PORPHYRINS

V.* FORMATION AND PROPERTIES OF STABILIZED CARBONIUM IONS OF METALLOPORPHYRINS

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The electronic spectra of solutions of copper complexes of a number of meso-substituted derivatives of etioporphyrin I in dichloroethane and carbon tetrachloride in the presence of trifluoroacetic acid and antimony pentachloride were investigated. It is shown that the development of broad intense bands at 450 and **1010-1020** nm is associated with the formation of stabilized carbonium ions of the metalloporphyrins. Copper complexes of meso-methoxymethyl- and meso-ethoxymethyletioporphyrin I were synthesized by reaction of the copper complexes of meso-hydroxymethyletioporphyrin and meso-dimethylaminomethyletioporphyrin with alcohols in the presence of acid catalysts or methyl iodide.

The introduction of substituents in the meso position of octaalkylporphyrins in most cases appreciably changes the general appearance of the electronic spectrum both with respect to the form and intensity of the bands in the visible region and with respect to the bathochromic shift as compared with the meso-unsubstituted porphyrins. At the same time, the spectra of complexes of such porphyrins with divalent metals usually have a classical form consisting of two bands in the visible region of the spectrum and an intense Soret band at 400-420 nm [2]. Stable (with respect to organic acids) copper complexes of porphyrins do not change their spectral characteristics when solutions of them are acidified.

The aim of the present research was to explain the appearance of the unusual electronic spectra in the case of a number of copper complexes of meso-substituted derivatives of etioporphyrin I in the presence of strong proton acids and Lewis acids.

As previously observed [3], the spectral changes that occur when even minimal amounts of acids (HCl, HCOOH, CF_3COOH, AcOH, etc.) are added to a solution of the copper complex of meso-aldiminoetioporphyrin I (I, R = H) are impossible to explain only by protonation of the nitrogen atom of the meso substituent. The practically complete disappearance of the α and β bands, the very strong bathochromic shift of the Soret band (~50 nm), and the development of a new intense broad band at 720 nm (Fig. 1) constitute evidence for a considerable change in the electronic structure of the porphyrin ring. In our opinion, these changes in the spectrum can be explained by assuming partial charge transfer from the nitrogen atom of the meso substituent to the π system of the porphyrin ring with the formation of a stabilized cation (II), for which the representation of 19 resonance structures is formally possible under the condition of retention of two pyrrole and two pyrrolene nitrogen atoms.

Similar spectral changes were also observed when various Schiff bases of the copper complex of meso-formyletioporphyrin with aliphatic amines (I, R = alkyl) [1] were protonated. The reaction of the aldimine and the Schiff bases with proton acids takes place so rapidly and the change in the color of the solutions from bright-red to green is so appreciable that these compounds may serve as indicators for the presence of free protons in organic solvents.

After we had completed this research these appeared a brief communication [4] in which the development of a band at 720 nm was also noted for the Schiff base of the copper complex of meso-formyloctaethylporphyrin

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* See [1] for communication IV.

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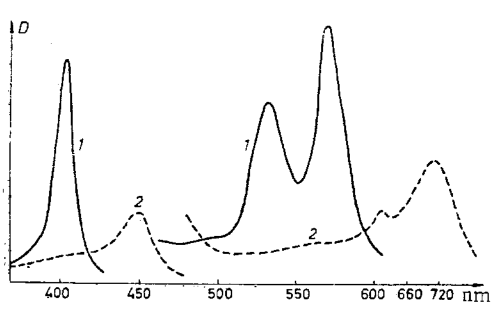
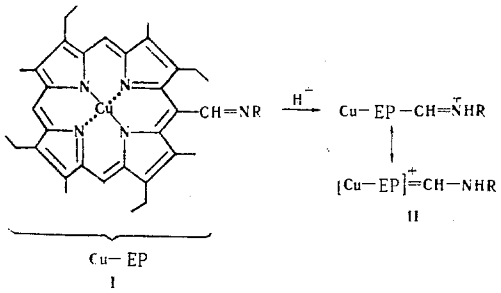
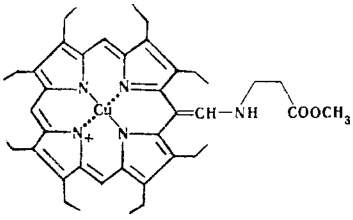


Fig. 1. Spectrum of complex I in dichloroethane (1) and when trifluoroacetic acid is added (2). Here and subsequently, the spectra in the region of the Soret band (350-450 nm) were recorded at the same concentrations but in a cuvette with a layer thickness of 0.5 mm.

with β-alanine when the solution was acidified. Witte and Fuhrhop [4] interpret the spectrum as being the consequence of the formation of a "fluorenoid" structure (III) with fixation of the charge on the nitrogen atoms of the pyrrole rings.



As seen from structure III, this representation does not sufficiently clearly reflect the surprising stability of the metal complex in acidic media.

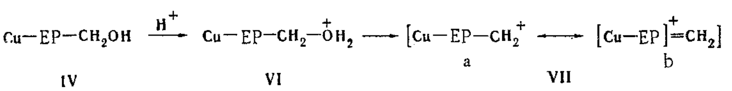


III

It is most likely that a structure with distribution of the positive charge over the entire molecule of the porphyrin ring, for which II and III are possible boundary states, actually exists.

We obtained interesting and unexpected electronic spectra in the case of protonation of the copper complex of meso-hydroxymethyletioporphyrin I (IV) [5] with trifluoroacetic acid (TFA) in specially purified dry dichloroethane, in which decomposition of complex IV to the copper complex of etioporphyrin I (V) did not occur. An appreciable change in the color of the solution from red to bright-yellow was observed when TFA was added. The α, β, and Soret bands vanished in the electronic spectrum, and intense bands with λ_{max} 380 and 452 nm and a broad band at 1015 nm appeared (Fig. 2).

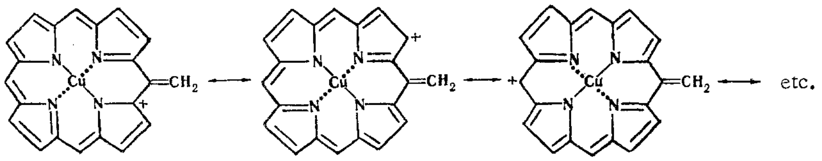
The appearance of a spectrum of this sort cannot be explained exclusively by the formation of an oxonium ion (VI). When the spectra of I and IV in acidic media are compared, one may note one important general feature — the presence of broad long-wave bands, which, in our opinion, are of identical nature and correspond to the excited state of the metalloporphyrin, in which a definite fraction of the positive charge is distributed over the π system of the porphyrin ring. This state can arise only as a result of splitting out of a water molecule from oxoniom ion VI and stabilization of the resulting carbonium ion (VII) via the following scheme:



$$\underset{\mathrm{IV}}{\mathrm{Cu{-}EP{-}CH_2OH}} \xrightarrow{H^+} \underset{\mathrm{VI}}{\mathrm{Cu{-}EP{-}CH_2{-}\overset{+}{O}H_2}} \longrightarrow \underset{\mathrm{a}}{[\mathrm{Cu{-}EP{-}CH_2^+}]} \longleftrightarrow \underset{\mathrm{b}}{[\mathrm{Cu{-}EP}]\overset{+}{=}\mathrm{CH_2}]}$$

VII

where form VIIb can also be depicted by means of 19 possible resonance structures, such as, for example:



One might have expected that changes of this sort in the electronic spectra would also be observed in the case of protonation of copper complexes of meso-dimethylaminomethyletioporphyrin I (VIII) [5] and meso-methoxymethyletioporphyrin I (IX). In the latter case, the electronic spectrum of the TFA-acidified solutions would be practically completely identical to the spectrum of complex IV in acidic media.

Using dry distilled carbon tetrachloride as the solvent, we observed that the electronic spectrum of VIII changed immediately in the same manner as those of complexes IV or IX when TFA was added (Fig. 2). However, in the latter case we also observed appreciable splitting out of the meso substituents and formation of complex V. Consequently, the product of protonation of complex VIII had a structure close to the structure of carbonium ion VII.

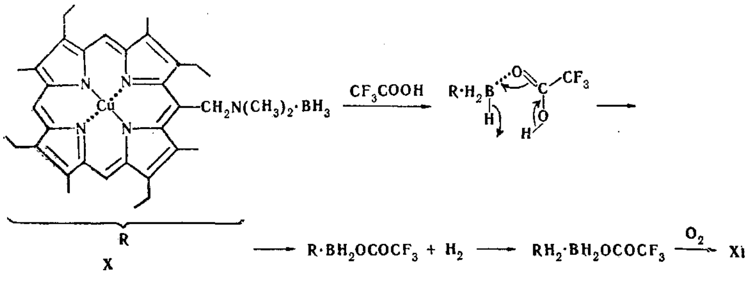
The spectrum of the carbonium ion from complex VIII cannot be obtained in dichloroethane and chloroform solution, since very rapid decomposition of the complex and formation of complex V occur when even small amounts of TFA are added.

The fact of the considerable change in the electronic spectrum of complex VIII on passing from carbon tetrachloride to chloroform or dichloroethane was surprising. It is apparent from Fig. 3 that in dichloroethane the α and β bands of complex VIII have an unusually broad form as compared with the spectrum in CCl_4 (Fig. 2). After the addition of TFA, the spectrum changes rapidly and becomes similar to the spectrum of the copper complex of meso-dimethylaminomethylboranoetioporphyrin I (X) [6]. This change in the spectrum when TFA is added can be explained by protonation of the dimethylaminomethyl group. The protonated complex then undergoes gradual decomposition, and bands characteristic for the spectrum of complex V appear in the spectrum of the reaction mixture, but an increase in the region of the Soret band at 396 nm (the Soret band of V) is not observed, and a new broad band with a shoulder at 460 nm appears at 380 nm. The addition of traces of moisture or alcohol rapidly leads to disappearance of the band at 380 nm, and the spectrum of the solution coincides completely with the spectrum of complex V.

Consequently, protonated complex V arises as a result of splitting out of trimethylamine from complex VIII. The spectrum of a solution of complex V in dichloroethane containing a large amount of TFA serves as proof for this assumption.

It seemed of interest to compare the ability to form a carbonium ion in the case of complexes VIII and X, since the latter has increased resistance to the action of TFA because of the presence of a very strong bond between nitrogen and boron [6].

In contrast to unstable complex VIII, the spectrum of the carbonium ion always develops when a considerable amount of TFA is added to a solution of X in chloroform, dichloroethane, or carbon tetrachloride. When small amounts of TFA in carbon tetrachloride are added, it always reacts with borane, and the liberated hydrogen partially reduces the porphyrin ring; this shows up in the appearance of a band at 725 nm (Fig. 4). The reduced product (with fluorene character) is readily oxidized by air oxygen, as the solvent is evaporated, to the corresponding trifluoroacetoxy derivative (XI) via the scheme



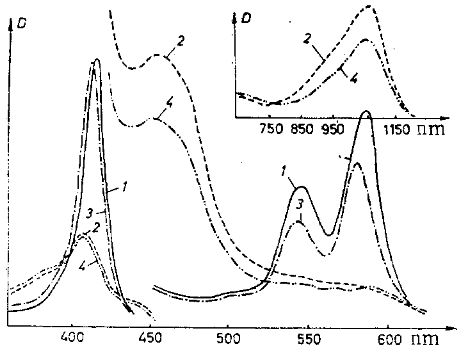


Fig. 2

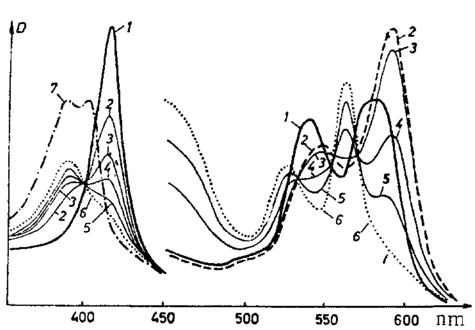


Fig. 3

Fig. 2. Spectra of complex IV in dichloroethane (1) and in TFA−acidified dichloroethane (2) and of complex VIII in CCl_4 (3) and in TFA−acidified CCl_4 (4).

Fig. 3. Spectrum of complex VIII in dichloroethane (1), immediately after the addition of TFA (2), and at 3-4 min intervals thereafter (3-6); spectrum (7) of complex V in dichloroethane−TFA (1 : 1).

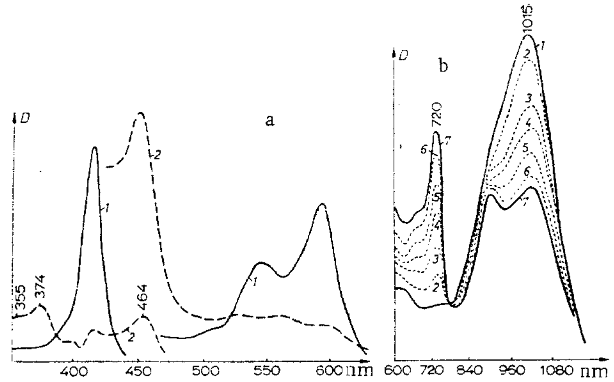
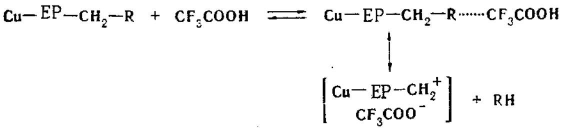


Fig. 4. a) Spectrum of complex X in CCl_4 (1) and after the addition of TFA (2); b) decomposition of the carbonium ion (1-7) recorded every 5 min.

A yellow product with λ_{max} 1020 nm, which is converted to the starting complex when alcohol is added rapidly, is formed immediately when TFA is added to a solution of X in chloroform or dichloroethane. This fact indicates that the carbonium ion is initially an "unseparated" ion pair. However, this state lasts a few seconds, after which at least four simultaneous reactions begin to take place: 1) reaction of TFA with borane; 2) decomposition of the intermediate to complex V; 3) hydrogenation to fluorene products; 4) oxidation to complex XI.

Since the stabilities of the carbonium ions obtained in identical solvents from complexes IV, VIII, and X are extremely different, it can be assumed that an "unseparated" ion pair, the stability of which depends both on the molecule (water or diethylamine) departing during anionoid detachment and on the nature of the solvent, is actually present for a short time in solution.

By comparing the abilities of the investigated compounds to form carbonium ions in the presence of TFA we measured the equilibrium constants (K_{eq}) for them in carbon tetrachloride and dichloroethane from the following equations:



$$\begin{array}{ccc} \text{Cu—EP—CH}_2\text{—R} + \text{CF}_3\text{COOH} & \rightleftharpoons & \text{Cu—EP—CH}_2\text{—R}\cdots\cdots\text{CF}_3\text{COOH} \\ & & \downarrow \\ & & \left[\begin{array}{c}\text{Cu—EP—CH}_2^{+} \\ \text{CF}_3\text{COO}^{-}\end{array}\right] + \text{RH} \end{array}$$

It is known that the "unseparated" ion pair, which exists for a short time, differs little spectrally from a separated ion pair [7]. We therefore used the band at 1020 nm for the determination of the carbonium ion concentration.

TABLE 1. Electronic Spectra and K_{eq} Values of Copper Complexes of Porphyrins

Compound (solvent)	K_{eq}	λ_{max}, nm ($\varepsilon \cdot 10^{-3}$)	
		without TFA	with TFA
Cu—EP—CH_2—NMe_2 (VIII) (dichloroethane)		410 (200) 542 (9,45) 584 (10,9)	410 548 (8,5) 593 (14,1)
(CCl_4)	$3{,}3 \cdot 10^{-4}$	408 (240) 538 (9,96) 582 (15,5)	380 (36,6) 398 (61,0) 448 (19,5) 1020 (10,9)
Cu—EP—CH_2—NMe_2BH_3 (X) (dichloroethane)	$1{,}21 \cdot 10^{-4}$	411 (207) 546 (7,97) 592 (13,1)	355 (25,2) 374 (28,4) 454 (25,2) 1020 (7,0)
(CCl_4)	$8{,}5 \cdot 10^{-5}$	412 (220) 548 (8,5) 578 sh 593 (14,3)	1020 (6,45)
Cu—EP—CH_2OMe (IX) (CCl_4)	$5{,}6 \cdot 10^{-4}$	408 (212) 540 (10,1) 580 (14,9)	380 (42) 396 (61,5) 450 (17,9) 1020 (10,1)
(dichloroethane)	$6{,}9 \cdot 10^{-3}$		1020 (10,8)
Cu—EP—CH_2OH (IV) (dichloroethane)	—	405 (198) 535 (9,65) 575 (12,8)	378 (50) 396 (66) 448 (18,4) 1020 (10,4)

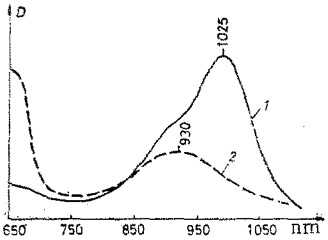


Fig. 5. Spectra of IX (1) and V (2) in dichloroethane with added $SbCl_5$.

Under the conditions of equal [$Cu-EP-CH_2^+$] and [RH] concentrations,

$$K_{eq} = \frac{[Cu-EP-CH_2^+]^2}{[Cu-EP-CH_2-R][CF_3COOH]}.$$

It is seen from Table 1 that a carbonium ion is most easily formed from ester IX. Transition from carbon tetrachloride to dichloroethane, i.e., an increase in the polarity of the solvent, also facilitates the formation of a carbonium ion.

Spectral changes characteristic for the carbonium ions are also observed when a weaker acid – trichloroacetic acid – is used. However, in this case a considerable amount of acid is required, and the stability of the carbonium ion decreases sharply.

For an independent confirmation of our conclusions that the band at 1020 nm corresponds to the formation of a carbonium ion, we investigated the effect of the addition of antimony pentachloride to copper complexes of meso-alkoxymethyletioporphyrin I, since reaction with strong Lewis acids is a characteristic feature of ethers [8]. When $SbCl_5$ was added, the spectra of the complexes changed in the same way as when TFA was added (Fig. 5), and this constitutes evidence in favor of the formation of an intermediate carbonium ion. The same changes are observed in the spectra when stannic chloride and titanium tetrachloride are added.

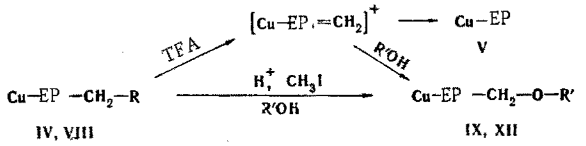
As seen from all of the figures presented, the band at 1020 nm has a shoulder at 930 nm. We also observed a band at 930 nm (Fig. 5) in the spectrum of unsubstituted complex V recorded in the presence of $SbCl_5$; this band apparently has the same nature as the shoulder at 930 nm in the spectra of carbonium ions of meso-substituted prophyrin and is a charge transfer band.

The reaction of ions of this sort with various nucleophiles may serve as synthetic proof for the existence of stabilized carbonium ions.

We investigated the reaction of complex VIII in the presence of TFA in CCl_4 solution containing methanol.

When excess methanol (or other lower aliphatic alcohol) is added to a yellow solution of the carbonium ion, the color of the solution rapidly changes to bright-red. A new complex, which, according to the results of elementary analysis and the IR and mass spectra, was identified as the copper complex of meso-methoxymethyletioporphyrin I (IX), was isolated after chromatographic separation of the reaction products. Its electronic spectrum was practically identical to that of complex IV. An intense band at 1150 cm^{-1}, which is characteristic for vibrations of the C−O group of ethers [9], was observed in the IR spectrum. The most intense peak, corresponding to the $[M - OCH_3]^+$ fragment, is observed in the mass spectrum along with the molecular ion peak. Ether IX may be similarly obtained by addition of methanol to the carbonium ion arising during the protonation of complex IV.

A substantial disadvantage of this method for the preparation of copper complexes of alkoxymethylporphyrins is partial destruction of the carbonium ion to complex V. Charge delocalization in the carbonium ion is evidently the reason for the ambiguous nucleophilic addition and the formation of complex V. This disadvantage is eliminated by another variant of the method for the preparation of the ethers, which consists in the addition of acid only as a catalyst to solutions of complex IV or VIII in a mixture of chloroform and a lower aliphatic alcohol. In this case the reaction proceeds through an activated complex rather than through a stabilized carbonium ion.



IV $R=OH$; VIII $R=N(CH_2)_2$; IX $R'=CH_3$; XII $R'=C_2H_5$

The reaction of complex IV with ethanol, present as a stabilizer in the chloroform, during the chromatography of the complex on silica gel may serve as a surprising example of the easy formation of ethers. Thus the copper complex of meso-ethoxymethyletioporphyrin I (XII) was isolated in quantitative yield when IV was passed through a column filled with silica gel in ethanol-stabilized chloroform.

Copper complexes of meso-alkoxymethylporphyrins can also be synthesized by another method. We observed that heating complex VIII with ethanol, methanol, and other aliphatic alcohols in solution in carbon tetrachloride, chloroform, or dichloroethane in the presence of methyl iodide leads to the corresponding copper complex of meso-alkoxymethylporphyrin. The amount of side complex V decreases appreciably in this case. The formation of a quaternary salt, which is readily split out under the influence of the nucleophile, evidently occurs in the first step. The lability of the quaternary salt is explained by the development of considerable steric hindrance during the addition of methyl iodide. The quaternary salt cannot be isolated or even detected chromatographically in the absence of alcohols.

The use of ethyl iodide for activation of complex VIII leads to a considerable increase in the reaction time and a decrease in the yields of final products; this indicates the paramount importance of steric effects in the formation of the quaternary salt.

Thus the conclusion regarding the formation and expected properties of the stabilized carbonium ion drawn on the basis of a study of the electronic spectra has been completely confirmed in the case of the synthesis of alkoxymethylporphyrin complexes.

EXPERIMENTAL

The electronic spectra were obtained with Shimadzu MPS-50L and Hitachi EPS-3T spectrophotometers. Freshly distilled dry solvents were used for recording of the spectra. The equilibrium constants were determined for $0.5\text{-}1 \cdot 10^{-4}$ M concentrations for the copper complexes and $6 \cdot 10^{-3}\text{-}1.5 \cdot 10^{-1}$ M concentrations for TFA. The IR spectra of KBr pellets of the compounds were recorded with a UR-10 spectrometer.

Copper Complex (IX) of meso-Methoxymethyletioporphyrin I. A 100-mg (0.187 mmole) sample of complex VIII was dissolved in 100 ml of carbon tetrachloride, after which 0.5 ml of TFA was added. After 1 min, 20 ml of methanol was added rapidly with stirring to the yellow solution of the carbonium ion. After 5 min, the solution was poured into water, and the organic layer was washed several times with water and dried. The solvent was removed in vacuo, and the residue was chromatographed with a column filled with silica gel. Workup of the first fraction yielded 20 mg of complex V, and workup of the second fraction yielded, after crystallization from chloroform–methanol, 65 mg (66%) of bright-red needles of complex IX with mp > 300°. UV spectrum, λ_{max}, nm ($\varepsilon \cdot 10^{-3}$): 405 (298), 540 (10.9), and 581 (15.7). IR spectrum: ν_{C-O} 1150 cm^{-1}. Found: C 70.0; H 7.3; N 9.3%. $C_{34}H_{40}CuN_4O$. Calculated: C 70.0; H 6.9; N 9.6%.

Complex IX was similarly obtained from complex IV in 50-60% yield.

Copper Complex (XII) of meso-Ethoxymethyletioporphyrin I. A) A solution of 100 mg (0.187 mmole) of complex VIII was refluxed for 30 min in a mixture of 1 ml of methyl iodide, 1 ml of absolute alcohol, and 50 ml of dry chloroform. The solution was evaporated to dryness, and the residue was chromatographed on silica gel in chloroform to give 74 mg (74%) of ether XII with mp > 300°. UV spectrum, λ_{max}, nm ($\varepsilon \cdot 10^{-3}$): 405 (290), 540 (10.8), and 580 (15.8). Found: C 69.9; H 7.1; N 9.2%. $C_{35}H_{42}CuN_4O$. Calculated: C 70.1; H 7.1; N 9.3%.

B) A solution of 20 mg (0.0375 mmole) of complex IV was passed through a column (4 × 40 cm) filled with silica gel with elution by chloroform–ethanol (98 : 2). Workup gave 20 mg (quantitative yield) of complex XII. According to the data from the electronic and IR spectra and the chromatographic mobilities, the product was identical to the complex obtained by method A.

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