One-Electron Oxidation of the Porphyrin Ring of Cobaltous Octaethylporphyrin ($Co^{II}OEP$). Absorption and Resonance Raman Spectral Characteristics of the $Co^{II}OEP^{+\bullet}ClO_4^-$ π-Cation Radical

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Metalloporphyrins are subject to oxidation at both the metal and the porphyrin ligand to form metal- and porphyrin-centered oxidation products, respectively.[1] The ring-oxidized iron porphyrin cation radicals serve as transient intermediates in a variety of biological redox processes such as found in the catalytic cycles of cytochromes p-450 and horseradish peroxidase and catalase.[2] A number of factors contribute to the site of the oxidation including the electronegativity and oxidation state of the central metal,[3] the nature of peripheral substituents on the porphyrin moiety,[4] metal-axial ligand(s),[5] the medium,[6] and temperature.[7] Cobaltous porphyrins and their oxidized products have received considerable attention because cobalt, like iron, is capable of reversible redox reactions[8] and is present in vitamin B_{12}. Moreover, two-electron oxidation products of Co(II) octaethylporphyrin ($Co^{II}OEP$), for example, $Co^{III}OEP^{+\bullet}2ClO_4^-$ and $Co^{III}OEP^{+\bullet}2Br^-$, have been used to model the π-cation nature of compound I in peroxidases and catalases and to explore the nature of the porphyrin radical ground state.[9] It is well documented that $Co^{II}OEP$ (**1**) may be oxidized electrochemically[9] or chemically[10] in one-electron steps to $Co^{III}OEPX^-$ (**2**) and $Co^{III}OEP^{+\bullet}2X^-$ (**4**). During a chemical and spectroscopic study of these species we have observed an alternative one-electron oxidation product, $Co^{II}OEP^{+\bullet}ClO_4^-$ (**3**), a ring-centered oxidized species which contrasts with its well-documented metal-centered Co^{III} counterparts.[11] This report describes the preparation and preliminary characterization of this radical.

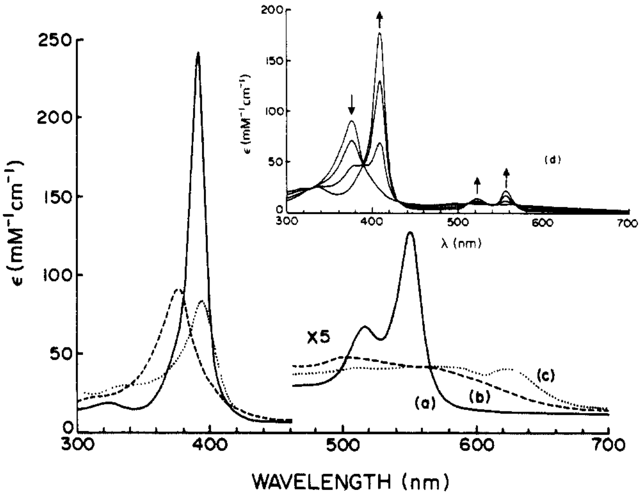

Figure 1. Electronic absorption spectra of $Co^{II}OEP$ derivatives: (a) $Co^{II}OEP$ (—); (b) $Co^{II}OEP^{+\bullet}ClO_4^-$ (---); (c) $Co^{III}OEP^{+\bullet}2ClO_4^-$ (···), in CH_2Cl_2; (d) spectral changes on addition of methanol to a methylene chloride solution of (b) producing $Co^{III}(CH_3OH)_2OEPClO_4^-$, total methanol content <0.01%.

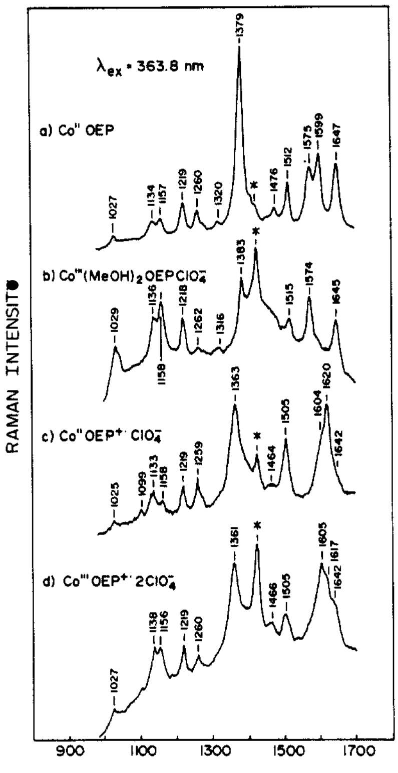

Figure 2. Resonance Raman spectra of (a) $Co^{II}OEP$, (b) $Co^{III}(CH_3OH)_2OEPClO_4^-$, (c) $Co^{II}OEP^{+\bullet}ClO_4^-$, and (d) $Co^{III}OEP^{+\bullet}2ClO_4^-$, excitation wavelength = 363.8 nm; samples were dissolved in dry CH_2Cl_2 except (b) which contained ~5% CH_3OH; spectra were measured in a quartz spinning cell with a laser power of 30-40 mW; the 1423-cm^{-1} band of CH_2Cl_2 is marked with an *.

3 is prepared by stirring a dry CH_2Cl_2 solution of **1** with a 3-fold excess of solid anhydrous $AgClO_4$ at room temperature for about 1 h. The bright red solution of **1** turns brownish red upon completion. The solution is then filtered and the product can be isolated by precipitation with hexane. In the optical spectrum of **3**, Figure 1a, the Soret band occurs at 376 nm (ε 9.24×10^4 M^{-1} cm^{-1}) and is ~1/3 as intense as that of **1** at 391 nm (ε 2.46×10^5 M^{-1} cm^{-1}). The region between 500 and 700 nm is broad and featureless, similar to that of other well-characterized porphyrin π-cation radicals.[1] The contribution of **3** is apparent in some previously reported optical spectra of "$Co^{III}OEPClO_4^-$" and $Co^{III}OEP^{+\bullet}2ClO_4^-$ (**4**) as a high-energy shoulder on the Soret absorptions. The presence of **3** was overlooked in earlier reports, most likely because this species is only stable in anhydrous noncoordinating solvents.[12] Titrative addition of water or methanol

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to a dry methylene chloride solution of **3** results in appearance of a species with absorption maxima at 409 (ϵ 1.80 × 10^5 M^{-1} cm^{-1}), 522, and 558 nm (Figure 1d). This new species presumably is $Co^{III}(ROH)_2OEPClO_4^-$ [13] as its optical characteristics are identical with those of typical Co^{III} porphyrin spectra;[14] i.e., the Soret peak is red-shifted by ~20 nm compared with that of **1**, and the relative intensities of the visible bands are decreased. The effect of "wet" solvent is reversible: if the solvent of the 409-nm species is evaporated to dryness and the residue is redissolved in dry CH_2Cl_2, the 376-nm species reappears. It seems that an authentic $Co^{III}OEPClO_4^-$ species, stripped of other coordinating solvents or ligands, does not exist.

3 is ESR silent.[15a,16] This indicates that the unpaired electron of low-spin Co^{II} in the d_{z^2} orbital of **3** is spin-coupled with the porphyrin unpaired electron.[17] The magnetic susceptibility of **3**[15b] at 50 K indicates a magnetic moment of 0.215 μ_B, most of which is likely to arise from contaminants,[16] and supports the quenching of the unpaired spins in **3**. This value may be contrasted with our measured values of 2.53 μ_B for **1** and 1.84 μ_B for **4** at this temperature.

Figure 2 shows the resonance Raman (RR) spectra of species **1**–**4** excited at 363.8 nm.[15c] Scattering from **1**, Figure 2a, is typical of Soret excited metalloporphyrin spectra and is dominated by totally symmetric vibrational modes.[18] The spectrum of **2**, Figure 2b, shows the effects of oxidation at the metal center. The high-frequency bands (above 1400 cm^{-1}) remain essentially unchanged in frequency, indicating little change in the core size of the ring.[19] Interestingly, ν_2,[20] occurring at 1599 cm^{-1} in **1**, is barely visible in **2** at 363.8 nm but is seen at 1596 cm^{-1} in spectra excited at 406.7 nm (not shown). The oxidation-state marker, ν_4, increases from 1379 to 1383 cm^{-1}, reflecting depopulation of porphyrin π^* orbitals caused by oxidation of the metal center.[18b] Except for some changes in the relative intensity of several of vibrational bands, the Raman spectra of **3** and **4** are essentially identical and radically different from RR spectra of **1** and **2** with unoxidized porphyrin rings. The most intense band in the RR spectra of both the π-cation species, Figure 2c,d, occurs at ~1362 cm^{-1} and is tentatively assigned to ν_4. The 20-cm^{-1} difference between this value and the value of ν_4 for **1** and **2** is presumably consistent with depopulation of the porpyrin a_{2u} π orbital.[15c,21] The IR spectra of **3** and **4**[15d] display bands at 1576 ± 5 and 1554 ± 5 cm^{-1}, respectively, diagnostic of porphyrin π-cation radicals.[22] The similarity between the vibrational spectra of $Co^{II}OEP^{+\bullet}ClO_4^-$ and of the authentic π-cation radical $Co^{III}OEP^{+\bullet}2ClO_4^-$ provides strong evidence that the former is also a π-cation radical.

The $AgClO_4/CH_2Cl_2$ oxidation method appears to be applicable in the preparation of other metalloporphyrin π-cation radicals such as $ZnTPP^{+\bullet}ClO_4^-$ (TPP = tetraphenylporphyrin), $ZnOEP^{+\bullet}ClO_4^-$, $CuOEP^{+\bullet}ClO_4^-$, and OEP itself. However, it fails to react with $Co^{II}TPP$, or $Cu^{II}TPP$, to give the corresponding divalent metal porphyrin radical. Assuming that this is due to the difference in the oxidation potential between OEP and TPP, the oxidizing power of the $AgClO_4/CH_2Cl_2$ is limited to ~+0.9 V (SCE).

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(12) (a) Electrochemical oxidation of $Co^{II}OEP$ carried out in CH_2Cl_2 and CH_3CN yields very different optical spectra; in CH_2Cl_2 it has features similar to that of **3** (Fujita, E.; Fajer, J., private communication). (b) Setsune et al. recently observed the 376-nm species but no assignment was made: Setsune, J.-i.; Ikeda, M.; Kishimoto, Y.; Kitao, T. *J. Am. Chem. Soc.* **1986**, *108*, 1309. (c) Sholz et al. have also suggested that oxidation of $Co^{II}TPP$ leads to a π-radical, $Co^{II}TPP^{+\bullet}SbCl_6^-$: Scholz, W. F.; Reed, C. A.; Lee, Y. A.; Scheidt, W. R.; Lang, G. *J. Am. Chem. Soc.* **1982**, *104*, 6791.

(13) Our preliminary optical and RR data (not shown) favor this assignement; nevertheless, the mixed diaxial Co^{III} $(CH_3OH)(ClO_4^-)OEP$ is not yet ruled out.

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(16) A residual ESR signal was often detected in the preparation, amounting to 3–4% of the spin density of **4**; however, it was verified to be due to contaminants for the following reasons. (a) Upon conversion by addition of methanol of **3** into **2**, which is a diamagnetic d^6Co^{III} species, the signal persisted with the same intensity. (b) Increasing the initial ratio of $AgClO_4$ to **1** resulted in a higher signal intensity. (c) The intensity of residual contaminant diminished upon repeated evaporating–redissolving **3** in CH_2Cl_2.

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Nuclear Spin Coherence Transfer in Photochemical Reactions

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The idea of labeling nuclear spin magnetization in the study of chemical reactions dates back to the famous saturation transfer experiment of Forsen and Hoffman.[1] This experiment, designed for chemically exchanging systems, has seen many applications, recently, for instance, in ^{31}P NMR studies of cell metabolism.[2] The two-dimensional analogue of it has been proposed by Jeener et al.[3] (2D exchange spectroscopy). Sagdeev and co-workers have applied radiofrequency labeling techniques to thee study of one-sided chemical reactions.[4] All these experiments involve *z*-magnetization labeling either through saturation or inversion of nuclear spins.

We propose here a two-dimensional experiment, whereby use is made of *xy*-magnetization labeling of nuclear spins. It can be used to study one-sided chemical reactions where the chemical change is brought about in a pulsed fashion, such as in flash photolysis. Comparison with a similar 2D experiment based on *z*-magnetization transfer shows that the coherence transfer experiment is inherently more sensitive. Furthermore a comparison of both may be particularly informative in situations where dephasing occurs (e.g., in the presence of paramagnetic intermediates), since the decay of *xy*-magnetization may be quite different from that of *z*-magnetization. In the latter case the two methods provide complementary information.

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