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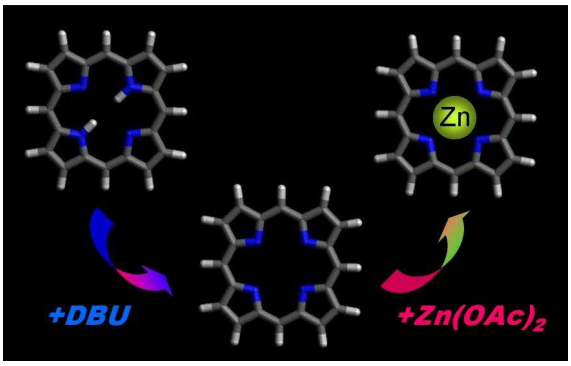

Easy formation of metalloporphyrins from the doubly deprotonated porphyrin P^{2-} is reported.

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COMMUNICATION

Acid-Base Equilibria and Coordination Chemistry of the 5,10,15,20-tetraalkyl-porphyrins: Implications for Metalloporphyrin Synthesis

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The spectrophotometric study of the acid-base equilibria and complexation with metal ions has been carried out for 5,10,15,20-tetrakis(trifluoromethyl)porphine and 5,10,15,20-tetrakis(*iso*-buthyl)porphine in acetonitrile solutions. Protonation and deprotonation of these porphyrins was found to be stepwise with sequential formation of mono- and doubly protonated/deprotonated species. The overall basicity and acidity constants have been determined. The porphyrin complexation with Zn^{2+} and Cu^{2+} ions were studied and the rates constants of the macrocycle metallation have been determined. The structure-property relationship derived from the metal chelation studies and the prospects of use of the above systems for the design of highly sensitive sensors for the metal ions were discussed in detail.

Introduction

Interest to the studies of the coordination and physical chemistry of tetrapyrrolic compounds, and, first of all, of the representatives of the porphyrin family, is due to the exceptionally important biological role of the metallocomplexes of these compounds which they play in the Life. The diversity of the functionalities relates to the diversity of their molecular structures, ability to form the complexes with different metal ions, possibility to form five- and six-coordinated axially ligated complexes as well as the ability to tune the oxidation state of the chelated metal ion according microenvironment properties.[1-9] The success of the porphyrin applications is directly related to the optimisation of the synthetic procedures, as well as to the detailed understanding of the structure-property relationships in the physico-chemical properties of these compounds. Selective modifications of the porphyrin macrocycle, especially those of non-symmetric type, frequently leading to the pronounced out-of-plane deformations of the tetrapyrrolic macrocycle, are considered to be the tool to understand and mimic the diversity of the biological functions of the tetrapyrroles.[10-12]

The results of the literature data analysis indicate that porphyrin macrocycle chelation with metal ions is able to proceed with two mechanisms: the molecular and ionic ones.[2,6,13-16] In the former case the complexation takes place between the metal salts and the porphyrin in the free base form (molecular form), whereas in the latter case deprotonated form of porphyrin undergoes the complexation. The first reaction is the generally accepted way to obtain the metalloporphyrins and has been studied in detail repeatedly,[2,6,17-18] while the macrocycle complexation with ionic mechanism was expected to be somewhat exotic and being far from the practical interest. However, our recent studies have demonstrated that the efficient metal chelation takes place also with doubly protonated forms of several porphyrin derivatives,[15,21] We have revealed that the rate of the porphyrin complexation with Zn^{2+} ions dramatically increases upon the addition to the solution of the deprotonating agent such as 1,8-diazabicyclo-[5,4,0]-undec-7-en (DBU), acting as "proton sponge" and ultimately leading to the full deprotonation of the porphyrin macrocycle core. Our findings are in line with few early communications on the ionic mechanism of complexation, where the possibility to obtain the metalloporphyrins has been reported for the core H-bonded and monodeprotonated porphyrins.[22-24]

Based on the above results, the extension of the metal complexation studies, involving the compounds with different substitution pattern of the porphyrin macrocycle, seems to be of interest. These studies aim to establish the structure-function relationship for the complexation of doubly deprotonated porphyrin macrocycles with different metal salts. The problem of metal ions determination in solutions is studied extensively during last two decades.[25-31] The reported to date conventional optical (spectrophotometric and luminescent) methods of the metal ion detection with porphyrin sensors approach to the detection limit of $1 \cdot 10^{-9}$ mole/L.[31] Increased complexation rate for ionic mechanism allows to extend the detection limit at least down to $5 \cdot 10^{-11} \div 1 \cdot 10^{-10}$ mole/L (according to difference in the porphyrin to metal salt ratio required for the metal ion chelating[15,21]). In this communication we report on the results of the studies of the acid-base equilibria and the complexation with $Cu(OAc)_2$ and $Zn(OAc)_2$ salts for two meso-alkyl-substituted porphyrins. The kinetic parameters related to the metal ion complexation by porphyrin macrocycle are also reported and discussed.

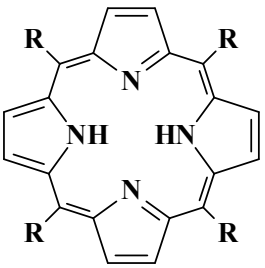
Results and Discussion

Free base porphyrin complexation

Molecular structures of studied 5,10,15,20-tetrakis-(trifluoromethyl)porphine (**1**) and 5,10,15,20-tetrakis(*iso*-buthyl)-porphine (**2**) are shown on the Scheme 1. It is accepted, that complexation of the free base porphyrins with divalent metal ions in nonaqueous solutions takes place according eq.1:

$$H_2P + [MX_2(Solv)_{n-2}] \rightarrow MP + 2HX + (n\text{-}2)Solv \quad (1)$$

where the H_2P is the porphyrin, M is the chelated metal ion, X is the salt anion, *Solv* is the solvent molecule serving as ligand.[2,6,8]



1 **R** = -CF_3
$H_2(CF_3)_4P$

2 **R** = -$CH_2CH(CH_3)_2$
$H_2(iBu)_4P$

Scheme 1

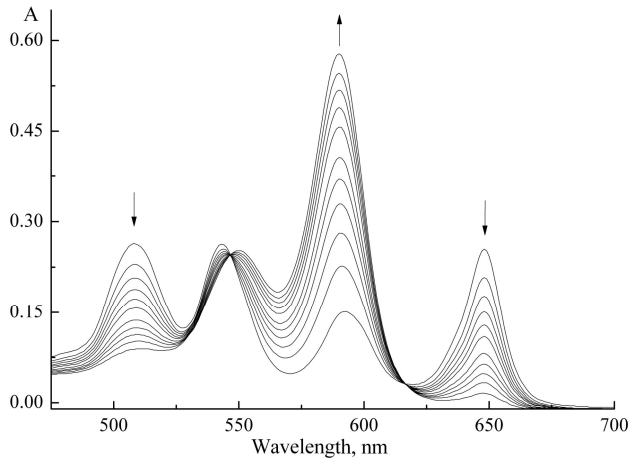


Fig. 1 Ground state absorption spectra changes in the course of the titration of porphyrin **1** with $Cu(OAc)_2$ in the acetic acid at 298 K. C_p = $5.20 \cdot 10^{-5}$ mole/L; C_{CuAc2} = $1.81 \cdot 10^{-3}$ mole/L. Arrows on this and following figures indicate the direction of the spectral changes upon increase in the titrant concentration.

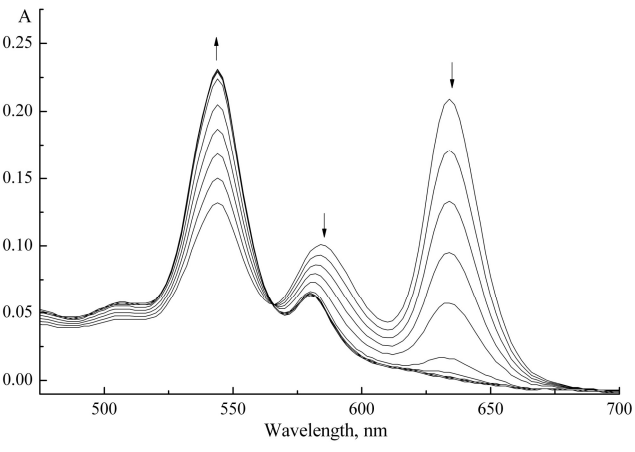


Fig. 2 Ground state absorption spectra changes in the course of the titration of porphyrin **2** with $Cu(OAc)_2$ in the acetic acid at 298 K. C_p = $1.79 \cdot 10^{-5}$ mole/L; $C_{CuAc2} = 3.62 \cdot 10^{-4}$ mole/L.

The kinetic parameters for the Cu-complexes formation of porphyrins **1** and **2** in the acetic acid are summarized in Table 1. Corresponding spectral changes measured during the spectrophotometric titrations are given at Figures 1, 2. Acetic acid has been chosen for the titration procedure since it forms relatively labile solvated complexes of transition metals, which can be easily broken in the presence of the porphyrin macrocycles to form metallocomplexes: thus, for example, 2,3,7,8,12,13,17,18-octamethylporphyrin complexation rate constant with Cu^{2+} was found to be about 10^5 times higher compared to that measured in pyridine.[32,33]

Table 1 Kinetic parameters of the Cu-complex formation for porphyrins **1** and **2** in acetic acid at 298 K.

	C_{CuAcO2}, mole/L	$k_{eff} \cdot 10^4$, s^{-1}	$k_v \cdot 10^4$, $(L/mole)^{0.5} \cdot s^{-1}$	E_a, κJ/mole	$\Delta S^{\neq}$, J/mole·K
1	$1.81 \cdot 10^{-3}$	1.77 ± 0.10	41.5 ± 2.3	79 ± 2	-34 ± 6
2	$3.62 \cdot 10^{-4}$	85.8 ± 0.9	4511 ± 135	75 ± 1	-7 ± 3

The obtained data on kinetic parameters of Cu-porphyrins formation indicate that electronic effects play the important role in the complexation. Replace of the electron donating substituents in porphyrin **1** for the electron withdrawing ones in the porphyrin **2** leads to almost 100-fold increase in the efficient rate constant k_{eff} of the complexation. At the same time, the energy of activation remains practically unchanged. Thus, four *iso*-butyl groups in the *meso*-positions of macrocycle in porphyrin **2** bring to the substantial changes of the electronic density of the tertiary nitrogens of pyrrole rings compared to that for porphyrin **1**. As a result, the basicity of porphyrin **2** is higher. According to bimolecular one stage mechanism of reaction (1), increase in basicity leads to more efficient interaction of porphyrin ligand with metal cation in the transition state, and, consequently, leads to substantial increase in the efficient rate constant of complexation.

Formation of mono- and doubly protonated porphyrin species

Porphyrins, is known, to be the amphoteric compounds, i.e. having both basic (N-bases) and acidic (weak NH-acids) properties.[1,4,10,34] There is a relationship between the coordination and acid-base properties of porphyrins; namely, the protonation of porphyrin macrocycle is the competing reaction with respect to the coordination of metal ion. Increase in the basicity of the porphyrin **2** as compared to that of porphyrin **1** are supported by the data obtained with the spectrophotometric titrations of both studied porphyrins in acetonitrile solutions with perchloric acid (Figures 3 - 6).

One can see that increase in the acid concentration leads to the formation of two series of spectral curves, with each of them has its own set of isosbestic points, indicating that protonation of porphyrins macrocycles takes place in two sages for both porphyrin **1** and porphyrin **2**. First of these series of spectral curves corresponds to the free base ↔ monoprotonated species equilibrium, whereas the second one relates to the equilibrium between the mono- and doubly protonated porphyrin species. Presence of the deflection point at the titration curve for the porphyrin **1** (Figure 4) enables the easy determining the acid concentration ranges where the porphyrin is in mono- and doubly protonated form. In case of the porphyrin **2** two basicity constants

are much closer each to other and therefore the titration curve does not reveal any deflection point (Figure 6).[35] The formation of the doubly protonated species can be treated with the overall basicity constant K_b describing the two-step formation of doubly protonated species. This value can be calculated with eq.2:

$$\lg K_b = \lg Ind - n \cdot \lg C_{HClO4}, \quad (2)$$

where, *Ind* is the indicator of concentration ratio $[H_4P^{2+}]/[H_2P]$, C_{HClO_4} is analytic value of the perchloric acid concentration $HClO_4$ in solution (mole/L), n=2 is the number of the protons attached.

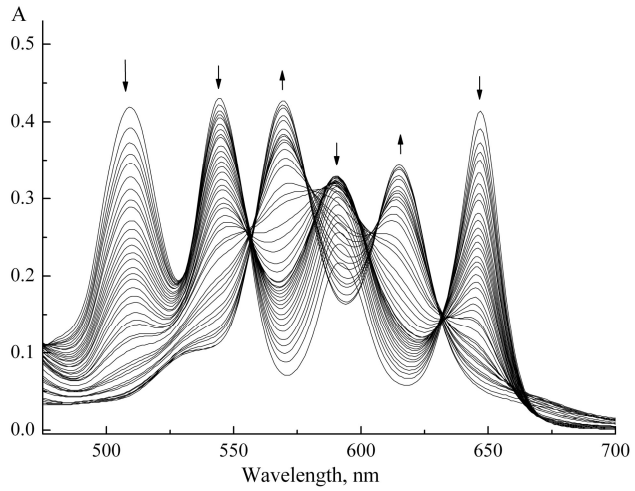


Fig. 3 Ground state absorption spectra changes in the course of the titration of porphyrin **1** with $HClO_4$ in acetonitrile at 298 K. $C_p = 3.04 \cdot 10^{-5}$ mole/L; $C_{HClO4} = 0 \div 0.576$ mole/L.

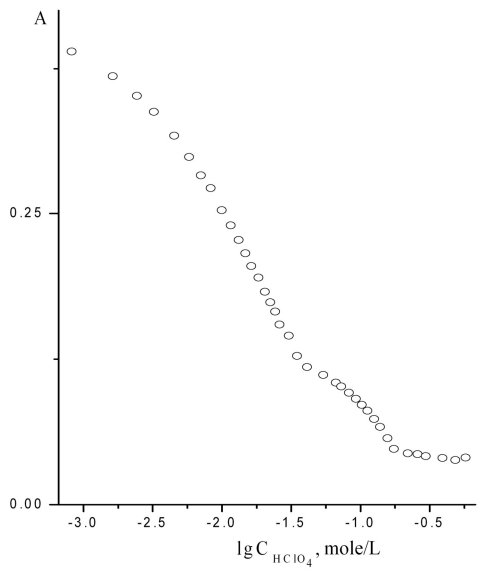


Fig. 4 The titration curve at λ = 509 nm for porphyrin **1** with $HClO_4$ in acetonitrile at 298 K.

The overall basicity constant K_b calculated with eq.2 amounts $\lg K_b$ =3.58 and $\lg K_b$ =9.04 at 298 K for porphyrins **1** and **2**, respectively. These values support the increase in the basicity in going from the porphyrin **1** to porphyrin **2**. No differences in the macrocycle planarity are expected to occur between two studied porphyrins based on the extensive crystallography data for the porphyrins with the same type of peripheral substitution,[36] and the macrocycle is suggested to be planar in both cases. Thus, the increase in the basicity of porphyrin **2** for almost 5 orders of magnitude needs to be assigned to pure electronic effects of substitution.

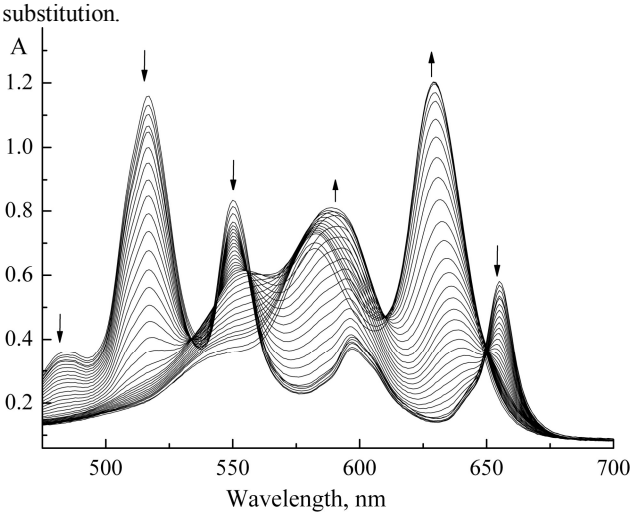


Fig. 5 Ground state absorption spectra changes in the course of the titration of porphyrin **2** with $HClO_4$ in acetonitrile at 298 K. $C_p = 1.10 \cdot 10^{-4}$ mole/L; $C_{HClO4} = 0 \div 2 \cdot 10^{-4}$ mole/L.

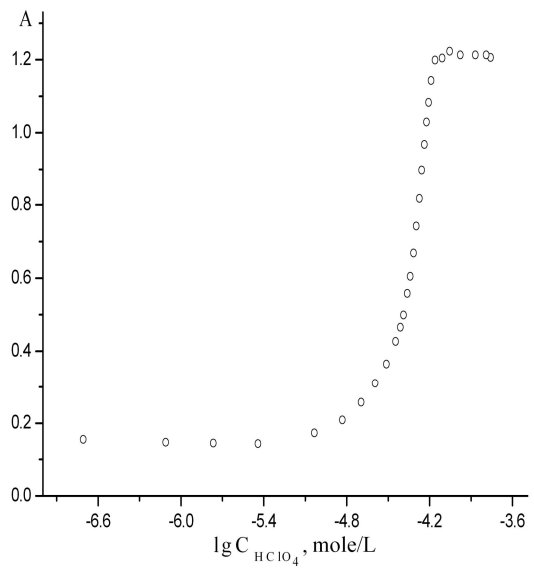


Fig. 6 The titration curve at λ = 629 nm for porphyrin **2** with $HClO_4$ in acetonitrile at 298 K.

Formation of mono- and doubly deprotonated porphyrin species

The acidic properties of studied porphyrins were evaluated with spectrophotometric titration in acetonitrile solution. The reactions between two organic compounds when one of them is used as the proton acceptor were reported.[37] The advantage of organic bases such as DBU over inorganic bases is the high solubility in organic solvents, enabling the use them in nonaqueous solutions.

The titration results revealed the difference in the acidity between porphyrin **1** and porphyrin **2**. Thus, even the maximum available DBU concentration have been applied to the solutions of porphyrin **2**, its doubly protonated form has not been obtained,

whereas at moderate DBU concentrations two sequential steps, corresponding to formation of mono- and doubly deprotonated species of porphyrin **1**, were observed (Figure 7). At the end of titration all the porphyrin **1** molecules have been converted into the doubly protonated species. The ground state absorption spectrum of the doubly deprotonated porphyrin **1:** λ_{max}, nm (lgε): 431 (4.96), 598 (4.00), 717(3.89).

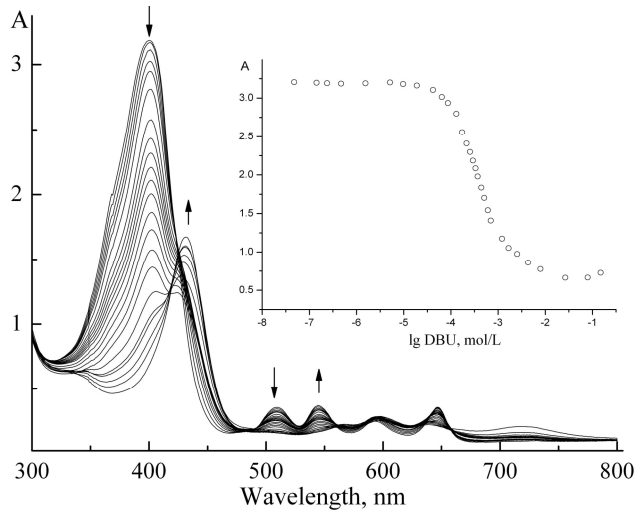


Fig. 7 Ground state absorption spectra changes in the course of the titration of porphyrin **1** with the DBU in acetonitrile at 298 K. C_p = $1.89 \cdot 10^{-5}$ mole/L; C_{DBU} = 0 ÷ $7.9 \cdot 10^{-3}$ mole/L. Insert shows the corresponding titration curve measured at λ = 400 nm.

+

The overall acidity constant was calculated with eq.3:

$$\lg K_a = \lg Ind + n \cdot \lg C_{DBU}, \quad (3)$$

where, *Ind* is the indicator of concentration ratio $[P^{2-}]/[H_2P]$, C_{HClO_4} is analytic value of the DBU in solution (mole/L), n=2 is the number of the protons attached. The calculations of the current concentrations of deprotonated forms and free base species, taking into account the material balance equation $C_o = C(H_2P) + C(P^{2-})$, show that all the porphyrin **1** molecules found themselves in the doubly deprotonated form at the DBU concentration ~ $7 \cdot 10^{-3}$ mole/L. The overall acidity constant was found to be $-\lg K_a = 9.69$.

Complexation of the doubly deprotonated porphyrin

The Zn-complex formation of the porphyrin **1** was studied in the acetonitrile solution containing the DBU amount (~$7 \cdot 10^{-3}$ mole/L, as was indicate above) required for the full conversion of the free base species into the doubly deprotonated ones. The spectral changes in the Soret band region measured during the titration of the free base porphyrin **1** are shown on Figure 8 for reference purposes. The spectral changes observed in course of the titration of the doubly deprotonated porphyrin **1'** are shown on Figure 9.

Table 2 summarizes the kinetic and thermodynamic parameters of the complexation. One can see that in going from the free base to the doubly deprotonated form, the rate of the complexation increases for more than 1000 times. The efficient rate constant of complexation reveals almost 200-fold increase.

Table 2 Kinetic parameters of the Zn-complex formation for the porphyrin **1** free base and its doubly deprotonated form **1'** in acetonitrile at 298 K.

	C_{ZnAcO2}, mole/L	$k_{eff} \cdot 10^4$, s^{-1}	$k_v \cdot 10^3$, (L/mole)·s^{-1}	E_a, κJ/mole	$\Delta S^{\neq}$, J/mole·K
1	$1.14 \cdot 10^{-2}$	6.9 ± 0.10	6.05 ± 0.08	52 ± 2	-175 ± 6
1'	$2.83 \cdot 10^{-4}$	115 ± 5	4006 ± 5	24 ± 1	-144 ± 5

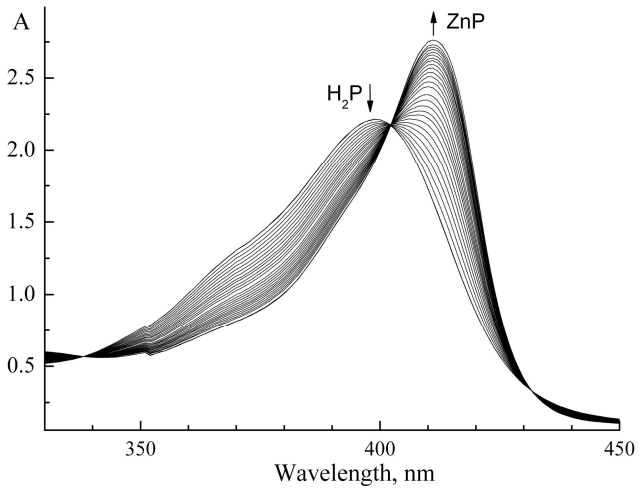


Fig. 8 Ground state absorption spectra changes in the course of the titration of the free base porphyrin **1** with $Zn(OAc)_2$ in acetonitrile at 298 K. $C_p = 1.31 \cdot 10^{-5}$ mole/L; $C_{ZnAc2} = 0 \div 1.14 \cdot 10^{-2}$ mole/L.

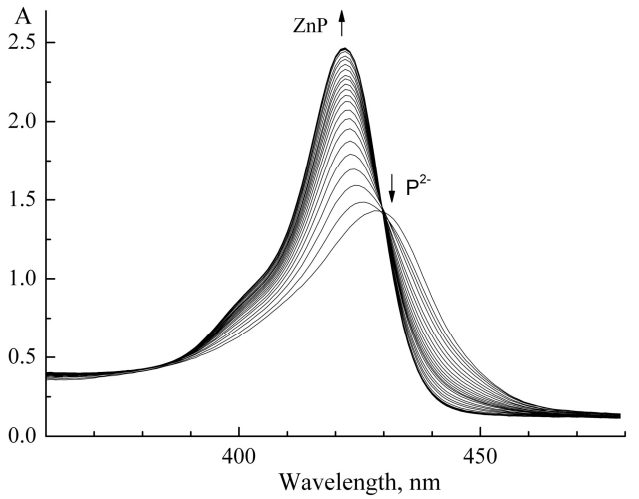


Fig. 9 Ground state absorption spectra changes in the course of the titration of the doubly deprotonated porphyrin **1'** with $Zn(OAc)_2$ in acetonitrile at 298 K. C_p = $1.67 \cdot 10^{-5}$ mole/L; C_{ZnAc2} = 0 ÷ $2.83 \cdot 10^{-4}$ mole/L; $C_{DBU} = 6.98 \cdot 10^{-3}$ mole/L.

At the same time, the activation energy value decreases twice compared to that measured for the complexation of the free base porphyrin **1**, which is followed with entropy decrease $\Delta S^{\neq}$ ~ 30 J/mole·K. These features are likely to be due to the absence of the

energy losses required for the deformation and rupture of the N−H bonds in the porphyrin core, as well as due to nonuniform charge distribution over the macrocycle, leading to polarization of the electronic cloud. As a result, the doubly deprotonated porphyrin **1'** may have higher solvation in the transition state which facilitates the metal ion chelation.

The Zn-porphyrin **1** molecules formed with two different procedures are identical each to other. Small long wavelength shift of the Soret band maximum (see Figures 8 and 9) for the Zn-complex of the porphyrin **1** formed with titration of doubly deprotonated form compared to that measured for Zn-complex obtained with titration of the free base porphyrin **1** is likely to be due to the solvent properties changes (most likely, the polarity), since in the former case the substantial amount of DBU was added to the acetonitrile solution. Stabilization of the electronic states with large transition dipole moment in (more) polar environment ultimately leads to the long wavelength shift of the absorption band.

Conclusions

The presented results unambiguously indicate that DBU can be successfully used for the formation of the mono- and doubly deprotonated porphyrins species in nonaqueous solutions. Introduction of the strong electron withdrawing substituents in the *meso*-positions of the porphyrin macrocycle increase the polarization of the N-H bonds, making difficult the complete deprotonation of the macrocycle. Provided that the macrocycle has low or moderate basicity, the full conversion of the free base porphyrins into the doubly deprotonated species is observed.

A significant decrease (down to 50 times) in the concentration of the metal salt required for the metal chelation and instant proceeding of the reaction appear to be the most promising features of the ionic mechanism of the metal complexation with the porphyrin macrocycles. This approach also needs substantially lower porphyrin to salt ratio (1:5) as compared with conventional molecular approach, where it amounts up to 1:100 or even higher value.[2, 23-24] All these facts taken together allow us to suggest the ionic mechanism of porphyrin metallocomplexes formation as the promising tool for the everyday practical use.

We hope also that the presented results to be of interest for the understanding of the synthesis and functioning of the endogenous porphyrins, since the formation of the metallocomplexes of endogenous porphyrins in the human and mammalian bodies occur also in the "very soft" conditions compared to those used for the synthesis of porphyrin metallocomplexes by conventional molecular procedure in the laboratory practice.

Experimental

Synthesis

The studied compounds were prepared according to the described earlier synthetic procedures.[38-40]

5,10,15,20-tetrakis-(trifluoromethyl)porphine (1) was purified by column chromatography (silica, eluent hexane-benzene 10:1) followed with recrystallization from the methylene chloride–methanol mixture. Elem.: calcd. for $C_{24}H_{10}N_4F_{12}$: C, 49.50; H, 1.73; N, 9.62; found: C, 49.53; H, 1.64; N, 9.33. ^{1}H NMR δ(ppm): 9.60 (s, 8 H), -2.08 (s, 2H, NH); Abs.: (CH_2Cl_2), λ_{max}, nm (lg ε): 403 (5.08), 510 (3.97), 545 (3.97), 593 (3.67), 649 (4.00).

5,10,15,20-tetrakis(*iso*-buthyl)porphine (2) was purified by column chromatography (Al_2O_3, type III by Brockman, eluent chloroform) followed with recrystallization from the chloroform–methanol mixture. Elem.: calcd. for $C_{36}H_{46}N_4$: C. 80.86, H 8.67, N 10.48; found: C 80.64, H 8.50, N 10.59. ^{1}H NMR δ(ppm): -2.65 (br, s, 2H, NH), 1.19 (d, 24H, CH_3), 2.62-2.81 (m, 4H, CH), 4.86 (d, 8H, CH_2), 9.45 (s, 8H, *β*-H). Abs.: (CH_2Cl_2), λ_{max}, nm (lg ε): 417 (5.65), 519 (4.15), 553 (4.04), 598 (3.7), 658 (3.95).

General experimental methods and instrumentation

NMR spectra in $CDCl_3$ solutions were acquired on commercial instrument Bruker Avance 500 MHz and chemical shifts (*δ*) are reported in parts per million (ppm) referenced to tetramethylsilane (TMS) or the internal (NMR) solvent signals. Mass spectra were run using a HP5989A apparatus (CI and EI, 70 eV ionisation energy) with Apollo 300 data system or a Thermo Finnigan LCQ Advantage apparatus (ESI). Ground state absorption spectra and spectrophotometric titration experiments were carried out with spectrophotometer Shimadzu UV-1800. The methods of the titration procedure and protocols of experimental data analysis were described in our previous papers.[41-42] The relative uncertainty in determined basicity and acidity constants did not exceeded 5 %.

$Cu(OAc)_2$ and $Zn(OAc)_2$ "for analysis" were purified by recrystallization with acetic acid followed with dehydration at 380-390 K according methods described.[43] Acetic acid "for analysis" was dehydrated by freezing followed with fractional distillation. Water contain was determined with Fischer method and did not exceeded 0.03%.[44] Dry acetonitrile (water contain no more then 0.03%) was used in the titration experiment. The 1,8-diazabicyclo-[5,4,0]-undec-7-en (DBU) was used as the deprotonating agent (pK_a = 13.2 in acetonitrile).[29] DBU and perchloric acid $HClO_4$ were used as received without further purification.

Complexation titration procedure and data treatment

Complexation was studied with the spectrophotometric method in the thermostated cuvettes at temperatures 293-308 K. Temperature during the titration set was kept with precision ± 0.1 K. Metalloporphyrin formation has the first order with respect to the porphyrin ligand.[2] Titration was carried out in the conditions of the 100-fold excess of metal salts $M(OAc)_2$ concentration over that of the porphyrin. In such conditions the efficient rate constant of the complexation reaction k_{eff} was calculated according to eq.4:

$$k_{eff} = (1/t)\ln[(A_o - A_\infty)/(A - A_\infty)], \quad (4)$$

where, A_0, A, A_∞ are the solution absorbance (at defined wavelength) before titration, at time t and at the end of titration, respectively. Rate constants of the n+1 order were calculated according to eq.5:

$$k_{n+1} = k_{eff}/c^n(M(OAc)_2), \quad (5)$$

where, n is the reaction order with salt, which is 0.5 for $Cu(OAc)_2$ in acetic acid,[45] and 1 for $Zn(OAc)_2$ in acetonitrile.[21] Activation energy E_a for the studied temperature range was calculated with Arrhenius equation (eq.6):

$$E_a = 19.1\cdot[(T_1\cdot T_2)/(T_2 - T_1)]\ \lg(k_2/k_1) \quad (6)$$

Entropy change for the formation of transition state $\Delta S^{\neq}$ was calculated with eq.7:

$$\Delta S^{\neq} = 19.1 \cdot \lg k_v + E_a/T - 253 \quad (7)$$

Acknowledgments

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Notes and references

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1 G.P. Gurinovich, A.N. Sevchenko, K.N. Solovyov Spectroscopy of chlorophyll and related compounds, Publishing house Science and Technology, Minsk, 1968, 520 p. [Engl. transl.: Nat. Tech. Informat. Serv. US Dept. of Commerce, Springfield, Virginia, 1971, 506 p.].

2 B. D. Berezin. *Coordination compounds of porphyrins and phthalocyanines*; Wiley: New York, Toronto, 1981.

3. D.J. Davis, in: D. Dolphin (Ed.), The Porphyrins, Academic Press, New-York, 1978, Vol. 5, p. 127

4 L. Latos-Grażyński, K. Rachlewicz, J. Wojaczyński, *Coord. Chem. Rev.*, 1999, **190–192**, 109

5 E.J. Baerends, G Ricciardi, A Rosa, S.J.A van Gisbergen, *Coord. Chem. Rev.*, 2002, **230**, 5

6 B.D Berezin, *J. of Porphyrins and Phthalocyanines*. 2003, **7**, 715.

7 Beletskaya, V. S. Tyurin, A. Yu. Tsivadze, R. Guilard, C. Stern, *Chem. Rev.*, 2009, ***109***, 1659.

8 M.G.H. Vicente, In: The Porphyrin Handbook. Vol. 1: Synthesis an Organic Chemistry; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: New York, 2000, pp 149-200.

9 M.O. Senge, In: The Porphyrin Handbook. Vol. 1: Synthesis an Organic Chemistry; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: New York, 2000, pp 239-348.

10 J.A. Shelnutt, In: The Porphyrin Handbook. Vol. 7: Theoretical and Physical Characterization; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: New York, 2000, pp. 167-223.

11 W.R. Scheidt, Y. Lee, *Structure and Bonding* (Berlin) 1987, **64**, 1-70.

12 O. A. Golubchikov,. S. G.; Pukhovskaya, E. M. Kuvshinova, *Russ. Chem. Rev.* 2005, ***74***, 249.

13 V. B. Sheinin, O. R. Simonova, E. L. Ratkova, *Macroheterocycles* 2008, **1,** 72

14 T. Sato, K. Ebisawa, K. Sue, S. Ito, T. Saito N. Itoh, *Ind. Eng. Chem. Res.*, 2012, **51**, 13908

15 Yu. B. Ivanova, D.T. Nam, S.A. Syrbu, M.M. Kruk, *Russian Journal of General Chemistry*, 2013, **83**, 1155

16 Y. Qi and Ji G. Pan, *Bull. Korean Chem. Soc*. 2014, **35**, 3313

17 P. Hambright, In : The Porphyrin Handbook. Vol.3: Synthetic Methodology; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: New York, 2000, pp. 129-210.

18 P Hambright, *Russ. Chem. Rev.*, 1977,**46**(7), 1207

19 Yu.B. Ivanova, S.G. Pukhovskaya, A.S. Semeykin, S.A.Surby, *Rus. J. Gener. Chem.*, 2013, **83**, 1406.

20 Yu.B. Ivanova, N.V. Chizhova, S.G. Pukhovskaya, N.Zh. Mamardashvili, *Rus. J. Gener. Chem.*, 2014, **84**, 848.

21 Yu.B. Ivanova, N.V. Chizhova, M.M.Kruk**,** *Russian Journal of General Chemistry*, 2013, **83**, 558.

22 P.A.Stuzhin, O.G.Khelevina, *Coordination Chemistry Reviews*, 1996. **147**, 41

23 P.A.Stuzhin, O.G. Khelevina, M.N.Ryabova, B.D.Berezin, *J. Applied Spectroscopy,* 1990, **52**, 70.

24 B.D.Berezin, O.G.Khelevina, P.A. Stuzhin, *Rus. J.l Phys. Chem. A*., 1985, **59**, 1295.

25 X.B. Zhang, C.C. Guo, Z.Z. Li, G.L. Shen, R.Q. Yu, *Anal Chem*., 2002 , **74**, 821

26 H.Y. Luo, X.B. Zhang , J.H. Jiang , C.Y. Li, J. Peng, G.L. Shen, R.Q. Yu, *Anal Sci*., 2007, **23**, 551

27 L. Lvova, P. Galloni, B. Floris, I. Lundström, R. Paolesse C. Di Natale, *Sensors,* 2013, **13**, 5841

28 V.K.Gupta, A.K. Jain, G. Maheshwari, H. Lang, Z. Ishtaiwi, *Sens. Actuators B Chem.,* 2006, **117,** 99

29 A. Kaljurand, L. Kütt, T. Sooväli, V. Rodima, I. Mäemets I., Leito, A. Koppel, *J. Org. Chem*., 2005, **70,** 1019

30 D. Vlascici, E. Fagadar, E.M. Pica, V.Cosma, O. Bizerea, G. Mihailescu, L. Olenic, *Sensors,* 2008, **8**, 4995

31 C.L. He, F.L. Ren, X.B. Zhang, Z.X. Han, *Talanta,* 2006, **70**, 364

32 S.G. Pukhovskaya, V.A. Efimovich, A.S Semeikin., O.A.Golubchikov *Rus. J. Inorg. Chem.,* 2010, **55**, 1494

33 S.G. Pukhovskaya., V.A. Efimovich, A.S Semeikin., E.A. Kolodina, O.A.Golubchikov, *Rus. J. Gener. Chem*., 2012, **82**, 476.

34 M. Kruk, A. Starukhin, W. Maes, *Macroheterocycles* 2011, **4**, 69.

35 I.Y. Bernstein, Y.L. Kaminsky, *Spectrophotometric Analysis in Organic Chemistry*; Khimiya: Leningrad, 1986, 202 p. (in Russian)

36 M.O. Senge, In: The Porphyrin Handbook. Eds. K. M. Kadish, K. M. Smith, R. Guilard. San Diego: Academic Press. 2000. V. 10. P. 1 – 218

37 A. F. Pozharskii, *Russ. Chem. Rev.* 1998, **67**, 1.

38 Y. Xie, J.P. Hill, R. Charvet, K. Ariga *J. Nanosc. and Nanotechn.*, 2007, **7**, 2969.

39 J. G Goll., K. T Moore., A. Ghosh, M. J. Therien, *J. Amer. Chem. Soc.*, 1996, **118**, 8344

40 A. M. d'A Rocha Gonsalves., J. M. T. B. Varejao., M. M. Pereira, *J. Heterocyclic Chem.,* 1991, **28**, 630

41 Ivanova Yu.B., Sheinin V.B., Mamardashvili N.Zh, *Rus. J. Gener. Chem.*, **2007**, 77, 1458.

42 Yu. B. Ivanova, Yu. I. Churakhina and N. Zh. Mamardashvili, *Rus. J. Gener. Chem.*, 2008, **78**, 673.

43 Yu.V. Karyakin., I.I. Angelov *Chistye Khimicheskie Veschestva (Pure Chemical Reactants)*. Moscow: Khimiya, 1974, 407 p.

44 A. J. Gordon and R. A. Ford, The chemists's companion: a handbook of practical data, techniques, and references, A Wiley-Interscience publication, John Wiley and Sons, New-York-London-Sydney-Toronto, 1972, 541 p.

45 T. A. Ageeva., E. L Ponomareva., O.A.Golubchikov., B. D. Berezin, *Koordinatsionnaia khimia (Coordination chemistry)*, 1987, **13**, 886.

