Octaethylcorrphycene and Its Metal Complexes. Radiolytic Reduction Studies

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Received: October 15, 1997; In Final Form: November 10, 1997

One-electron and multielectron reductions of 2,3,6,7,11,12,17,18-octaethylcorrphycene (H_2OECn) and its Sn(IV), Fe(III), Co(II), Ni(II), Cu(II), and Ag(II) complexes in 2-propanol (2-PrOH) solutions have been studied by radiolytic techniques. Formation and decay of unstable intermediates formed upon one-electron reduction have been followed by kinetic spectrophotometric pulse radiolysis. The absorption spectra of stable reduction products have been recorded following γ-radiolysis. H_2OECn is reduced to a transient π-radical anion, $(H_2OECn)^{\bullet -}$, which decays by disproportionation to form a product with a chlorin-like spectral signature. $Sn^{IV}OECn$ is reduced to a stable π-radical anion and subsequently to the dianion, which protonates to a species that, on the basis of its spectral characterization, is considered to be a phlorin-anion-type product. Fe(III), Co(III), Co(II), and Ag(II) corrphycenes undergo radiolytic reduction at the metal center. The Fe(II) and Co(I) corrphycenes produced are stable, and upon further reduction in neutral solutions they yield species with chlorin-like spectral signatures. When similar reductions are carried out in alkaline solutions, species with phlorin-anion-like characteristics are produced. $Ag^{I}OECn$, due to its large ionic radius, undergoes demetalation. $Cu^{II}OECn$ is reduced at the ligand in neutral 2-PrOH, but in alkaline solutions it forms an unstable $Cu^{I}OECn$ complex, which disproportionates and demetalates. In contrast, reduction of $Ni^{II}OECn$ yields the π-radical anion in acidic, neutral, and alkaline 2-PrOH solutions. These results suggest that the larger size of the corrphycene core, as compared with that of porphycenes, results in greater stability of complexes with metal ions of and larger radii. Ni(II), Co(II), and Fe(II) corrphycenes also react rapidly with $^{\bullet}CH_3$ radicals to form σ-bonded $CH_3{-}M^{III}OECn$ complexes. Whereas the $CH_3{-}Ni^{III}OECn$ complex decays within <1 ms, the $CH_3{-}Fe^{III}OECn$ complex proved stable in the absence of oxygen, and the corresponding $CH_3{-}Co^{III}OECn$ species was found to be stable even in the presence of O_2.

Introduction

Porphyrinoid macrocycles form coordination complexes with a wide variety of metal ions in a range of different oxidation states. The stability of these complexes is known to depend in part on a proper size on the matching between the metal ion and the macrocycle cavity. For example, porphyrinoid macrocycles with a larger cavity size may stabilize complexes with metal ions of lower oxidation states and larger radii.[2] Porphyrin−metal complexes with unusually low or high oxidation states are of interest in that they serve as intermediates in a range of catalytic and electron-transfer processes.[3]

Porphycenes and corrphycenes are nonnatural porphyrin isomers with cavity sizes that differ from those of the porphyrins. In porphycenes, the four nitrogens define a rectangle with N−N distances of 2.83 and 2.63 Å. They thus stand in contrast to the porphyrins, where the four nitrogens form a square with N−N distances of 2.89 Å. The smaller size of the porphycene cavity restricts the accommodation of reduced metal ions of large ionic radii.[2j] This has been demonstrated in the reduction of Ni(II) and Co(II) tetrapropylporphycene, which leads to the formation of π-radical anions,[4] whereas the analogous metalloporphyrins are reduced at the metal center.[5] Conversely, the smaller size of the porphycene cavity serves to stabilize higher transition-metal oxidation states and has allowed the formation of stable Ni(III) porphycene.[6]

Corrphycene is a relatively new porphyrin isomer that contains its four nitrogens arranged in a planar trapezoid with N−N distances of 2.539, 2.799, and 3.447 Å (Figure 1).[2] Despite this unsymmetrical pattern, a variety of transition metals (Fe(III), Co(II), Ni(II), Cu(II), Ag(II), and Sn(IV)) can be incorporated into the corrphycene ring. In the present study we examine the reduction of free base octaethylcorrphycene and several metallocorrphycenes by radiolytic methods. We find that, in comparison to what is true for porphyrins and porphycenes, the larger cavity size results in the stabilization of lower oxidation states.

Experimental Section

Free base 2,3,6,7,11,12,17,18-octaethylcorrphycene (H_2-OECn) and its Fe(III), Co(II), Ni(II), Cu(II), Ag(II), and Sn(IV) complexes were prepared as described elsewhere.[8] The divalent metal complexes were neutral, $M^{II}OECn$, while those of higher valence, namely $ClFe^{III}OECn$ and $Cl_2Sn^{IV}OECn$, were studied in the form of the chloride complexes. In discussing the redox reactions of these compounds, we omit the chloride (or solvent) axial ligands and the positive charges of species

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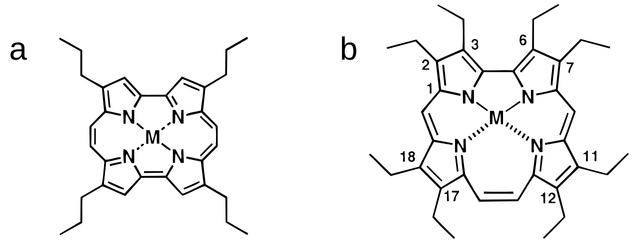
S1089-5639(97)03341-0 CCC: $15.00



$M^{II}TPrPc$ $M^{II}OECn$

Figure 1. Structures of metalloporphycenes and metallocorrphycenes (TPrPc = 2,7,12,17-tetrapropylporphycene; OECn = 2,3,6,7,11,12,17,18-octaethylcorrphycene).

such as $Fe^{III}OECn$ and $Sn^{IV}OECn$ in order to emphasize the negative charges added upon reduction of the ligand. The other materials used were analytical reagents, mainly from Mallinckrodt.[9] Solutions containing 5×10^{-6} to 1×10^{-4} mol L^{-1} corrphycene or metallocorrphycene were freshly prepared and were irradiated after purging with N_2 or Ar. Most experiments were done using 2-PrOH as the solvent. In some experiments this solvent was made acidic by adding $HClO_4$ or basic by adding NaOH or KOH. Steady-state irradiations were done in a Gammacell 220 ^{60}Co source with a dose rate of $\approx$1 Gy s^{-1}. Irradiation times were up to several minutes. Optical absorption spectra were recorded within several minutes before and after irradiation. Pulse radiolysis experiments were performed by utilizing 50 ns pulses of 8 MeV electrons from a Model TB-8/16-1S electron linear accelerator. Basic details of the equipment and the data analysis have been described elsewhere.[10] Dosimetry was based on the oxidation of SCN^- to $(SCN)_2^{\bullet-}$. The dose per pulse was varied between 14 and 27 Gy, which in aqueous solutions gives between $(8-16) \times 10^{-6}$ mol L^{-1} of radicals. Kinetic traces were recorded at various wavelengths, showing bleaching of the starting corrphycene or formation of the corrphycene product. Differential absorption spectra were measured after the completion of the kinetic process observed and were not corrected for the bleaching of the parent compound. All experiments were carried out at room temperature, 21 ± 2 °C.

Results and Discussion

Reduction of corrphycene (H_2OECn) and metallocorrphycenes (MOECn) was carried out by irradiating in deoxygenated 2-PrOH solutions. The radiolysis of this solvent produces two strong reductants, e_{sol}^- and $(CH_3)_2{}^{\bullet}COH$ (or $(CH_3)_2{}^{\bullet}CO^-$ in basic solution), which have been shown to reduce many porphyrins and porphycenes.[7,14,16] The reduction potential of $(CH_3)_2{}^{\bullet}COH$ in water is -1.39 V vs NHE, and that of $(CH_3)_2{}^{\bullet}CO^-$ is -2.1 V.[11] Therefore, these species are expected to transfer an electron to metallocorrphycenes with less negative reduction potentials (eq 1).[12]

$$\mathrm{MOECn} + (\mathrm{CH_3})_2{}^{\bullet}\mathrm{COH} \rightarrow (\mathrm{MOECn})^{\bullet-} + (\mathrm{CH_3})_2\mathrm{CO} + \mathrm{H}^+ \qquad (1)$$

The spectra of transient species and stable products were recorded using standard techniques (see Experimental Section) and were used to characterize the reduction products. On the basis of what is observed with porphyrins and porphycenes, it was considered likely that reduction of metallocorrphycenes could take place at either the macrocylic ligand or the metal center.[4a,13,16] It was thus deemed important to establish which process, if any, was dominant for a given MOECn complex. This, in turn, required an assignment of the optical absorption spectra characteristics of the ligand-reduced and metal-reduced species. This is done by studying the free base corrphycene in comparison with the metallocorrphycenes.

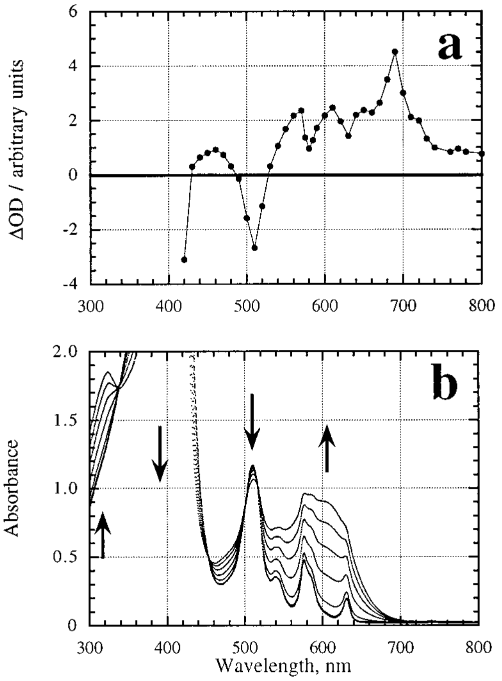


Figure 2. Radiolytic reduction of H_2OECn in deoxygenated 2-PrOH solutions. (a) Differential absorption spectrum monitored by pulse radiolysis, 200 μs after the pulse, after completion of the reduction reaction. (b) γ-Radiolytic reduction. The doses were 0, 25, 75, 175, 275, 475, 675, and 875 Gy; the arrows indicate the direction of absorption changes during the course of irradiation.

Free Base Corrphycene (H_2OECn). The differential absorption spectrum recorded upon pulse radiolysis of a deoxygenated 2-PrOH solution of H_2OECn (1×10^{-5} mol L^{-1}) (Figure 2a) exhibits a broad band at 650−750 nm and bleaching of the starting material (the Soret peak at 414 nm, $\epsilon = 151\,900$ L mol^{-1} cm^{-1}, and the Q-band at 511 nm, $\epsilon = 15\,800$ L mol^{-1} cm^{-1}). It is further noticed that the broad band at 650−750 nm contains two minima at ~590 and 630 nm (Figure 2a) which correspond to the minor peaks of H_2OECn (at 585 nm, $\epsilon = 4400$ L mol^{-1} cm^{-1}, and 630 nm, $\epsilon = 2600$ L mol^{-1} cm^{-1}). Since radiolysis of deoxygenated 2-PrOH leads to the formation of reducing species, and since one-electron reduction of H_2OECn can yield only the π-radical anion, the spectral changes observed are attributed to the π-radical anion, $(H_2OECn)^{\bullet-}$. As in the case of porphyrins and porphycenes, this is characterized mainly by a broad absorption feature in the 650−750 nm region; this band was thus used to identify π-radical anions obtained from metallocorrphycenes (see below).

The radical anion is formed in two steps, by a diffusion-controlled reaction with the solvated electron and a slower electron transfer from $(CH_3)_2{}^{\bullet}COH$, occurring with a rate constant of 5×10^8 L mol^{-1} s^{-1}.

To examine the stable products of reduction, γ-radiolysis experiments were carried out with similar solutions. The optical absorption spectra recorded before and after several irradiation intervals (Figure 2b) show a gradual decrease in the intensity of the peaks of the starting material and a growing in of a broad absorption feature in the 550−650 nm region. (Isosbestic points are also observed at 450, 500, and 520 nm.) This spectrum is different than that observed at short times after the pulse and leads us to suggest that a stable product is formed by disproportionation and protonation of the unstable π-radical anion.

The finding that the product formed from H_2OECn absorbs near 600 nm and is stable under O_2 allows us to assign it as being a chlorin-type product, i.e., a product of two-electron reduction which is doubly protonated at a pyrrole ring (eq 2).[14] The absorption peak for this presumed chlorin-type product is much broader than that of the chlorins derived from typical porphyrins. This is unexpected since several isomeric products with slightly different peaks should be formed in the case of corrphycene.

$$2H_2OECn^{\bullet -} + 2H^+ \rightarrow H_2OECn + H_2OECnH_2 \qquad (2)$$

Upon continued radiolysis this product transforms into a species absorbing weakly at lower wavelengths (with maxima at 349 and 500 nm), which we attribute to bacteriochlorin-type products, wherein two of the pyrrole ring have become partly saturated.

Radiolytic reduction of H_2OECn in alkaline 2-PrOH solutions also gives rise to stable products with chlorin-like spectral features. However, it was noticed in these experiments that the spectrum recorded within several seconds after irradiation exhibited absorptions similar to those of $H_2OECn^{\bullet -}$, which is believed to decay to a chlorin-like product. In light of this, it is assumed that the alkaline conditions somewhat stabilize $H_2OECn^{\bullet -}$ by (i) eliminating radiolytically generated protons and (ii) suppressing the putative proton-induced disproportionation.

The spectrum of H_2OECn was the same in neutral and in alkaline solutions, indicating that no deprotonation of the pyrrolic NH protons takes place in 2-PrOH containing 0.01 mol L^{-1} KOH. In contrast, in acidic solution (0.01 mol L^{-1} $HClO_4$) the absorption maxima shifted to 416, 556, and 600 nm. This result is considered consistent with further protonation taking place on the pyrrolic nitrogen to form, presumably, species such as H_4OECn^{2+}. Radiolysis of this acidic form resulted in the formation of a product that exhibits an intense absorption at 710 nm and that may be oxidized by O_2 to regenerate the starting material H_2OECn. On this basis, the reduction product produced in acid solutions is ascribed to a phlorin-type product (protonated at a meso position, not at a pyrrole ring). The absorption characteristics of free base corrphycene and of the various metallocorrphycenes studied as well as those of their reduction products are summarized in Table 1.

Tin Corrphycene ($Cl_2Sn^{IV}OECn$). The stability of π-radical anions of metalloporphyrins and metalloporphycenes has been shown to increase as the reduction potential becomes more positive.[4a,14] This effect is particularly notably in the case of Sn(IV) porphyrins; as a general rule, these form stable π-radical anions even in neutral aqueous solutions (in the absence of O_2). Accordingly, we expected Sn^{IV}OECn, which has a reduction potential of −0.97 V vs SCE in CH_2Cl_2, as compared with −1.32 V for the free base,[12] to form a stable $Sn^{IV}OECn^{\bullet -}$ radical anion. As detailed below this expectation was met albeit only in part.

The differential absorption spectrum recorded upon pulse radiolytic reduction of a deoxygenated 2-PrOH solution of Sn^{IV}OECn (Figure 3a) exhibits absorption maxima at 610, 680, 700, and ~780 nm. Such spectral features are consistent with the formation of $Sn^{IV}OECn^{\bullet -}$. The spectra monitored following γ-radiolytic reduction of the same solution also contain peaks at 680, 700, and 780 nm (Figure 3b, dashed line) that resemble those found in the time-resolved experiments. The product formed under conditions of γ-radiolysis is thus also ascribed to the π-radical anion. This product was not stable and was converted within several minutes into a stable product that is characterized by absorptions at 655 and 760 nm. Further radiolytic reduction led to a complete conversion of Sn^{IV}OECn into this latter product (i.e., the one absorbing at 655 and 760 nm) (Figure 3b, dotted line). The intense broad peak at 760 nm is considered consistent with the formation of a phlorin-anion-type product. Support for this conclusion came from studies of its reactivity with O_2. Both the π-radical anion initially and the putative phlorin anion derived from it were found to be quantitatively oxidized by O_2 to regenerate Sn^{IV}OECn. It should be noted that the π-radical anion was unstable even in alkaline 2-PrOH solutions and underwent disproportionation within several minutes.

$$2Sn^{IV}OECn^{\bullet -} + H^+ \rightarrow Sn^{IV}OECn + Sn^{IV}OECnH^- \quad (3)$$

Radiolytic reduction of Sn^{IV}OECn in acidic 2-PrOH solutions resulted in the formation of a product with chlorin-like spectral features that was not reoxidized by O_2.

Iron Corrphycene (FeOECn). This complex was synthesized and studied in the form of its chloride derivative, $ClFe^{III}$OECn. Although initially prepared in this manner, the spectrum of this complex was found to be strongly dependent on the actual solution phase conditions (i.e., on the actual axial ligands bound to the iron). In neutral and acidic 2-PrOH solutions the Soret band falls at 407 nm and the Q-bands appear at 524 and 665 nm. In alkaline 2-PrOH there is a split Soret band; the peaks are at 360, 400, 445, and 572 nm. These shifts probably are due to ionization of the $(CH_3)_2CHOH$ axial ligand in alkaline solutions. In the presence of pyridine (1.2×10^{-2} mol L^{-1}) the Soret band was similar to that observed in neutral 2-PrOH, but slightly shifted to the blue (i.e., λ_{max} 407 → 404 nm) with the other peaks appearing at 520 and 668 nm (Table 1). At this low concentration of pyridine the complex is most probably in the form of $Cl(Py)Fe^{III}$OECn. Replacement of the chloride to form $[(Py)_2Fe^{III}OECn]^+$ likely requires a much higher concentration of pyridine, as is the case with iron porphyrins. Consistent with this thinking is the observation that in the presence of 0.6 mol L^{-1} pyridine the Soret band appeared also split with maxima at 380 and 402 nm.

γ-Radiolysis of any of the above Fe(III) corrphycene solutions in the absence of O_2 resulted in the formation of Fe^{II}OECn. The spectral changes are similar to those observed in the case of iron porphyrins. In particular, the Soret band of Fe^{II}OECn was found to be much sharper than that of Fe^{III}OECn. This peak is found at 438 nm in neutral and alkaline 2-PrOH and in the presence of pyridine. The main Q-band was at 558 nm, with an additional small peak near 600 nm (Figure 4 and Table 1). The Fe^{II}OECn species produced in this way react rapidly with O_2 to regenerate the original Fe^{III}OECn. Reduction of Fe^{III}OECn by Pd/H_2 gave the same spectra.

The reduction behavior of Fe^{III}OECn in acidic 2-PrOH solutions, however, was quite different. Although the spectrum of starting Fe^{III}OECn complex was similar to that recorded in neutral 2-PrOH, that of the Fe^{II}OECn complex produced upon radiolytic reduction was shifted; specifically, the Soret peak appeared at 418 nm instead of 438 nm. Furthermore, the Fe^{II}OECn species formed under these acidic conditions was not oxidized by O_2. This is interpreted in terms of a shift in the Fe^{II}/Fe^{III} reduction potential due to protonation of the $(CH_3)_2CHO^-$ axial ligand. When the acidic 2-PrOH solution of Fe^{II}OECn was made alkaline, the complex was readily reoxidized to Fe^{III}OECn in the presence of O_2.

Further radiolytic reduction of Fe^{II}OECn in alkaline 2-PrOH solutions led to formation of a product that exhibits a broad absorption at 760 nm and a weak Soret band (similar to Figure 3b). This product is rapidly oxidized by O_2 to regenerate Fe^{III}-

TABLE 1: Absorption Peaks of the Corrphycenes and Their Radiolytic Reduction Products

corrphycens and products	medium	peaks, nm (relative intensity)
H_2OECn	2-PrOH	410 (100), 508 (15), 540 (4), 576 (6), 630 (2)
H_2OECnH_2	2-PrOH	322 (100), 410, 511 (61), 576 (55), 605 (50)
H_2OECnH_4	2-PrOH	349 (100), 500 (10)
H_2OECn	2-PrOH/KOH	410 (100), 508 (15), 540 (4), 576 (6), 630 (2)
$H_2OECn^{\bullet-}$	2-PrOH/KOH	650−750
H_2OECnH_2	2-PrOH/KOH	322 (100), 410, 511 (61), 576 (55), 605 (50)
H_4OECn^{2+}	2-PrOH/$HClO_4$	416 (100), 556 (6), 600 (3)
$H_4OECnH_2^{2+}$	2-PrOH/$HClO_4$	548 (100), 710 (93)
$Sn^{IV}OECn$	2-PrOH	374 (30), 424 (100), 554 (16), 592 (5)
$Sn^{IV}OECn^{\bullet-}$	2-PrOH	424 (100), 632 (1), 680 (4), 700 (3), 780 (2)
$Sn^{IV}OECn^{2-}$	2-PrOH	355 (50), 413 (100), 472 (20), 635 (20), 762 (38)
$Sn^{IV}OECn$	2-PrOH/KOH	374 (30), 424 (100), 552 (16), 592 (5)
$Sn^{IV}OECn^{\bullet-}$	2-PrOH/KOH	424 (100), 632 (1), 680 (4), 702 (2), 780 (1)
$Sn^{IV}OECn^{2-}$	2-PrOH/KOH	424 (100), 510 (7), 790 (14)
$Sn^{IV}OECn$	2-PrOH/$HClO_4$	374 (30), 424 (100), 554 (16), 592 (5)
$Sn^{IV}OECnH_2$	2-PrOH/$HClO_4$	322 (100), 511 (61), 576 (55), 605 (50)
$ClFe^{III}OECn$	2-PrOH	360 (sh), 406 (100), 520 (10), 668 (3)
$Fe^{II}OECn$	2-PrOH	380 (20), 436 (100), 526 (8), 558 (10), 596 (5)
$ClFe^{III}OECn$	2-PrOH/KOH	364 (88), 402 (100), 446 (63), 574 (16)
$Fe^{II}OECn$	2-PrOH/KOH	361 (20), 438 (100), 558 (10), 596 (5)
$Fe^{II}OECnH^-$	2-PrOH/KOH	350 (100), 520−540 (38), 780 (70)
$ClFe^{III}OECn$	2-PrOH/$HClO_4$	360 (sh), 404 (100), 520 (10), 668 (3)
$Fe^{II}OECn$	2-PrOH/$HClO_4$	418 (100), 557 (6), 601 (4)
$Cl(py)Fe^{III}OECn$	2-PrOH/py (0.1 vol %)	360 (sh), 404 (100), 520 (10), 668 (3)
$Cl(py)Fe^{II}OECn$	2-PrOH/py (0.1 vol %)	381 (30), 438 (100), 526 (8), 558 (11), 597 (4)
$(py)_2Fe^{III}OECn$	2-PrOH/py (5 vol %)	380 (87), 402 (100), 440 (50), 570 (10), 664 (2)
$(py)_2Fe^{II}OECn$	2-PrOH/py (5 vol %)	434 (100), 524 (13), 555 (12), 590 (4)
$CH_3{-}Fe^{III}OECn$	2-PrOH/CH_3Cl	415 (90), 432 (100), 558 (12), 640 (5), 730 (5)
$Co^{III}OECn$	2-PrOH	386 (75), 444 (100), 563 (19), 602 (16)
$Co^{II}OECn$	2-PrOH	405 (100), 525 (15), 640 (10)
$Co^{I}OECn$	2-PrOH	413 (100), 533 (11), 622 (8)
$Co^{I}OECnH_2$	2-PrOH	413 (100), 540 (20), 640 (16), 690 (14)
$Co^{II}OECn$	2-PrOH/KOH	404 (100), 560 (11), 608 (10)
$Co^{I}OECn$	2-PrOH/KOH	410 (100), 520 (10), 640 (5)
$(py)_2Co^{III}OECn$	2-PrOH/py	386 (75), 444 (100), 553 (19), 592 (16)
$(py)_2Co^{II}OECn$	2-PrOH/py	410 (100), 540 (9), 650 (5)
$(py)_2Co^{I}OECn$	2-PrOH/py	414 (100), 458 (18), 535 (14), 575 (14)
$(py)_2Co^{I}OECnH^-$	2-PrOH/py	630 (80), 680 (100), 710 (80), 780 (10)
$Co^{II}OECn$	CH_2Cl_2	405 (100), 528 (11), 630 (4)
$ClCo^{III}OECn$	CH_2Cl_2	382 (100), 440 (71), 558 (24), 602 (18)
$CH_3{-}Co^{III}OECn$	2-PrOH/CH_3Cl/KOH	414 (100), 495 (12), 540 (10), 640 (5), 680 (5)
$Co^{II}OECn$	2-PrOH/CH_3Cl/HCl	390 (55), 440 (100), 550 (12), 592 (10)
$CH_3{-}Co^{III}OECn$	2-PrOH/CH_3Cl/HCl	414 (100), 490 (10), 545 (9), 640 (4), 680 (4)
$Ni^{II}OECn$	2-PrOH	395 (100), 458 (23), 537 (10), 622 (11)
$Ni^{II}OECnH^-$	2-PrOH	395 (100), 625 (8), 786 (26)
$Ni^{II}OECnH_2$	2-PrOH	310 (100), 500 (30)
$Ni^{II}OECn$	2-PrOH/KOH	395 (100), 458 (23), 537 (10), 622 (11)
$Ni^{II}OECnH^-$	2-PrOH/KOH	312 (25), 395 (100), 622 (10), 804 (20)
$Cu^{II}OECn$	2-PrOH	435 (100), 551 (13), 594 (10)
$Cu^{II}OECnH_2$	2-PrOH	322 (100), 511 (61), 576 (55), 605 (50)
$Cu^{II}OECn$	2-PrOH/KOH	435 (100), 551 (13), 594 (10)
$Cu^{II}OECnH^-$	2-PrOH/KOH	330, 435, 623, 764
$Ag^{II}OECn$	2-PrOH/KOH	382 (32) 445 (100), 551 (14), 594 (10)
H_2OECn	2-PrOH/KOH	410 (100), 508 (15), 540 (4), 576 (6), 630 (2)
$Ag^{II}OECn$	2-PrOH	382 (32) 445 (100), 551 (14), 594 (10)
H_2OECn	2-PrOH	410 (100), 508 (15), 540 (4), 576 (6), 630 (2)

OECn. In light of the results discussed above and in consideration of previous findings with metalloporphyrins, this product is ascribed to a phlorin-anion-type species, $Fe^{II}OECnH^-$. This product was not observed when $Fe^{II}OECn$ was radiolytically reduced in neutral 2-PrOH. In this latter instance, unidentified degradation products were formed, and very little of the original iron corrphycene was found to be regenerated upon air oxidation. Reduction in acidic solutions, however, did give rise to a product with a strong absorption in the red, similar to that of a phlorin anion. However, its lowest energy absorption was found to fall at 710 nm (instead of 760 nm), leading us to propose that it may be a protonated form of the same species. This product was found to undergo oxidation in the presence of O_2, although much more slowly than the product obtained in alkaline solutions. Interestingly, it is oxidized to form $Fe^{II}OECn$ and not $Fe^{III}OECn$.

The above phlorin-type products are thought to arise as the result of disproportionation and protonation of the initial unstable one-electron reduction products. One-electron reduction of Fe^{II}-OECn is expected to lead to formation of $Fe^{I}OECn$, but this putative product was not sufficiently stable to be detected in the solutions studied above by γ-radiolysis. In an attempt to examine whether $Fe^{II}OECn$ is indeed reduced to a transient Fe^{I}-OECn or to a π-radical anion, we carried out pulse radiolysis

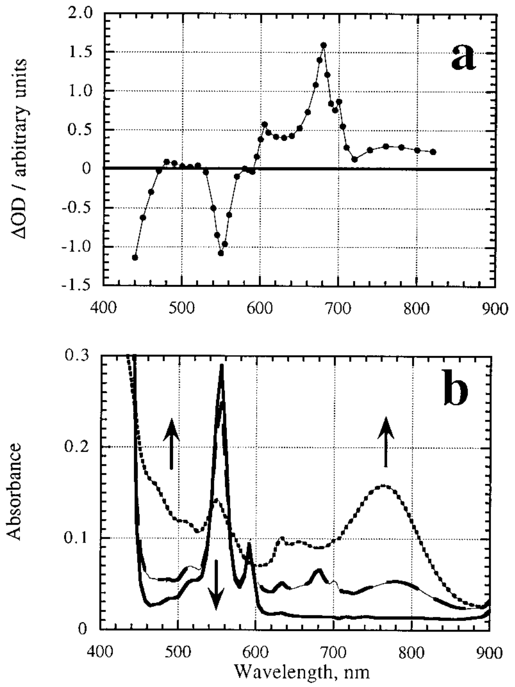


Figure 3. Radiolytic reduction of $Cl_2Sn^{IV}OECn$ in deoxygenated 2-PrOH solutions. (a) Differential spectrum monitored by pulse radiolysis, 200 μs after the pulse. (b) γ-Radiolytic reduction. The doses were 0, 185, and 1285 Gy; the arrows indicate the direction of absorption changes during the course of irradiation, showing the spectrum of the π-radical anion (dashed line) and the phlorin-anion-type product (dotted line).

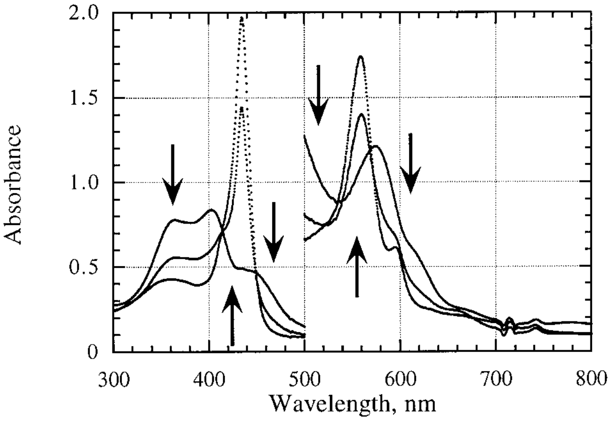


Figure 4. Radiolytic reduction of $ClFe^{III}OECn$ in deoxygenated 2-PrOH solutions. γ-Radiolytic reduction. The doses were 0, 275, and 475 Gy; the arrows indicate the direction of absorption changes during the course of irradiation.

experiments with $Fe^{II}OECn$ in alkaline 2-PrOH. The $Fe^{II}OECn$ solutions were prepared by quantitative reduction of $Fe^{III}OECn$ solutions, either by γ-radiolysis or by H_2 over Pd. Unfortunately, the handling of these solutions during the pulse radiolysis experiments led to partial oxidation by traces of O_2, and the mixtures of the resulting $Fe^{II}OECn$ solutions containing a small fraction of $Fe^{III}OECn$ were found to undergo reduction processes that involved predominantly the latter species.

Although we cannot confirm at this time that $Fe^{II}OECn$ is reduced to $Fe^{I}OECn$, we may assume that this reaction takes place, in analogy to the behavior of iron porphyrins.[15] $Fe^{I}OECn$ then may undergo two possible reactions. It may react with a proton from the solvent, to form a hydride complex (a species that would likely decompose to yield H_2 and $Fe^{II}OECn$). Alternatively, it may undergo disproportionation and protonation to form $Fe^{II}OECn$ and $Fe^{II}OECnH^-$. Since radiolytic reduction of $Fe^{II}OECn$ leads to the efficient production of what is thought to be the phlorin anion, $Fe^{II}OECnH^-$, we conclude that the latter route reflects the more likely mechanism for in in-situ decomposition.

Fe(II) porphyrins are known to form stable σ-bonded alkyl−iron complexes.[15b] To examine whether such products might be formed from the corrphycenes, we irradiated $Fe^{III}OECn$ in 2-PrOH solutions saturated with CH_3Cl. The latter solute reacts with solvated electrons to generate methyl radicals, while the solvent radicals reduce $Fe^{III}OECn$.

$$CH_3Cl + e_{sol}^- \rightarrow {}^{\bullet}CH_3 + Cl^- \tag{4}$$

$$Fe^{III}OECn + (CH_3)_2{}^{\bullet}COH \rightarrow Fe^{II}OECn + (CH_3)_2CO + H^+ \tag{5}$$

Subsequent reaction between these two products was expected to form the sought-after σ-bonded methyl adduct.

$$Fe^{II}OECn + {}^{\bullet}CH_3 \rightarrow CH_3{-}Fe^{III}OECn \tag{6}$$

As it transpired, the spectral changes recorded after γ-radiolysis of the above solution are indeed significantly different from those recorded in the absence of CH_3Cl (Table 1). They are thus ascribed to the formation of an $CH_3{-}Fe^{III}OECn$ complex. Upon exposure to O_2 the starting material, $Fe^{III}OECn$, is recovered quantitatively.

Cobalt Corrphycene (CoOECn). This metallo derivative was originally prepared in the form of the $Co^{II}OECn$ complex. However, when dissolved in 2-PrOH and stored under air, gradual oxidation to the Co^{III} form was observed (as in the corresponding porphyrin). The spectrum of the latter product was similar to that obtained upon oxidative radiolysis, such as irradiation in aerated CH_2Cl_2. To accelerate the air oxidation of $Co^{II}OECn$ and to obtain quantitative conversion, pyridine was added to the solution. Coordination of pyridine as an axial ligand makes the reduction potential of the cobalt complex more positive. In the presence of 5% pyridine the cobalt complex was rapidly converted into $(Py)_2Co^{III}OECn$. Radiolytic reduction of this product (i.e., reductive conversion back to the Co^{II} state) was followed by pulse radiolysis (Figure 5a, ●) and γ-radiolysis (Figure 5b) with the peak positions for the two species being given in Table 1. The spectral changes are somewhat similar to those observed with the corresponding iron complex.

Pulse radiolytic reduction of $Co^{II}OECn$ in 2-PrOH solution (in the absence of pyridine) resulted in absorption changes (Figure 5a, ○) that somewhat resemble those observed upon reduction of $Co^{III}OECn$ (Figure 5a, ●). This similarity and the lack of absorption near 700 nm are interpreted in terms of reduction of $Co^{II}OECn$ to $Co^{I}OECn$. This putative product was also observed following γ-radiolysis, leading us to consider this spectral assignment as secure. (Relevant peak positions are summarized in Table 1.) Exposure to O_2 resulted in quantitative recovery of $Co^{II}OECn$. Further radiolysis of $Co^{I}OECn$ led to reduction of the corrphycene ligand. The resulting species, with a chlorin-type absorption at 640 and 690 nm, was quite stable in the presence of oxygen. Indeed, only very slow recovery to the starting $Co^{II}OECn$ complex was observed.

Although time-resolved reduction of $Co^{II}OECn$ in acidic 2-PrOH leads undoubtedly to the formation of the monovalent cobalt complex (vide supra), γ-radiolysis of a similar solution did not reveal any noticeable changes in the absorption spectrum.

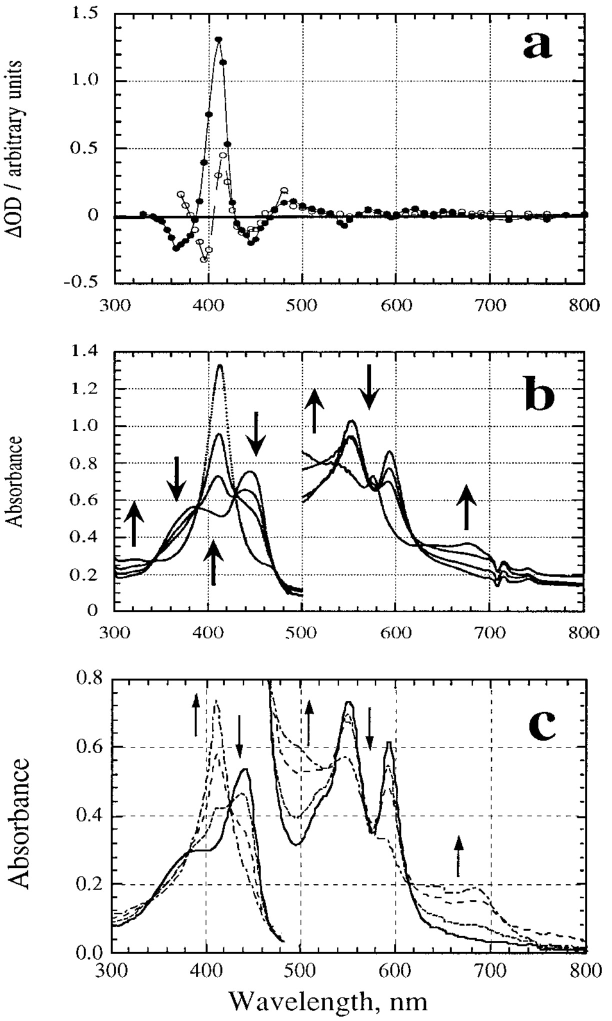


Figure 5. Radiolytic reduction of CoOECn in deoxygenated 2-PrOH solutions. (a) Comparison of the differential absorption spectra monitored by pulse radiolysis upon reduction of $Co^{III}OECn$ and Co^{II}-OECn. (●) $Co^{III}OECn$, in the presence of pyridine (5 vol %), recorded 100 μs after the pulse, (○) $Co^{II}OECn$, recorded 5 μs after the pulse. (b) γ-Radiolytic reduction of $Co^{III}OECn$ in the presence of pyridine. The doses were 0, 50, 100, and 200 Gy; the arrows indicate the direction of absorption changes during the course of irradiation. (c) γ-Radiolysis of $Co^{II}OECn$ in the presence of CH_3Cl, showing formation of CH_3-$Co^{III}OECn$. The doses were 0, 50, 100, and 200 Gy.

This can be rationalized in terms of a fast reoxidation (on the γ-radiolysis time scale) of the transient $Co^{I}OECn$ by the acidic medium.

The reaction of $Co^{II}OECn$ with $^{\bullet}CH_3$ radicals was studied via the γ-radiolysis of CH_3Cl-saturated 2-PrOH solutions. Under these conditions, new absorptions at 414, 490, 545, 640, and 680 nm appeared (Figure 5c) that are ascribed to $CH_3-Co^{III}OECn$. This presumed product was stable in the presence of O_2 in alkaline solutions but was found to be reoxidized readily in acidic solutions to regenerate the starting complex. The observation of the above absorption features in acidic media stands in contrast to what is found in the absence of CH_3Cl, where reoxidation of the initially formed $Co^{I}OECn$ complex by the acid precluded the detection of any stable product.

Production of methyl radicals during the radiolysis of 2-PrOH, although in small yield (~0.1 μmol J^{-1}), gives rise to the possibility that $Co^{II}OECn$ in the above reduction experiments may react with $^{\bullet}CH_3$ radicals. Comparison between Figure 5a (○) and Figure 5c reveals that the spectral changes, in particular around 410 nm, are distinctly different from each other. This confirms that reduction of $Co^{II}OECn$ is the predominant process in the radiolysis of the divalent Co complex in neat 2-PrOH.

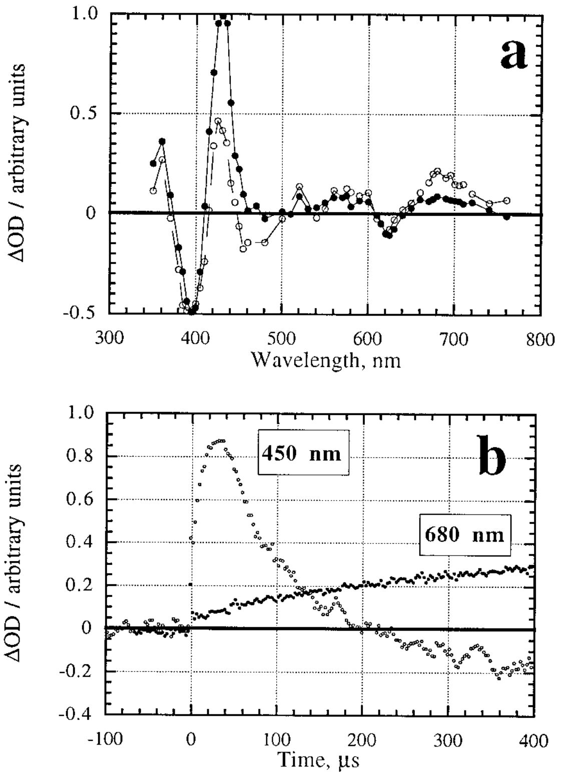


Figure 6. Radiolytic reduction of $Ni^{II}OECn$ in deoxygenated 2-PrOH solutions. (a) Differential absorption spectra monitored by pulse radiolysis, 40 μs (●) and 400 μs (○) after the pulse, the former showing formation of a sharp absorption at 430 nm ascribed to transient CH_3-$Ni^{III}OECn$ and the latter showing formation of the broad absorption around 680 nm ascribed to $Ni^{II}OECn^{\bullet-}$. (b) Representative traces showing the formation and decay of the transient absorptions at 450 and 680 nm.

Nickel Corrphycene (NiOECn). The differential spectrum recorded by pulse radiolysis of alkaline 2-PrOH solutions of $Ni^{II}OECn$ indicates the formation of a species absorbing at 680 nm (Figure 6a). By comparison with the results obtained with $H_2OECn^{\bullet-}$ and $SnOECn^{\bullet-}$, we ascribe this new absorption feature to the π-radical anion, $Ni^{II}OECn^{\bullet-}$ (eq 7).

$$Ni^{II}OECn + e^{-} \rightarrow Ni^{II}OECn^{\bullet-} \quad (7)$$

Based on a kinetic analysis, this species is thought to arise predominantly from the reaction of $Ni^{II}OECn$ with $(CH_3)_2{}^{\bullet}COH$ over the course of ~200 μs. In addition to this product, another species was observed at short times; it is characterized by a sharp peak at 430 nm and is seen to decay with a half-life of $\tau_{1/2} = 40$ μs. Representative kinetic traces for these two transients are shown in Figure 6b. In acidic solutions, the decay of the species characterized by the absorption at 430 nm was considerably faster ($\tau_{1/2} = 25$ μs), whereas that of the species absorbing at 680 nm remained the same.

The 430 nm peak is ascribed to the product of the reaction of methyl radicals (produced in small yields (~0.1 μmol J^{-1}) upon radiolysis of neat 2-PrOH) with $Ni^{II}OECn$, to form the unstable species $CH_3-Ni^{III}OECn$. A similar short-lived product has been shown to be produced upon reaction of Ni(II) porphyrins with methyl radicals.[17] Nonetheless, to confirm this assignment, we irradiated a 2-PrOH solution of $Ni^{II}OECn$ saturated with CH_3Cl, where the yield of methyl radicals is much higher. In fact, the yield of the species absorbing at 430 nm increased by a factor of 3.5, relative to what was seen in the absence of CH_3Cl. Also, the peak at 680 nm was not observed. Further evidence for the σ-bonded species was obtained from pulse radiolysis experiments involving the study of Ni^{II}OECn in N_2O-saturated *t*-BuOH solutions. These conditions produce significant quantities of $^{\bullet}CH_2(CH_3)_2COH$ radicals and gave rise to a short-lived species absorbing around 450 nm.

γ-Radiolytic reduction of Ni^{II}OECn in basic 2-PrOH led to the formation of a transient, ascribed to $Ni^{II}OECn^{\bullet-}$. Within minutes this latter species is transformed into a species (absorbing at 804 nm) that is considered to be a phlorin-like anion. Both products were oxidized by O_2 to regenerate the starting Ni^{II}OECn complex.

Copper Corrphycene (CuOECn). Pulse radiolytic reduction of Cu^{II}OECn in neutral 2-PrOH solutions forms a transient species absorbing at 680 and 780 nm (similar to Figures 2a and 3a) that is ascribed to the π-radical anion, $Cu^{II}OECn^{\bullet-}$. This species undergoes disproportionation over several hundred milliseconds to form a species with chlorin-type spectral properties This latter product, observed also in the γ-radiolysis experiments, is similar to that produced upon radiolysis of acidic Sn^{IV}OECn solutions and is similarly inert toward O_2.

By contrast, pulse radiolysis in alkaline 2-PrOH solutions indicated formation of a different product, i.e., one lacking an absorption feature near 680 nm (not shown, but differential changes resemble those depicted in Figure 5a). Because of the lack of resemblance to what is produced under conditions of neutral pulse radiolysis, this species is considered to be a metal-centered product, Cu^{I}OECN. It has been noticed before that reduction may take a different route in alkaline 2-PrOH as compared to neutral solution. In the case of Co porphycene,[4f] base-promoted reduction took place at the ligand rather than at the metal. That behavior was rationalized in terms of the alkaline conditions providing a stronger axial ligands (2-PrO$^-$ vs 2-PrOH) which increased the electron density at the metal center and militated against a metal-centered reduction process. In the present case the trend is reversed. This is ascribed to a change in the coordination geometry of the copper complex. The 2-PrO$^-$ ligand in the alkaline medium is a stronger ligand than 2-PrOH. As a result, the starting square-planar (tetracoordinated) Cu^{II}OECn is transformed into one with a pyramidal (pentacoordinated) geometry. This geometric change may place the copper out of the corrphycene plane and thus facilitate its reduction.

The above considerations aside, Cu^{I}OECn is not observed as a stable product under conditions of γ-radiolysis. Instead, the product exhibits absorptions at 330, 435, 623, and 764 nm, indicating the formation of a phlorin-anion-type product. This latter putative product changes over minutes and, after exposure to O_2, generates the free base form of corrphycene (H_2OECn). Such an observation leads us to suggests that Cu^{I}OECn does not undergo demetalation directly, despite the large radius of Cu(I) (0.96 Å). Rather it is $Cu^{II}OECnH^-$ that demetalates slowly.

Silver Corrphycene (AgOECn). Reduction of Ag^{II}OECn by the $(CH_3)_2{}^{\bullet}COH$ radical in neutral 2-PrOH solutions was too slow to be observed by pulse radiolysis at the low concentrations used, although γ-radiolysis resulted in reduction. Addition of 0.01 mol L^{-1} KOH leads to partial dissociation of $(CH_3)_2{}^{\bullet}COH$ into $(CH_3)_2{}^{\bullet}CO^-$, under which conditions Ag^{II}OECn is reduced more rapidly. Specifically, under these latter conditions, the spectral changes observed by pulse radiolysis show a sharp band around 460 nm and no noticeable absorbance in the 600−800 nm region (not shown), features that lead us to suggest that Ag^{I}OECn is being formed. This product did not change for several milliseconds.

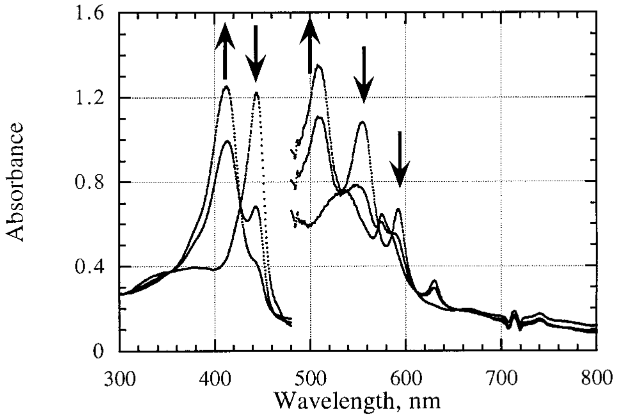


Figure 7. Radiolytic reduction of Ag^{II}OECn in deoxygenated 2-PrOH solutions containing 0.01 mol L^{-1} KOH. γ-Radiolytic reduction. The doses were 0, 50, and 100 Gy; the arrows indicate the direction of absorption changes during the course of irradiation.

Interestingly, γ-radiolysis of Ag^{II}OECn under these same basic conditions resulted in the transformation of the starting Ag^{II}OECn complex into a stable product with absorption features that are similar to those of H_2OECn (Figure 7, Table 1). This is taken as an indication that reduction to Ag^{I}OECn leads eventually to demetalation. This postulated demetalation process was observed even in the presence of KOH and is considered reasonable in view of the larger ionic radius of Ag(I) (1.26 Å) compared to Cu(I) (~0.96 Å);[18] certainly, it parallels what happens with a silver porphyrin in aqueous solution.[19]

Conclusion

The behavior of octaethylcorrphycene and most of its metal complexes, upon one-electron and multielectron reduction, is generally similar to that of the analogous porphyrins and porphycenes. All of these compounds are reduced very rapidly by solvated electrons and more slowly by the radicals derived from the 2-PrOH solvent. Reduction may take place at the metal center or at the macrocyclic ligand, and the spectral changes observed for each type of process are somewhat independent of the various macrocyclic structure. With specific metal complexes, however, the behavior was different for the different macrocycles. This difference may be ascribed to two factors: (a) variations in the size of the macrocycle cavity relative to the size of the metal ion (which can affect the stability of the complex) and (b) variations in the reduction potential of the macrocycle. As outlined above, porphycenes and porphyrins possess cavities of similar size (but not shape), whereas that of corrphycene is larger. This difference has been found to decrease the stability of porphycene complexes with low-oxidation state metal ions, relative to that of porphyrins. This results either in reduction of the macrocycle instead of the metal or in demetalation of the reduced complex. Corrphycenes, because of their larger cavity, exhibit the opposite effect, as demonstrated by the present results.

Independent of core size, changes in macrocycle reduction potential can determine whether reduction takes place at the metal center or at the ligand π-system. The reduction potential of the corrphycene ligand (−1.32 V vs SCE) is anodically shifted relative to that of porphycene (−0.94 V vs SCE). As a consequence, electron transfer to the corrphycene ligand is relatively inhibited and reduction of the metal center may predominate in certain cases. For comparison, the reduction potentials of porphyrins are −1.05 V vs SCE for H_2TPP and −1.46 V vs SCE for H_2OEP.

The reactions of the Ni(II), Co(II), and Fe(II) corrphycene complexes with methyl radicals were also found to reflect what is seen with porphyrins and porphycenes. In all cases, the corresponding σ-bonded $CH_3-M^{III}OECn$ complexes were formed. The stabilities of these species varied significantly and paralleled the behavior of the porphyrin and porphycene analogues. For instance, $CH_3Ni^{III}OECn$ was found to decay within <1 ms back to methyl radicals (which dimerize) and the starting Ni(II) complex. On the other hand, $CH_3Fe^{III}OECn$ was found to be stable in the absence of O_2, whereas $CH_3Co^{III}OECn$ was found to be stable even in the presence of O_2 in neutral solutions but unstable in acidic media.

Acknowledgment. This work was supported in part by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy. This is contribution No. NDRL-3999 from the Notre Dame Radiation Laboratory. J.L.S. acknowledges support from the National Science Foundation (CHE 9122161).

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