Compound I and II Analogues of a Chlorin

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Oxoferryl chlorin π-cation radicals are putative transients in the dismutation of hydrogen peroxide by chlorin-containing catalases[1] of organisms such as *Escherichia coli*[2] and *Neurospora crassa*[3] and are analogues of the compound I transients of catalases having iron protoporphyrin IX as the prosthetic group. To date, efforts to model the compound I analogues of chlorins have relied on the dihydro derivatives of *meso*-tetraarylporphyrins.[4−6] Generation of chlorin compound I analogues by the usual treatment of the ferric complexes with peracids is accompanied by considerable aromatization back to the porphyrin macrocycle, posing difficulties for characterization by EPR, Mössbauer, and resonance Raman spectroscopy. We have synthesized *trans*-2,3-dihydroxy-2,3-dimethylporphinatoiron(III) ($|Fe^{III} \mathbf{1}|^+$), an iron chlorin complex in which aro-

$|Fe^{III} \mathbf{1}|^+$
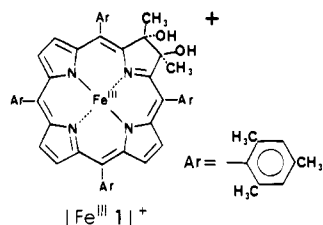
matization is prevented by *gem* substitution at both pyrroline β-carbons, and report generation of the compound I and one-electron-reduced compound II analogues. Absence of porphyrin contamination has permitted the definitive characterization of a chlorin compound I analogue.

The metal-free base ($|H_2 \mathbf{1}|$) was obtained (50%) by addition of methyllithium to 2,3-dioxotetramesitylporphyrin.[7] The 2,3-dimethyl-d_6 chlorin from addition of methyl-d_3-lithium permitted determination of the hyperfine shifts of the pyrroline methyl protons from the deuterium shifts observed by ^2H NMR.

Metalation with ferrous chloride ($^{57}FeCl_2$ for Mössbauer samples) gave $|Fe^{III}(Cl) \mathbf{1}|$. The *trans*-2,3-dimethyl configuration is established by the absence of a symmetry element evident in the inequivalence of the pyrroline methyl resonances and resolution of five pyrrole signals in a 1:1:1:1:2 ratio in the ^1H NMR spectrum; other data are consistent with the assigned structure.[8] By cyclic voltammetry (CH_2Cl_2, 0.1 M n-Bu_4N^+-PF_6^-, 200 mV s^{-1}), $|H_2 \mathbf{1}|$ and $|Fe^{III}(Cl) \mathbf{1}|$ undergo reversible one-electron oxidations at $E_{1/2} = 0.805$ and 0.896 V vs SCE, respectively, compared to 0.910 and 1.046 V for the first oxidation potentials of tetramesitylporphine and its chloroiron(III) complex. The well-resolved, reversible cyclic voltammogram of $|Fe^{III}(Cl) \mathbf{1}|$ at ambient temperature suggests that the first oxidation is ligand-centered.[9]

Solutions of the hydroxo complex[10] $|Fe^{III}(OH) \mathbf{1}|$ in butyronitrile or the trifluoromethanesulfonato (triflato) complex[10] $|Fe^{III}(Tf) \mathbf{1}|$ in 9:1 methylene-d_2-chloride/methanol-d_4 (for ^1H NMR) gave the compound I analogue on treatment with 1.5 molar equiv of *m*-CPBA at −80 °C. The integrity of the macrocycle in the compound I analogue was confirmed by UV−vis and ^1H NMR analysis of material recovered following reduction with n-$Bu_4N^+I^-$ and metathesis to the chloro complex. The UV−vis and ^1H NMR spectra of $|Fe^{IV}=O \mathbf{1}|^+$ are as follows: UV−vis (butyronitrile, −80 °C) [λ_{max} ($\epsilon \times 10^{-3}$)] 410 (13.16), 798 (1.13) nm; ^1H NMR (500 MHz, 9:1 methylene-d_2 chloride/methanol-d_4, −75 °C) −80, −42, −10 (2H each, pyrrole H); 1.06, 14.12 (pyrroline CH_3, from ^2H NMR of dimethyl-d_6 derivative); 10.5, 11.0, 12.7, 14.7, 20.8 (1:2:2:1:2, mesityl *o*-CH_3); 16.7, 26.6, 28.2 (4H:2H:2H, mesityl *m*-H) ppm. The UV−vis spectrum of $|Fe^{IV}=O \mathbf{1}|^+$ corresponds closely to that reported for the compound I analogue of 2,3-dihydrotetramesitylporphyrin.[4,5] The upfield ^1H NMR hyperfine shifts of the pyrrole protons are consistent with a π-spin delocalization mechanism and vacant $d_{x^2-y^2}$ orbital of low-spin ferryl iron.[11] As in the case of the oxidized dihydrotetramesityl chlorin complex,[5] the shifts and anisotropy of pyrrole H and mesityl *m*-H signals are in accord with the predicted electronic state counterpart of a_{1u} symmetry in the D_{4h} point group.[5,12] Such a_{1u} character is in contrast to the a_{2u} state assigned to the π-cation radical of the compound I analogue of tetramesitylporphyrin.[13] Resonance Raman spectra of $|Fe^{III}(Tf) \mathbf{1}|$ (Figure 1a) and $|Fe^{IV}=O \mathbf{1}|^+$ (Figure 1b) in the high-frequency range were obtained with 4067 Å (Soret band) excitation. The trace of $|Fe^{III}(Tf) \mathbf{1}|$ correlates with spectra of copper(II) tetraphenylchlorin under Soret excitation.[14,15] Upon oxidation, a significant decrease in band intensity is accompanied by broadening and shifts in band frequencies (Figure 1b), as expected for formation of the macrocycle π-cation radical. However, correlation of bands with established porphyrin modes is complicated by the

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(8) UV−vis (CH_2Cl_2) [λ_{max}($\epsilon \times 10^{-3}$)] 380 (40.06), 414 (43.57), 595 (11.15) nm. ^1H NMR (500 MHz, CD_2Cl_2, −75 °C): 4.32, 4.75 (s, mesityl *p*-CH_3); −4.2, −0.1, 8.5, 11.0, 13.1, 14.8 (bs, 6/8 mesityl *o*-CH_3); 7.9, 18.6 (bs, pyrroline CH_3 [^2H NMR]); 16.3, 17.5, 18.3, 20.7, 21.3, 21.9, 22.1, 25.5 (s, *m*-H); 102.5, 110.8, 123.3, 136.7, 142.5 (bs, 2:1:1:1:1, py-H) ppm. FAB/MS ($|Fe^{III} \mathbf{1}|^+$: *p*-nitrobenzyl alcohol) *m/z* (rel intensity) 898 (100) M$^+$, 881 (9) M − OH, 866 (15) M − OH − CH$_3$, 853 (21) M − CH$_3$-CHOH, 838 (15) M − OH − CH$_3$ − CO. HRMS (FAB): *m/e* calcd for C$_{58}$H$_{58}$N$_4$O$_2$Fe 898.3909, *m/e* found 898.3945. Anal. Calcd for C$_{58}$H$_{58}$-ClN$_4$O$_2$Fe: C, 74.55; H, 6.26; N, 5.99; Fe, 5.98. Found: C, 74.55; H, 6.53; N, 5.85; Fe, 5.60.

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(10) Metathesis of Cl$^-$ counterion to OH$^-$ was accomplished by chromatography of $|Fe^{III}(Cl) \mathbf{1}|$ over activity I basic alumina eluted with 4:1 CH$_2$Cl$_2$/methanol. The triflato complex was obtained by treating the hydroxo complex with 1 equiv of triflic anhydride in CH$_2$Cl$_2$.

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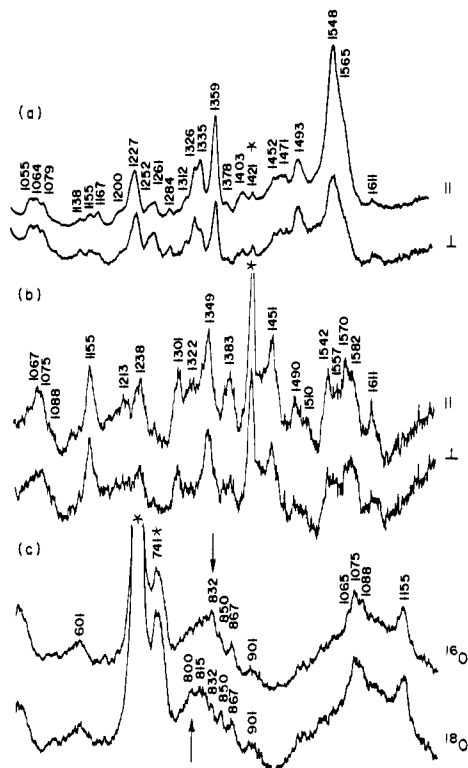
Figure 1. Resonance Raman spectra (4067 Å, 7 mW): (a) |Fe^{III}(Tf) 1| in the high-energy region in parallel (upper trace) and perpendicular (lower trace) polarizations; (b) the same after addition of *m*-CPBA; (c) low-energy region after addition of *m*-CPBA, indicating (arrow) ^{18}O-isotope sensitive band assigned $\nu_{Fe=O}$. Spectra obtained in a spinning cell cooled to −80 °C (measured by probe in cryostat) by cold N$_2$ gas; CH$_2$Cl$_2$ bands denoted by asterisks (*).

possibility of mode localization and mode mixing arising from lowered symmetry.[15,16] Interpretation of these data in terms of the symmetry state of the chlorin π-cation radical awaits detailed band assignments. In the low-frequency region, a band at 832 cm^{-1} shifting to 800 cm^{-1} on oxidation with [^{18}O]-*m*-CPBA (Figure 1c) is assigned as $\nu_{Fe=O}$ and corresponds closely to $\nu_{Fe=O}$ of the oxoferryl tetramesitylporphyrin π-cation radical in methylene chloride/methanol medium.[13]

In frozen butyronitrile solution, the first-derivative EPR trace of |Fe^{III}(OH) 1| (Figure 2a) consists of a major high-spin rhombic ferric species and small amounts of high-spin and low-spin components in different axial ligation states, possibly from coordinated solvent and H$_2$O. Oxidation produces a rhombic quartet spectrum integrating[17] to 85% of the initial spins (Figure 2b). Both the EPR and Mössbauer (Figure 3) spectra of the oxidized species support a parallel spin-coupled ferryl chlorin π-cation radical ($S_{total} \approx$ $^3/_2$) structure.[17] Simulations[17] of EPR and Mössbauer spectra (e.g., Figures 2b, 3) provided estimates of spin Hamiltonian parameters.

The Mössbauer spectrum of the compound II analogue |Fe^{IV}=O 1|, present as a 45% component of the measured spectrum of |Fe^{IV}=O 1|$^+$ in butyronitrile, was simulated as shown in Figure 3. Reduction of the chlorin cation radical is accompanied by an increase in ΔE_q. A parallel increase in ΔE_q is observed when the compound I analogue of tetramesitylporphyrin[18] is reduced to an oxoferryl complex under similar conditions. On standing in butyronitrile at −80 °C, the compound I analogue decayed to compound II, having the UV−vis spectrum [$\lambda_{max}(\epsilon \times 10^{-3})$] 409 (23.06), 595 (5.02) nm. For
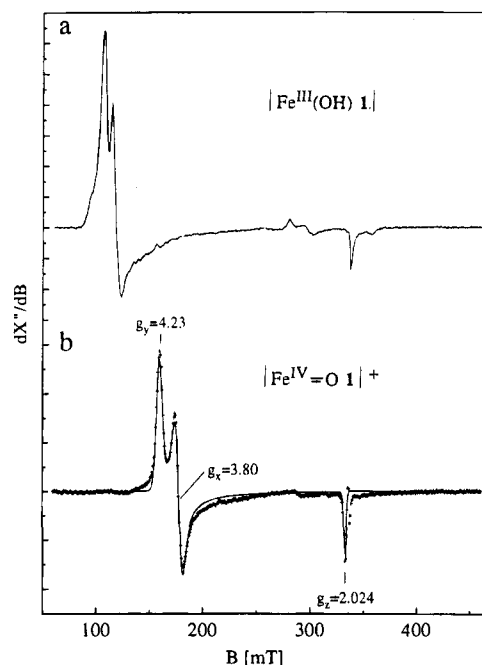
Figure 2. (a) X-band EPR spectrum of |Fe^{III}(OH) 1| in butyronitrile solution. Conditions: 10 K; ν = 9.4 GHz; microwave power, 20 μW; modulation amplitude, 2 mT. (b) X-band EPR spectrum of |Fe^{IV}=O 1|$^+$, same conditions as in part a; simulation (solid line) parameters: D = 23 cm^{-1}, E/D = 0.053, J_0 = 29.2 cm^{-1}, g_{eff} = (3.80, 4.23, 2.02), Gaussian line widths Γ = (7, 6, 2.8 mT).
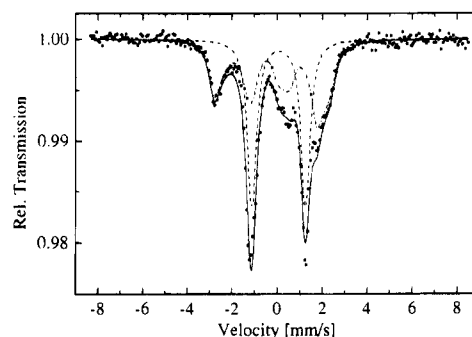
Figure 3. Mössbauer spectrum in butyronitrile. Conditions: 4.2 K, 20 mT field perpendicular to direction of γ-irradiation. Subspectrum of |Fe^{IV}=O 1|$^+$ (55%; dash-dotted line) simulated by parameters: δ = 0.01 mm s^{-1} ΔE_q = +1.25 mm s^{-1}, A = (−31.6, −27.4, −10 T) and Γ = 0.45 mm s^{-1}. Subspectrum of |Fe^{IV}=O 1| (45%; dashed line) simulated by parameters: δ = 0.07 mm s^{-1}, ΔE_q = 2.37 mm s^{-1}, Γ = 0.45 mm s^{-1}. Heavy line is sum of curves.

resonance Raman spectroscopy, the compound II analogue was generated by *m*-CPBA oxidation of |Fe^{III}(OH) 1| in 9:1 CH$_2$-Cl$_2$/THF at −80 °C. The resonance Raman spectra of the compound II analogue (traces not shown) are similar to that of the nonradical complex |Fe^{III}(OH) 1|. A weak band in the low-frequency region at 833 cm^{-1}, shifting to 812 cm^{-1} on oxidation with [^{18}O]-*m*-CPBA, is assigned to $\nu_{Fe=O}$ and is similar to $\nu_{Fe=O}$ of oxoferryl tetraarylporphyrins.[13,19] For both chlorin 1 and tetramesitylporphyrin,[16] $\nu_{Fe=O}$ of the compound I analogue with methanol as probable axial ligand is very close to that of the compound II analogue.

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