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Synthesis, Characterization, and Electrochemistry of Copper(II) and Palladium(II) Hydroporphyrins: The Copper(I) Octaethylisobacteriochlorin Anion

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The Cu(II) and Pd(II) complexes of *trans*-octaethylchlorin (OEC) and octaethylisobacteriochlorin (OEiBC) were synthesized and characterized. The redox behavior of these complexes and of the octaethylporphyrin complexes Cu(OEP) and Pd(OEP) were investigated in nonaqueous media. Potentials were determined by cyclic voltammetry in butyronitrile, methylene chloride, and dimethylformamide solutions. Oxidized and reduced species derived from these complexes were characterized by spectroscopic means. The first oxidation of all six complexes afforded M(II) cation radicals. The palladium(II) hydroporphyrin cation radicals were unstable on the time scale of electrolysis in all three solvents. With the exception of Cu(OEiBC), electrochemical reduction of the complexes afforded M(II) anion radicals. Chemical reduction of these complexes did not give the anion radicals, but instead proceeded directly on to the phlorin anion or chlorin–phlorin anion complexes, M(OEPH)$^-$ and M(OECH)$^-$, respectively. Electrochemical or chemical reduction of Cu(OEiBC) afforded the stable diamagnetic Cu^{I}(OEiBC)$^-$ anion. Unlike other Cu^{I}N$_4$ complexes, Cu^{I}(OEiBC)$^-$ does not appear to have measurable affinity for additional ligands. The rate of oxidation of the highly reducing Cu^{I}(OEiBC)$^-$ anion by O$_2$ or by alkyl halides is slower than for Ni^{I}(OEiBC)$^-$, an anion with a nearly equal reduction potential.

Work in our laboratory established that hydroporphyrin ligands stabilize the less common oxidation states Ni(I) and Ni(III).[1-3] In certain cases, Ni(III) is accessible in porphyrins, too.[4-7] However, authentic nickel(I) tetrapyrrole complexes have only been isolated upon reduction of either nickel(II) isobacteriochlorins[1,2,8] or factor F430,[9] the Ni(II) hydrocorphinoid prosthetic group found in the methanogenic bacterial enzyme methyl-coenzyme M reductase.[10] Reduction of nickel(II) porphyrins results in redox processes that most workers[11] consider to be wholly or predominantly ligand based.[2,7,8,12] Regardless of the correct description, the initial species afforded by reduction of nickel(II) porphyrins are kinetically and thermodynamically unstable in bulk solution with respect to the formation of meso-saturated phlorin anions. The unambiguous accessibility and stability of Ni(I) complexes of the hydroporphyrins reflects the greater flexibility, somewhat smaller ligand field, and more negative reduction potential of hydroporphyrins compared to porphyrins.[1,2,8] These properties of hydroporphyrin ligands can be expected to affect the chemistries of other coordinated metal ions.

Copper and palladium, like nickel, have extensive coordination chemistries in the 2+ oxidation state, but have more limited chemistries in the 1+ oxidation state. Of particular interest here is the ability of certain tetraaza macrocycles to stabilize Cu(I)[13-18] and Pd(I).[19] Where comparisons can be made, the reduction potentials of these complexes and of the corresponding nickel complexes suggest that hydroporphyrin ligands might also be able to stabilize Cu(I) and Pd(I).

Very little information exists on the redox reactions of palladium porphyrins and palladium and copper hydroporphyrins.[20,21] All reactions reported to date are ligand centered. The redox processes of copper porphyrins have been more thoroughly investigated.[22] Although no direct reduction of a neutral copper(II) porphyrin complex to a Cu(I) anion complex has been claimed, several reports of Cu(I) in a porphyrin environment exist. Changes in the X-ray photoelectron spectrum of solid Cu(TPP) upon exposure to sodium metal vapor were advanced as evidence for Cu^{I}(TPP)$^-$.[23] Electrochemical reduction of the Cu(II) dianion complex of copper tetracyanotetraphenylporphyrin (which is already reduced by two electrons) was reported to afford a Cu(I) dianion complex.[24] Finally, the first reduction of cationic copper(II) N-substituted porphyrin complexes was assigned to a Cu(II)/Cu(I) process.[25] The evidence for this assignment was that the potential of the reduction fell in a region intermediate between the two electrode processes generally attributed to ligand oxidation and the two processes generally attributed to ligand reduction. Additionally, the potential of the reduction was sensitive to the nature of the axial ligand on copper. Spectroscopic data were not reported.

This paper describes the synthesis and electrochemistry of the Cu and Pd complexes of OEP,[26] OEC, and OEiBC. Our results

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provide unambiguous spectroscopic evidence for Cu^{I}(OEiBC)$^{-}$. Preliminary investigations suggest that the reactivity of this anion differs significant from that of copper(I) tetraaza macrocyclic complexes[15] and of Ni^{I}(OEiBC)$^{-}$.[12,27]

Experimental Section

All manipulations were carried out under a nitrogen or argon atmosphere by use of either Schlenk techniques or a Vacuum Atmospheres Co. drybox. Column chromatographic procedures involving hydroporphyrin complexes were performed in the drybox. Reagents and solvents were treated as previously reported[27,28] and were thoroughly degassed prior to use. H$_2$(OEP),[29] H$_2$(OEC),[30,31] and H$_2$(OEiBC)[32] were prepared by published methods. Absorption spectra were recorded on a Perkin-Elmer Lambda 4C spectrophotometer. Spectra of electrochemically generated species were obtained with an optically transparent thin-layer electrode cell (OTTLE) whose design and use was described elsewhere.[2,32] Other spectroscopic and electrochemical measurements were obtained as before.[27,28]

Cu(OEP) was prepared by the reaction of H$_2$(OEP) with Cu(C$_2$H$_3$O$_2$)$_2$·H$_2$O in DMF.[33] UV–vis (benzene), λ_{max}, nm (10^{-3} ϵ_M, M^{-1} cm^{-1}): 327 (19.3), 395 (136.6), 525 (14.7), 562 (32.3).

Cu(OEC) was prepared and purified by the method reported for the *cis*-Cu(OEC) isomer.[31] Spectral data agree with those reported[31] for Cu(OEC) prepared by a different method.[34]

Cu(OEiBC). A solution of 50 mg of Cu(C$_2$H$_3$O$_2$)$_2$·H$_2$O in 2 mL of methanol was added to a solution of 50 mg of H$_2$(OEiBC) in 10 mL of chloroform. The solution was stirred at room temperature for 5 min, during which time the bright magenta color of the solution turned dark violet. The solvent mixture was removed under vacuum, and the resulting residue was washed with 25-mL portions of degassed water until the washings were no longer blue and then dried. The UV–vis spectrum of the crude product was examined for the presence of Cu(OEC), which can result from an H$_2$(OEC) impurity in the H$_2$(OEiBC) or from oxidation during reaction or workup. If present, the crude product was purified by chromatography on alumina. Elution with 20% toluene in hexane afforded a purple band of Cu(OEiBC) followed by a small blue band of Cu(OEC). The solid recovered from the eluate was recrystallized from chloroform/methanol to give the product in 50% yield. (Additional product can be recovered from the mother liquid.) UV–vis (benzene), λ_{max}, nm (10^{-3} ϵ_M, M^{-1} cm^{-1}): 362 (42.6), 380 (63.0), 391 (84.0), 550 (13.7), 593 (65.5).

Cu^{I}(OEiBC)$^{-}$. Cu(OEiBC) in either acetonitrile or THF solution was reduced with excess sodium amalgam (1%). Reductions were carried out inside the drybox. Protiated solvents were pretreated with an aliquot of amalgam prior to use in reductions. Deuteriated solvents were from freshly opened ampules and were used without amalgam treatment. ^{1}H NMR (CD$_3$CN), δ: 0.99 and 1.00 (t, 6 H each, 2,8- and 3,7-CH$_3$); 1.56 and 1.60 (t, 6 H each, 12,18- and 13,17-CH$_3$); 1.95 and 2.06 (m, 4 H each, 2,8- and 3,7-CH$_2$); 3.35 (q, 4 H, 12,18-CH$_2$); 3.47 (q, 4 H, 13,17-CH$_2$); 3.78 (m, 4 H, 2,3,7,8-H); 6.89 (s, 1 H, 5-H); 7.54 (s, 2 H, 10,20-H); 8.62 (s, 1 H, 15-H).

Pd(OEP) was prepared by the reaction of H$_2$(OEP) with PdCl$_2$ in DMF.[33] Traces of unreacted H$_2$(OEP) were removed from the crude product by chromatography on silica gel. Elution was with chloroform. The product was recrystallized from chloroform/methanol. UV–vis (benzene), λ_{max}, nm (10^{-3} ϵ_M, M^{-1} cm^{-1}): 393 (174.9), 513 (12.9), 546 (46.3). ^{1}H NMR (CDCl$_3$), δ: 1.95 (t, 24 H, CH$_3$), 4.03 (q, 16 H, CH$_2$), 10.05 (s, 4 H, *meso*-H).

Pd(OEC). A 45-mg sample of solid Pd(C$_2$H$_3$O$_2$)$_2$ (2.0×10^{-4} mol) was added to a solution of 100 mg of H$_2$(OEC) (1.86×10^{4} mol) in 20 mL of chloroform and 10 mL of methanol. The stirred solution was heated in a bath of boiling water. The progress of the reaction was monitored by TLC and UV–vis spectroscopy. Typically, the color of the solution became deep blue within 15 min. The reaction was halted when the extent of metalation stopped increasing or Pd(OEP) began to appear. The solution was taken to dryness, and the residue was purified by chromatography on silica gel. Elution with a 1:1 hexane/toluene solvent mixture gave an small unidentified blue band, which was followed by the major blue Pd(OEC) band. An orange-pink Pd(OEP) band follows. It can coelute with the tail of the Pd(OEC) band if the column loading is too high or the conversion to Pd(OEP) is appreciable. In this event, the sample was repurified on a Harrison Research Chromatron using a silica rotor developed with a 7:3 hexane/toluene solvent mixture. The solid recovered from the pure Pd(OEC) band was recrystallized from chloroform/methanol. UV–vis (benzene), λ_{max}, nm (10^{-3} ϵ_M, M^{-1} cm^{-1}): 383 sh (74.4), 395 (84.9), 483 (4.0), 518 (4.9), 559 (6.9), 575 (7.0), 600 (59.7). ^{1}H NMR (CDCl$_3$), δ: 1.04 (t, 6 H, 2,3-CH$_3$); 1.73, 1.75, and 1.77 (t, 6 H each, 7,18- 8,17-, and 12,13-CH$_3$); 2.10 and 2.23 (A and B parts of ABX multiplet, 4 H total, 2,3-CH$_2$); 3.70, 3.81, and 3.84 (q, 4 H each, 7,18- 8,17-, and 12,13-CH$_2$); 4.47 (X part of ABX multiplet, 2 H, 2,3-H); 8.75 (s, 2 H, 5,20-H); 9.58 (s, 2 H, 10,15-H). ^{13}C NMR (C$_6$D$_6$), δ: 10.65 (2,3-CH$_3$); 18.11, 18.58, and 18.62 (7,18-, 8,17-, and 12,13-CH$_3$); 19.79, 19.85, and 19.94 (7,18-, 8,17-, and 12,13-CH$_2$); 31.19 (2,3-CH$_2$); 53.37 (2,3-C); 94.75 (5,20-C); 102.58 (10,15-C); 155.04 (1,4-C); 135.84, 136.45, 137.05, 138.50, 142.18, and 143.31 (unassigned macrocycle carbons).

Pd(OEiBC). A 22.5-mg sample of solid Pd(C$_2$H$_3$O$_2$)$_2$ (1.0×10^{-4} mol) was added to a solution of 50 mg of H$_2$(OEiBC) (9.3×10^{-5} mol) in 2 mL of chloroform and 10 mL of methanol. The stirred solution was heated in a hot water bath for 30 min, during which time the color of the solution changed from magenta with an orange fluorescence to deep red. The solution was taken to dryness, and the residue was purified by chromatography on silica gel. A red-violet band of Pd(OEiBC) was eluted with a 7:3 hexane/toluene solvent mixture and was followed by a small blue Pd(OEC) band. Any remaining traces of Pd(OEC) can be removed by repurification on a Harrison Research Chromatron using a silica rotor developed with hexane. The solid recovered from the pure Pd(OEiBC) band was recrystallized by slow evaporation of a diethyl ether solution to afford 43 mg of product (72% yield). UV–vis (hexane), λ_{max}, nm (10^{-3} ϵ_M, M^{-1} cm^{-1}): 360 sh (40.0), 380 (67.3), 510 (7.0), 536 (12.8), 577 (57.5). ^{1}H NMR (CDCl$_3$), δ: 0.99 (m, 12 H, 2,3,7,8-CH$_3$); 1.58 (m, 12 H, 12,13,17,18-CH$_3$); 1.7–2.2 (m, 8 H, 2,3,7,8-CH$_2$); 3.41 (q, 4 H, 12,18-CH$_2$); 3.52 (q, 4 H, 13,17-CH$_2$); 3.8–4.0 (m, 4 H, 2,3,7,8-H); 7.22 and 7.26 (s, 1 H combined, 5-H of *ttt* and *tct*); 7.89 and 7.91 (s, 2 H combined, 10,20-H of *ttt* and *tct*); 8.90 and 8.92 (s, 1 H combined, 15-H of *ttt* and *tct*).

Results

Syntheses of the Cu and Pd complexes of OEC and OEiBC were reported first by Eisner.[34–36] Quantitative UV–vis spectra and analytical data were reported for the OEC complexes, both of which were isolated as crystalline solids. The claims for the OEiBC complexes, which were not isolated, are open to question. The wavelengths of UV–vis absorptions reported for Pd(OEiBC) differ from later reports by 50–100 nm. The wavelengths reported for Cu(OEiBC) absorption bands are correct, but the absorptivity of 2.08×10^5 M^{-1} cm^{-1} reported for the Soret band is suspiciously larger than that of any other known OEiBC complex. Furthermore, the ratio of the intensity of the Soret band to the Q (visible) band is 3.5, which is significantly greater than the range of 1–2 typical for isobacteriochlorin compounds.[31]

Cu(OEC) has been reasonably well investigated in subsequent years.[31,37,38] Additional reports of the other complexes have been few, however, and their characterization has been incomplete.

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(26) Abbreviations: OEP, 2,3,7,8,12,13,17,18-octaethylporphyrin dianion; OEC, *trans*-2,3-dihydro-2,3,7,8,12,13,17,18-octaethylporphyrin dianion (chlorin); OEiBC, mixture of *ttt*- and *tct*-2,3,7,8-tetrahydro-2,3,7,8,12,13,17,18-octaethylporphyrin dianion (isobacteriochlorin); OEPH, 5-hydro-2,3,7,8,12,13,17,18-octaethylporphyrin trianion (phlorin); OECH, 2,3,(5 or 10)-trihydro-2,3,7,8,12,13,17,18-octaethylporphyrin trianion (chlorin–phlorin); cyclam, 1,4,8,11-tetraazacyclotetradecane; tmc, 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane; *t*-tetramine, *trans*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; tbc, 1,4,8,11-tetrabenzyl-1,4,8,11-tetraazacyclotetradecane; LBF$_2$, difluoro[3,3′-trimethylenedinitrilobis(2-butanoneoximato)]borate; TIM, 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene.

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Fuhrhop measured the potential of the one-electron oxidation of both OEC complexes by potentiometric titration and reported UV–vis and ESR data for their cation radicals.[21] Gradyushko and co-workers examined the phosphorescence of all four complexes.[39] The UV–vis and EPR spectra of Cu(OEiBC) were reported.[32,40] Recently, Pd(OEC) and Pd(OEiBC) were prepared and characterized by Angst, who worked in the Eschenmoser group.[41]

Preparation of palladium hydroporphyrin complexes is not trivial. The relative inertness of Pd(II) necessitates longer reaction times, vigorous conditions, and excess Pd. All exacerbate the oxidative dehydrogenation of hydroporphyrin compounds by Pd(II). Eisner's procedure, which employs $PdCl_2(C_6H_5CN)_2$ in benzene, resulted in substantial conversion of H_2(OEC) to Pd(OEP).[36] The yield of Pd(OEC) after chromatography and recrystallization was less than 10%. Pd(OEiBC) did not survive this procedure, as judged by the UV–vis data that were reported. Fuhrhop attempted to prepare Pd(OEC) from H_2(OEC) and $PdCl_2$ in acetic acid but obtained Pd(OEP) in quantitative yield.[21] Addition of a 3-fold excess of 2,4-pentanedione to the system stabilized Pd(II) through complexation and afforded a mixture of Pd(OEP) and Pd(OEC), whose yields after chromatographic purification were not reported. We examined variations of this approach that started with $PdCl_2$, $Pd(C_2H_3O_2)_2$, or $Pd(acac)_2$. The reactions are excessively slow and give about 50% conversion to Pd(OEP). Gradyushko used Adler's method[33] of $PdCl_2$ in DMF and obtained after chromatography at least enough Pd(OEC) and Pd(OEiBC) for spectroscopic studies.[39] Details were not reported. In our hands, this method is also too slow and results in more oxidation of the hydroporphyrins than is acceptable. Angst employed $Pd(C_2H_3O_2)_2$ in a chloroform/methanol solvent mixture.[41] Our method of choice is a modification of his approach. One advantage of this approach is that the reactions are faster than in most of the other methods. Although the reactions do not go to completion, they can be run to roughly 80% conversion before significant amounts of oxidation products appear. The small amount of oxidation product present simplifies the chromatographic workup. Furthermore, the unreacted free base hydroporphyrin can be recovered and recycled, if desired. We report here details of the method and characterization data for the palladium hydroporphyrin complexes because Angst's thesis is not readily accessible and is not indexed under the Pd complexes in *Chemical Abstracts*.

Preparation of copper hydroporphyrin complexes only requires combining a Cu(II) salt and the hydroporphyrin free base in a solvent mixture in which both are soluble. Indeed, the reaction is so facile and quick that metalation of H_2(OEiBC) by adventitious traces of copper can be an unwanted side reaction during insertion of iron and other metals.

Spectral data for complexes are reported in the Experimental Section. Our data are in reasonable agreement with those reported earlier. The variation of the absorptivities reported for Pd(OEC) was a source of concern, however. It could imply that different workers had crystallized different solvates. Although we were unable to obtain satisfactory analyses for this complex, X-ray structural data confirm the identities of Pd(OEC) and Pd(OEiBC) and the absence of solvent molecules in their lattices.[42]

Electrochemistry. The electrochemical behavior of copper and palladium octaethylporphyrin and octaethylhydroporphyrin complexes in butyronitrile (*n*-PrCN), CH_2Cl_2, and dimethylformamide (DMF) was investigated by use of cyclic voltammetry. Potentials vs SCE are reported in Table I. Ferrocene was added as an internal standard at the conclusion of each experiment. The average of the potentials (vs SCE) that we measured for the ferrocenium/ferrocene couple in each solvent are reported in Table I. Individual measurements were within 15 mV of the mean.

Table I. Potentials of Copper(II) and Palladium(II) Porphyrin and Hydroporphyrin Complexes

complex	solvent	E,[a,b] V 2+/1+	1+/0	0/1−	other
Cu(OEP)	CH_2Cl_2	1.25	0.75		−1.50,[c,f] −1.76,[f] −1.49[e]
	DMF	1.20[c,e]	0.82	−1.47	
	n-PrCN	1.27[c,e]	0.80	−1.54	
Cu(OEC)	CH_2Cl_2	1.09	0.47	−1.52	−2.15[c,f]
	DMF	1.00[e,g]	0.53	−1.44	−2.03,[f,g] −1.94[e]
	n-PrCN	1.02[h]	0.51	−1.51	
Cu(OEiBC)	CH_2Cl_2	0.87	0.20		−1.69,[c,f] −1.48[e]
	DMF	0.79[e,g]	0.23	−1.50[i]	
	n-PrCN	0.80[h]	0.21	−1.56	
Pd(OEP)	CH_2Cl_2	1.54[c,h]	0.82	−1.52[j]	
	DMF	1.34[c,e]	0.90	−1.46	
	n-PrCN	1.70[e]	0.87	−1.51[j]	
Pd(OEC)	CH_2Cl_2	1.32[c,e]	0.56	−1.52	−1.89[f]
	DMF	1.23[c,e]	0.68	−1.44	
	n-PrCN	1.27[c,e]	0.62	−1.51	
Pd(OEiBC)	CH_2Cl_2	1.15[c,e]	0.28		−1.9[k]
	DMF	0.98[c,e]	0.39	−1.79	
	n-PrCN	1.08[c,e]	0.33	−1.86	
ferrocene	CH_2Cl_2		0.45		
	DMF		0.50		
	n-PrCN		0.47		

[a] $E = E_{1/2} = {}^1/_2(E_{p,a} + E_{p,c})$ unless process is otherwise noted as irreversible. [b] At 25 °C in a solution 0.1 M in TBAP with a Pt disk working electrode and 100 mV/s scan rate. [c] Greater than one-electron process. [d] Irreversible. [e] $E_{p,a}$ (irreversible). [f] $E_{p,c}$ (irreversible). [g] Two-electron process. [h] $i_{p,c} < i_{p,a}$. [i] Peak to peak separation is larger than for a reversible process. [j] $i_{p,a} < i_{p,c}$. [k] Inflection point of a multielectron electrocatalytic wave.

(a) Oxidations. The oxidations of the Cu complexes are typical of porphyrin and hydroporphyrin complexes.[3,7,31,32,43–45] Two one-electron oxidations are observed for each complex. The potentials of the reversible first oxidations shift negatively by about 250–300 mV for each increase in the level of saturation of the macrocycle. The second oxidations of the complexes are reversible only in CH_2Cl_2. Cu(OEC) and Cu(OEiBC) have chemically irreversible ($i_{p,c}$ less than $i_{p,a}$) second oxidations in *n*-PrCN. The second oxidation process of these complexes in DMF consists of a two-electron anodic peak, as judged by comparison to the one-electron first oxidation. A corresponding cathodic peak is absent. However, a new cathodic wave appears at a potential that corresponds to the reduction of the cation radical of the next most unsaturated complex in the series. These observations are consistent with an ECE process in which the initially generated $Cu(OEC)^{2+}$ dehydrogenates to afford Cu(OEP), which in turn is immediately oxidized to $Cu(OEP)^{\bullet+}$ at the potential of the electrode. In an analogous process, $Cu(OEiBC)^{\bullet+}$ is converted to $Cu(OEC)^{\bullet+}$. Similar behavior was observed for the dications of Ni(OEC) and Ni(OEiBC) in DMF.[3]

One distinctive feature of the oxidations of the Pd complexes is the unusually large difference in potential between the first and second oxidations. The first oxidations are reversible. In contrast, all of the second oxidations are irreversible and have peak currents which are larger than that which corresponds to a one-electron process. The second oxidation of Pd(OEP) in CH_2Cl_2 is the only one for which a well-defined cathodic peak is detected. Consequently, the potentials reported in Table I for the second oxidations are of the anodic peak. The difference between the peak potential

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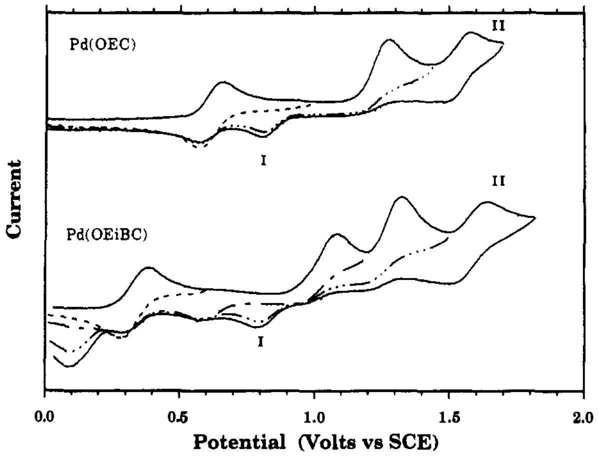

Figure 1. Cyclic voltammograms of the oxidations of Pd(OEC) and Pd(OEiBC) recorded at 100 mV/s in butyronitrile solution, 0.1 M in TBAP. The effects of varying the switching potential are illustrated. Peaks labeled I and II correspond, respectively, to the reduction and oxidation of $Pd(OEP)^{\bullet+}$, which is formed by oxidative dehydrogenation of the hydroporphyrin complexes.

of the second oxidation and the $E_{1/2}$ of the first oxidation is larger than Δ_{ox}, the difference in $E_{1/2}$'s. Nonetheless, the differences observed here are so great that by necessity Δ_{ox} would be larger than typically observed for M(OEP), M(OEC), and M(OEiBC) complexes. The nature and site of the second oxidation process for Pd(OEP) is unknown. However, the −250- to −290-mV shift in the potential of this process (vs Fc/Fc^+) in DMF relative to the other solvents could suggest a metal-centered oxidation in DMF.

Another noteworthy feature is the marked instability of oxidized palladium hydroporphyrin complexes. The second oxidations of Pd(OEC) and Pd(OEiBC) result in oxidative dehydrogenation processes like those described above for the Cu and Ni complexes in DMF. However, unlike the Cu and Ni complexes, the Pd complexes are subject to the reaction in all three solvents. The instability of the Pd complexes is nearly comparable to that of *cis*-OEC complexes,[31] which are the least stable hydroporphyrin complexes with which we have worked. This could explain the difficulties experienced in preparing palladium hydroporphyrin complexes.

Figure 1 shows the cyclic voltammograms of Pd(OEC) and Pd(OEiBC) in *n*-PrCN. The first oxidation of Pd(OEC) is reversible when scanned separately. A cathodic peak at 0.82 V, I, corresponding to reduction of $Pd(OEP)^{\bullet+}$ appears in the reverse scan after the potential is swept through the irreversible second oxidation peak at 1.27 V. The current of this second oxidation peak is larger than that of a one-electron peak, because it includes contributions from both the oxidations of $Pd(OEC)^{\bullet+}$ and of the Pd(OEP) formed by dehydrogenation of $Pd(OEC)^{2+}$. No coupled reduction peak is present. When the potential is swept to even more positive values, oxidation of $Pd(OEP)^{\bullet+}$ is observed, II. The cyclic voltammogram of Pd(OEiBC) exhibits analogous processes. A cathodic peak corresponding to reduction of $Pd(OEC)^{\bullet+}$ appears after the potential is swept through an irreversible second oxidation peak at 1.08 V. As would be expected after a process that generates $Pd(OEC)^{\bullet+}$, an irreversible third oxidation peak is observed at a potential near that of the second oxidation process of Pd(OEC). The cathodic peak I then appears in the reverse sweep. Finally, II is observed when the potential sweep is continued to even more positive potentials. One unexplained feature in the voltammogram of Pd(OEiBC) is the appearance of a cathodic peak at 0.1 V. The current of this peak increases as the switching potential is increased.

(b) Reductions. The Cu and Pd complexes undergo reversible one-electron reductions in DMF and *n*-PrCN, with two exceptions. Reduction of Cu(OEiBC) in DMF is chemically reversible ($i_{p,c} = i_{p,a}$), but the exceptionally large peak to peak separation (190 mV) precludes Nernstian reversibility. The reduction of Pd(OEP) in *n*-PrCN is chemically irreversible. The reduction potentials of most of the complexes are within 0.06 V of −1.50 V. However, Pd(OEiBC) is reduced at a potential that is some 350 mV more negative.

A second, irreversible reduction of Cu(OEC) is observed in DMF at a potential in excess of −2.0 V. Irreversible second reduction processes appear to lie just beyond the accessible potential window for Pd(OEP) in DMF and for Pd(OEC) and Pd(OEiBC) in DMF and *n*-PrCN. Evidence for this conclusion include a significant increase in current above the expected background and the several small anodic peaks that appear in the cyclic voltammogram of Pd(OEiBC) when the switching potential is more negative than −2.0 V.

Reductions in CH_2Cl_2 are much less well-behaved. Cu- and Pd(OEC) have reversible one-electron first reductions and irreversible second reductions. The reduction of Pd(OEP) is chemically irreversible. The reduction process for Cu(OEP) consists of two overlapping cathodic peaks at −1.56 and −1.76 V and a anodic peak at −1.49 V. The current of the first cathodic peak is greater than that of a one-electron process, whereas that of the second is smaller. The current of the anodic peak is somewhat smaller than that of the first cathodic peak. Cu(OEiBC) exhibits a large cathodic peak at −1.69 V and a small anodic peak at −1.48 V. Finally, a multielectron catalytic wave is observed with Pd(OEiBC). The inflection point of the wave is at a potential comparable to the reduction potential of Pd(OEiBC) in DMF or *n*-PrCN.

(c) Coulometry. Controlled-potential electrolysis of a solution of Cu(OEiBC) in *n*-PrCN at −1.70 V results in a color change from blue-violet to red-violet and in the addition of 1.0 ± 0.2 equiv of electrons. The same number of coulombs is passed upon reoxidation at 0.00 V, and Cu(OEiBC) is recovered. Satisfactory results are not obtained in coulometric measurements with other complexes, owing to the instability of both singly oxidized and singly reduced species on the time scale of a bulk electrolysis. With the exception of Pd(OEiBC), reduction of the other complexes results in the passage of a current that is greater than 1 equiv of electrons and affords a phlorin or chlorin–phlorin complex. The copper and palladium hydroporphyrin complexes undergo partial or complete dehydrogenation when oxidized in bulk at a potential about 100 mV beyond the first $E_{1/2}$.

Spectroelectrochemistry. The UV–vis spectra of the species generated by electrochemical oxidation or reduction of the Cu and Pd complexes of OEP, OEC, and OEiBC were obtained by use of an OTTLE cell. *n*-PrCN was the solvent of choice for these experiments because the reversibility of both oxidations and reductions is greatest in this solvent. Spectral data for electrogenerated species are presented in Table II.

(a) Oxidations. Oxidation of Cu(OEP) at 0.95 V leads to the loss of the Soret band at 395 nm and the visible bands at 523 and 559 nm. These are replaced by broad, weak bands centered at 357.5 and 555 nm. Another new feature observed in the spectrum is one side of an extremely broad band that has a maximum at wavelengths greater than 900 nm. The spectrum neither agrees with a previous report for $Cu(OEP)^{\bullet+}$ in chloroform[21] nor resembles a typical metallooctaethylporphyrin cation radical. However, it does resemble closely the spectra of the dimeric cation radicals $[M(OEP)^{\bullet}]_2^{2+}$, where M = Mg, Ni, and Zn.[3,46,47] Apparently, $Cu(OEP)^{\bullet+}$ like $Ni(OEP)^{\bullet+}$ is monomeric in chloroform but dimeric in *n*-PrCN. Reduction of $[Cu(OEP)^{\bullet}]_2^{2+}$ at 0.0 V resulted in quantitative recovery of Cu(OEP).

Oxidation of Cu(OEC) at 0.65 V and of Cu(OEiBC) at 0.40 V results in parallel changes in their UV–vis spectra. The prominent visible bands, which are characteristic of hydroporphyrin complexes, are replaced by several broad, weak bands at both longer and shorter wavelengths. The changes in the Soret bands are comparatively small. Both blue shift, broaden, and decrease in intensity. The final spectrum obtained in each case

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Table II. Quantitative Absorption Spectral Data for Copper and Palladium Porphyrin and Hydroporphyrin Complexes in Butyronitrile Solution[a]

complex	λ_{max}, nm (ϵ, mM)
Cu(OEP)	325.5 (6.6), 395 (136.6), 523 (4.7), 559 (10.3)
Cu(OEP)$^{\bullet+}$ [c]	357.5 (38.0), 555 (3.0)
Cu(OEP)$^{2+}$ [b]	300 (16.7), 334 (15.5), 390 (13.0), 504 (3.0), 544 (3.1), 657 (8.4)
Cu(OEP)$^{\bullet-}$	315 (18.8), 404 (74.2), 419 sh (55.4), 586 sh (8.2), 614 (14.4), 817 (7.5)
Cu(OEPH)$^-$	301 (38.5), 370 (20.0), 422 sh (34.7), 446 (68.5), 590 (1.3), 758 (12.6)
Cu(OEC)	396 (143.0), 493.5 (5.6), 528.5 (5.7), 567.5 (8.8), 611 (47.8)
Cu(OEC)$^{\bullet+}$	394 (113.2), 485.5 (8.8), 521.5 (7.9), 559 (9.0), 612 (4.8), 643 (6.9)
Cu(OEC)$^{2+}$ [b]	357 (52.8), 402 (23.7), 548 (7.2)
Cu(OEC)$^{\bullet-}$	384 (59.8), 440 sh (17.8), 563 (12.3), 587 (10.5), 748 (14.4)
Cu(OECH)$^-$	307 (34.7), 365 (32.9), 527 (16.9), 688 (9.7)
Cu(OEiBC)	359.5 (45.8), 379 (67.2), 390.5 (84.0), 522.5 (6.9), 549 (12.8), 593 (59.8)
Cu(OEiBC)$^{\bullet+}$	380.5 (61.2), 480 (10.3), 612.5 (2.1), 648.5 (2.3)
Cu(OEiBC)$^{2+}$ [b]	355 (60.6), 552 (4.7)
Cu^{I}(OEiBC)$^-$	392 (86.1), 481 (5.3), 516 (6.8), 548 (11.1), 590 (50.1)
Pd(OEP)	328 (19.3), 390 (174.9), 510 (13.1), 544 (43.5)
Pd(OEP)$^{\bullet-}$	421.5 (63.4), 595 (22.8), 738 (3.5), 824.5 (12.1)
Pd(OEPH)$^-$	304.5 (59.1), 367 (23.3) 421 sh (33.8), 448 (75.2), 786.5 (14.7)
Pd(OEC)	391 (109.5), 481 (6.4), 516 (7.2), 556 (9.7), 598.5 (66.3)
Pd(OEC)$^{\bullet-}$	381.5 (55.7), 412 sh (34.2), 436.5 (23.7), 513 (7.6), 563 (20.6), 643 (5.4) 715.5 (27.3)
Pd(OECH)$^-$	303 (37.2), 358.5 (36.5), 449.5 (6.7), 495 sh (11.7), 528.5 (20.2), 702.5 (9.1)
Pd(OEiBC)	357 sh (40.9), 382.5 (67.3), 510 (7.2), 538 (12.3), 580 (53.1)
Pd(OEiBC)$^{\bullet-}$	369.5 (28.1), 394 (30.2), 518 (11.7), 662 (6.3)

[a] 0.1 M in TBAP. [b] See text for discussion of the identity of this complex. [c] Dimeric.

is consistent with formation of a cation radical. Both are quite similar to those observed previously for the corresponding Ni complexes in nitrile solvents.[3] The spectrum of Cu(OEC)$^{\bullet+}$ is in reasonable agreement with previously reported spectra of this cation radical in other solvents.[21,38b] Recovery of the initial neutral complexes upon reduction is nearly quantitative.

None of the species generated by electrolysis of the Cu complexes at their second oxidation potential have been identified. For ease of discussion, though, we will refer to them as Cu(P)$^{2+}$ (P = OEP, OEC, or OEiBC). The spectrum of Cu(OEP)$^{2+}$ consists of a well-defined band at 657 nm and a very broad, ill-defined band or overlapping bands, which extend from 300 to 420 nm. The spectra of Cu(OEC)$^{2+}$ and of Cu(OEiBC)$^{2+}$ each have Soret-like bands near 355 nm, a smaller band near 550 nm, and rising absorbance at long wavelengths, which imply a band with a wavelength maximum greater than 900 nm. Once formed, the spectra of the two-electron-oxidized complexes do not change further. Very little Cu(OEP) is recovered when Cu(OEP)$^{2+}$ is reduced. Cu(OEC)$^{2+}$ and Cu(OEiBC)$^{2+}$ afford Cu(OEP) and Cu(OEC), respectively, when reduced. The Cu(P)$^{2+}$ spectra do not resemble the typical UV–vis spectra of metalloporphyrin and metallohydroporphyrin dications, which consist of a single Soret-like feature at 330–345 nm. At wavelengths greater than 450 nm, dication spectra are featureless and have absorptivities that decrease monotonically and are essentially negligible. Another possible formulation for Cu(P)$^{2+}$ is a Cu(III) cation-radical complex. The few metal-oxidized porphyrin or hydroporphyrin cation radicals known (M = Ni) have UV–vis spectra that largely resemble the spectra of the M(II) cation radical.[3,7] This is not a good description of the Cu(P)$^{2+}$ spectra. In fact, for the hydroporphyrin Cu(P)$^{2+}$ complexes, the spectra most closely resemble that of the dimeric cation radicals [M(P)$^{\bullet}$]$_2^{2+}$. This interpretation is feasible. The second oxidation of Cu(OEC) occurs at a potential positive of the first oxidation of Cu(OEP). Thus, any Cu(OEP) formed by oxidative dehydrogenation of Cu(OEC) will itself be oxidized. The potentials of Cu(OEiBC) and Cu(OEC) are similarly related. The interpretation requires that dimerization of hydroporphyrin cation radicals be slow if direct oxidation of Cu(OEC) in *n*-PrCN favors a monomeric cation radical but oxidation of Cu(OEC) generated during electrolysis of Cu(OEiBC) favors the dimer. The second process occurs over a considerably longer time period. Apparently, the dication Cu(OEP)$^{2+}$ reacts irreversibly with the solvent or an impurity in it. Additional experimental data are required for an unequivocal identification of these complexes.

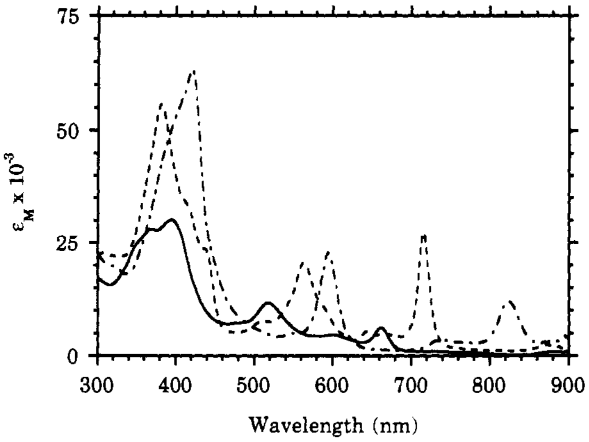

Figure 2. UV–vis spectra of Pd(OEP)$^{\bullet-}$ (–·–), Pd(OEC)$^{\bullet-}$ (--), and Pd(OEiBC)$^{\bullet-}$ (—) in butyronitrile containing 0.1 M TBAP recorded in the OTTLE cell. These anion-radical complexes were produced by electrolysis at −1.70, −1.65, and −2.10 V vs SSCE, respectively.

The spectral changes observed upon oxidation of Pd(OEP) appear to be consistent with formation of the dimeric cation radical [Pd(OEP)$^{\bullet}$]$_2^{2+}$ in the first oxidation and the dication Pd(OEP)$^{2+}$ in the second oxidation. However, the quality of the spectra is poor. This is a consequence of the limited solubility of Pd(OEP) in *n*-PrCN, the short path length of the thin-layer cell, and the broadness and low absorptivity of the visible bands in the spectra of the oxidized complexes. Reduction of either oxidized complex at 0.0 V affords nearly quantitative recovery of Pd(OEP).

Oxidation of Pd(OEiBC) in the OTTLE cell at a potential slightly positive of the first $E_{1/2}$ results in a spectrum that appears to be a superposition of the spectra of Pd(OEiBC) and Pd(OEC) and some weak broad bands that could be due to Pd(OEiBC)$^{\bullet+}$. The intensity of the Pd(OEC) bands increases as the electrolysis is continued for longer times. Early in the electrolysis, reduction at 0.0 V affords what is clearly a mixture of Pd(OEiBC) and Pd(OEC). Prolonged electrolysis or repeated oxidation/reduction cycles leads to complete conversion to Pd(OEC). Oxidation at a potential positive of the second $E_{1/2}$ results in immediate conversion to Pd(OEC) and gradual conversion to Pd(OEP). As would be expected, electrolytic oxidation of Pd(OEC) affords Pd(OEP) in an analogous fashion. Consequently, we are unable to report spectroscopic data for the oxidized Pd complexes. Oxidation of the copper hydroporphyrin complexes in DMF results in similar changes, except that no evidence is observed for an intermediate species.

(b) Reductions. The UV–vis spectra observed upon reduction of the complexes in *n*-PrCN solution are reported in Table II. Nearly identical spectra were obtained with DMF solutions.

There are striking similarities in the spectra of all of the one-electron-reduced complexes, with the exception of Cu(OEiBC)$^-$. The spectra of Pd(OEP)$^-$, Pd(OEC)$^-$, and Pd(OEiBC)$^-$, Figure 2, and of Cu(OEP)$^-$ and Cu(OEC)$^-$, Figure 3, consist of three major bands: a Soret-like feature centered near 400 nm and two prominent visible bands that occur in the wavelength ranges 500–600 and 660–830 nm. The Soret-like band

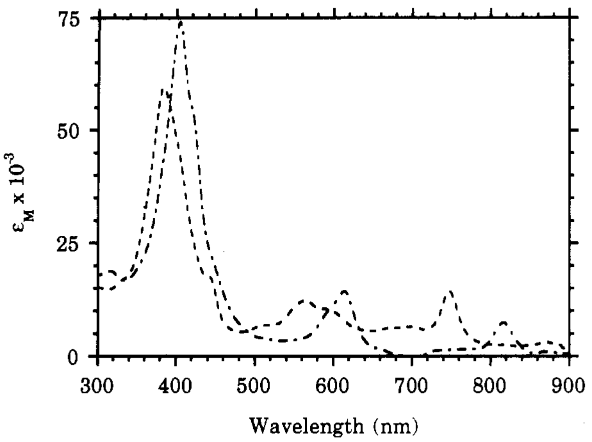

Figure 3. UV–vis spectra of Cu(OEP)$^{\bullet-}$ (–·–) and Cu(OEC)$^{\bullet-}$ (- -) in butyronitrile containing 0.1 M TBAP recorded in the OTTLE cell. These anion-radical complexes were produced by electrolysis at −1.63 and −1.75 V vs SSCE, respectively.

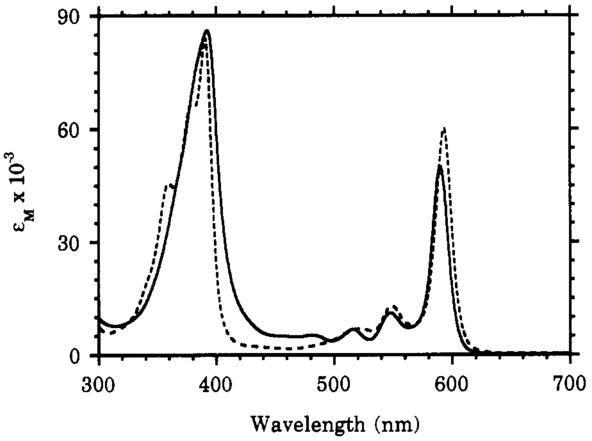

Figure 4. UV–vis spectra of Cu(OEiBC) (- -) and Cu^{I}(OEiBC)$^-$ (—) in butyronitrile containing 0.1 M TBAP recorded in the OTTLE cell. Cu^{I}(OEiBC)$^-$ was produced by electrolysis at −1.75 V vs SSCE.

is red shifted relative to the position of the Soret band of the neutral complex (center of gravity if not wavelength of the absorbance maximum) and drops to roughly one-third of the intensity. The two visible bands shift to progressively shorter wavelengths in these ranges as the extent of saturation of the macrocycle increases. The absorbtivities of the visible bands are roughly (1–2) × 10^4 M^{-1} cm^{-1}. The spectra bear a very close family resemblance to the spectra of Zn(TPP)$^{\bullet-}$[48] and the radical anion of chlorophyll *a*.[49] Thus, the five one-electron-reduced species are anion radicals. To the best of our knowledge, the spectrum of Pd(OEiBC)$^{\bullet-}$ is the first reported for an isobacteriochlorin anion radical. It should be noted in passing that the spectra of the Cu and Pd(OEP) anion radicals differ in band structure and wavelength from the spectrum of Ni(OEP)$^-$.[2] This suggests either that different electronic ground states can exist for metalloporphyrin anion radicals or that some mixing of metal and ligand orbitals occurs in the electronic states of Ni(OEP)$^-$.

Reduction of Cu(OEiBC) at −1.75 V, Figure 4, results in subtle changes in the UV–vis spectrum. The visible band shifts about 3 nm to shorter wavelengths and decreases slightly in intensity. The changes in the Soret band are even smaller. The Soret band loses its shoulders and shifts 1.5 nm to longer wavelengths, but has nearly identical intensity. The minimal changes in the spectrum suggest that the site of reduction is the metal rather than the tetrapyrrole ring. Other results, discussed below, confirm the formation of Cu^{I}(OEiBC)$^-$. Cu(OEiBC) is recovered quantitatively upon reoxidation of Cu^{I}(OEiBC)$^-$.

Second reductions are observed in the cyclic voltammograms of the OEC complexes in DMF. Thus, we examined the reduction of all complexes in DMF and in *n*-PrCN solutions at the extreme potential limit accessible in the OTTLE cell. The nominal value of this limit is −2.10 V, but the actual value is probably less negative owing to the *IR* drop in the OTTLE cell. No further changes are seen when Cu(OEiBC) and Pd(OEiBC) are reduced in either solvent under these conditions. However, reduction of the Cu and Pd complexes of OEP and OEC at very negative potentials results in the initial rapid formation of the corresponding anion radical and is followed by another change at longer times. The final spectra obtained with the OEP complexes closely resemble the spectrum of the meso-saturated, phlorin anion complex Ni(OEPH)$^-$.[2] Similarly, the final spectra obtained with the OEC complexes closely resembles the spectrum of the chlorin–phlorin anion complex Ni(OECH)$^-$.[2] No evidence of an intermediate dianion is observed during the reduction of any of the complexes. Assignments of the final spectra to M(OEPH)$^-$ and M(OECH)$^-$ complexes, where *M* = Cu and Pd, is confirmed by the behavior of these complexes when reoxidized. Oxidation does not occur until the applied potential is well positive of the reduction potential of the neutral complex. Reoxidation proceeds quantitatively and directly to the neutral complex without intermediate formation of the anion-radical complex. Reoxidation at 0.0 V of the anion-radical complexes affords quantitative recovery of the starting neutral complex in all cases.

Chemical Reductions. Reduction of an acetonitrile or THF solution of Cu(OEiBC) by excess sodium amalgam results in a subtle color change from blue-violet to red-violet. Typically, the reduction is complete in about 2 h, but the actual time depends on the solvent and other reaction conditions. The UV–vis spectra of the product in acetonitrile and in THF are quite similar to that of Cu(OEiBC)$^-$ generated by electrolysis in *n*-PrCN in the OTTLE cell. Two minor differences are that for chemical reductions the blue-shift of the visible band is smaller and the Soret band retains the two shoulders on the short wavelength side. Interactions with the TBAP electrolyte, which is present in the electrochemical reductions but absent in the chemical reductions, may be responsible. Cu(OEiBC)$^-$ is stable to further reduction in the presence of excess amalgam. On one occasion, though, a solution of Cu(OEiBC) in THF bleached when reacted overnight with a large excess of amalgam. We suspect a protic impurity was also present.

The ^{1}H NMR spectrum of Cu(OEiBC)$^-$ in THF-d_8, Figure 5, and in acetonitrile-d_3 confirms the Cu^{I}(OEiBC)$^-$ formulation proposed above. Cu(I) is d^{10} and diamagnetic. The chemical shifts, multiplet patterns, and narrow line widths observed are all consistent with a diamagnetic OEiBC complex. Loss of Cu on reduction is ruled out by the UV–vis spectrum and the absence of NH peaks in the NMR spectrum. Furthermore, line widths in the spectrum of the free base H_2(OEiBC) in these solvents are noticably greater than in the Cu^{I}(OEiBC)$^-$ spectrum. Finally, reoxidation of the sample to afford the paramagnetic Cu(OEiBC) leads to total loss of a detectable NMR spectrum.

Sodium amalgam reductions of acetonitrile or THF solutions of Cu(OEP), Cu(OEC), Pd(OEP), and Pd(OEC) result in final spectra that are identical with those obtained in the OTTLE cell when the respective complex is electrolyzed at a very negative applied potential. The reduced products were identified above as phlorin anions on the basis of the similarity of the spectra to those of authentic phlorins. UV–vis spectra recorded during the reaction show that these reductions do not proceed in discrete stages. Although the absence of isosbestic points could imply that anion-radical complexes are intermediates in the reduction, at no point is their concentration significant. A similar situation occured in the reductions of Ni(OEP) and Ni(OEC).[2] Any chemical agent that was capable of reducing these complexes reduced them directly to the phlorin anion.

Attempts to reduce Pd(OEiBC) with sodium amalgam are unsuccessful when typical reaction conditions are employed. Nearly complete reduction of the complex can be achieved,

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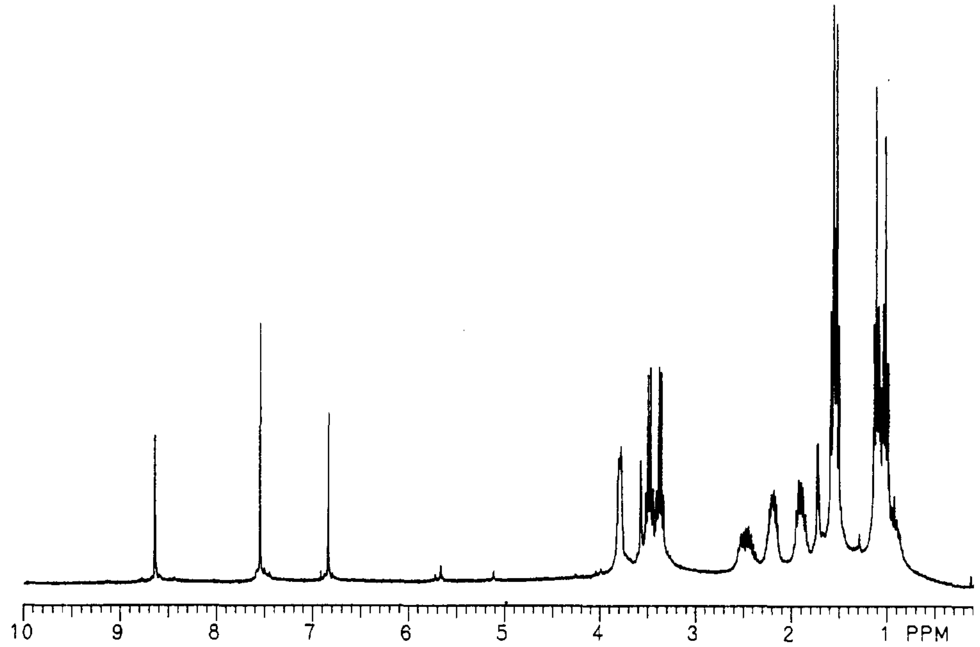

Figure 5. ^{1}H NMR spectrum of $Cu^I(OEiBC)^-$ in tetrahydrofuran-d_8.

Table III. M(II)/M(I) Reduction Potentials of Palladium, Nickel, and Copper Tetraaza Macrocycle Complexes[a]

	ref electrode	$[M(t\text{-tetramine})]^{2+}$	$[M(cyclam)]^{2+}$	$[M(tmc)]^{2+}$	$[M(tbc)]^{2+}$	lit. ref
Pd	Fc/Fc$^+$	−1.99	−2.10[b]	−1.53[c]	−1.27[c]	19
Ni	Fc/Fc$^+$	−1.64	−1.80	−1.25		19
	$Ag/AgNO_3$[d]	−1.57	−1.70[b]	−1.19[c]		56
	$Ag/AgNO_3$[d]	−1.58				57
Cu	$Ag/AgNO_3$[d]	−1.16				14[e]
	Fc/Fc$^+$		−1.50[f,g]			17
	Fc/Fc$^+$		−1.48[f,h]			58

[a] $E_{1/2}$, V, measured at Pt working electrode in acetonitrile solution. [b] Complex adopts *R,S,S,R* or *trans*-III configuration. [c] Complex adopts *R,S,R,S* or *trans*-I configuration, which places all four alkyl groups on the same face of the ligand. [d] Ag/0.1 M $AgNO_3$. [e] Same authors as ref 57. [f] E_p, irreversible—Cu stripping peak observed on anodic scan. [g] Reported value of −1.10 V vs SCE was corrected by the average value of the Fc/Fc$^+$ couple (+0.40 V). [h] Reported value of −0.90 V vs Ag/AgCl was corrected by the reported value of the Fc/Fc$^+$ couple (+0.58 V).

however, by reaction with an extremely large excess of amalgam, which contains a higher sodium concentration. The product of the reduction is not the anion radical. Its UV–vis spectrum in THF consists of broad, overlapping absorption bands with maxima at 329, 448, and 545 nm. The band positions could suggest an isobacteriochlorin–phlorin anion species. No such complex is currently known, although other hydroporphyrin complexes of comparable saturation level have been characterized. To the best of our knowledge, none of these complex has a comparable spectrum. The reduced complex is readily reoxidized. Brief exposure to air results in the immediate formation of Pd(OEiBC).

Because of the instability of oxidized Pd complexes and the inaccessibility of the anion-radical complexes upon chemical reduction, magnetic resonance data were not obtained for oxidized or reduced complexes other than $Cu^I(OEiBC)^-$. Interpretation of the EPR spectra of the Cu(II) anion- and cation-radical complexes will not be straighforward given the possible range of interactions between the two spins.

Reactivity of $Cu^I(OEiBC)^-$. The reactivity of $Cu^I(OEiBC)^-$ was examined in bulk and by electrochemical means. The cyclic voltammogram of Cu(OEiBC) in acetonitrile is not significantly affected by addition of such potential axial ligands as CO, C_5H_5N, PPh_3, Cl^-, and t-C_4H_9NC. The only change observed that is larger than the error in measurement was a +30-mV shift in the Cu(II)/Cu(I) potential in the presence of 10 equiv or more of pyridine. In contrast to these observations, addition of CH_3I results in significant changes in the voltammogram. The reversible one-electron reduction becomes an irreversible, electrocatalytic process as the concentration of CH_3I is increased. At comparable CH_3I concentrations, the electrocatalytic current, and by extension the rate of reaction, is smaller for $Cu^I(OEiBC)^-$ than for $Ni^I(OEiBC)^-$.[27]

Bulk solutions of $Cu^I(OEiBC)^-$ were reacted with excesses of the ligands listed above. There was no discernible change in the UV–vis spectra. In addition, the ^{1}H NMR spectrum of $Cu^I(OEiBC)^-$ under an atmosphere of CO was identical with the spectrum under a nitrogen atmosphere.

Solutions of $Cu^I(OEiBC)^-$ are slowly oxidized to Cu(OEiBC) when exposed to air (minutes to tens of minutes). This contrasts strongly with the immediate reoxidation of $Ni^I(OEiBC)^-$. Addition of unpurified THF, which contains traces of peroxides, results in rapid reoxidation of $Cu^I(OEiBC)^-$.

Discussion

The coordination environments preferred by Cu(II) and Cu(I) are distinctly different. The d^9 Cu(II) ion generally adopts Jahn–Teller distorted six-coordinate (tetragonal) or five-coordinate geometries, when solvent or counterion ligation is included.[50] The d^{10} Cu(I) ion, which does not experience ligand field stabilization, generally prefers four-coordinate tetrahedral environments or even lower coordination numbers. The structural differences between Cu(II) and Cu(I) complexes are sufficiently large that in several cases electron transfer is observed to produce a Cu(I) complex with a Cu(II)-like coordination environment, which subsequently relaxes to a stable Cu(I) complex.[51,52] The coordination spheres

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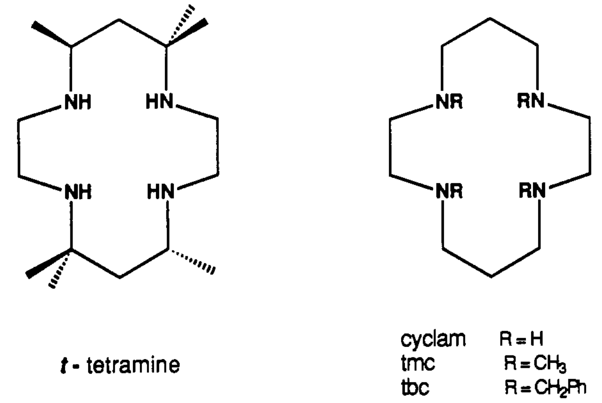
of Cu(II) and Cu(I) complexes are labile toward structural rearrangement and ligand substitution. This can limit the stability of Cu(I) complexes because many complexes, including macrocyclic complexes, undergo ligand loss[51] and/or disproportionate to Cu(II) and metallic copper.[17,53] Early studies showed that ligands that have amine donor groups or rigid square-planar structures were less favorable for Cu(I) than flexible ligands that have unsaturated nitrogen donor groups.[14,54] Recently, the generalization was offered that Cu(I) is favored by ligands with weak σ-donor ability and good π-acceptor properties.[17,53]

Too few Pd(I) complexes (nonorganometallic) are known to determine their preferred coordination environment. Pd(II) is difficult to reduce, because the large ligand field splitting of Pd raises the $d_{x^2-y^2}$ LUMO orbital to rather high energy. This is illustrated by direct comparisons of reduction potentials, which can be made for the Pd and Ni complexes of the macrocyclic ligands cyclam, tmc, and *t*-tetramine,[26] Table III. Pd(I) is produced at potentials 280–350 mV negative of that required for Ni(I). The Cu complexes of *t*-tetramine and cyclam, which already have one electron in the metal-ligand antibonding $d_{x^2-y^2}$ LUMO orbital, are even easier to reduce than the Ni complexes. The electrochemical data show that Pd(I) is favored by a decrease in the σ-donor ability of the ligand. N-Peralkylation of $[Pd(cyclam)]^{2+}$ shifts the Pd(II)/Pd(I) redox potential from −2.10 to −1.53 V for $[Pd(tmc)]^{2+}$ and to −1.27 V for $[Pd(tbc)]^{2+}$.[26] Related changes in reduction potential are observed for the *N*-peralkylcyclam complexes of Cu[18,55] and Ni[56] and are attributed to the greater length of M–N(tertiary) bonds relative to M–N(secondary) bonds.[56] The average Pd–N bond length increases from 2.05 Å in $[Pd(cyclam)]^{2+}$ to 2.06 and 2.10 Å in $[Pd(tmc)]^{2+}$ and $[Pd(tbc)]^{2+}$, respectively.[19] The four benzyl groups of $[Pd(tbc)]^{2+}$ also induce a substantial tetrahedral distortion to the square-planar stereochemistry around Pd(II). The nitrogen atoms alternate 0.21 Å above and below the least-squares N_4 plane. $[Pd(tmc)]^{2+}$ does not have a tetrahedral distortion, but does have a pyramidal distortion. The authors attribute the shifts in reduction potentials to these distortions and suggest that Pd(I) is favored by tetrahedral coordination.[19] N-Peralkylation of macrocycles also increases the stability and lifetime of Cu(I) and Pd(I) complexes by steric inhibition of dimerization and of reaction at the metal.[18,19]



Tetrapyrrole ligands generally have smaller M–N distances and stronger ligand fields and are more rigidly square planar than the tetraaza macrocyclic ligands that were considered here. M(II) tetrapyrrole complexes are neutral whereas M(II) macrocycle complexes are dications. These factors should render the tetrapyrroles less effective than the macrocycles in stabilizing Cu(I) or Pd(I). In their favor, the nitrogen donors of tetrapyrroles are conjugated imines rather than saturated amines. Overall, the unfavorable effects should predominate. Our results bear out this expectation. The reduction potentials of the copper and palladium porphyrin and hydroporphyrin complexes are all significantly cathodic of the potentials for the corresponding complexes of cyclam. Yet, of the tetrapyrrole complexes, only Cu(OEiBC) undergoes reduction at the metal rather than at the π-system of the ligand. Thus, for the others, the energy of the M(I) tetrapyrrole configuration is even higher than the cathodic shift of the reduction potentials alone would seem to suggest.

The site of reduction of $Cu(OEP)^-$ and $Cu(OEC)^-$ necessitates that the singlet state arising from the electronic configuration with a filled $d_{x^2-y^2}$ orbital, $(\pi)^2(d)^2$ or $Cu^I(P)$, is higher in energy than one of the states arising from the configuration with one electron each in the $d_{x^2-y^2}$ orbital and π^* (e_g) orbitals, $(\pi)^2(d)^1(\pi^*)^1$ or $Cu^{II}(P^-)$. The opposite must be true for $Cu(OEiBC)^-$. Emission spectra establish that the order of states in the anions parallel the order of the excited states in the respective neutral complexes. Cu(OEP)[59,60] and Cu(OEC)[39] phosphoresce. The emission is from "tripdoublet" (^2T) and quartet (^4T) states, which arise from the electronic configuration $(\pi)^1(d)^1(\pi^*)^1$, $Cu^{II}(P^*)$. Phosphorescence is quenched if a charge-transfer state lies below the $^{2,4}T$ states.[59] One such charge-transfer state arises from the electronic configuration $(\pi)^1(d)^2(\pi^*)^0$, $Cu^I(P^+)$, a ligand to metal charge transfer.[61] Cu(OEiBC) does not phosphoresce.[39] Thus, for Cu(OEiBC), the charge-transfer state is lower in energy than the $^{2,4}T$ states. The electronic states $Cu^I(P)$ and $Cu^{II}(P^-)$ of the anions are generated from the respective excited states $Cu^I(P^+)$ and $Cu^{II}(P^*)$ of the neutrals by the formal addition of one electron to the π-HOMO orbital. Thus, the energy difference between the respective anion and neutral states should be the same to the first approximation. Undoubtedly, the higher energy of both the π-HOMO and π^*-LUMO orbitals of OEiBC plays a major role in changing the order of the states relative to OEP and OEC.[45d] It is also possible that the $d_{x^2-y^2}$ orbital of Cu(OEiBC) lies somewhat lower in energy than in the other two complexes, given that the reduction potentials of Cu(OEP), Cu(OEC), and Cu(OEiBC) are essentially the same.

Our results for Pd(OEP), Pd(OEC), and Pd(OEiBC) require that the $d_{x^2-y^2}$ orbital lies higher in energy than the π^* orbitals. This is not surprising, because the Pd–N bond lengths in these complexes are significantly shorter than in $[Pd(cyclam)]^{2+}$.[42] This ordering of orbitals is consistent with the emission spectra of these complexes. All exhibit phosphorescence and weak fluorescence.[39,62] Emissions would be quenched by a low-lying, empty d orbital.

Cu(I) Reactivity. Several four-coordinate, macrocyclic complexes of Cu(I) form square-pyramidal complexes in the presence of added ligand.[15,16] Ligand types include amines, phosphines, phosphites, isocyanides, and CO. This reaction was most thoroughly investigated for $Cu^I(LBF_2)$. Measurements of formation constants for this and other macrocyclic complexes of Cu(I) establish that the thermodynamic stability of the adducts follow the increasing π-acceptor and decreasing σ-donor abilities of the ligand.[15b,15d,16] The macrocycle structure is also important. The complexes $Cu^I(LBF_2)$, $Cu^I(LB_2F_4)^-$, and $Cu^I(TIM)^+$ have comparable electronic and steric environments, yet the equilibrium constants for binding CO are 1.2×10^5, 8.8×10^5, and 42 M^{-1}, respectively.[15d] The differences suggest either that the BF_2 bridges assist CO binding (dipole interactions?) or that the charge of the complex is important. Molecular orbital calculations for $Cu^I(LBF_2)CO$ suggest that CO is bound to Cu through interactions of the CO σ orbital and the metal 4s and 4p orbitals supplemented

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(61) Another possible charge-transfer state is $(\pi)^2(d)^0(\pi^*)^1$, $Cu^{III}(P^-)$, a metal to ligand charge transfer. Although calculations do not agree on which of these two charge-transfer states is lowest in energy for porphyrin, evidence discussed in ref 60 suggests that it is the ligand to metal charge transfer. This is certainly the most chemically reasonable possibility for hydroporphyrins, which are much easier to oxidize and harder to reduce (OEiBC) than porphyrin.

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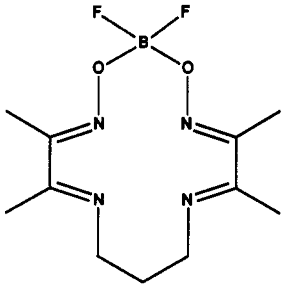
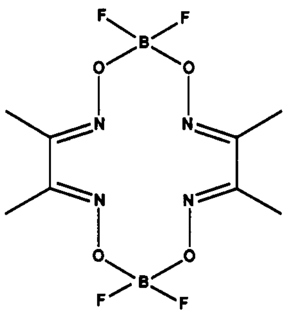
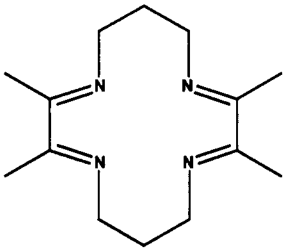


LBF$_2$



LB$_2$F$_4$



TIM

by π-back-donation from the filled metal dπ orbitals to the unoccupied CO π* orbitals.[63] The metal d orbitals are not believed to contribute to the metal–CO σ bond. For the purposes of the calculations, the copper atom was constrained to lie in the plane of the four nitrogen atoms. This is not a good approximation of the structure of Cu^I(LBF$_2$)CO.[15b] The copper atom lies 0.96 Å out of the basal plane of the four nitrogen atoms. Cu–N bond lengths are 2.10–2.16 Å. These features represent extremely large changes from the structure of the four-coordinate Cu^I(LBF$_2$) complex. In Cu^I(LBF$_2$), the Cu–N bond lengths average 1.94 Å and the coordination sphere is tetrahedrally distorted.[15c] The nitrogen atoms alternate 0.3 Å above and below the least-squares N$_4$ plane, which contains the copper atom.

We find no evidence that Cu^I(OEiBC)$^-$ binds added ligands. It is possible that binding occurs, but major structural changes make the reaction too slow to be detected by cyclic voltammetry. This is unlikely given the absences of changes in the spectra of Cu^I(OEiBC)$^-$ in the presence of CO and other ligands for extended times. Although it is possible that ligand addition would not significantly perturb the OEiBC π,π* transitions that dominate the UV–vis absorptions, it is difficult to argue that major structural changes upon ligand coordination would have no effect on the ^{1}H NMR spectrum.

Several explanations can be offered to rationalize the apparent inability of Cu^I(OEiBC)$^-$ to bind ligands and form square-pyramidal complexes. The tetrapyrrole ligand may not be sufficiently flexible to permit the necessary structural changes. The copper 4s and 4p orbitals in Cu^I(OEiBC)$^-$ may be too high in energy to interact effectively with the σ orbital of CO. Finally, OEiBC may function as a π-acceptor and thus compete with an added ligand for the π-electron density on copper.

Another interesting aspect of the reactivity of Cu^I(OEiBC)$^-$ is the sluggishness of its reaction with O$_2$. Cu^I(LBF$_2$) is more than 1 V weaker as a reducing agent ($E_{1/2}$ = −0.40 V vs SCE[16]) yet is reported to react rapidly and irreversibly with oxygen.[15b] Ni^I(OEiBC)$^-$ is formed at about the same potential as Cu^I(OEiBC)$^-$, but reacts more rapidly with O$_2$ and with CH$_3$I. Apparently, an activation barrier exists to the reoxidation of Cu^I(OEiBC)$^-$. This is not without precedent for Cu(I) complexes. The Cu(II)/Cu(I) self-exchange rate constants calculated from the cross-reaction of outer-sphere oxidants with certain Cu(I) complexes are smaller than those calculated from the reduction of the corresponding Cu(II) complex.[52a] The disparity was attributed to large structural differences between the two oxidation states. Structural data for Cu^I(OEiBC)$^-$ would help establish whether or not a similar effect operates here.

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