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Solution Characterization of Copper(II) and Silver(II) Porphyrins and the One-Electron Oxidation Products by Nuclear Magnetic Resonance Spectroscopy

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Abstract: The Cu(II) and Ag(II) complexes of tetraphenylporphyrin, octaethylporphyrin, etioporphyrin I, and the one-electron oxidation products of these metalloporphyrin species have been examined by nuclear magnetic resonance (NMR) spectroscopy. Deuterium NMR spectroscopy of selectively labeled porphyrin derivatives has permitted unambiguous assignment of signals, detection of signals with large line widths, and observation of porphyrin signals for solutions containing large concentrations of organic supporting electrolyte salts. The pyrrole deuteron chemical shift value for Cu(II) tetraphenylporphyrin correctly predicts the nuclear hyperfine coupling constant previously measured by ENDOR spectroscopy. Mixtures of electrochemically oxidized copper tetraphenylporphyrin species show a mole-weighted average chemical shift indicating fast electron exchange and reversibility of the oxidation process. Large alternating chemical shifts for the phenyl deuterons of oxidized copper tetraphenylporphyrin serve to confirm the a_{2u} radical character of this compound. Oxidized copper octaalkylporphyrins exhibit relatively small chemical shifts for the methine deuteron residue and a_{1u} radical character is inferred. Oxidized copper octaalkylporphyrins exist in dimeric form in frozen glasses at low temperature. Dimeric or higher order mixed aggregates are also formed between oxidized and parent Cu(II) compounds. Oxidized silver porphyrins exhibit NMR spectra consistent with those of diamagnetic species and show no fast electron exchange with the parent species in dichloromethane solution. Metal-centered oxidation is thus apparent for the Ag(II) complexes, whereas porphyrin-centered oxidation is the case for Cu(II) analogues.

Nuclear magnetic resonance spectroscopy has become a vital tool for examination of metalloporphyrin compounds in solution. Copper(II) and silver(II) porphyrin compounds on the other hand have not been amenable to thorough study by proton NMR spectroscopy as a consequence of extreme line broadening by efficient nuclear relaxaton from the metal center.[1] However, it is demonstrated here that deuterium NMR spectroscopy may be used to observe otherwise undetectably broad copper(II) and silver(II) metalloporphyrin signals,[2] and to avoid dynamic range problems from supporting electrolyte signals for in situ electrochemically oxidized metalloporphyrin species.

Oxidation of metalloporphyrin complexes can potentially take place at either the metal center or the porphyrin ring. An early study showed that oxidation of copper(II) octaethylporphyrin ((OEP)Cu) produced a species that was EPR silent at room temperature.[3] It was suggested that this could be due to the formation of a copper(III) porphyrin product. However, it has since been shown by electrochemical[4] and visible-UV spectral data[5] that one-electron oxidation of copper porphyrins is associated with formation of a π-cation radical species. The absence of EPR signals at moderate temperatures could be due to the following: (i) strong coupling with cancellation of radical and copper spins; (ii) efficient spin-spin relaxation by noninteracting spins; or (iii) large zero-field splitting for an $S = 1$ state. Solution magnetic susceptibility measurements on both chemically and electrochemically oxidized copper(II) tetraphenylporphyrin ((TPP)Cu) show no evidence for coupling between the unpaired electrons.[4,6] Thus, it is now thought that $[(TPP)Cu]^+$ is paramagnetic in solution with two unpaired electrons and that in the solid state the two spins are coupled, giving rise to a diamagnetic species. The nature of the π-cation radical species generated here has been monitored by deuterium NMR spectroscopy, and an unusual aggregation process has been delineated for copper(II) octaalkylporphyrins.

Unlike the copper porphyrin species discussed above, one-electron oxidation of silver(II) porphyrins apparently produces silver(III) complexes and not porphyrin π-cation radicals. It has been shown that both (OEP)Ag(II)[7] and (TPP)Ag(II)[8] have an unusually low first oxidation potential. Further work with $[(OEP)Ag]ClO_4$ revealed this compound had no EPR spectrum and was diamagnetic.[7] Also, an X-ray photoelectron study of both (OEP)Ag and $[(OEP)Ag]ClO_4$ shows a significant charge buildup on the silver atom on going from (OEP)Ag to $[(OEP)Ag]ClO_4$.[9] The above data and the NMR results presented here are consistent with the formation of silver(III) porphyrin species upon one-electron oxidation rather than a silver(II) porphyrin π-cation radical species.

Experimental Section

Materials. Heptane and dimethylformamide (MCB) were reagent grade and were used without further purification. Methylene chloride and chloroform were purified by washes with concentrated H_2SO_4 (until the acid layer was colorless), twice with water, twice with 10% Na_2CO_3 solution, and twice with water followed by equilibration overnight with $CaCl_2$ and distillation into brown bottles containing activated 4 Å molecular sieves. The bottles were purged with nitrogen or argon and stored in the refrigerator until use. Deuterated methylene chloride (Aldrich, gold label) was stored over 3 Å molecular sieves and was used as received. Deuterated chloroform was stirred over Na_2CO_3 overnight and was then distilled into vials that contained activated 3 Å molecular sieves. The vials were purged with nitrogen or argon and stored in the freezer.

The supporting electrolytes used for cyclic voltammetry and electrochemical oxidations were either tetra-*n*-propylammonium perchlorate or tetra-*n*-butylammonium perchlorate. These salts were purified by recrystallization from ethyl acetate or 4:1 acetonitrile/water.[10] The supporting electrolyte salts were dried under vacuum and stored in a re-

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frigerator. (**CAUTION**: Detonation of perchlorate compounds is well documented and although no shock sensitivity was observed for the metalloporphyrin perchlorates studied here, preparation of only milligram quantities is urged.)

Porphyrin Compounds. The free base porphyrin compounds, tetraphenylporphyrin (H_2TPP), octaethylporphyrin (H_2OEP), and etioporphyrin I (H_2ETIO), were prepared by literature methods.[11,12] The other tetraarylporphyrin derivatives, tetra-*p*-tolylporphyrin (H_2TTP) and tetrakis(3,4,5-trimethoxyphenyl)porphyrin (H_2-3,4,5-$(OCH_3)_3$TPP), were synthesized in the same manner as H_2TPP with *p*-tolualdehyde and 3,4,5-trimethoxybenzaldehyde, respectively.

The deuterated tetraphehylporphyrins, H_2TPP-d_8 (pyrrole deuterated) and H_2TPP-d_{20} (phenyl deuterated), were also synthesized by the pyrrole–aldehyde condensation method. Preparation of the pyrrole deuterated compound involved a 30-min reflux of pyrrole in propionic acid-d_1 (from D_2O and propionic anhydride) before the aldehyde was added.[13] The phenyl-deuterated compound was synthesized from benzaldehyde-d_6 that was obtained through oxidation of toluene-d_8 (Aldrich, gold label, 99+ atom % D) with ceric ammonium nitrate.[14]

Methine (meso) deuteration of H_2OEP and H_2ETIO was carried out by fusion of a mixture of the desired free base porphyrin and *p*-toluenesulfonic acid-d_1 to 115–120 °C for 8 h.[15] This method gave 80–85% meso deuteration. Simultaneous ring adjacent and meso deuteration of H_2OEP and H_2ETIO was carried out by an 8-day reflux reaction with *p*-toluenesulfonic acid-d_1, NaCl, and the porphyrin of interest in *o*-dichlorobenzene.[15] This method gave approximately 60% deuteration at the ring adjacent positions and >90% deuteration at the meso position. Ring methyl and ring methylene deuteration of H_2ETIO was also carried out by facile exchange in Me_2SO-d_6 in the presence of base.[16]

Copper and silver were inserted in all porphyrins by the dimethylformamide reflux method[17] through the use of copper(II) acetate and silver(I) acetate, respectively. After addition of the metal salt to the refluxing porphyrin–DMF solution the mixture was heated at reflux for an additional 30 min. The solution was allowed to cool and a 2–4 volume excess of an aqueous NaCl solution was added to promote precipitation. The solution was placed in the refrigerator overnight. After filtration and vacuum drying the solid was dissolved in CH_2Cl_2 and purified on an alumina column (CH_2Cl_2 eluent). Metalloporphyrins were obtained in microcrystalline form by the concurrent removal of CH_2Cl_2 and the slow addition of heptane. Homogeneity of the final product was determined by thin-layer chromatography (silica gel, 15% heptane in methylene chloride eluant). The visible–UV spectra of the products matched those previously reported.[3,4,7,18-20]

Physical Measurements. Proton NMR spectra were recorded on a Bruker WM-360 pulsed FT spectrometer operating at 360.13 MHz. The deuterium spectra were also obtained on the above instrument operating at 55.28 MHz. Metalloporphyrin compounds ranged in concentration from 1 to 9 mM. All NMR signal positions were obtained through use of the solvent signal as a secondary reference. The solvent signals for $CHCl_3$ ($CDCl_3$) and CH_2Cl_2 ($CHDCl_2$) were assigned as 7.24 and 5.32 ppm vs. Me_4Si, respectively.

Visible–UV spectra were recorded on a Beckman Model 25 spectrophotometer in either 1.0- or 0.10-cm cells with methylene chloride as the solvent.

Cyclic voltammetry and controlled potential coulometry were performed in methylene chloride solutions that were 0.10 M in supporting electrolyte and 1.5 to 3.5 mM in porphyrin. The supporting electrolytes were either tera-*n*-butylammonium perchlorate or tetra-*n*-propylammonium perchlorate. The working electrode was either a platinum bead (cyclic voltammetry) or a platinum basket (bulk oxidations), and the counterelectrode was a platinum coil separated from the bulk solution by a very fine fritted glass filter. The reference electrode was a silver wire immersed in a 0.10 M $AgNO_3$/acetonitrile solution that was separated from the bulk solution by a porous Vycor tip. An experimentally determined conversion factor of 0.38 V vs. SCE was used and all potentials in this paper are reported vs. the SCE. Measurements were made with a Princeton Applied Research Model 173 potentiostat driven by a Model 175 Universal Programmer.

Electron paramagnetic resonance measurements were made on a Varian E-104A X-band spectrometer equipped with an Air Products LTD-3-110 Heli-Tran low-temperature system. Oxidized samples were run in methylene chloride solutions that were approximately 0.1 M in tetra-*n*-propylammonium perchlorate and 3.5 mM in total metalloporphyrin.

Magnetic susceptibility measurements were obtained by the method of Evans[21] in CH_2Cl_2 solutions containing 1% Me_4Si. Solutions of oxidized porphyrin were obtained by concentration of the solution from the electrolysis cell after the completion of bulk electrolysis. After transfer of a known volume of the porphyrin solution to a small vial the appropriate amount of Me_4Si was added with a microsyringe. The solution in the reference tube was approximately 0.5 M in supporting electrolyte (CH_2Cl_2 solvent) with 1% Me_4Si. The concentration of oxidized porphyrin in the outer tube was determined by transfer of a known amount of solution to a volumetric flask, reduction to the parent compound with excess tetra-*n*-butylammonium iodide, TBAI, dilution to known volume, and determination of the concentration from the absorption at a specific wavelength. The molar absorptivity values used were ϵ_{413} = 492 L/mM cm[22] for (TPP)Cu and ϵ_{399} = 305 L/mM cm[3,23] for (OEP)Cu. At 25 °C magnetic moment values of 2.4 ± 0.1 and 2.3 ± 0.1 μ_B were obtained for [(TPP)Cu]ClO_4 and [(OEP)Cu]ClO_4, respectively.

Titrations of oxidized copper octaalkylporphyrins with tetra-*n*-butylammonium iodide, TBAI, were conducted as follows. After the porphyrin had been oxidized by electrochemical means and the solution volume was reduced under a nitrogen stream, 2 mL of the concentrated solution was transfered to a 2-mL volumetric flask. The concentration of this solution was then determined spectrophotometrically, and the remainder of the undiluted solution was transferred to a 10-mm NMR tube. A standard solution of TBAI in CH_2Cl_2 was utilized such that 10-μL increments would cause the reduction of 8 to 12.5% of the oxidized copper porphyrin.

The titration of [(OEP)Cu]ClO_4 with TBAI, for EPR spectroscopy, was conducted as follows. After electrochemical oxidation of the porphyrin was complete a portion of the solution was transfered to a vial. The concentration of this solution was determined spectrophotometrically, and a standard solution of TBAI was prepared. A small amount of the oxidized porphyrin solution was transfered to a vial, the appropriate amount of the TBAI solution was added, and the mixture was transfered to an EPR tube.

Infrared spectra were recorded on a Beckman IR-20A spectrometer in Nujol mulls on sodium chloride plates. Crystalline oxidized metalloporphyrins were prepared by immediate removal of the CH_2Cl_2 after electrolysis by vacuum evaporation, followed by addition of acetonitrile to dissolve the supporting electrolyte (the oxidized porphyrins were also slightly soluble in acetonitrile). The mixture was filtered, and the solid oxidized metalloporphyrin was washed with a small amount of acetonitrile and dried under vacuum.

Results

Copper(II) Porphyrin NMR Spectroscopy. The proton NMR spectra of (TPP)Cu, (TPP)Cu, and (3,4,5-$(OCH_3)_3$TPP)Cu are shown in Figure 1. The two signals in the phenyl region of (TPP)Cu at 7.62 and 7.48 ppm can be assigned to the *p*- and *m*-phenyl protons, respectively, from the following observations. The proton NMR spectrum of (3,4,5-$(OCH_3)_3$TPP)Cu shows a broad *o*-phenyl signal located at 6.9 ppm. In the NMR spectrum of (TTP)Cu a broad, presumably *o*-phenyl proton signal can also be seen partially obscured by the *m*-phenyl signal. The proton NMR spectrum of (TTP)Cu shows a *m*-phenyl signal at 7.30 ppm. It is known that the *m*-phenyl signal is shifted upfield 0.21 ppm for the TTP derivative as compared with the TPP derivative in both Co(III)[24] and unmetalated[25] porphyrins. Thus, the signal

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(20) Absorption maxima for metalloporphyrin compounds dissolved in CH_2Cl_2: (TPP)Cu, 391 (shoulder), 413 (Soret), 500, 537, 570, and 614 nm; (TTP)Cu, 395 (shoulder), 415 (Soret), 470, 503, 539, 573, and 616 nm; (3,4,5-$(OCH_3)_3$TPP)Cu, 395 (shoulder), 417 (Soret), 500, 537, and 569 nm; (TPP)Ag, 400 (shoulder), 425 (Soret), 504, 540, 572, and 604 nm; (OEP)Ag, 406 (Soret), 523, and 557 nm; (ETIO)Ag, 407 (Soret), 522, and 556 nm.

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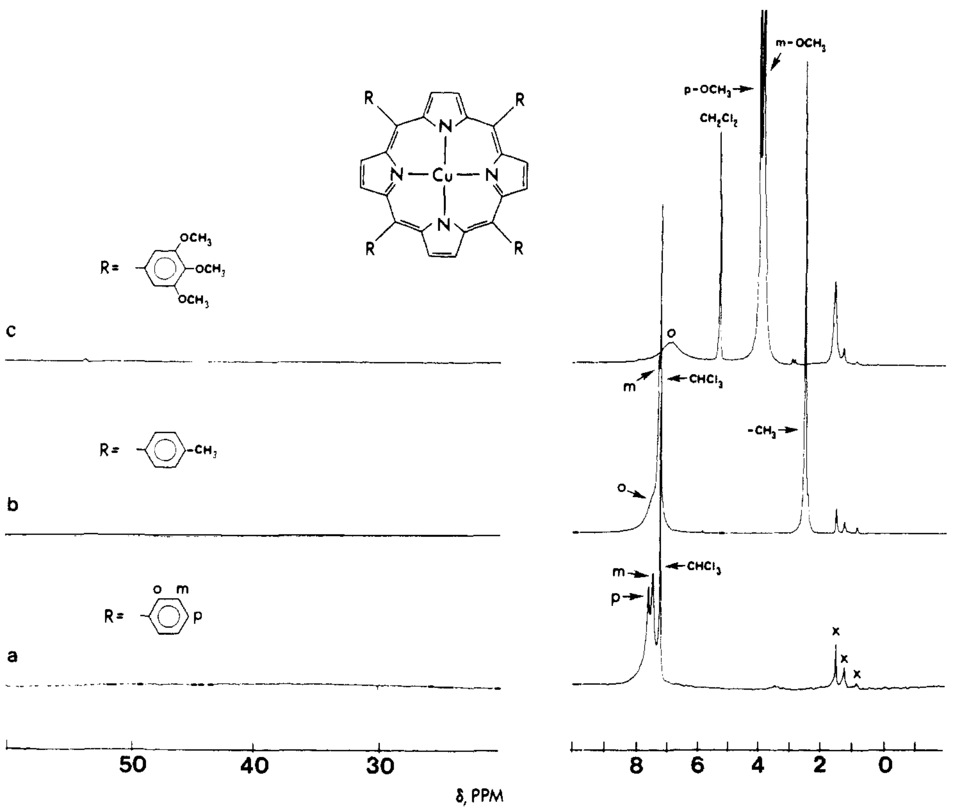

Figure 1. Proton NMR spectra of copper tetraarylporphyrins: (a) (TPP)Cu in $CDCl_3$, (b) (TTP)Cu in $CDCl_3$, and (c) (3,4,5-$(OCH_3)_3$TPP)Cu in CD_2Cl_2. All spectra referenced to $(CH_3)_4Si$ at 25 °C.

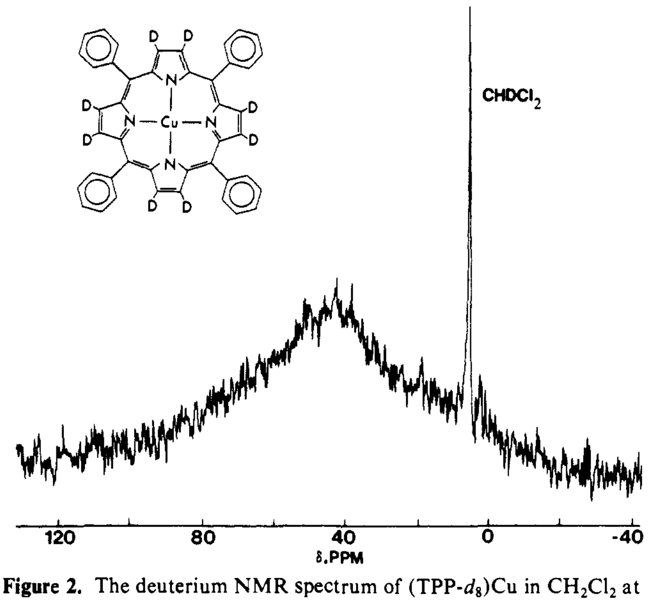

Figure 2. The deuterium NMR spectrum of (TPP-d_8)Cu in CH_2Cl_2 at 25 °C, referenced to $(CD_3)_4Si$.

at 7.48 ppm in the spectrum of (TPP)Cu can be assigned to the *m*-phenyl protons. The remaining sharp signal at 7.62 ppm in the spectrum of (TPP)Cu must therefore arise from the *p*-phenyl proton. Relatively small hyperfine shifts for phenyl protons are indicative of only minor magnetic anisotropy for the Cu(II) ion as described below.

No pyrrole proton signal was detectable for the spectra shown in Figure 1. However, the resonance was observable in the deuterium spectrum of pyrrole-d_8-(TPP)Cu. In the limiting case of electron-nuclear dipolar relaxation the NMR line width is directly proportional to the square of the gyromagnetic ratio of the nucleus.[2] Thus, the NMR line width for a proton signal can be as much as 42 times greater than that of the deuterium signal. The deuterium NMR spectrum of pyrrole-deuterated (TPP)Cu-(TPP-d_8)Cu is shown in Figure 2. The pyrrole deuteron exhibits a broad resonance (line width = 1150 Hz at half-height) located 41 ppm downfield from Me_4Si. No broad feature of this type was apparent in the spectrum for the nondeuterated compound.

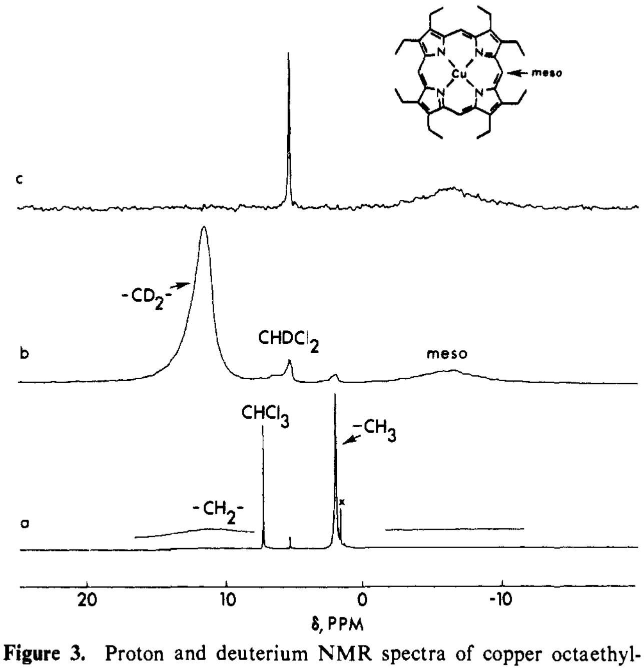

Figure 3. Proton and deuterium NMR spectra of copper octaethylporphyrin: (a) proton spectrum of OEPCu in $CDCl_3$, (b) deuterium spectrum of (OEP-d_{20})Cu in CH_2Cl_2, and (c) deuterium spectrum of (OEP-d_4)Cu in CH_2Cl_2. All spectra were taken at 25 °C and are referenced to $(CH_3)_4Si$ or $(CD_3)_4Si$.

The proton and deuterium NMR spectra of (OEP)Cu and its deuterated analogues are shown in Figure 3. The proton NMR

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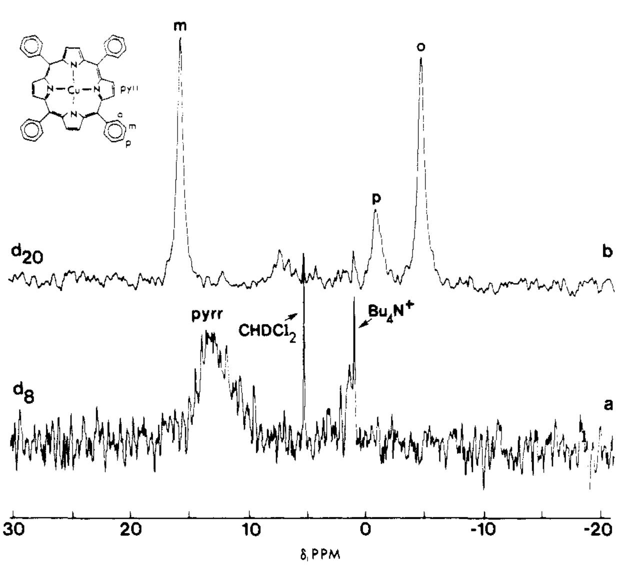

Figure 4. The deuterium NMR spectra of oxidized (TPP)Cu: (a) $[(\mathrm{TPP}\text{-}d_8)\mathrm{Cu}]\mathrm{ClO_4}$ and (b) $[(\mathrm{TPP}\text{-}d_{20})\mathrm{Cu}]\mathrm{ClO_4}$. Both spectra were taken in CH_2Cl_2 at 25 °C and are referenced to $(CD_3)_4Si$.

spectrum of OEPCu (Figure 3a) shows signals at 11.5 (br) and 1.88 ppm, and the deuterium NMR spectrum of $(\mathrm{OEP}\text{-}d_{20})\mathrm{Cu}$ (Figure 3b) shows signals at 11.5 and −6.2 ppm. The signal at −6.2 ppm is also seen in the spectrum of $(\mathrm{OEP}\text{-}d_4)\mathrm{Cu}$ (Figure 3c) and thus can be assigned to the meso deuterons. The signal at 11.5 ppm is due to the ring methylene protons because of its presence in the spectrum of $(\mathrm{OEP}\text{-}d_{20})\mathrm{Cu}$ and because the ring methylene protons are expected to have a larger paramagnetic shift and a larger linewidth than the ethyl-CH_3 protons.

The proton NMR spectrum of (ETIO)Cu shows signals at 11.1 (br), 6.4, and 1.86 ppm. The deuterium NMR spectrum of $(\mathrm{ETIO}\text{-}d_{24})\mathrm{Cu}$ shows signals at 11.3, 6.5, and −6.2 ppm. These data along with that previously obtained for (OEP)Cu allow assignment of the signals as follows: 11.3, ring methylene; 6.5, ring methyl; 1.86, ethyl CH_3; −6.2 ppm, meso proton.

Oxidized Copper Porphyrins. Copper(II) tetraphenylporphyrin was exhaustively oxidized at the first oxidation wave and the process was monitored by visible–UV spectroscopy and a drop in potentiostat current to 1% of the initial value. The visible–UV spectrum of $[(\mathrm{TPP})\mathrm{Cu}]^+$ in CH_2Cl_2 (λ_{max} 385 (shoulder), 408 (Soret), 435 (shoulder), 587, and 640 nm) resembled the spectrum previously reported for the same species in benzonitrile.[4] The deuterium NMR spectra of $[(\mathrm{TPP}\text{-}d_8)\mathrm{Cu}]^+$ and $[(\mathrm{TPP}\text{-}d_{20})\mathrm{Cu}]^+$ are shown in Figure 4. The pyrrole signal in $[(\mathrm{TPP}\text{-}d_8)\mathrm{Cu}]^+$ is shifted upfield to 13.4 ppm and the line width of this peak is decreased significantly with respect to that of the parent species. Addition of $(\mathrm{TPP}\text{-}d_8)\mathrm{Cu}$ to this sample caused the pyrrole signal to shift downfield and its line width to increase, indicating fast electron exchange between $(\mathrm{TPP}\text{-}d_8)\mathrm{Cu}$ and $[(\mathrm{TPP})\mathrm{Cu}]\mathrm{ClO_4}$ in solution, as well as totally reversible electrochemical oxidation. The NMR spectrum of $[(\mathrm{TPP}\text{-}d_{20})\mathrm{Cu}]^+$ showed three peaks at 15.8 (*m*-phenyl), −1.01 (*p*-phenyl), and −4.90 ppm (*o*-phenyl).

The first oxidation potential for (OEP)Cu (ring oxidation) was determined to be 0.85 ± 0.03 V in CH_2Cl_2 (a first oxidation potential of 0.79 V is known for the same species in 4:1 chloroform/methanol[3]). Oxidation of the bulk solution was carried out at 0.98 V. A visible–UV spectrum of the resulting oxidized species in CH_2Cl_2 (λ_{max} 380 (Soret), 471, 511, 558, and 612 nm) compared favorably with the spectrum for the species in 4:1 chloroform/methanol.[3] The deuterium NMR spectrum of $[(\mathrm{OEP}\text{-}d_{20})\mathrm{Cu}]\mathrm{ClO_4}$ shows signals at 17.1 and −4.1 ppm. The signal at −4.1 ppm is due to the meso deuterons, as this signal is also seen in the spectrum of $[(\mathrm{OEP}\text{-}d_4)\mathrm{Cu}]\mathrm{ClO_4}$. The signal at 17.1 ppm is due to the ring methylene deuterons.

The first oxidation potential of (ETIO)Cu was determined to be 0.84 ± 0.03 V in CH_2Cl_2. After complete oxidation the visible–UV spectrum (λ_{max} 380 (Soret), 510, 558, and 615 nm) closely resembled that of $[(\mathrm{OEP})\mathrm{Cu}]\mathrm{ClO_4}$. The deuterium NMR spectrum of $[(\mathrm{ETIO}\text{-}d_{24})\mathrm{Cu}]\mathrm{ClO_4}$ (see Figure 5a) shows signals at 12.7 and −10 ppm.

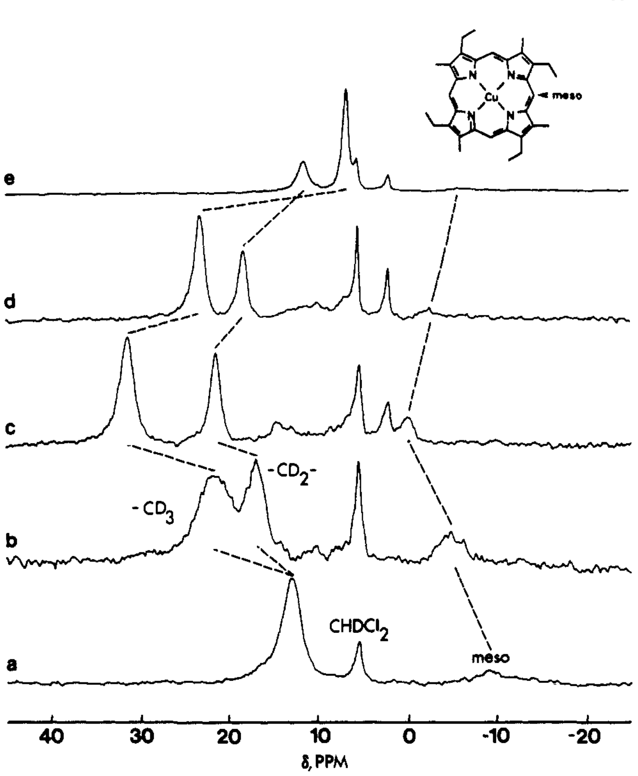

Figure 5. Deuterium NMR spectra for the titration of $[(\mathrm{ETIO}\text{-}d_{24})\mathrm{Cu}]\mathrm{ClO_4}$ with tetra-*n*-butylammonium iodide: (a) 0% reduced, (b) 12.5% reduced, (c) 37.5% reduced, (d) 62.5% reduced, (e) 1.125 equiv of I^- added. All spectra were taken at 25 °C in CH_2Cl_2 which was approximately 0.5 M in tetra-*n*-propylammonium perchlorate and 7.4 mM in total porphyrin. All spectra are referenced to $(CD_3)_4Si$.

Addition of parent compound or an appropriate reducing agent to either of the oxidized copper octaalkylporphyrins causes a downfield shift of all of the porphyrin signals. This is not the expected result for fast electron exchange between the parent and ozidized porphyrin species in which case the mole fraction weighted average of the signals for the two species should be seen. The NMR spectra associated with the titration of $[(\mathrm{ETIO}\text{-}d_{24})\mathrm{Cu}]\mathrm{ClO_4}$ with the reducing agent tetra-*n*-butylammonium iodide are shown in Figure 5. As the amount of reductant was increased the overlapping ring methylene and ring methyl signals split and both signals moved downfield to 21.4 and 31.5 ppm, respectively (Figure 5c). After 37.5% of the porphyrin had been reduced, the signals began to move upfield until reduction was complete, at which point the spectrum was the same as that of the parent species. The meso deuteron signal moved in the same manner. A titration of $[(\mathrm{OEP}\text{-}d_{20})\mathrm{Cu}]\mathrm{ClO_4}$ (not included) showed the same downfield and upfield shift pattern for progressive reduction, with the maximum downfield shift occurring when 33% of the porphyrin was reduced. The fact that the furthest downfield shifts of both the octaalkylporphyrins occurred at the same fraction of added reductant indicates the formation of the same type of species in both cases. The NMR titration data thus demonstrate existence of at least one additional species in solutions containing parent Cu(II) octaalkylporphyrins and their π-cation radical derivatives.

Electron spin resonance spectral data for the titration of $[(\mathrm{OEP})\mathrm{Cu}]\mathrm{ClO_4}$ with TBAI are shown in Figure 6. In agreement with NMR results the EPR spectra for solutions containing mixtures of Cu(II) octaalkylporphyrins and the corresponding π-cation radical species reveal the presence of new components. Interpretations of the spectra are offered in the Discussion section.

Silver Porphyrins. The proton NMR spectrum of (TPP)Ag in CD_2Cl_2 shows two signals at 7.77 and 7.65 ppm. These two signals presumably represent phenyl protons that are unshifted by the relatively isotropic paramagnetic silver(II) center. A deuterium NMR spectrum of $(\mathrm{TPP}\text{-}d_8)\mathrm{Ag}$ reveals no signal that

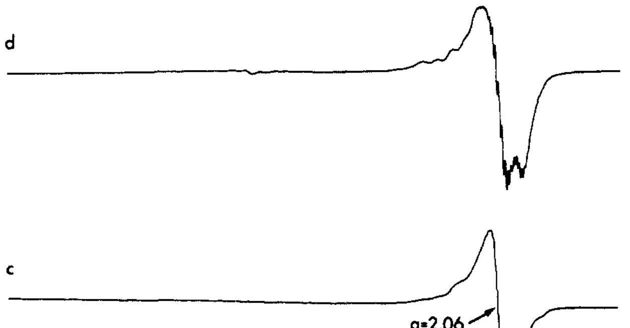

Figure 6. EPR spectra of the reduction of [(OEP)Cu]ClO_4 with tetra-*n*-butylammonium iodide: (a) 0% reduced, (b) 8.3% reduced, (c) 24.9% reduced, and (d) 74.7% reduced. All spectra were run at 5.5 K in CH_2Cl_2 which was approximately 0.1 M in tetra-*n*-propylammonium perchlorate.

can be assigned to the β-pyrrole deuterons; the signal is presumably broadened beyond the detection limits of the spectrometer.

The proton NMR spectra of both (OEP)Ag (see Figure 7) and (ETIO)Ag exhibit a single, sharp peak at 2.31 ppm. As with the copper(II) octaalkylporphyrins discussed above the ethyl-CH_3 proton is adequately removed from the metal center to sense little or no paramagnetic shift, and the sharp signal at 2.31 ppm is thus assigned to this residue. The assignment is also confirmed by the deuterium NMR spectra of (OEP-d_4)Ag and (OEP-d_{20})Ag (see Figure 7). Two signals located at −15.1 and 17.3 ppm are observed in the spectrum of (OEP-d_{20})Ag, whereas (OEP-d_4)Ag shows only one signal at −15.1 ppm. The upfield signal is therefore assigned to the meso deuteron and the downfield signal is assigned to the ring-CH_2 group.

It has been determined that the first oxidation potential for (TPP)Ag(III) is at 0.54 V in CH_2Cl_2 solution.[8] Oxidation of (TPP-d_8)Ag(II) was carried out at 0.66 V and the reaction was judged complete when the current reading had dropped to 1% of the initial value. The deuterium NMR spectrum of the resulting [(TPP-d_8)Ag]ClO_4 shows a sharp pyrrole signal at 9.65 ppm. Addition of (TPP-d_8)Ag to the tube does not cause a shift in the position of this signal, indicating no fast electron exchange between the parent and oxidized species. The infrared spectrum of solid [TPPAg]ClO_4 isolated from the supporting electrolyte shows no signal in the 1270–1295-cm^{-1} range characteristic of a π-cation radical.[26]

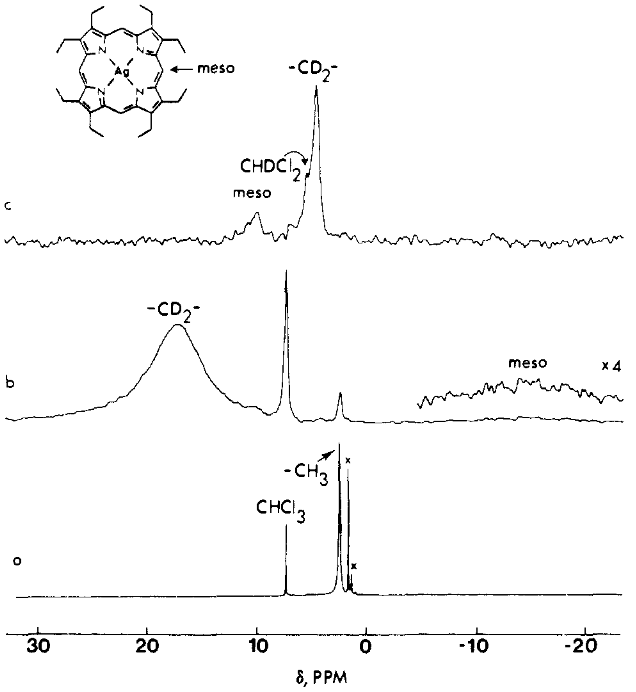

Figure 7. Proton and deuterium NMR spectra of silver octaethylporphyrins: (a) proton spectrum of (OEP)Ag in $CDCl_3$, (b) deuterium spectrum of (OEP-d_{20})Ag in $CHCl_3$, and (c) deuterium spectrum of [(OEP-d_{20})Ag]ClO_4 in CH_2Cl_2. All spectra were taken at 25 °C and are referenced to $(CD_3)_4Si$.

The first oxidation potential for (OEP)Ag has been determined to be 0.44 V in CH_2Cl_2 solution.[8] Oxidation of (OEP-d_{20})Ag was carried out at 0.61 V. A visible–UV spectrum of the oxidized species shows little change in band positions from the parent compound, but there is a change in the relative intensity of the two bands in the 500–600-nm region as was reported for the same species in chloroform/methanol solution.[7] The deuterium NMR spectrum of [(OEP-d_{20})Ag]ClO_4 is presented in Figure 7. The spectrum shows signals located at 9.9 and 4.39 ppm for the methine and ring methylene protons, respectively.

Discussion

It is of interest to discuss the pattern of NMR hyperfine chemical shift values detected for Cu(II) and Ag(II) porphyrins in the context of spectra measured for other paramagnetic metalloporphyrin complexes. Copper(II) and silver(II) porphyrins presumably exhibit an electronic structure in which the unpaired spin is located in the $d_{x^2-y^2}$ orbital. To first order the resulting σ-symmetry unpaired spin should be delocalized into a porphyrin molecular orbital of compatible symmetry such that only downfield porphyrin contact shifts would be expected. The 41-ppm pyrrole proton signal for (TPP)Cu is thus consistent with signals seen in the 30–60-ppm region for other 2+ metallotetraarylporphyrins bearing unpaired spin in the $d_{x^2-y^2}$ orbital.[1,27] Likewise, downfield ring CH_2 and CH_3 proton NMR signals are observed for other paramagnetic metalloporphyrin complexes in which unpaired σ-spin density is prevalent. The upfield shifted meso proton signal in Cu(II) and Ag(II) octaalkylporphyrins is, however, counter to the expectation of consistent downfield shifts. The magnitude of the upfield shift cannot be explained by a dipolar shift term. An upfield shift of comparable magnitude is observed for the meso proton signal of paramagnetic nickel(II) porphyrin complexes.[1] The anomalous signal position has been rationalized in the nickel(II) case through hypothetical polarization of nickel(II) π-symmetry paired spin by the $d_{x^2-y^2}$ spin. Such σ–π spin polarization has also been invoked to explain nonaxial pyrrole hyperfine tensors derived from analysis of the (TPP)Cu and (TPP)Ag ENDOR data.[28,29]

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Table I. Proton and Deuteron NMR Chemical Shifts for Copper and Silver Porphyrins and Their One-Electron Oxidation Products[a]

porphyrin	*o*-phenyl	*m*-phenyl	*p*-phenyl	β-pyrrole	meso	ring $-CH_2-$	ring $-CH_3$	ethyl $-CH_3$
(TPP)Ag[b]	×	7.65 (?)	7.77 (?)	×				
(ETIO)Ag[b]					×	×	×	2.31 (61)
(OEP)Ag[b]					×	×		2.32 (56)
(OEP-d_{20})Ag[c]					-15.1 (674)	17.3 (317)		
[(TPP-d_8)Ag]ClO_4[b]				9.65 (135)				
[(OEP-d_{20})Ag]ClO_4[b]					9.9 (84)	4.39 (35)		
(TTP)Cu[b]	7.48 (144)	7.30 (32)	2.52 (10)[e]	×				
(3,4,5-$(OCH_3)_3$TPP)Cu[d]	6.9 (274)	3.86 (32)[f]	3.98 (17)[g]	×				
(TPP)Cu[b]	×	7.48 (35)	7.62 (39)	×				
(TPP-d_8)Cu[c]				41 (1150)				
[(TPP-d_8)Cu]ClO_4[c]				13.4 (177)				
[(TPP-d_{20})Cu]ClO_4[c]	-4.90 (24)	15.8 (23)	-1.01 (37)					
(OEP)Cu[b]					×	11.5 (1275)		1.88 (49)
(OEP-d_{20})Cu[c]					-6.2 (240)	11.5 (85)		
[(OEP-d_{20})Cu]ClO_4[c]					-4.1 (230)	17.1 (122)		
(ETIO)Cu[b]					×	11.1 (1000)	6.4 (303)	1.86 (39)
(ETIO-d_{24})Cu[c]					-6.2 (205)	11.3 (66)	6.5 (19)	
[(ETIO-d_{24})Cu]ClO_4[c]					-10 (400)	12.7 (150)	12.7 (150)	

[a] All spectra were obtained at 25 °C and chemical shift values are referenced to Me_4Si. Line widths, in parentheses, are given in Hz, "×" entries indicate signals not detected due to large line width and/or overlap with other signals. [b] $CDCl_3$ solvent. [c] CH_2Cl_2 solvent. [d] CD_2Cl_2 solvent. [e] *p*-CH_3 signal. [f] *m*-OCH_3 signal. [g] *p*-OCH_3 signal.

Assuming equivalent chemical shifts for deuterons and protons, the proton hyperfine coupling constant, A_s, can be calculated for the pyrrole proton signal of (TPP)Cu by use of the following relationship

$$\frac{\Delta H}{H_0} = -\frac{g\beta S(S+1)}{(\gamma_N/2\pi)3kT}A_s$$

where g is the rotationally averaged g value, β is the absolute value of the Bohr magneton, γ_N is the nuclear gyromagnetic ratio, and ΔH is the isotopic shift at an applied magnetic field H_0.[30] With use of a value of 32 ppm for the hyperfine contact shift an A_s value of 1.2 MHz is obtained for the proton hyperfine coupling constant. This is to be compared with a value of 1.32 MHz for the proton hyperfine coupling constant of the β-pyrrole protons of (TPP)Cu obtained by Brown and Hoffman from ENDOR spectroscopy at 30 K.[28] Through application of deuterium NMR spectroscopy it is thus possible to measure and determine the sign of electron–nuclear coupling constants in systems with long T_{1e} values. The pyrrole deuteron signal of (TPP)Ag is, however, seemingly broadened beyond the detection limits of high-resolution NMR instrumentation; the ENDOR coupling constant of 2.13 MHz for the corresponding proton signal indicates that the NMR resonance should be found at 65 ppm.

In several paramagnetic metalloporphyrin complexes the hyperfine chemical shifts for *meso*-phenyl substituents are due entirely to the through-space dipolar term.[1,27] Relatively small upfield shifts for the phenyl protons of (TPP)Cu are indicative of small magnetic anisotropy, but the magnitude of shifts precludes reliable calculation of the anisotropy. The general upfield bias of phenyl signals as compared with those of diamagnetic analogues would indicate magnetic anisotropy of the form $\chi_\parallel > \chi_\perp$ consistent with the known ordering of $g_\parallel > g_\perp$ from EPR spectra.

The general case of oxidation of heavier metals within a given periodic group is apparent for copper(II) and silver(II) in the porphyrin environment. This difference is manifested in oxidation of Ag(II) to Ag(III) in the porphyrin complex, whereas porphyrin ring oxidation is more facile for the Cu(II) analogue. Presence of the diagnostic infrared band at 1295 cm^{-1} has previously confirmed the radical character of the $[(TPP)Cu]^+$ product.[26] The resulting Cu(II) tetraphenylporphyrin cation radical has been variously described as having a strongly coupled $S = 0$ state,[31] a ferromagnetically coupled $S = 1$ state,[4] and as a molecule bearing only weakly interacting $S = {}^1/_2$ centers.[6] Previous workers have noted that the crystalline product is diamagnetic, whereas the solution species has $\mu_{eff} = 2.4\ \mu_B$.[6] the solution magnetic moment of 2.4 ± 0.1 μ_β for $[(TPP)Cu]^+$ was reproduced for the electrochemically oxidized material during the course of magnetic resonance studies reported here. This value matches the expected combination of two noninteracting $S = {}^1/_2$ centers as compared with the value of 2.83 μ_B for a "spin-only" $S = 1$ molecule.

Deuterium NMR results confirm the radical nature of $[(TPP)Cu]^+$ in that large phenyl deuteron shifts of alternating sign are seen only for metallotetraarylporphyrin radicals. Chemical shifts are, however, attenuated for phenyl signals of $[(TPP)Cu]^+$ as compared with those for $(TPP)Fe^{III}$ radical complexes. For example, the *o*-phenyl deuteron signal in $(TPP)Fe(ClO_4)_2$ is located at -16.2 ppm;[32] the signal for $[(TPP)Cu]^+$ is located at -4.90 ppm. On the basis of a 0.316 G *o*-phenyl proton–electron coupling constant for $(TPP)Zn(ClO_4)$,[33] an *o*-phenyl proton (deuteron) signal is expected at -15 ppm for a TPP–metal π-cation radical species. Perhaps the unusually large "ruffling" of the porphyrin core seen in the crystal structure[6] for $[(TPP)Cu](SbCl_6)$ serves to attenuate the π-cation radical spin transfer to the meso carbon residues. Significant chemical shifts for the phenyl protons (deuterons) do indicate major spin density transfer to the meso carbon atom consistent with classification of $[(TPP)Cu]^+$ as an a_{2u} type radial. This radical type is expected to have large spin density at the meso carbon and the pyrrole nitrogen atoms, whereas an a_{1u} radical would have little spin density at the meso position and major spin density at the α-pyrrole carbon atom.[33]

The pyrrole deuteron signal of (TPP)Cu at 41 ppm is shifted upfield to 13.4 ppm and the line width is greatly reduced upon oxidation of the porphyrin ring. The upfield shift may be rationalized by a strong contribution of radical π-spin density at the β-pyrrole carbon atoms that induces an upfield bias to the signal for the attached proton (deuteron). The balance between the downfield σ-spin contribution of the Cu(II) $d_{x^2-y^2}$ spin and the π-radical spin reasonably could result in near cancellation of the hyperfine chemical shift. Reduced line width for the 13.4-ppm resonance likely reflects metal–radical spin–spin interactions that must shorten the effective T_{1e} value and cause loss of the EPR signal at temperatures down to 77 K.[4]

Rationalization of NMR signal positions for the Cu(II) octaalkylporphyrin radical species may be complicated by the apparent aggregation of these species. Existence of $[(OEP)Cu]^+$ dimers

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is suggested by the EPR measurements described below. At ambient temperature, however, any occurrence of such dimerization does not result in spin pairing, as the magnetic moment per copper porphyrin unit is 2.3 ± 0.1 μ_B. Chemical shifts are surprisingly small for ring CH_2 and CH_3 residues (see Figure 5a) of the $[(ETIO)Cu]^+$ product in that the combination of σ-spin density from the metal center and the π-spin density from the porphyrin radical would be expected to induce large downfield shifts. Magnification of chemical shifts for these residues is apparent in the spectrum of the mixture of oxidized and parent (ETIO)Cu (Figure 5c), and the greater shift of the CH_3 signal as compared with the CH_2 signal confirms a major contribution of π-spin density at the β-pyrrole carbon atom. The position of the meso deuteron signal in the near upfield region for all the oxidized tetraalkylporphyrin copper(II) species is significant in that only small π-spin density must be present at the meso carbon atom. This observation is contrary to classification of $[(OEP)Cu]^+$ as an a_{2u} radical type as has been offered on the basis of MCD measurements.[34] Thus, a_{2u} radicals typically exhibit spin densities of 0.12 at the meso carbon atom,[23] and this value would translate as a proton chemical shift of some 200 ppm upfield. The −4.1 ppm meso proton (deuteron) signal is clearly indicative of an a_{1u} radical type.

Aggregation of metallooctaalkylporphyrins and corresponding cation radicals has been delineated by EPR measurements in a number of cases.[35] Zinc and magnesium porphyrin cation radicals are known to dimerize in frozen solutions at low temperature, and the resulting π–π stacked aggregates are diamagnetic.[3,36,37] Although problems have been reported with detection of EPR signals for the $[(OEP)Cu]^+$ species,[3] dichloromethane solutions containing this ion and supporting electrolyte from the electrochemical preparation scheme readily gave signals at 5.0 to 80 K. A series of spectra recorded with progressive reduction are shown in Figure 6. The fully oxidized material in trace "a" exhibits a spectrum equivalent to that reported for the octaethylchlorin copper(II) radical cation at 100 K.[38] The spectrum is characteristic of a dimeric Cu(II) triplet state, and the seven-line, 100-G hyperfine structure (upon expansion) in the 1800-G region confirms the interaction of two copper centers. This spectrum differs from that produced by γ-ray irradiation of a frozen solution of (TPP)Cu in that the low-field signal for the γ-irradiated glass consists of only a four-line component from the interaction of only one Cu(II) center.[39] The radiation-induced oxidation in a frozen glass most likely yields a transient, monomeric copper radical species.

Partial reduction of $[(OEP)Cu]^+$ does not produce spectra (traces "b" and "c" in Figure 6) that are sums of spectra for $[(OEP)Cu]^+$ and (OEP)Cu. Mixtures of the oxidized and parent materials yield spectra with a prominent broad $g = 2.06$ band that is devoid of hyperfine splitting. Such spectra are reminiscent of those seen for coupled, highly delocalized $S = {}^1/_2$ species. Hence the predominant species present when $[(OEP)Cu]^+$ and (OEP)Cu are mixed in equal quantities is thought to be a dimer or higher aggregate in which the radical spin is delocalized over the porphyrin centers. Precedent exists for formation of partially oxidized chlorophyll[40,41] and vanadyl porphyrin[42] aggregates of this type. The unique deuteron NMR spectra obtained for mixtures of the oxidized and parent Cu(II) porphyrin compounds also suggest formation of such aggregates with $S = {}^1/_2$ and/or $S = {}^3/_2$ character.

Conclusions

Magnetic resonance methods have provided additional molecular and electronic structural characterization of Cu(II) and Ag(II) porphyrins and their one-electron oxidation products. Unpaired spin delocalization patterns reflect not only contributions from the singly occupied σ-symmetry $d_{x^2-y^2}$ orbital but also the presence of π-spin density likely as a consequence of σ–π polarization. Relatively small phenyl proton NMR hyperfine shifts in (TPP)Cu and (TPP)Ag reflect only minor dipolar shift contributions from the rather isotropic metal ion centers. Porphyrin-centered oxidation of the Cu(II) and metal-centered oxidation of the Ag(II) derivatives has been confirmed. For the tetraarylporphyrin series rapid electron transfer is seen between Cu(II) porphyrin–Cu(II) porphyrin radical species, but electron transfer is slow on the NMR time scale for Ag(II)–Ag(III) analogues. The resulting Cu(II) tetraarylporphyrin cation radicals are shown to be of the a_{2u} type, whereas the Cu(II) octaalkylporphyrin radicals are best classified as a_{1u} type. Dimerization of the Cu(II) octaalkylporphyrin radicals is apparent at low temperature. Formation of aggregates involving Cu(II) octaalkylporphyrins and Cu(II) octaalkylporphyrin radicals is apparent at low temperature in EPR spectra and at ambient temperature in the NMR spectra.

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