the reported spectra.<sup>5a</sup> Figure 2 shows the resonance Raman spectra of the green complex. Spectra (A) and (C) were observed for the green complexes obtained from the  $^{16}\text{O}$ - and  $^{18}\text{O}$ -*m*-CPBA, respectively. Only the 828-cm<sup>-1</sup> band in spectrum (A) was a new band upon the formation of the green complex and this band was shifted to 792 cm<sup>-1</sup> with  $^{18}\text{O}$  as shown in spectrum (C). For an isolated  $\nu_{\text{Fe}=\text{O}}$  vibration, the  $\nu(^{18}\text{O})/\nu(^{16}\text{O})$  frequency ratio is calculated to be 0.956, and accordingly the expected isotopic frequency shift ( $\Delta\nu$ ) is 0.044 $\nu_{\text{Fe}=\text{O}}(^{16}\text{O})$ . If we assume  $\nu_{\text{Fe}=\text{O}}(^{16}\text{O}) = 828\text{ cm}^{-1}$ , the expected shift would be  $\Delta\nu = 36.4\text{ cm}^{-1}$ , which agrees remarkably well with the observed shift. When the green complex was derived from (TMP)<sup>5a</sup>Fe<sup>III</sup>Cl and  $^{16}\text{O}$ -*m*-CPBA, spectrum (E) was obtained. The 4-cm<sup>-1</sup> shift of the 828-cm<sup>-1</sup> band to a higher frequency is coincident with the expected isotopic frequency shift (3.4 cm<sup>-1</sup>). Consequently, the 828-cm<sup>-1</sup> band is assigned to the  $\nu_{\text{Fe}=\text{O}}$  band of the green complex. The good agreement between the observed and calculated isotopic frequency shifts means that this mode is scarcely coupled with other porphyrin vibrations.

When the spinning of the cell was stopped without raising temperature, spectra (B) and (D) were obtained for the  $^{16}\text{O}$ - and  $^{18}\text{O}$ -derivatives, respectively. The  $\nu_{\text{Fe}=\text{O}}$  bands disappeared and a new band appeared at 843-844 cm<sup>-1</sup> for both derivatives. This band was present in the spectrum of the ferric compound and exhibited a frequency shift of  $-4\text{ cm}^{-1}$  upon  $^{15}\text{N}$  substitution of four pyrrole nitrogens.<sup>22b</sup> Therefore, the 844-cm<sup>-1</sup> band cannot be assigned to the  $\text{Fe}^{\text{IV}}=\text{O}$  stretching mode of the neutral ferryl complex. At the same time as the spectral change around the 800-850-cm<sup>-1</sup> region, the spectrum in the higher frequency region above 1200 cm<sup>-1</sup> changed drastically, and the resultant spectrum resembled that of the ferric complex, suggesting the occurrence of photoreduction by two oxidative units. The one-electron reduced species could not be identified in the present experiment.

Previously we pointed out that the oxo oxygen atom of compound II is exchanged with oxygen atoms of bulk water only when the oxo oxygen atom is hydrogen bonded to the distal histidine.<sup>17b,d</sup> In the original report of the green complex,<sup>5a</sup> on the other hand, incorporation of the  $^{18}\text{O}$  atom into olefin upon addition of  $\text{H}_2^{18}\text{O}$  to the green complex was noted. Hence we measured the Raman

spectrum of the  $^{16}\text{O}$  derived green complex in the presence of  $\text{H}_2^{18}\text{O}$ , but the  $\nu_{\text{Fe}=\text{O}}$  band remained unshifted. Therefore, the oxo oxygen atom in the green complex was not easily exchanged with bulk water under the present conditions.

The  $\nu_{\text{Fe}=\text{O}}$  frequency of (TMP)Fe<sup>IV</sup>=O in toluene was 843 cm<sup>-1</sup>,<sup>22a</sup> but this frequency is reported to change with surroundings. Out of the reported  $\nu_{\text{Fe}=\text{O}}$  frequencies of the ferryl complexes, that in the oxygen matrix at 15 K is highest (852 cm<sup>-1</sup>),<sup>19</sup> and the frequency decreases in coordinating solvents: 829 cm<sup>-1</sup> in THF<sup>20</sup> and 807-820 cm<sup>-1</sup> in *N*-methylimidazole.<sup>20,21</sup> The coordination number of the green complex has not been clarified yet. The NMR study<sup>24</sup> suggested the presence of weak interactions between the iron ion(IV) and methanol. However, the  $\nu_{\text{Fe}=\text{O}}$  Raman band was identified at the same frequency for the green complex derived in the absence of methanol and also upon addition of acetic acid to it. Judging from this insensitivity of the  $\nu_{\text{Fe}=\text{O}}$  frequency and also from the absence of the EXAFS peak corresponding to the Fe-trans ligand pair,<sup>13</sup> it seems more likely that the green complex which gives rise to the  $\nu_{\text{Fe}=\text{O}}$  Raman band adopts the five coordinate structure. Then, the present observation implies that the oxidation of the porphyrin ring to the cation radical results in slight reduction of the double bond character of the axial  $\text{Fe}^{\text{IV}}=\text{O}$  bond.

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### Insertion of Carbon Monoxide into Transition-Metal-Acyl Bonds To Form $\alpha$ -Ketoacyl Complexes

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Migratory insertion of CO into transition-metal-alkyl bonds to form acyl ligands is one of the most studied of all transition-metal organometallic reactions.<sup>1</sup> In contrast, the insertion of a second CO into a metal-acyl bond to form an  $\alpha$ -ketoacyl ligand has never been observed, even though a number of the important "double carbonylation" reactions<sup>2-4</sup> could involve such a transformation. However, the only mechanistically studied "double carbonylation" catalyst has been shown to form  $\alpha$ -ketoamide

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