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PHYSICAL CHEMISTRY OF SOLUTIONS

Structure and Stability of H^+ Associates of (5,10,15,20-Tetraphenylporphinato)silver(II) in Trifluoroacetic Acid

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Abstract—Direct experimental confirmation of the formation of ion–molecular associates of (5,10,15,20-tetraphenyl-21H,23H-porphinato)silver(II) (AgTPP) with solvent protons in CF_3COOH is obtained by means of ^1H NMR spectroscopy. Their structure and spectral properties, as well as the kinetics of dissociation on metal–nitrogen bonds, depending on the concentration of CF_3COOH (89–100%) and temperature (298–328 K), are studied It is shown that AgTPP acts as a C-base during the formation of H^+ associates, the coordination centers of which have a high stability.

Keywords: metalloporphyrin, silver, formation of H^+ associates, stability, ^1H NMR spectroscopy.

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INTRODUCTION

The acid–base properties of tetrapyrrole macrocyclic compounds have been thoroughly studied using a variety of physicochemical methods of analysis [1–10], due to the need to develop the practical aspects of their chemistry. The conjugate acids of porphyrins in particular are promising compounds for developing anion receptors, especially in solutions. Such solid-phase receptors are already well known [11–13]. In all of the above works, the focus was tetraazaporphyrins or their complexes, where nitrogen atoms in the aza bridges exhibit pronounced basicity and can be protonated (accept protons) in media with sufficiently high proton contents. The protonation of free bases on intracyclic nitrogen atoms, which is not observed when we move to complexes, is also possible. Despite the absence of such basicity centers in metalloporphyrins (MPs), very stable protonated forms of some MPs were detected in concentrated sulfuric acid media from their characteristic two-band UV–Vis spectrum as long as twenty years ago [14]. It was found that further protonation in media with high proton contents can also be observed for free base porphyrins, which are doubly protonated in acidic media to yield H_4P^{2+} species (H_2SO_4 at concentrations of over 17.5 mol/L).

It was concluded from UV–Vis spectra that the aromatic macrocycle is stable after the protonation of MP and H_4P^{2+}, indicating the incomplete transfer of protons to macrocycles, as is observed with aza-substituted analogues. Based on this data, the structure of ion–molecular associate MP...H^+_{Solv} (an H^+ associate), in which the proton is retained by a hydrogen bond with one of the carbon atoms of the macrocycle, was attributed to the detected protonated form of MPs.

Incomplete proton transfer was defined as incomplete or partial protonation. The existence of H^+ associates of metalloporphyrins in media of other acids was demonstrated later [15], and the first direct experimental confirmation of the presence of an additional proton in the H^+ associated form of metalloporphyrins was found. We now need to perform further studies on the properties of H^+ associates of MPs. In this work, the structure and spectral properties of ion–molecular forms of (5,10,15,20-tetraphenyl-21H,23H-porphinato)silver(II) (AgTPP) and the kinetic stability of their coordination centers were therefore studied. The formation of H^+ associates and the kinetics of dissociation of a partially protonated complex were observed in a trifluoroacetic acid.

EXPERIMENTAL

(5,10,15,20-Tetraphenyl-21H,23H-porphinato)-silver(II), AgTPP. This complex was obtained using the procedure described in [16] and modified in product isolation. H_2TPP was dissolved in 50 mL of chloroform. Ag(OAc) (0.1 g) was dissolved in 50 mL of acetic acid. The two solutions were mixed, and the reaction mixture was refluxed in a reaction flask equipped with a reflux condenser for 15 min. The reaction mixture was cooled and washed with water to remove any acetic acid. It was then placed on a column packed with silica gel (100/250) and chromatographed using a hexane–benzene mixture (volume ratio, 1 : 2) as an eluent. The AgTPP formed a dark red

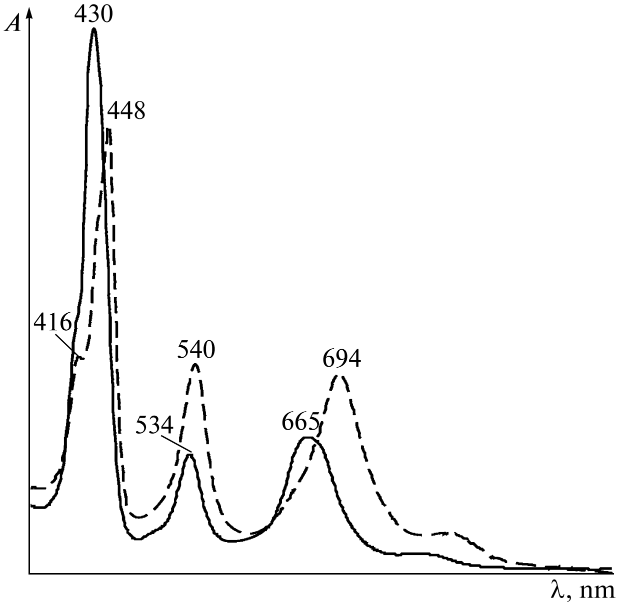

Fig. 1. UV–Vis spectra of AgTPP after dissolution in (solid line) 97.3% CF_3COOH and (dotted line) 95.2% H_2SO_4 at 298 K.

zone. UV–Vis spectrum of AgTPP ($CHCl_3$), $\lambda_{max}(\log\varepsilon)$, nm: 426 (5.25), 509 (3.86), 541 (4.12), 574 (3.83). The IR spectrum (KBr), ν, cm^{-1}: phenyl substituents 670 (γ(C=C)), 735 (γ(C–H)), 1076 (δ(C–H)), 1482 (ν(C=C)); 3040, 3060 (ν(C–H)); pyrrole fragments 800 (γ(C–H)); 974, 1008 (C_3–C_4, ν(C–N), δ(C–H)); 1320, 1360 (ν(C–N)); 1440 (ν(C=N)); coordination center 454 (Ag–N).

The ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.77 (s, $8H_\beta$), 7.65 (s, $8H_o$), 7.1 (m, $8H_m$), 6.55 (m, $4H_p$).

UV–Vis spectra were recorded on an Agilent 8453 with automatic registration of the spectrum, software for automatic metrological certification of the system and our qualitative and quantitative analysis, and a Specord M-400. The IR spectra were recorded on a VERTEX 80v; the ^1H NMR spectra, on a Bruker AVANCE III-500.

The dissociation rates for the H^+ associated complex in trifluoroacetic acid were determined spectrophotometrically by the concentrations excess method. AgTPP solutions in concentrated CF_3COOH ($C_{AgTPP} = 10^{-6}$ mol/L) were thermostated in a cuvette placed in the spectrophotometer's cell compartment. The error in determining temperature was ±0.1 K.

The numerical values of the dissociation rate constants and activation energies (k_{eff}, E_{eff}) were performed by the least squares method in Microsoft Excel software with $\log[(A_0 - A_\infty)/(A_\tau - A_\infty)] - f(\tau)$, $\ln k_{eff} - f[1/T]$ dependencies, respectively. Here, A_0, A_∞, and A_τ are the optical densities of the solutions at the working wavelength, at moments 0 and τ, and at the end of the reaction; T is temperature. The activation entropies ($\Delta S^{\neq}_{eff}$) were determined with the Eyring equation used for liquid systems in the second steady state.

RESULTS AND DISCUSSION

The attempt in [14] to obtain a high-quality ^1H NMR spectrum of the H^+ associates of all investigated MPs in order to identify the protons of the associates failed. The metalloporphyrins studied earlier either formed no associate in deuterated acids or underwent dissociation on M–N bonds with the release of double-protonated porphyrin ligands. Neither did the admixture of H_2SO_4 in deuterated sulfuric acid help to perform successful experiments. Only AgTPP was found to be suitable for such studies, as it forms a stable ion–molecular associate with protons in a medium of strong acids like CF_3COOH, which remains stable under the conditions of ^1H NMR spectrum registration.

UV–Vis spectra of AgTPP in organic solvents (AgTPP spectrum in $CHCl_3$ ($\lambda_{max}(\log\varepsilon)$, nm) is 426 (5.25), 509 (3.86), 541 (4.12), 574 (3.83)) are the hypso-type spectra of MPs [17]. The general spectrum view of the complex in an acid medium (Fig. 1) being characteristic of $MP...H^+_{Solv}$ [15], allows us to accurately identify it as belonging to the H^+ associated form of AgTPP. The absorption maxima of the H^+ associate of AgTPP in CF_3COOH are hypsochromically shifted relative to those observed in concentrated aqueous sulfuric acid [18] (Fig. 1). There are no theoretical interpretations of the MP H^+ associate UV–Vis spectra in the literature. However, the nature of two intense broad bands in the visible region of the spectra of all conceivable metalloporphyrins in this form can be interpreted from the published data on MPs π-radical cations, i.e., in the complete removal of one electron from a metalloporphyrin macrocycle [19]. ZINDO calculations of the molecules, cations, and anions of ZnPc (Pc being a dianion of tetrabenzotetraazaporphyne) and ZnTPP performed using a 16-orbital model and data from magnetic circular dichroism spectroscopy showed that a highly symmetric ZnTPP has an orbitally degenerate ground state, i.e., the two frontier HOMOs are degenerate. The degeneracy is removed with the reduction of the macrocyclic ring in the $ZnTPP^-$ anion, leading to such catastrophic changes in the UV–Vis spectrum as the emergence of absorption bands at λ_{max} 538 and 910 nm associated with $\pi^* \longrightarrow \pi^*$ transitions within unoccupied MOs and a bathochromic shift of 145 and 168 nm for two Q bands in the spectrum of the initial ZnTPP (605 and 560 nm). Using the example of the transition from ZnPc to $ZnPc^+$, it was shown that a similar degeneracy was eliminated and new bands attributable to a $\pi \longrightarrow \pi$ transition emerged within the closed

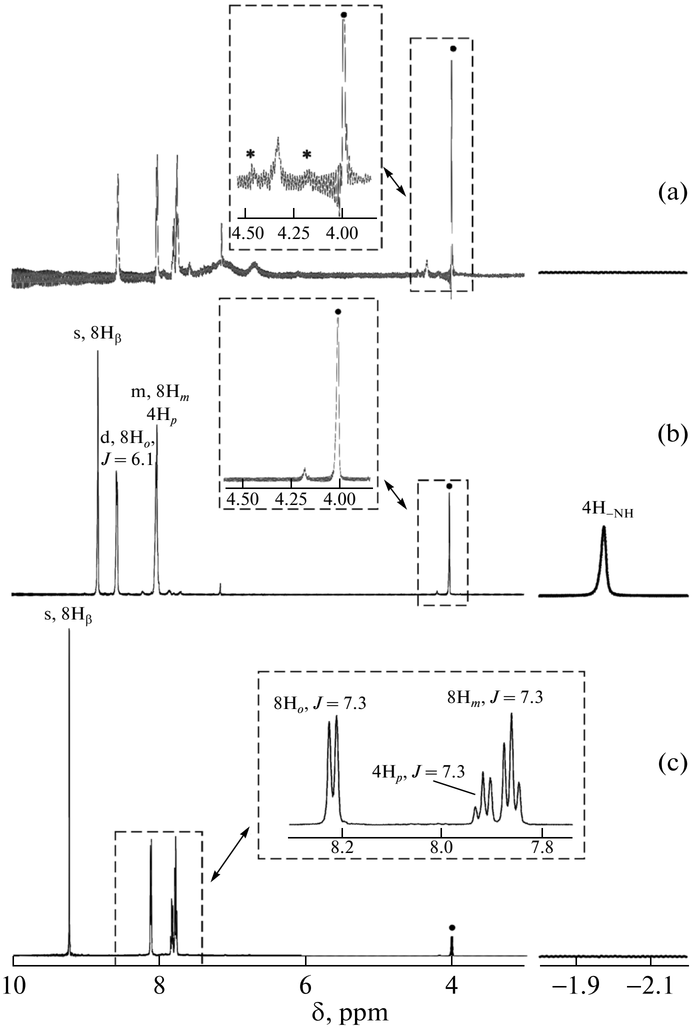

Fig. 2. ^{1}H NMR spectra of (a) AgTPP, (b) H_2TPP, and (c) (Cl)AuTPP in 99.8% CF_3COOH. The signals of additional protons in the H^+ associate are marked with asterisks; the signals of H_2O protons, with dots.

shells. Along with bathochromically shifted Q bands at 958 and 925 nm, the band of a second $\pi \longrightarrow \pi^*$ transition at 300–450 nm and bands arising from B_1, B_2, and $n \longrightarrow \pi^*$ transitions were observed in the spectrum upon the removal of a single electron. The partial redistribution of the electron density between the macrocycle and the proton in the MP H^+ associate probably produces similar changes in the spectrum. In light of the above data from [19], it is believed that the two bands near 700 and 540 nm in the spectrum of MP...H^+_{Solv} are nothing but a bathochromically shifted Q band and an absorption band corresponding to a $\pi \longrightarrow \pi$ transition that occurs within the HOMO due to the vacancy arising from the displacement of one electron in the direction of H^+.

The NMR spectrum provides direct quantitative information about the stoichiometry of absorbing nuclei of different types in a particular molecule. It is worth comparing the spectra of MP H^+ associates and those of MP complexes that exist in molecular form and the double-protonated free base porphyrin H_4TPP^{2+}. The ^{1}H NMR spectrum of a freshly prepared solution of AgTPP in CF_3COOH (δ, ppm, J, Hz) in molecular form is 7.84 (s, $8H_\beta$), 7.66 (m, $8H_o$), 7.23 (m, $4H_p$), 7.15 (m, $8H_m$); that of H^+ in associated form is 8.67 (s, $8H_\beta$), 8.14 (d, $8H_o$, $J = 7.3$), 7.55 (m, $4H_p$), 7.48 (m, $8H_m$), 4.25 (m, 1H, H^+_{meso}), 4.46 (m, 1H, H^+_β). Compared to the ^{1}H NMR spectra of free H_2TPP and (Cl)AuTPP, which form no H^+ associated form in any of the solvents [18], two signals at 4.20 and 4.46 ppm and broad resonance signals attributable to an exchange of protons belonging to the H^+ associate and the *meta* and *para* protons in the phenyl rings (6.5–7.8 ppm) were detected in the spectrum of a freshly prepared solution of AgTPP in CF_3COOH (Fig. 2), confirming the formation of the H^+ associate

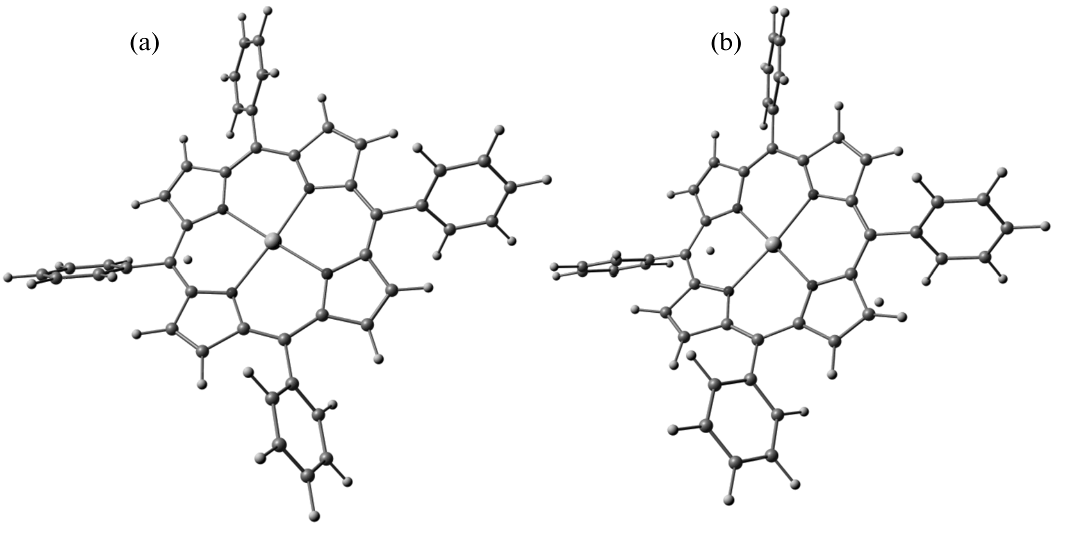

Fig. 3. Optimized structures of (a) AgTPP...H^+_{meso} and (b) AgTPP...$H^+_{meso}H^+_{\beta}$, calculated using the ZINDO quantum-chemical method.

of AgTPP. From calculations of the integrated intensities of the proton signals, it follows that the stoichiometry of the H^+ associate present in the solution was AgTPP : H^+ = 1 : 2.

The structures of AgTPP and its H^+ associates were optimized by S.V. Zaitseva and S.A. Zdanovich (Institute of Solution Chemistry, Russian Academy of Sciences) using the PM3 and ZINDO quantum-chemical techniques [20–23] under the condition that the calculations end at a preassigned gradient of 0.04 kJ/(mol Å). The angles and bonds of the average structure of metalloporphyrins were taken as an initial approximation for the macrocycle [24]. The energy of partial protonation E_{prot}, internuclear distances l, and Mulliken charges Z on the reaction centers were determined during the quantum-chemical calculations. The partial monoprotonation of AgTPP is most likely to occur at the *meso* position of the macrocycle (Fig. 3a) resulting in the formation of AgTPP...H^+_{meso} (E_{prot} = –320.22 kcal/mol, $l_{C_{meso}...H^+}$ = 1.10 Å). The generation of an associated form with two H^+, e.g., AgTPP...$2H^+$, is most favorable energetically when there is interaction on the *meso* and β positions (Fig. 3b) of the pyrrole fragment in a nonneighboring macrocycle (E_{prot} = –286.08 kcal/mol, $l_{C_{meso}...H^+}$ = 1.10 Å, $l_{C_\beta...H^+}$ = 1.102 Å, $Z_{C_{meso}}$ = –0.080, Z_{C_β} = –0.092 electron charge). C_{meso} and C_β are descreened in different by the ring current that arises in the porphyrin macrocycle under the influence of an electromagnetic field in the radio frequency range. According to these data, the additional signals in the ^1H NMR spectrum of AgTPP in CF_3COOH can be attributed to protons bonded to C_{meso} and C_β atoms (Fig. 3).

On the basis of the spectrophotometric titration data, the authors of [15] demonstrated that in concentrated H_2SO_4, the stable complex (Cl)InTPP forms an ion–molecular associate with one proton of the solvent. Quantum-chemical calculations for indium(III) complex showed that despite the high effective charges on the C_{meso} and C_β atoms in (Cl)InTPP...H^+_{Solv} (–0.093 and –0.096 to –0.154, respectively), the addition of a second proton is accompanied by strong distortion of the molecule and it becomes less energetic (E_{prot} ~ –140.02 kcal/mol) [15]. These data agree with the greater stability of AgTPP in concentrated H_2SO_4, compared to (Cl)InTPP (dissociation rate constants k^{298} are 0.24 × 10^{-8} s^{-1} mol^{-2} L^2 and 0.36 × 10^{-6} s^{-1} mol^{-1} L, respectively [18, 14]).

When a solution of AgTPP is heated in 89–100% CF_3COOH, its initial spectrum is transformed over time, as is shown in Fig. 4. The spectral curve of the final product corresponds to the double-protonated porphyrin H_4TPP^{2+}. This process proceeds notably slower at 298 K.

In a trifluoroacetic acid medium, silver complex in solution, being in the form of an H^+ associate, thus undergoes dissociation over time on the M–N bonds according to first order reaction (1) with respect to the concentration of H^+ associate:

$$\begin{aligned}&\mathrm{AgTPP...2(H^+...R) + 2(H^+...R)}\\&\xrightarrow{k_1} \mathrm{[Ag]^{2+} + H_4TPP^{2+} + 4R},\end{aligned} \tag{1}$$

where R is an anion or a molecule of acid. The first order of (1)

$$-dC_{\mathrm{AgTPP...2(H^+...R)}}/d\tau = k_{\mathrm{eff}}C_{\mathrm{AgTPP...2(H^+...R)}} \tag{2}$$

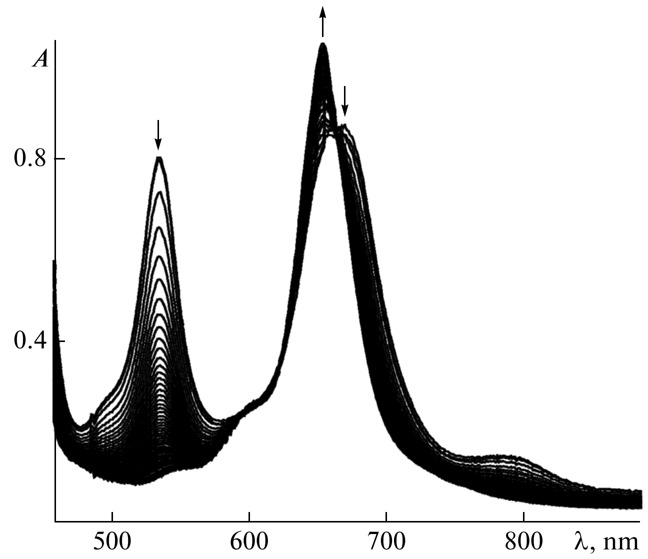

Fig. 4. Changes in the electronic absorption spectrum of AgTPP in 99.8% CF_3COOH at 318 K and τ in the range 0 to 10700 s.

is evident from the constancy of the effective dissociation rate constants (see above) of AgTPP in CF_3COOH (Table 1).

No linear correlation between the logarithms of k_{eff} and C_{CF_3COOH} was found in attempting to determine the reaction order with respect to a proton–donor species H^+...R. The rate of reaction (1) rises with an increase in the initial concentration of CF_3COOH in the range of 89.11–97.31%, reaching its maximum value at 97.31% and dramatically declining in 99.80% acid.

According to the data of [25], the dependence of acidity function H_0 on the initial concentration of CF_3COOH is not linear and has an extremum in the concentration range of 97.3–98.0 mol/L, explaining the tendency toward change in the rate of the process (1). The reaction order with respect to acid likely remains constant during the transition from the initial concentration of CF_3COOH to the equilibrium concentration of a certain type of proton–donor species in the medium of the solvent that is used. The lack of data on the equilibrium composition of concentrated aqueous CF_3COOH thus prevents us from determining the total kinetic equation and considering the mechanism of dissociation using this equation. Our results allow us only to establish an activation mechanism for reaction (1) (Table 1). It is impossible to determine the energy and solvation contributions to the activation of the system from the obtained data, since the value of k_{eff} could include an equilibrium constant in aqueous trifluoroacetic acid that becomes apparent in its temperature dependence.

Effective kinetic parameters of the dissociation of AgTPP in CF_3COOH

$C^0_{CF_3COOH}$, %	$-H_0$ [11]	T, K	$k_{eff} \times 10^4$, s^{-1}
99.80	2.7	298	1.3 ± 0.1
	–	308	3.5 ± 0.3
	–	318	5.8 ± 0.5
	–	328	19.0 ± 2.6
97.31	2.80	298	9.0 ± 0.5
95.96	2.78	298	8.0 ± 0.3
92.41	2.55	298	7.5 ± 0.1
89.11	2.25	298	4.4 ± 0.6

True parameters of the dissociation of AgTPP in H_2SO_4 [10]: $k^{298} = 0.24 \times 10^{-8}$ s^{-1} mol^{-2} L^2; E = 116 kJ/mol; $\Delta S^{\#}$ = −28 J/(mol K); E_{eff} = 82 kJ/mol, $\Delta S^{\neq}_{eff}$ = −56 J/(mol K). H_0—is the acidity function.

It is also worth noting that according to the data presented in [26], in which a special comparative study of the kinetics of dissociation of (AcO)MnTPP...H^+_{Solv} and its tetrakis–*o*-amino derivative (AcO)MnT(*o*-NH_2)PP forming no H^+ associate in solution was performed, the protons of H^+ associate are not involved in the protonation of coordinated N atoms during the dissociation of coordination centers. The same second-order rate equations were derived experimentally, and the same mechanism of dissociation was proven for the reactions of both compounds in concentrated H_2SO_4, the first in the form of H^+ associate and the second in molecular form.

For the same reasons, it is impossible to calculate the dissociation rate constants of AgTPP in CF_3COOH, which do not depend on the concentration of the acid, as was done for the AgTPP–H_2SO_4 system (table). However, we may suggest that the reaction rate in CF_3COOH is higher than for H_2SO_4, because even when AgTPP is dissolved in CF_3COOH at concentrations close to 100% (Fig. 1, line *1*), a shoulder corresponding to H_4TPP^{2+} appears on the *Q* band. It is the presence of double-protonated ligands in the reaction mixture that determines the overall hypsochromic shift of the spectrum indicated at the beginning of this section.

CONCLUSIONS

We have presented new data on the properties of MP H^+ associates in solutions with high concentrations of protons that characterize them as compounds with stable coordination centers and hydrogen bonds (i.e., C-bases) in excesses of H^+. Since the two-banded visible spectrum of metalloporphyrin is clearly attributable to its H^+ associated form, we can avoid incorrect conclusions about the stability and form of MPs in solvents of different natures when studying the reaction and catalytic activity of complexes.

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