in rate. These results are also consistent with complex formation and indicate that if a very stable copper complex is formed, the porphyrin is unable to "extract" the metal ion from it. The failure of the other metal ions examined to show any signs of incorporation, especially Zn(II), is less easily explained. However, these results can be interpreted within the framework of complex formation. If the cofactor (e.g., quinoline) acted only as a base to aid in proton removal, then its effectiveness would not depend on the particular metal ion. However, for a given ligand, the metal ion does affect the nature (stoichiometry, stability, lability, and geometry) of the complex.

Registry No. Copper, 7440-50-8; tetraphenylporphine, 917-23-7; benzene, 71-43-2; cyclohexanol, 108-93-0; potassium oleate, 143-18-0; sodium cetyl sulfate, 1120-01-0; octadecyl acetate, 822-23-1; albumin, 9048-46-8; quinoline, 91-22-5.

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Reactions in Microemulsions. II. Stabilization of Intermediates by Triphenylphosphine in the Incorporation of Copper(II) by Tetraphenylporphine

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We have investigated the effect of triphenylphosphine on the incorporation of aqueous copper(II) by tetraphenylporphine in a benzene in water microemulsion containing cyclohexanol and sodium cetyl sulfate as surfactants. The Lewis base stabilizes the formation of a copper–porphyrin complex in the interphase region of the oil microdroplet. Two additional copper–porphyrin species can be isolated as detergent aggregates. Spectral and chemical evidence is presented which indicates that these species are intermediates in the formation of the metalloporphyrin and that their visible absorption spectrum depends primarily on the charge in the ring center rather than its source (protons and/or metal ions). The nature of these species is discussed.

Introduction

In the preceding paper we reported an exploratory investigation of the incorporation of divalent metal ions by tetraphenylporphine in microemulsion media.[1] Of the metal ions examined, only Cu(II) was found to react at room temperature in oil–water micellar emulsions stabilized by anionic surfactant. A number of Lewis bases, as cofactors, accelerated the rate of formation of metalloporphyrin. This was attributed to the formation of a copper–cofactor complex in the surface (interphase) region of the oil microdroplet, although the presence of such a complex in the reaction mixture was not directly detected.

There have been numerous studies of the kinetics of metal ion incorporation by porphyrins in various solvent media.[2] The initial step in the reaction mechanism is often postulated to be the equilibrium formation of a metal ion–porphyrin "sitting-atop" complex (SAT). The existence of a complex has been reported in aqueous solution for water-soluble porphyrins.[3–5] The rate of reaction of magnesium(II) with deuteroporphyrin dimethyl ester is accelerated by pyridine and a variety of bases[6] and is attributed to the formation of a reactive pyridine–magnesium(II)–porphyrin complex on the basis of kinetic data. In this case, no direct spectroscopic evidence for the existence of the complex was obtained.

The actual existence of a SAT has been the subject of some dispute, particularly in light of the fact that the spectra attributed to these complexes resemble those of the corresponding porphyrin dications (diacid salts). There is evidence that, in nonaqueous solvents, the spectra are due to diacid salt–ion pair complexes resulting from the solvolysis of the metal salt by traces of water or other hydroxylic solvent.[7] Recently, the "SAT complexes" of water-soluble tetrapyridylporphines in aqueous solution have been attributed to dication formation due to an increase in ionic strength as a result of addition of the metal salt.[8] However, the preparation and characterization of an SAT complex of tetraphenylporphine and chlorodicarbonylrhodium(I) dimer isolated from dry benzene has just been reported.[9] In continuing our study of the effect of cofactors on the formation of copper tetraphenylporphine in anionic oil–water microemulsions, we find that triphenylphosphine stabilizes a copper–porphyrin complex, and we present evidence for the stabilization of further intermediates along the reaction path.

Experimental Section

Microemulsion Preparation. The oil in water micellar emulsions were prepared by mixing water, benzene, cyclohexanol, and detergent. Agitation was not required, but the mixture was normally stirred to speed formation of the transparent microemulsion. The composition employed was, by weight, 54.54% water, 6.12% benzene, 23.49% cyclohexanol, and 15.85% sodium cetyl sulfate (SCS).

Reaction Mixture. Since tetraphenylporphine ($TPPH_2$) dissolves very slowly in the microemulsion, it was usually first dissolved in the benzene which was then combined with the (premixed) other three components. Triphenylphosphine, aqueous $CuSO_4$, and additional water were then added to give an overall composition diluted 40% (by volume) with water with respect to the weight percent composition given above. The concentrations of $TPPH_2$ and $CuSO_4$ were about

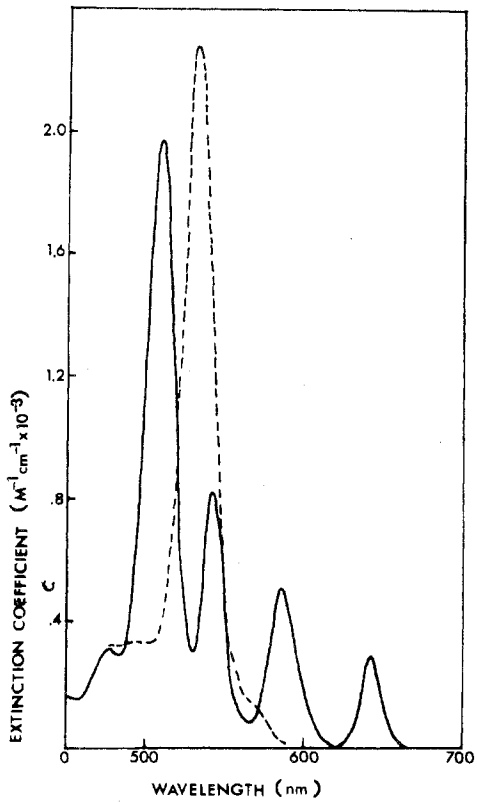


Figure 1. Visible absorption spectra of $TPPH_2$ (solid line) and CuTPP (dashed line).

10^{-4} and 10^{-2} *M*, respectively. The Ph_3P concentration was about 10^{-2} *M*.

Spectral Measurements. All uv–visible absorption spectra were obtained with a Cary 14 spectrophotometer in 1-cm quartz cells using the solvent as reference. Emission and excitation spectra were obtained with an Aminco-Bowman spectrophotofluorometer. ESR spectra were obtained with a Varian E-12 spectrometer system operating at approximately 9.1 GHz with 100-kHz field modulation. Infrared spectra were obtained with a Perkin-Elmer 457 grating spectrometer, and a Hitachi Perkin-Elmer RMU-6 was employed for the mass spectra.

Chromatographic Separations. The products from the reaction of $CuSO_4$ with tetraphenylporphine and triphenylphosphine in the SCS microemulsion were extracted and separated. The micellar emulsion was broken by the addition of half a volume of acetone, which caused phase separation and the precipitation of detergent. After filtration, the acetone layer in the filtrate was drawn off, evaporated to a small volume, and placed on preparative TLC plates (silica, Quantum Industries). To isolate the green product A615, the plates were successively developed with 3:2 v/v benzene–*n*-hexane, twice with 3:1 v/v acetone–cyclohexane, and then with acetone (final R_f of green complex 0.38–0.57). The material was scraped off the plate and removed from the silica with acetone. The extract was evaporated to dryness (cold) and the residue redissolved in chloroform, filtered, and again evaporated to dryness yielding the product (A615) as a paste.

Analyses. Total copper was determined on a Perkin-Elmer 303 atomic absorption spectrometer using an air–acetylene flame and acetone as the solvent. Solutions of $CuCl_2$ in acetone were used as standards and checked with a pure sample of copper tetraphenylporphine (CuTPP). Analysis for copper (as CuTPP) was performed by dissolving the sample in benzene and shaking with a small amount of aqueous 4 *N* KOH until the visible spectrum indicated only the presence of CuTPP. The concentration of CuTPP was determined from the measured extinction coefficient of the 538-nm band. All samples were weighed on a Cahn Electrobalance (±0.001 mg). Elemental phosphorus analysis was performed by Chemalytics Inc., Tempe, Ariz.

Results and Discussion

Copper(II) Ion Incorporation. The internal structure of the benzene–cyclohexanol–sodium cetyl sulfate (SCS)–water microemulsion system employed for these studies may be described as a stable collection of monodisperse benzene "oil" microdroplets measuring a few hundred ångstroms in diameter and surrounded by a 20–30 Å thick surface phase (interphase) composed of SCS and cyclohexanol, dispersed in an aqueous continuous phase. The tetraphenylporphine ($TPPH_2$) is located in the droplet, and the Cu(II) ion is bound to the (negatively charged) droplet surface.[1] The net reaction is given by eq 1. In the absence of added cofactors and under the

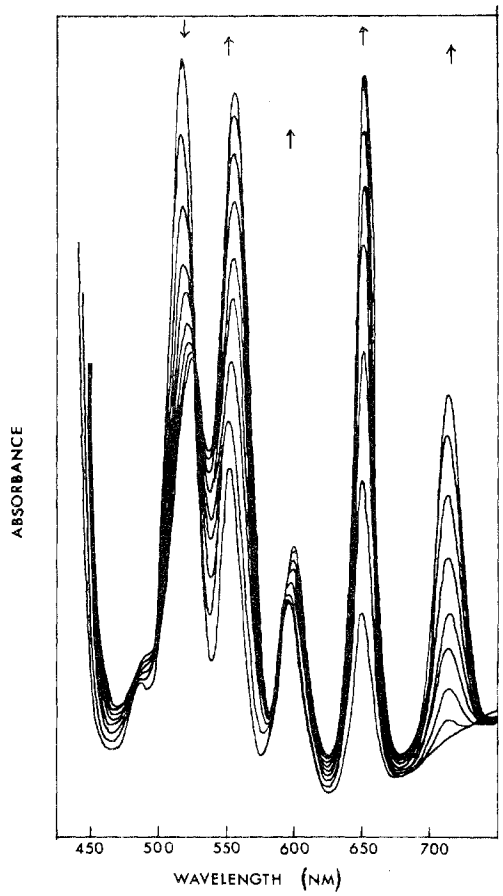


Figure 2. Spectrum of $TPPH_2$, copper(II), and Ph_3P ($\sim 10^{-2}$ *M*) in the microemulsion at various times after mixing.

$$Cu^{2+} + TPPH_2 \rightarrow CuTPP + 2H^+ \quad (1)$$

conditions employed in this investigation (25°C, ca. 8×10^{-5} *M* $TPPH_2$ and $(5-10) \times 10^{-3}$ *M* $CuSO_4$), the half-life for the formation of copper tetraphenylporphine (CuTPP) was over 12 hr. If quinoline (ca. 10^{-3} *M*) is added, the half-life is reduced to 1–2 min.[1] As the reaction proceeds, the characteristic etio spectrum of $TPPH_2$ with visible bands at 513, 547, 590, and 647 nm is converted into the CuTPP spectrum with a major visible absorption band at 538 nm (Figure 1). With or without added cofactor (e.g., quinoline), no spectral evidence of any intermediate porphyrin species was obtained.

Formation of A650. If triphenylphosphine (Ph_3P; ca. 10^{-2} *M*) is added to the microemulsion reaction mixture containing Cu(II) and $TPPH_2$, unusual spectral changes begin to take place. Absorption maxima are observed at 513, 555, 598, 650, and 710 nm. The bands at 650 and 598 nm grow in intensity with time and the 513-nm band decreases. The 710-nm band either remains approximately constant or increases, and correspondingly the 555-nm band either decreases slightly or increases. After a period of hours, the spectral changes reach equilibrium (Figure 2). Control experiments utilizing all possible combinations of reactants and product (Cu^{2+}, $TPPH_2$, Ph_3P, CuTPP) confirm that all three initial components (Cu^{2+},

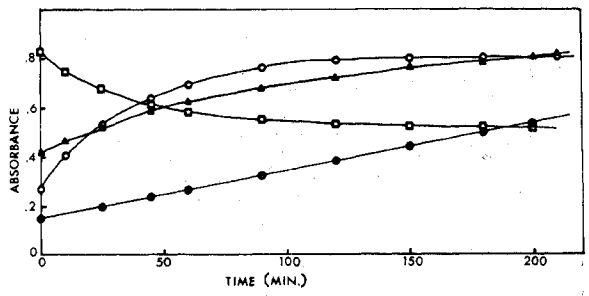


Figure 3. Absorbance at 513 nm (squares), 555 nm (triangles), 650 nm (open circles), and 710 nm (closed circles) vs. time for a microemulsion reaction mixture containing $TPPH_2$, Cu(II), and Ph_3P.

$TPPH_2$, Ph_3P) are necessary to produce the spectral changes. A plot of the absorbance of the 513-, 555-, 650-, and 710-nm bands vs. time is shown in Figure 3. The absorbance (A) of the 710-nm band increases *linearly* with time, while the *ca.* 555-nm band parallels it but with some curvature. It also appears that the increase of the 650-nm band and the decrease of the 513-nm band are related. This is confirmed by plots of log ($A_\infty - A_{650}$) and log ($A_{513} - A_\infty$) vs. time which are both linear and have essentially equal slopes (0.027 and 0.024 min^{-1}, respectively). A plot of A_{650} vs. A_{513} is also linear, providing additional confirmation. At this point we may thus conclude that $TPPH_2$ is slowly converted to a species which has a principal absorption maximum at 650 nm (A650). At "equilibrium", some $TPPH_2$ still remains as determined by its characteristic fluorescence spectrum. A third porphyrin species (vide infra) with a principal absorption maximum at 710 nm (A710) and a second major band at 550 nm is also present. Neither A650 nor A710 absorbs appreciably at 513 nm. Lower temperature (e.g., 15°C) shifts the equilibrium in favor of A650.

Acid–Base Equilibrium. The tetraphenylporphine dication ($TPPH_4^{2+}$) also has its principal visible absorption maximum at about 650 nm. However, the species A650 is *definitely not* the dication or dication–ion pair complex.[7] In support of this statement we present the following data.

(a) The acid–base equilibrium is "instantaneous". The addition of HCl to the A650 "equilibrium" mixture produces $TPPH_4^{2+}$ from the remaining $TPPH_2$ (vide supra) and all bands *broaden* appreciably. This would not occur if $TPPH_4^{2+}$ and A650 were the same species.

(b) Independent studies (with HCl) show that the effective equilibrium constant (K) in the microemulsion for the reaction

$$TPPH_2 + 2H^+ = TPPH_4^{2+} \quad (2)$$

is $K \simeq 6 \times 10^3\ M^{-2}$. Thus, in order to convert only 10% of the $TPPH_2$ to $TPPH_4^{2+}$ in the microemulsion, a H^+ concentration in excess of $10^{-3}\ M$ is required. None of the components present could (or do) produce this.

(c) In anticipation of results to be presented below, the addition of a base (e.g., quinoline) to a $TPPH_4^{2+}$ solution instantly converts it back to $TPPH_2$. In contrast, addition of quinoline to the A650 "equilibrium" reaction mixture produces no immediate change and slowly *decreases* the absorption band at 650 nm.

Formation of A615. If the equilibrium (A650) reaction mixture in the microemulsion is heated or dilute NaOH added, the A650 (and $TPPH_2$) decreases with the formation of CuTPP, as evidenced by the appearance of an absorption band at 538 nm. Control experiments show that the 615-nm band does not arise from the presence of CuTPP. Increasing the concentration of hydroxide leads to complete conversion to CuTPP.

A very important observation results from the addition of quinoline to the A650 equilibrium mixture (Figure 4). The

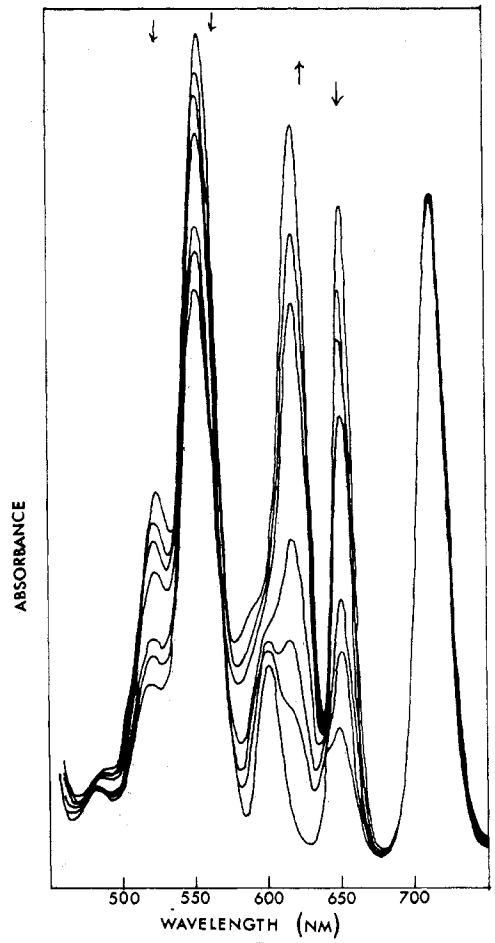


Figure 4. Spectrum of A650 equilibrium reaction mixture to which quinoline ($\simeq 10^{-2}\ M$) has been added, at various times after addition of the quinoline.

A650 decreases while the band at 615 nm increases and the band at ~552 nm decreases slightly. The A710 remains constant. A plot of A_{650} vs. A_{615} is linear, which is consistent with the formation of a new porphyrin species (A615) *from* A650. After the A650 has completely reacted, fluorescence spectra show that no detectable $TPPH_2$ remains, and the addition of HCl has no effect. The two major species present in the absorption spectrum are A615 (615 nm) and A710 (710 and 550 nm), as shown in Figure 4. We may therefore conclude that $TPPH_2$ produces A650, which in turn produces A615. The species A710 is a minor "side product" probably derived from $TPPH_2$, A650, or both. The CuTPP is produced by further reaction of A615.

In examining the fluorescence of the microemulsion for the presence of $TPPH_2$, other species which give rise to visible emissions were discovered. These are discussed below.

Formation of F464. The A615 reaction mixture has a fluorescent emission spectrum with maxima at 464 and 725 nm. By obtaining the excitation spectra, the 725-nm emission is shown to arise from A710 (excitation maxima of 550 and 710 nm). We may thus conclude that, in addition to the species A710, a species F464 is present in the A615 reaction mixture in an amount too small to be observed in absorption. Evidence will be presented below which indicates that F464 is in fact an intermediate between A615 and CuTPP.

Separation of A615 and F464. If the microemulsion containing the equilibrium mixture of $TPPH_2$ and A650 is broken by the addition of acetone, all of the color is present in the acetone layer. The spectrum of the separated acetone layer shows that the A650 is decreased and both A615 and CuTPP are present. The lower the temperature of the mi-

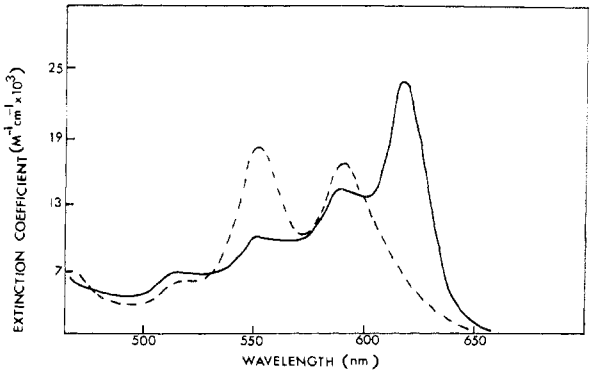


Figure 5. Visible absorption spectra of A615 (solid line) and F464 (dashed line) in benzene. The molar extinctions are based on the porphyrin content (Table I).

croemulsion, the larger is the A615:CuTPP ratio in the acetone layer. The components present in the acetone were separated by means of thin-layer chromatography (TLC) on silica gel plates. We were able to separate a green band, which was removed from the plate and dissolved in acetone. The absorption spectrum shows a visible absorption maximum at 615 nm and a Soret band at 428 nm. The material can be repeatedly rechromatographed with no change in the spectrum. By comparison of this spectrum with that of the microemulsion reaction solution, this porphyrin species is identified as A615. If treated with aqueous hydroxide, it is converted to CuTPP. Removal of the solvent on a rotary evaporator yields thick green paste. Various efforts to obtain A615 as a solid powder were unsuccessful. The A615 (paste) is insoluble in water and unaffected by it. It is soluble in acetone, benzene, chloroform, and methanol. If A615 which has been "purified" by repeated TLC is dissolved in acetone and let stand at room temperature, its spectrum slowly changes to give visible absorption maxima of about equal intensity at 550 and 590 nm and a Soret band at 427 nm. Acetone solutions of A615 do not convert if kept cold (below about 10°C). In methanol, a conversion of the A615 spectrum occurs more rapidly. Removal of solvent yields a greenish red paste, insoluble in water but soluble in methanol, acetone, benzene, and chloroform. The spectrum is the same in all of the solvents. This species, which subsequently was found to fluoresce at 464 nm (F464), does not exhibit any further spectral changes if let stand at room temperature in solution. The visible absorption spectra of A615 and F464 in benzene are shown in Figure 5. As was the case for A615, solutions of F464 which are heated or shaken with aqueous hydroxide are converted to CuTPP. No trace of $TPPH_2$ or other porphyrin species was detected in the CuTPP spectrum.

Analysis of A615 and F464. Although both A615 and F464 could only be isolated as pastes, analysis of composition was attempted. Samples of the pastes were weighed out and then dissolved and made up to volume in the appropriate solvent. Conversion of samples in benzene to CuTPP was accomplished via shaking the solution with aqueous hydroxide. The concentration of CuTPP was determined from the measured extinction coefficient of the 538-nm band of CuTPP in benzene. This method of analysis (spectrophotometric) gives total porphyrin, as well as copper present as CuTPP. Atomic absorption was also employed for the determination of copper. The analytical results are given in Table I. Several points may be noted. First, the mole ratio of copper to porphyrin is greater than 1. There are apparently 2–3 g-atoms of copper/mol of porphyrin. Second, phosphorus is present, presumably as Ph_3P, in about an equimolar ratio with copper. Third, after taking into account the weight percent of CuTPP, Ph_3P, and the additional copper assumed to be present as copper cetyl sulfate, 65 wt % of the material for F464 remained

Table I. Copper Analysis of A615 and F464 Complexes[a]

Complex	Method of separation	Wt % Cu	Method of determination[b]
A615	Column chromotography	0.60	Spectrophotometic
A615	Preparative TLC	1.04	Atomic absorption
F464[c]	Preparative TLC	0.73	Spectrophotometric
F464	Preparative TLC	2.40	Atomic absorption

[a] See text. [b] See text, including Experimental Section. [c] Phosphorus 1.03 wt %.

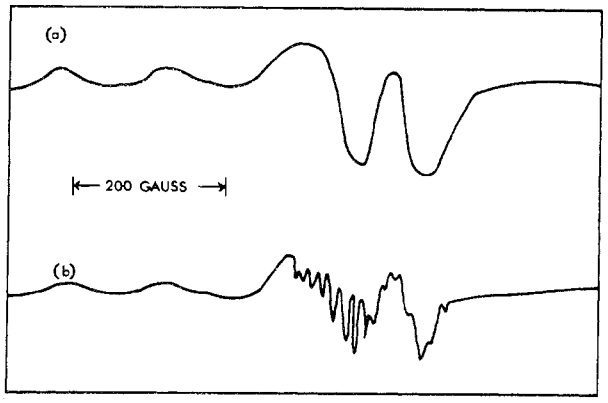


Figure 6. ESR derivative spectra of (a) A615 and (b) F464 in acetone at 77 K. The hfs on the A615 spectrum has been surpressed (via modulation amplitude).

unaccounted for. The dominant features in the mass spectrum corresponded to those produced by a C_{16} hydrocarbon chain, and the bulk of the remaining material in the complex is thus considered to be SCS. On this basis, there are about 16 mol of SCS/mol of porphyrin. Finally, the lower weight percent of copper in A615 indicates that this complex contains more SCS, and possibly Ph_3P, than F464.

An infrared spectrum of F464 was obtained by placing the paste between NaCl plates. The major features observed in the SO stretching region were peaks at 1090, 1055, and 1015 cm^{-1}, with a very weak band at 965 cm^{-1}. In SCS (Nujol mull), the split sulfate fundamental gives peaks at 1260 and 1235 cm^{-1}. The complete splitting of the triply degenerate (SO_4^{2-}) band and the considerable shift to lower frequency are consistent with close binding of the cetyl sulfate and counterion.[10]

The composite of all the above data suggests that the (isolated) substances A615 and F464 are triphenylphosphine–copper(II)–porphyrin complexes aggregated with SCS. We speculate that the complex is present in the core of a reversed SCS micelle. This is consistent with the solubility, relatively low aggregation number, the ir spectrum, and the isolation of the material as a paste. The role of the "extra" copper is less clear. It is possible that its presence is responsible for the rather remarkable stability of the aggregate, since a micelle would normally be expected to dissociate in dilute solution.

The formation of F464 from A615 would appear to involve some loss of SCS, and possibly Ph_3P. We wish to emphasize, however, that the complexes A615 and F464 are porphyrin species as shown by their electronic spectra. Aggregate formation is likely a result of breaking the micellar emulsion. Once formed, the aggregate remains intact. Since some F464 is formed in the microemulsion (vide supra), loss of Ph_3P and/or a proton from the complex is probably the controlling factor since no gain or loss of SCS is involved.

ESR Spectra. With the idea in mind that a 1:1 copper–porphyrin complex was the essential species with the remainder of the material only providing stabilization upon removal from the microemulsion, the ESR spectra of A615 and F464 were

Table II. ESR Parameters at 77 K

Compd	Solvent	$g_{\parallel}$[a]	$-A$,[b] cm^{-1}	a,[c] G
CuTPP	Benzene–acetone (1:2 v/v)	2.18_9	0.020	16.7 ± 0.5
A615	Acetone	2.19_1	0.018	17.0 ± 0.5
F464	Acetone	2.18_7	0.018	16.1 ± 0.7

[a] ±0.003. [b] Copper hyperfine splitting ($g_{\parallel}$ component), ±0.001 cm^{-1}. [c] Nitrogen hyperfine splitting (on $g_{\perp}$ components).

Table III. Emission and Excitation Spectra of F464

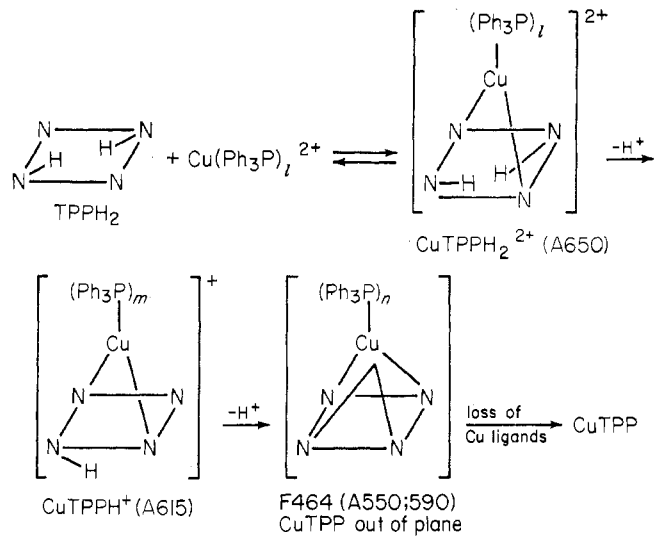
	Room temp–total emission		Liquid nitrogen temp–rotating shutter	
Solvent	Excitation max, nm	Emission max, nm	Excitation max, nm	Emission max, nm
Benzene	366[e] 464	464[a]	290	464[b,d]
$CHCl_3$	366[e] 464	464[a]	310	495[c,d]

[a] Normal fluorescence (F). No delayed fluorescence (DF) or phosphorescence (P). [b] DF; some weak P (495 nm) observed if excited above ca. 320 nm. [c] P; total emission shows some F if excited above 310 nm; no DF observed. [d] Some indication of weak features at about 570 and 615 nm; however, no emission at all is observed by exciting above 500 nm. [e] Strongest excitation maximum.

obtained in frozen acetone solutions at 77°K. Both A615 and F464 had essentially identical spectra, as shown in Figure 6. The spectrum of A615 in Figure 6 is shown without nitrogen hyperfine structure (hfs). The spectra are characteristic of copper complexes with axial symmetry. The nitrogen hfs shows that the species responsible for the spectra are copper–porphyrin complexes. In fact, the ESR spectra of A615 and F464 are quite similar to that of CuTPP. The values of $g_{\parallel}$, the copper hyperfine splitting A, and the nitrogen hyperfine splitting a are readily obtained from the spectrum. These parameters are tabulated in Table II. The values of $g_{\parallel}$ are the same within experimental error. The average nitrogen hyperfine splitting is much the same for all three complexes, although the range of a values is somewhat wider for A615 and F464 than for CuTPP. This may indicate some anisotropy in the nitrogen hfs. The copper hyperfine splitting A is essentially the same for both A615 and F464 and slightly smaller than that for CuTPP. Since the addition of Ph_3P does not affect the CuTPP spectrum, this is taken as an indication of some difference in geometry between CuTPP and the two complexes. It may be noted that no signal due to any other Cu(II) species was observed in the A615 or F464 spectra and no signal could be obtained at room temperature.

Emission Spectra. In an attempt to discriminate further between the complexes and/or characterize the complexes, they were examined for emission at both room and liquid nitrogen temperatures. Tetraphenylporphine fluoresces at 660 and 718 nm in benzene, while CuTPP phosphoresces (77 K) at 730 nm in benzene but does not fluoresce. It was found that A615 does not luminesce, while F464 exhibits fluorescence, delayed fluorescence, and phosphorescence. The results are summarized in Table III. Good controls were more difficult to obtain in this case, but it does not appear that Ph_3P or a Cu^{II}–Ph_3P complex is responsible for the emission. The excitation maxima do not correspond to any absorption maxima, and no emission could be obtained by excitation of the visible (550, 590 nm) or Soret (428 nm) bands. If the 464-nm emission is from the 428-nm Soret band of the porphyrin complex, then it would be expected that the fluorescence excitation maximum would be 428 nm rather than 366 nm. The SCS has very weak absorption maxima at 238 and approximately 365 nm, and it is possible that energy absorbed by the SCS aggregate or interphase is transferred

Scheme I



to a porphyrin state buried under the Soret band.

In any event, it is clear that the species A615 may be converted into the fundamentally different species F464 (A550,590), which in turn can be converted to CuTPP by base. It may be noted that addition of dilute NaOH to A615 in the microemulsion also leads to its conversion to F464. The results up to this point are summarized

$$\underset{\text{CuTPP}}{\text{TPPH}_2} \xrightleftharpoons{Ph_3P,\ Cu^{2+}} \text{A650} \xrightarrow{\text{quinoline}} \text{A615} \xrightarrow{\text{NaOH}} \text{F464} \xrightarrow{\text{NaOH}}$$

Assignment of Structures. Before offering an interpretation of the results, we make note of the following observations concerning tetraphenylporphine electronic spectra:[11] (a) increasing the π-electron density at the periphery of the ring (less positive center) tends to red shift the bands; (b) metalloporphyrins with available d orbitals have blue-shifted spectra with a very depressed first (low-energy) band; (c) metalloporphyrins which have available only s and p orbitals are red shifted with respect to those in (b) above, with a much more intense first vibrational band (e.g., Mg, Ba, Zn, Cd, Sn).

The spectrum of F464 is red shifted with respect to CuTPP and resembles the spectra of the nontransition metal porphyrins. This is consistent with the copper being out of the plane of the porphyrin ring, as indicated by the ESR spectrum, since this should lead to an increase in the s and p character of the hybrid atomic orbitals (AO's) employed by the Cu(II). In A615, the copper should also be out of the plane. The increased intensity of the first band would tend to indicate a further decrease in d character of the copper hybrid AO's, and the red shift, a more electropositive center. In this regard it may be noted that this is equivalent to an increase in positive charge of the complex by metal ion and/or protons, since both reside in or near the center of the ring (e.g., $TPPH_4^{2+}$). The increased complexity of the A615 spectrum also may indicate a lowering of symmetry. The spectrum of A650 is further red shifted and, as mentioned earlier, resembles that of the dication.

All of the above considerations are consistent with the initial formation of a $CuTPPH_2^{2+}$ complex which eventually reaches equilibrium with $TPPH_2$. The factor which stabilizes the complex must be Ph_3P coordinated to the Cu(II). Upon subjecting the A650 to more vigorous conditions (heat or base), a proton may be lost to form $CuTPPH^+$. This is stabilized by the coordinated Ph_3P and quite possibly by the low-dielectric, anionic interphase region of the microemulsion. It is known that the porphyrin monocation tends to be stabilized,

relative to the dication, by anionic detergent.[12] From the ESR and electronic spectra, this would correspond to the species A615. Loss of the remaining proton and Ph_3P ligand(s) produces CuTPP. If the proton and Ph_3P are not lost in a concerted fashion, then it seems likely that proton loss would be the first of a two-step process. This would produce a neutral "incipient" CuTPP species. The species F464 appears to be a neutral metalloporphyrin in which the copper is out of plane. This would thus correspond to CuTPP, in which the copper is out of plane and still contains at least one coordinated Ph_3P ligand or any solvent molecules or detergent anions which may be associated with the copper or the complex itself. (See Scheme I.)

Although we have no conclusive evidence for the exact nature of the proposed species, we do feel that they are chemically reasonable and consistent with the experimental data. If correct, they provide considerable insight into the details of a mechanism of metal ion incorporation by porphyrins at water–oil interfaces.

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Registry No. Copper, 7440-50-8; tetraphenylporphine, 917-23-7; benzene, 71-43-2; cyclohexanol, 108-93-0; sodium cetyl sulfate, 1120-01-0; triphenylphosphine, 603-35-0; CuTPP, 14172-91-9.

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Dissymmetric Arsine Complexes. An Interpretation of the d–d Electronic Absorption Spectra of Five-Coordinate Nickel(II), Palladium(II), and Platinum(II) Complexes and Their Axial-Group Interchange and Exchange Mechanisms

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A series of five-coordinate complexes of the type $[M(tetars)X]^+$, where tetars is a linear quadridentate tetra(tertiary arsine) ligand, where M = Ni(II), Pd(II), or Pt(II) and where X is a halide ligand, have been prepared and characterized. The absorption and circular dichroism spectra of these square-pyramidal complexes show consistent patterns and suggest that the d-orbital functions have the ordering $d_{xy} < d_{xz}, d_{yz} < d_{z^2} << d_{x^2-y^2}$. The halogeno ligands, although very stable in nonpolar solvents, are at the same time very labile at 30°. A variable-temperature NMR study indicates that both axial-site interchange and intermolecular exchange can occur by three different bimolecular mechanisms which involve halogen attack of the metal, as well as attack by either a four- or a five-coordinate complex resulting in the formation of dimers.

The diamagnetic five-coordinate complexes of Ni(II), Pd(II), and Pt(II) containing soft donor atoms such as arsenic and/or phosphorus have been the subject of continuing interest since the early work of Nyholm,[1-3] who isolated and characterized derivatives of the type $[M(diars)_2X]ClO_4$. All of these species are square-pyramidal complexes and it was only later that Venanzi[4-6] showed that, with appropriately designed ligands, diamagnetic trigonal-bipyramidal complexes of Ni(II) were equally accessible and were apparently of similar stability. In addition, Venanzi characterized the d–d spectra of the latter and showed them to be diagnostic of the geometry.

We recently described the preparation of a series of Co(III) complexes containing the quadridentate ligand tetars[7,8] and showed how the isomers of the ligand could be separated and resolved by means of their metal complexes. The *ms*-tetars ligand was shown to prefer a trans arrangement of its four arsenic atoms but the racemic ligand was flexible in its topological proclivities, giving cis-α, cis-β, and trans isomers in varying proportions depending upon the nature of the other coordinating ligands.[8] It was therefore of interest to see if this topological flexibility would extend to the d^8 systems, particularly those of divalent nickel, where the square-pyramidal and trigonal-bipyramidal stereochemistries might be of similar energies. We will show, however, that this is not the case for these ligands; all contain a planar array of arsenic donor atoms in a large variety of solvents. Besides this stereochemical aspect, only one report[9] of a systematic interpretive study of the electronic spectra of square-pyramidal systems has appeared. The assignments in this recent study[9] were based on the temperature-dependent profiles of the d–d bands and their energy displacements upon axial substitution. In the present work we amplify, and essentially confirm, the assignments of the previous study by an analysis of the circular dichroism spectra, which provide a precise probe into the magnetic dipole character of the transitions and are capable of resolving features which are hidden beneath the broad manifolds observed in the normal linear absorption. The final aspect of interest is that the fifth coordinated ligand, X, which is usually a halogen or pseudohalogen, is very stable,[10] although chemical evidence suggests that, at the same time, it is very labile in solution at room temperature. The $[Ni(diars)_2X]^+$ ions, although having some of the convenient simplicity in their