Metalloporphyrin receptors for bases

T. N. Lomova,★ E. V. Motorina, E. N. Ovchenkova, and M. E. Klyueva

Institute of Solution Chemistry, Russian Academy of Sciences,
1 ul. Akademicheskaya, 153045 Ivanovo, Russian Federation.
Fax: +7 (493 2) 33 6237. E-mail: tnl@isc-ras.ru

The review summarizes data on the reversible addition of inorganic and organic biologically active bases at the coordination sites of mixed complexes containing the porphyrin dianion as one of ligands. An analysis of the thermodynamic parameters revealed new receptors for small cyclic molecules holding promise for analytical purposes and sensorics.

Key words: metalloporphyrins, hydrogen sulfide, organic bases, reversible coordination, replacement of ligands.

Porphyrins (H_2P) form simple and mixed coordination compounds (MP) with metal cations.[1—3] Simple complexes can have the cation : ligand composition 2 : 1, 1 : 1, 1 : 2, or 2 : 3. Complexes of the latter two compositions have a sandwich structure.[4,5] The coordination spheres of mixed complexes contain, in addition to porphyrin, molecular, acido, or chelating ligands. Although sandwich complexes with a 2 : 3 stoichiometry belong to simple coordination compounds, each metal atom in these complexes is bound to two structurally different macrocyclic ligands (X-ray diffraction data[6]), *viz.*, to the central planar ligand and the terminal dish-shaped ligand.

Among mixed complexes, complexes with aromatic macrocyclic ligands are distinguished by the nearly planar arrangement of the donor and other atoms of the macrocyclic ligand, a high charge density at the bonds in the coordinated aromatic ligand, and the delocalized electronic state of the latter. In other classes of mixed complexes, cyclic ligands can contain only double and triple bonds or heteroatoms with several lone electron pairs as sterically rigid units, whereas the macrocycle in metalloporphyrins is rigid by itself. In other words, one of the ligands in mixed metalloporphyrins is characterized by the maximum steric rigidity. Upon coordination, the metal cation cannot impose stoichiometric constraints on this ligand corresponding to the optimal polyhedron of the complex. Hence, the overall coordination sphere of mixed porphyrin-containing complexes is rather specific. Although the specificity of the replacement of small (nonmacrocyclic) acido ligands in mixed porphyrin-containing complexes of highly charged metal cations is well known, these reactions have received little quantitative study.

Metalloporphyrins, in which the maximum possible coordination number of the metal cation is not achieved, can bind bases and form mixed coordination compounds. Until recently, these additional ligands in the coordination sphere have been commonly called extra ligands.[3,7] However, it is already evident that additional coordination processes is a special case of reactions of MP with bases. Nowadays, the coordination or replacement reactions of ligands involving porphyrin complexes of highly charged metal cations ($z \geq 3$) are of considerable interest for coordination and applied chemistry, because these complexes not only have vacancies in the first coordination sphere but are also coordinatively unsaturated and are characterized by a high effective positive charge of the central atom due to high diversity of possible coordination polyhedra.

In the overwhelming majority of cases, the coordination of inorganic and organic ions and molecules by metalloporphyrins is reversible. The reversible addition (transfer) of small cyclic molecules characterized by moderately high equilibrium constants can be successfully used for the separation of mixtures of organic isomers, quantitative analysis, and environmental and medical purposes. Hence, studies of quantitative characteristics and stoichiometry of equilibria of additional coordination to metalloporphyrins and the replacement of noncyclic ligands are not only of academic interest in the coordination chemistry of metalloporphyrins but also for a practical search for receptors and carriers of small cyclic molecules or ions.

The number of mixed porphyrin-containing complexes is very large compared to that of the above-mentioned complexes with a homoleptic coordination sphere. The formation of mixed complexes is statistically more favorable than the formation of simple complexes.[8] For example, the statistical probability of the formation of mixed MABC complexes in the case of ML_3 complexes (L = A, B, or C) with the coordination number of 3 is twice as high as that of MA_2B, MAB_2, MB_2C, or MBC_2 com-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 636—654, April, 2007.

plexes. The characteristic features of changes in the thermodynamic parameters depending on the nature of the cation and ligand do not correspond to those for the reactions giving rise to ML complexes, as it was exemplified by ethylenediamine derivatives.[9—11] Hence, the thermodynamic parameters of the formation of MEdtaL complexes cannot be predicted based on correlations with the parameters of ML complexes. Because of experimental problems, the thermodynamic stability constants of mixed porphyrin-containing complexes remained unknown. Attempts to estimate the relative stability of simple and macrocyclic ligands were made only in indirect experiments.[12—14] Hence, the thermodynamics of the formation of mixed complexes from available metalloporphyrins remains the only way of estimating the possibility of the simultaneous presence of an aromatic macrocycle and structurally simpler ligands (small molecules or acid anions) in the same coordination sphere.

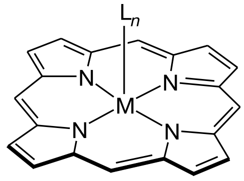
The present review summarizes data on the thermodynamics and kinetics of coordination reactions of bases with porphyrin complexes of highly charged metal cations, which are most numerous, practically important but poorly studied compounds. Complexes of doubly charged M^{2+} cations are considered as the simplest example of molecular complexation involving metalloporphyrins. The role of the additional coordination and replacement of ligands in catalysis by metalloporphyrins and prospects for the practical use of mixed porphine-containing highly charged metal complexes are analyzed.

1. Reversible coordination of hydrogen sulfide and organic nitrogen-containing bases by mixed porphyrin-containing transition metal complexes

The stoichiometric mechanism of the reactions of MP with bases is determined by the presence or absence of ligands of the non-porphyrin nature in the starting MP. Highly charged cations form mixed complexes with porphyrins because the charge of the cation higher than two is compensated by coordination of an anionic ligand, usually, of an acid residue of the starting metal salt, from which MP is derived. Hence, the reactions of doubly charged metal cation complexes with bases belong to a specific group of MP. To understand the nature of the reactions of mixed porphyrin-containing complexes, let us briefly consider some characteristic features of the reactions with $M^{2+}P$.

1.1. Doubly charged cation complexes

Porphyrin complexes of doubly charged metal cations form mixed complexes L_nMP (**1**) by coordinating H_2O, O_2, CO, organic solvent, nitrogen heterocycle, aliphatic or aromatic amine, polypeptide, or protein molecules, as well as acido ligands, *viz.*, halides, acetates, CN^-, OH^-, O^{2-}, HO_2^-, *etc.*, as additional ligands.



1

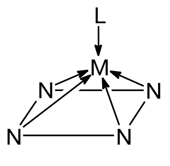
Additional coordination of molecular ligands by porphyrin complexes can give rise to one- and two-ligand metalloporphyrin complexes with small organic molecules:

$$MP + L_1 \rightleftharpoons (L_1)MP, \quad (1)$$

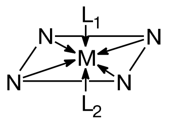
$$(L_1)MP + L_2 \rightleftharpoons (L_1)(L_2)MP. \quad (2)$$

Data on quantitative studies of equilibria (1) and (2) were summarized in the review.[15] These equilibria can easily be shifted in the desired direction by changing the concentrations of molecular ligands, the nature of the solvent, or the temperature. The coordination of additional ligands is accompanied by a shift of absorption bands in the optical spectrum with respect to those in the spectrum of the starting MP by 5—35 nm. The value and direction of the shift depend on the nature of the central atom and the molecular ligand and on the structure of porphyrin. The addition of the first ligand (Eq. (1)) leads to a bathochromic shift of the first absorption band corresponding to the low-frequency $\pi\rightarrow\pi^*$ transition, if MP is planar and weakly binds solvent molecules. The addition of the second molecular ligand (Eq. (2)) results in pushing of the metal atom into the center of the porphyrin cavity, strengthening of the $M\leftarrow N$ σ bond, and the stronger electrostatic influence on the N_4 atoms of the porphyrin. This should lead to a hypsochromic shift of the band I of the complex; however, the band I in the spectrum of the $(L)_2MP$ complex is less hypsochromic than that in the spectrum of metalloporphyrin due to the mutual influence of the $M\leftarrow L$ and $M\leftarrow N$ bonds (in porphyrin).

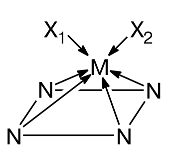
Due to the diversity of geometric polyhedra in porphyrin complexes with metal cations, there are many coordination modes of additional ligands. In Fe^{II}, Co^{II}, Mn^{II}, Zn^{II}, *etc.* complexes with one extra ligand, (L)MP, the metal ion is pushed out from the N_4 plane, and the MN_4 coordination unit can be described as a pyramid with the M metal atom in the apical position (structure **2**). As a result of the addition of the second ligand of the same nature or a ligand having a similar donor-acceptor ability, the metal atom is again pushed into the center of the N_4 plane, and the $(L_1)(L_2)MN_4$ coordination unit becomes planar (structure **3**). In highly charged metal cation complexes, anionic ligands X^- occupy the sites of molecular ligands L. Complexes of triply charged ions M^{3+} are, as a rule, nonplanar. Generally, the small anionic ligand (X^- = Cl^-, Br^-, CN^-, OH^-, *etc.*) involved in (X)MP is very strongly coordinated to the metal atom and pushes the latter from the plane of the macrocycle by 0.1—0.5 Å (structure analogous to **2**). Metalloporphyrins containing a cation with a formal charge of 4+ also form planar $(X_1)(X_2)MP$ complexes if X^- anions are identical or similar in nature (formula analogous to **3**). Porphyrin complexes with metals in oxidation state 5+ or 6+ form coordination units having even a higher symmetry, such as **4** and **5**.[3,16] For complexes with the already present ligands X^{n-}, the reaction with base molecules proceeds as the additional coordination only if the coordination sphere has vacancies; otherwise, the reaction leads to the replacement of ligands.



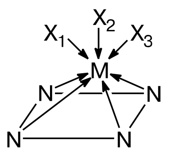
2



3



4



5

The $(Cl)_2ZrTPP$ and $(Cl)_2HfTPP$ complexes provide interesting examples. Due to very large sizes, the location of the Zr and Hf cations in the center of the N_4 cavity is energetically unfavorable because it would be accompanied by strong deformation of the porphyrin molecule. Hence, the metal atoms are located above the N_4 plane, and two acido ligands Cl^- are located on one side of the plane of the macrocycle (structure **4**), which is reflected in the character of additional coordination reactions.

Reactions (1) and (2) in solution are generally studied by optical spectroscopy[17,18] allowing the monitoring of the formation of complexes with molecular ligands, the determination of the number of coordinated molecular ligands, and measurements of the stability constants of molecular complexes and their temperature dependence. Data on the thermodynamic parameters of reactions (1) and (2) involving porphyrin complexes with Fe^{II}, Co^{II}, Zn^{II}, Ni^{II}, Hg^{II}, Cd^{II}, Cu^{II}, and Mg^{II}, as well as with Mn^{III}, Fe^{III}, and Co^{III}, were obtained for a large number of additional ligands of different nature.[19—24] The influence of the nature of the molecular ligand on stability of mixed complexes was considered in several studies.[21—25] The main conclusion drawn in these publications is that the thermodynamic constants of substitution (of anions and solvent molecules) in porphyrin complexes with molecular ligands of different nature does not, in the general case, linearly correlate with the basicity constants, except for sterically unhindered structurally similar ligands of similar nature. The same conclusion was drawn[26] for the reaction of $(Br)Fe^{III}OPTAP$ (OPTAP is the octaphenyltetraazaporphine dianion) with aromatic amines (imidazole (Im), Py, and its derivatives) yielding the $(L)_2Fe^{II}OPTAP$ complex. The thermodynamic stability of the $(L)_2Fe^{II}OPTAP$ complexes linearly correlates with $pK_{BH^+}(L)$ only in the series of sterically unhindered Py derivatives (2-ClPy, Py, 4-MePy, and 3,4-Me_2Py). Stability of complexes with the sterically hindered 2-MePy and 2,4,6-Me_3Py ligands is substantially lower than that expected based on pK_{BH+} of these bases. On the contrary, the complex with Im is more stable than could be expected based on the correlation diagram for substituted pyridines and pK_{BH+}(Im). This is attributed to the different degree of involvement of the dative π effect in coordination of molecular ligands of different nature.

The presence of molecular ligands substantially influences the properties of coordinated macrocyclic ligands and complexes as a whole. The influence of the Fe, Ru, and Os cations on the properties of MOPTAP containing isocyanides or five- and six-membered nitrogen heterocycles (1-MeIm, Py, Pyz, *etc.*) in the mixed coordination sphere was studied.[27] Investigations of protonation of Fe, Ru, and Os complexes led to the conclusion that the basic properties of MOPTAP strongly depend on the nature of additionally coordinated ligands. An increase in the electron-withdrawing properties of organic bases, on the one hand, decreases the basicity of the *meso*-N atoms, and, on the other hand, stabilizes the metal ion in oxidation state +2. The presence of molecular ligands containing additional basic centers also results in a strong decrease in the equilibrium constants of protonation of the macrocycle, however, mainly due to the electrostatic factor.

Analogous studies of porphyrin complexes with highly charged metal cations are scarce. Additional coordination by metalloporphyrins should attract much more attention in view of an extension of applied aspects in porphyrin chemistry. The catalytic and biological activity of MP, (X)MP, and $(X)_nMP$ and their stability in solution particularly strongly depend on the effects of additional coordination. Our data were obtained for mixed highly charged metal cation complexes, which are considered in the next section.

1.2. Highly charged cation complexes

In coordination chemistry of porphyrins with highly charged metal cations,[3] considerable attention was given to the synthesis of these mixed complexes, whereas the additional coordination of base molecules by metalloporphyrins have received little study. Investigations of the thermodynamics of additional coordination of small heterocyclic molecules by metalloporphyrins are of great interest, because these studies provide data on thermodynamic stability of complexes in solution and the character of the bond between the metal atom and the donor atom of the molecular ligand.

The reactions of mixed porphyrin-containing complexes with bases are very specific depending on the composition and structure of the coordination sphere and involve, as a rule, several equilibrium and irreversible steps. Hence, it is reasonable to consider the results successively for structurally similar complexes.

1.2.1. Complexes with Hf^{IV} and Zr^{IV}. 5,10,15,20-Tetraphenyl-21*H*,23*H*-porphinehafnium(IV) dichloride $(Cl)_2$HfTPP was synthesized[28—30] by analogy with the octaethylporphine complex (H_2OEP)[31] by the reaction of H_2TPP with anhydrous $HfCl_4$. The individuality and spectral purity (ESR parameters remain unchanged after additional purification steps) of the $(Cl)_2$HfTPP complex, which was synthesized in 60% yield, were confirmed by elemental analysis (FlashEA 1112 analyzer), the complete agreement between the ESR spectrum of the complex and the spectrum published in the study,[32] and the similarity of the IR spectra (in toluene and KBr) with the data published in the same study, where the complex was synthesized and identified for the first time.

5,10,15,20-Tetraphenyl-21H,23H-porphinezirconium(IV) dichloride $(Cl)_2$ZrTPP was synthesized and identified according to know procedures.[33] The electronic absorption spectra in chloroform (λ_{max}, nm (logε): 563.0 (shoulder), 535.0 (4.16), 497.0 (3.67), 461.0 (3.91), 414.0 (4.64)) are in complete agreement with the published data.[33]

The equilibria of the reactions of MP with H_2S, Py, Pyz, Im, and 1-Me—Im were studied[28—30,34—36] in toluene (by spectrophotometric titration). Toluene is regarded as a good solvent for metalloporphyrins in spite of low solubility of MP in this solvent (~10^{-3} mol L^{-1}); it is mixed with organic bases and is involved in chemical reactions with neither of these compounds.

The reaction of $(Cl)_2$HfTPP with Py was studied at 298 K in a broad pyridine concentration range from $8.27 \cdot 10^{-6}$ to 2.07 mol L^{-1} (Fig. 1). It was demonstrated[30] that an increase in the Py concentration leads to changes in the spectrum of $(Cl)_2$HfTPP in three series of spectral bands, for each series the titration curve being measured (Fig. 2), *i.e.*, the reaction of $(Cl)_2$HfTPP with Py proceeds in three steps. The compositions of the coordination spheres in the products of stepwise reactions were confirmed by spectroscopic data for the starting and final reaction products in the UV-Vis and IR regions (see Fig. 1, Table 1).

The stoichiometry of the first step of the reaction of $(Cl)_2$HfTPP with Py was determined as 1 : 1 based on the $\log A - \log C_L$ plot, where $A = (A_p - A_o)/(A_\infty - A_p)$ (Fig. 3,

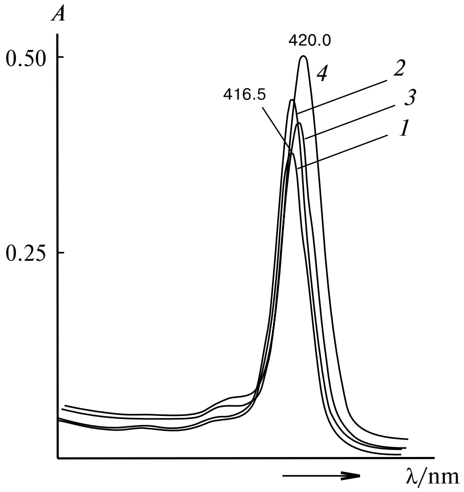


Fig. 1. Electronic absorption spectra of $(Cl)_2$HfTPP in toluene depending on the Py concentration, C_{Py}/mol L^{-1}: 0 (*1*), $8.27 \cdot 10^{-4}$ (*2*), $5.17 \cdot 10^{-1}$ (*3*), and 2.07 (*4*); $C_{(Cl)_2HfTPP} = 1.5 \cdot 10^{-6}$ mol L^{-1}.

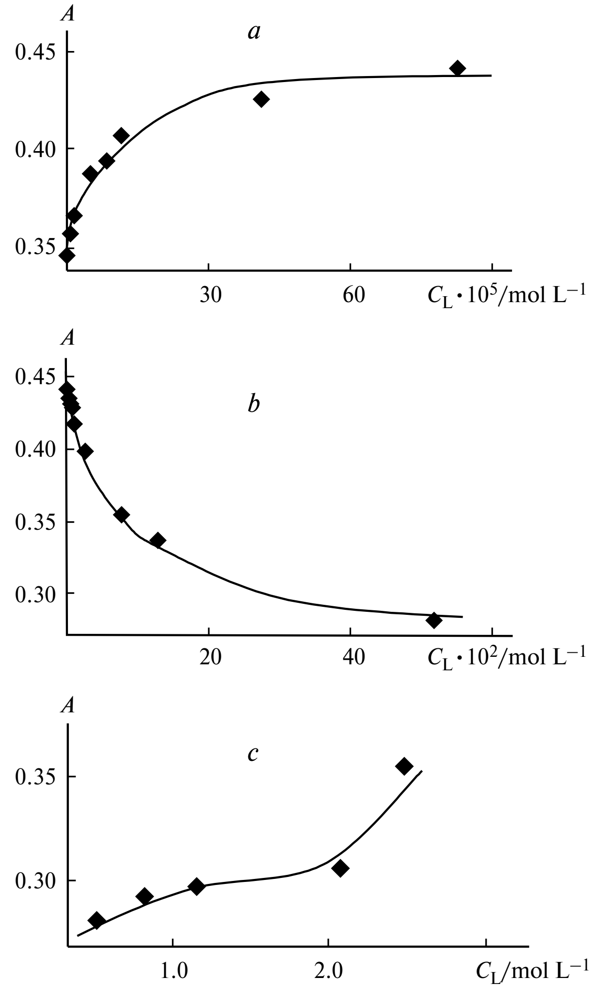


Fig. 2. Spectrophotometric titration curves for the reaction of $(Cl)_2$HfTPP with pyridine in toluene, C_{Py}/mol L^{-1}: $(8.27 \cdot 10^{-6})$—$(8.27 \cdot 10^{-4})$ (*a*), $(8.27 \cdot 10^{-4})$—$(5.17 \cdot 10^{-1})$ (*b*), $(5.17 \cdot 10^{-1})$—2.07 (*c*). The operating wavelength was 414 nm.

Table 1. Band frequencies (ν/cm^{-1}) in the IR spectra of tetraphenyl-21*H*,23*H*-porphinehafnium(IV) dichloride before and after the treatment of the latter with pyridine (toluene, 400—4000 cm^{-1}, Specord M80)

Band in the spectrum (Cl)$_2$HfTPP	(Cl)$_2$HfTPP	[(Py)$_3$HfTPP]$^{2+}\cdot$2Cl$^-$	Band assignment
1	—	405	ν(Hf—N$_{\text{Py}}$)
	445	—	ν(Hf—Cl)
2	464	465	ν(Hf—N)
	—	602	Stretching vibrations of Py
6	694	694	γ(C—H) of the benzene ring
	—	696	γ(C—H) of pyridine
7	731	731	γ(C—H) of the benzene ring
	—	733	γ(C—H) of pyridine
8	796	796	γ(C—H) of the pyrrole ring
11	891	905	δ(C—H) of the pyrrole ring
	—	990	δ(C—H) of pyridine
15	1030	1030	ν(C$_3$—C$_4$), ν(C—N)
	—	1068	ν(C—C), ν(C—N) of pyridine
17	1081	1081	δ(C—H) of the benzene ring
	—	1145	δ(C—H) of pyridine
20	1180	1180	δ(C—H) of the benzene ring
	—	1216	δ(C—H) of pyridine
25	1380	1380	ν(C—N)
	—	1436	ν(C=N) of pyridine
26	1454	1454	ν(C=N)
27	1495	1495	ν(C=C) of the benzene ring
28	1525	1525	Vibrations of the pyrrole ring
	—	1577	ν(C=C) of pyridine
30	1604	1600	ν(C=C) of the benzene ring
	Region is not studied	2920	ν(C—H) of the pyrrole ring
		2960	*Ditto*
		3071	ν(C—H) of the benzene ring
		3110	*Ditto*

straight line *1* ($\tan\alpha = 0.92$)). The equilibrium constant K_1 in the first step of the reaction of (Cl)$_2$HfTPP with Py (Eq. (3)[37]) is $(1.5\pm0.2)\cdot10^4$ L mol^{-1} (Table 2), which is substantially higher than that usually determined for coordination reactions of bases with metalloporphyrins.[15]

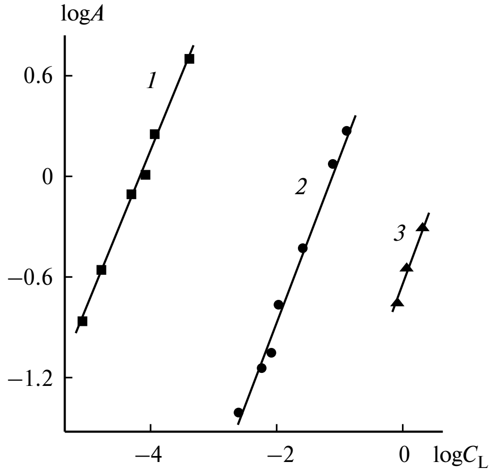


Fig. 3. Plot of log$A$ *vs* logC_{L}, where $A = (A_{\text{p}} - A_{\text{o}})/(A_\infty - A_{\text{p}})$, for the reaction of (Cl)$_2$HfTPP with Py in toluene in the first (*1*), second (*2*), and third (*3*) steps (ρ 0.998, 0.995, and 0.994, respectively).

$$K = A/(1 - A)(C_{\text{L}} - C^0_{\text{MP}}A), \qquad (3)$$

where $A = (A_{\text{p}} - A_{\text{o}})/(A_\infty - A_{\text{p}})$, C^0_{MP} and C_{L} are the initial concentrations of metalloporphyrin and Py, respectively, in toluene, A_{o}, A_{p}, and A_∞ are the absorbances at the operating wavelength for solutions of metalloporphyrin, the equilibrium mixture at a particular Py concentration, and the reaction product, respectively.

After the equilibration of the first reaction step in the case of all the additives of Py used, a slow irreversible reaction proceeds, as evidenced by a decrease in the absorbance of equilibrium mixtures. For this reaction, the apparent rate constants were calculated by Eq. (4) (Tables 2 and 3).

$$k^{\text{app}} = (1/\tau)\ln A', \qquad (4)$$

where $A' = (A_0 - A_\infty)/(A_\tau - A_\infty)$, A_o, A_τ, and A_∞ are the absorbances at the operating wavelength at the initial instant of time, at the instants of time τ, and after completion of the reaction.

Table 2. Example of calculations of the equilibrium constants and the reaction rates for tetraphenyl-21*H*,23*H*-porphinehafnium(IV) dichloride with pyridine

Equilibrium in the first step				$C_{Py} = 1.16 \cdot 10^{-4}$ mol L^{-1}			
$C_{Py}10^5$ /mol L^{-1}	A_p	K_1	$(K_1 \pm \delta K_1) \cdot 10^{-4}$ /L mol^{-1}	τ /min	Transmittance (414 nm)	$k^{eff}{}_1 \cdot 10^4$	$(k^{eff}{}_1 \pm \delta k^{eff}{}_1) \cdot 10^4$ /s^{-1}
0	0.3449		1.5±0.2	0	0.409		3.6±0.2
0.827	0.3565	16909		5	0.412	3.20	
1.65	0.3658	17114		15	0.4183	3.67	
4.96	0.3872	15975		35	0.427	3.69	
8.27	0.3936	12459		40	0.429	3.80	
11.6	0.4067	15526		65	0.435	3.79	
41.3	0.4253	12204		105	0.439	3.46	
82.7	0.4413			∞	0.443		

Table 3. Apparent rate constants k^{app} for the reaction of $(Cl)_2HfTPP$ with Py in toluene at 298 K ($C_{(Cl)_2HfTPP} = 1.5 \cdot 10^{-6}$ mol L^{-1})

Step 1		Step 2	
$C_{Py} \cdot 10^5$ /mol L^{-1}	$(k^{eff}{}_1 \pm \delta k^{eff}{}_1) \cdot 10^4$ /s^{-1}	$C_{Py} \cdot 10^2$ /mol L^{-1}	$(k^{eff}{}_2 \pm \delta k^{eff}{}_2) \cdot 10^4$ /s^{-1}
0.83	2.7±0.2	0.25	3.1±0.1
1.65	2.9±0.2	0.58	3.4±0.2
4.96	3.2±0.1	0.83	3.5±0.2
8.27	3.4±0.1	1.07	3.7±0.1
11.6	3.6±0.2	2.59	4.1±0.2
41.3	4.10±0.03	7.76	4.6±0.1
82.7	4.5±0.2	12.9	4.9±0.5
		51.7	5.5±0.2

Processing of the linear dependence

$$\log k_1{}^{app} = \log k_1 + m_1 \log C_{Py} \quad (5)$$

resulted in the rate constant $k_1 = 9.74 \cdot 10^{-4}$ s^{-1} and the order of reaction (6) m_1 with respect to C_{Py} equal to 0.11 (Fig. 4, straight line *1*).

$$(Cl)_2HfTPP + Py \xrightleftharpoons{K_1} (Cl)_2(Py)HfTPP \longrightarrow$$
$$\longrightarrow [(Cl)(Py)\,HfTPP]^+ \cdot Cl^-, \quad (6)$$

$$(Cl)_2(Py)HfTPP + Py \xrightleftharpoons{K_2}$$
$$\rightleftharpoons [(Cl)(Py)_2HfTPP]^+ \cdot Cl^- \longrightarrow$$
$$\longrightarrow [(Py)_2HfTPP]^{2+} \cdot 2Cl^-, \quad (7)$$

$$[(Cl)(Py)_2HfTPP]^+ \cdot Cl^- + Py \xrightleftharpoons{K_3}$$
$$\rightleftharpoons [(Py)_3HfTPP]^{2+} \cdot 2Cl^-. \quad (8)$$

The second equilibrium step of the reaction of $(Cl)_2HfTPP$ with one Py molecule (see Fig. 3, straight line *2*, tanα = 1.02) proceeds at Py concentrations of $8.27 \cdot 10^{-4}$—$5.17 \cdot 10^{-1}$ mol L^{-1} with the constant K_2 equal to 14±2 L mol^{-1}. For the irreversible reaction in the second step, the apparent rate constants $k_2{}^{app}$, which were determined for different initial Py concentrations, are given in Table 3. The true rate constant $k_2 = 6.05 \cdot 10^{-4}$ s^{-1} and the reaction order m_2 with respect to C_{Py} is 0.11 (see Fig. 4, straight line *2*), which is not contradictory with the reaction scheme for the second step (Eq. (7)).

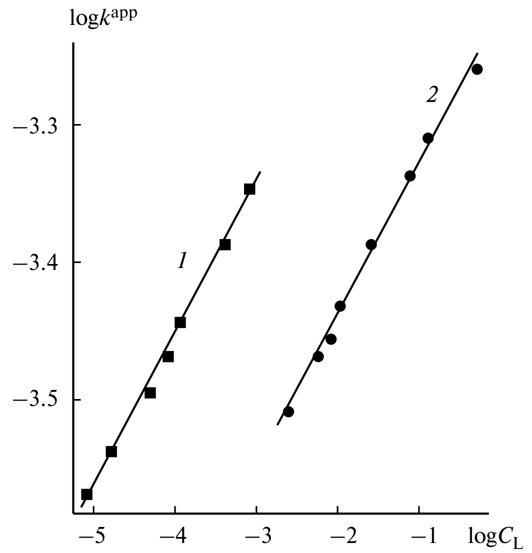


Fig. 4. Plot $\log k^{app}$—$\log C_L$ for the reaction of $(Cl)_2HfTPP$ with Py in toluene at 298 K in the first (*1*) and second (*2*) steps (ρ 0.998 and 0.997, respectively).

In the third step of the reaction of $(Cl)_2HfTPP$ with Py (Eq. (8)) at Py concentrations of $5.17 \cdot 10^{-1}$—2.07 mol L^{-1}, the changes in the electronic absorption spectra at different C_{Py} were found to be more substantial than those in steps (1) and (2) (see Fig. 1). The number of Py molecules involved in the reaction is close to 1 (1.11) (see Fig. 3, straight line *3*). The equilibrium constant K_3 = 0.23±0.01 L mol^{-1}.

Therefore, the first step involves coordination of the Py molecule at the seventh coordination site followed by the slow irreversible displacement of Cl^- in the resulting mixed complex to the second coordination sphere. Instability of the coordination sphere is apparently attributed to the *cis* configuration of the acido ligands in $(Cl)_2HfTPP$ and deviation of the Hf atom from the N_4 plane, which precludes the effective attack of the nucleophilic Py molecule on the central atom. The equilibrium constant K_2 is three orders of magnitude lower than that of K_1. The latter fact is indicative of worse conditions for additional coordination of the Py molecule by the seven-coordinate complex and the necessity of the displacement of the Cl^- ion from the coordination sphere (Eq. (7), the equilibrium reaction).

The third step involves the reversible replacement of Cl^- by the second Py molecule and the irreversible displacement of the second acido ligand to the outer sphere. The displacement of charged noncyclic ligands from the coordination sphere of the complex in the third reaction step giving rise to $[(Py)_3HfTPP]^{2+}\cdot 2Cl^-$ leads to a bathochromic shift of the band in the electronic absorption spectrum (λ_{max} = 420.0 nm). The difficulty of replacement of the acido ligands (Eq. (8)) is manifested in a decrease in the equilibrium constant K_3 compared to the constants K_1 and K_2 in steps (1) and (2), respectively.

The structure of the product generated in reaction (8) is confirmed by the IR spectra of the starting $(Cl)_2HfTPP$ complex and the complex isolated from a solution in Py by vacuum distillation of the latter (see Table 1). The spectrum of the starting $(Cl)_2HfTPP$ complex shows an absorption band at 445 cm^{-1}, which presumably belongs to Hf—Cl stretching vibrations.[38] This band disappears in the IR spectrum of $[(Py)_3HfTPP]^{2+}\cdot 2Cl^-$. The IR spectrum of the complex isolated from a solution in Py ($[(Py)_3HfTPP]^{2+}\cdot 2Cl^-$) has new absorption peaks assigned to stretching vibrations of coordinated pyridine (see Table 1).[39]

Overall reactions (6) and (7) and reaction (8) result in the replacement of ligands in the first coordination sphere of the hafnium(IV) porphyrin complex. The reaction mechanism in the first and second steps (Eqs (6) and (7), respectively), for which the kinetics of the irreversible displacement of the acido ligands was studied, resembles, on the whole, the associative mechanism of the replacement of ligands[40]

$$M(X_n) + L \rightleftharpoons M(X)_nL \rightleftharpoons M(X)_{n-1}L + X^-, \qquad (9)$$

but it has specific features.

Like the dissociative mechanism of the reactions of (AcO)CrTPP with Im,[41] the associative mechanism differs from the classical substitution mechanism of ligands in that rather stable complexes with the stability constants substantially larger than unity ($K_1 = 1.50\cdot 10^4$ L mol^{-1} and K_2 = 14.15 L mol^{-1} for Hf complexes) are produced instead of unstable intermediates, *viz.*, complexes having, correspondingly, the extended ($M(X)_nL$ in Eq. (9)) or ionized (Cr complex) coordination sphere with a high or intermediate coordination number.

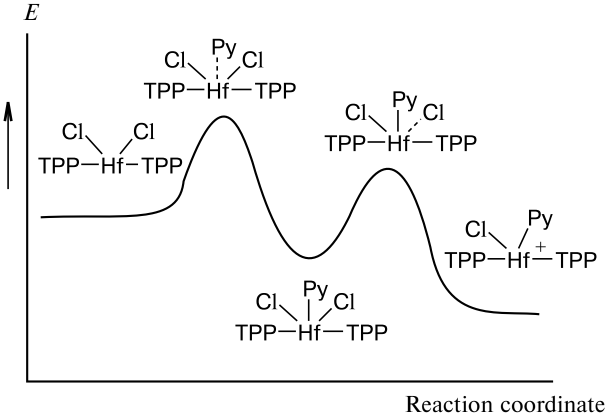


Fig. 5. Cross-section of the potential energy surface for reactions (6)—(8). The deviation of Hf from the porphyrin plane is not shown in the figure.

The proceeding of reaction (7) by this mechanism is provided by several factors: the accessibility of the vacant d orbitals of Hf for the formation of the direct N_{Py}—Hf dative π bond, the coordination number > 6 in Hf complexes, and the nonplanar arrangement and the large covalent radius of Hf in metalloporphyrins.

Analogous studies of the reaction with Py were carried out for some other H_2TPP complexes.[42] The constant K_1 for the reaction of Py with mixed porphyrin-containing chromium, molybdenum, and tungsten complexes changes in the series

$$\underset{(K_1 = 13300)}{O{=}W(OH)TPP} > \underset{(K_1 = 9100)}{O{=}Mo(OH)TPP} > \underset{(K_1 = 2.8)}{(AcO)CrTPP}. \qquad (10)$$

A sharp decrease in the stability constant of the pyridine complex with Mo is associated with a change, compared to reaction (6), in the nature of the equilibrium

$$O{=}Mo(OH)TPP + Py \rightleftharpoons [O{=}Mo(Py)TPP]^+OH^-. \qquad (11)$$

In the stability constant, the $(Cl)_2(Py)HfTPP$ complex ($K_1 = 1.50\cdot 10^4$ L mol^{-1}) is the first compound in series (10), *i.e.*, among the known mixed complexes, this complex is the best receptor for organic bases. The latter fact, along with reversibility of the reaction with Py, can be used for analytical purposes, *viz.*, for the membrane separation of mixtures of organic compounds. It is also important that the reactions with excess Py involving coordinated Cl^- anions (above-considered reactions (7) and (8)) are characterized by the equilibrium constants many orders of magnitude lower than K_1.

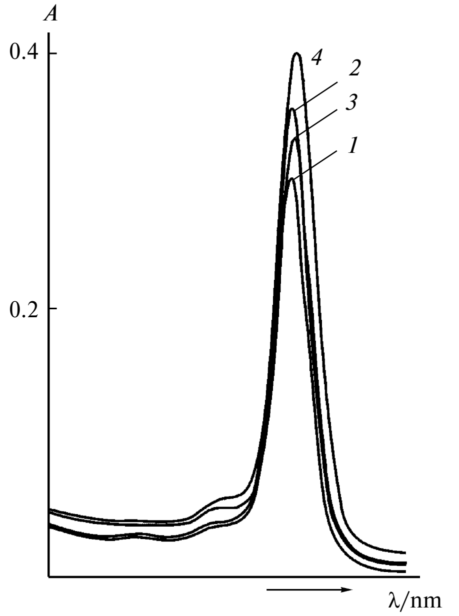


Fig. 6. Electronic absorption spectra of $(Cl)_2HfTPP$ in toluene depending on the Im concentration; C_{Im}/mol L^{-1}: 0 (*1*), $1.20 \cdot 10^{-5}$ (*2*), $2.39 \cdot 10^{-3}$ (*3*), $1.39 \cdot 10^{-2}$ (*4*), $C_{(Cl)_2HfTPP} = 1.5 \cdot 10^{-6}$ mol L^{-1}.

The reaction of $(Cl)_2HfTPP$ with Im was studied[29] in a broad Im concentration range ($1.20 \cdot 10^{-6}$—$1.39 \cdot 10^{-2}$ mol L^{-1}) at 298 K. Figure 6 shows the electronic absorption spectra of $(Cl)_2HfTPP$ in toluene depending on the Im concentration. The reaction of $(Cl)_2HfTPP$ with Im in toluene involves three equilibrium steps. The equilibrium constant K_1 for the first reaction step is rather high ($(2.3 \pm 0.2) \cdot 10^5$ L mol^{-1}). The reaction product in the first step is unstable and gradually undergoes a slow and irreversible transformation into a complex spectrally identical to the reaction product of metalloporphyrin $(Cl)_2HfTPP$ with Im in the second step (see Fig. 6, spectral curve *3*). Table 4 gives the apparent rate constants for this transformation k_1^{app}, which were determined for different initial Im concentrations. The second step of the reaction proceeds at Im concentrations of $1.20 \cdot 10^{-5}$—$2.39 \cdot 10^{-3}$ mol L^{-1}. The equilibrium constant K_2 is $(1.4 \pm 0.1) \cdot 10^4$ L mol^{-1}. In the second step, Cl^- is replaced by the second Im molecule, and the second acido ligand undergoes slow irreversible displacement to the outer sphere with the rate constant k_2^{app} (see Table 4). The third equilibrium step of the reaction with Im at Im concentrations of $2.39 \cdot 10^{-3}$—$1.39 \cdot 10^{-2}$ mol L^{-1} is characterized by the equilibrium constant $K_3 = 27.4 \pm 0.9$ L mol^{-1}.

Table 4. Formal first-order apparent rate constants k^{app} for the reaction of $(Cl)_2HfTPP$ with Im in toluene at 298 K ($C_{(Cl)_2HfTPP} = 1.5 \cdot 10^{-6}$ mol L^{-1})

Step 1		Step 2	
$C_{Im} \cdot 10^6$ /mol L^{-1}	$(k^{eff}_1 \pm \delta k^{eff}_1) \cdot 10^4$ /s^{-1}	$C_{Im} \cdot 10^4$ /mol L^{-1}	$(k^{eff}_2 \pm \delta k^{eff}_2) \cdot 10^4$ /s^{-1}
3.59	6.2±0.4	0.20	4.2±0.2
5.98	6.4±0.2	0.36	4.4±0.2
7.18	6.6±0.2	0.60	4.6±0.3
9.57	6.7±0.2	1.20	4.9±0.2
12.0	6.8±0.2	3.59	5.4±0.4
		5.98	5.9±0.5
		23.9	6.7±0.6

Therefore, the elementary steps of the reactions of $(Cl)_2HfTPP$ with Im are identical to those of the reactions with Py (Eqs (6)—(8)).

The coordination and replacement of the ligands in $(Cl)_2HfTPP$ with the S base, *viz.*, molecular H_2S, have been studied.[28] The reaction with H_2S was found to proceed in toluene reversibly with the step constants $K_1 = 82$ and $K_2 = 289$ L mol^{-1}:

$$(Cl)_2HfTPP + H_2S \rightleftharpoons (Cl)_2(H_2S)HfTPP, \qquad (12)$$

$$(Cl)_2(H_2S)HfTPP + H_2S \rightleftharpoons (Cl)_2(H_2S)_2HfTPP. \qquad (13)$$

The reaction of $(Cl)_2ZrTPP$ with Py in toluene in a broad Py concentration range ($8.27 \cdot 10^{-6}$—4.96 mol L^{-1}) at 298 K involves several equilibrium and irreversible steps. The reaction is manifested in the spectra as follows: initially, the band absorbance at 418.6 nm gradually increases as the Py concentration increases and then, at a Py concentration from $1.16 \cdot 10^{-4}$ to $1.29 \cdot 10^{-1}$ mol L^{-1}, the intensity of the band at 418.6 nm decreases and the maximum of this band is slightly bathochromically shifted to 420.9 nm. At the maximum Py concentrations ($1.29 \cdot 10^{-1}$—4.96 mol L^{-1}), a band at $\lambda_{max} = 421.4$ nm appears. The number of molecular ligands, which are bound in each of the three observed equilibrium steps of the reaction of $(Cl)_2ZrTPP$ with Py, is ~1. In the first and second steps, the equilibrium mixture is unstable. Based on these data, a stoichiometric reaction mechanism was suggested involving equations analogous to Eqs (6)—(8) derived for the reaction of the tetraphenylporphyrin hafnium(IV) complex with Py. Therefore, the reaction of $(Cl)_2ZrTPP$ with Py can be described as follows: 1) coordination of the Py molecule in the first coordination sphere ($K_1 = 36500$ L mol^{-1}), 2) the replacement of Cl^- by the second pyridine molecule ($K_2 = 160$ L mol^{-1}), 3) coordination of the third Py molecule as a result of replacement of Cl^- ($K_3 = 0.56$ L mol^{-1}). The formation of $[(Py)_3ZrTPP]^{2+} \cdot 2Cl^-$ is accompanied by the appearance of the band at $\lambda_{max} = 421.4$ nm in the electronic absorption spectrum.

The irreversible transformations are associated with the displacement of the acido ligands Cl^- from the first coordination sphere of $(Cl)_2ZrTPP$ to form the outer-sphere complexes $[(Cl)(Py)ZrTPP]^+ \cdot Cl^-$ and $[(Py)_2ZrTPP]^{2+} \cdot 2Cl^-$.

The reaction of $(Cl)_2ZrTPP$ with Im, which is the stronger base than Py (pK_a are 7.03 and 5.21, respectively),[39,43] is also a complex multistep process consisting of several reversible and irreversible steps (14)—(16):

$$(Cl)_2ZrTPP + Im \xrightleftharpoons{K_1} (Cl)_2(Im)ZrTPP \longrightarrow$$
$$\longrightarrow [(Cl)(Im)ZrTPP]^+ \cdot Cl^-, \qquad (14)$$

$$(Cl)_2(Im)ZrTPP + Im \xrightleftharpoons{K_2}$$
$$\rightleftharpoons [(Cl)(Im)_2ZrTPP]^+ \cdot Cl^- \longrightarrow$$
$$\longrightarrow [(Im)_2ZrTPP]^{2+} \cdot 2Cl^-, \qquad (15)$$

$$[(Cl)(Im)_2ZrTPP]^+ \cdot Cl^- + Im \xrightleftharpoons{K_3}$$
$$\rightleftharpoons [(Im)_3ZrTPP]^{2+} \cdot 2Cl^-. \qquad (16)$$

The first step involves coordination of the Im molecule in the first coordination sphere (K_1 = 179000 L mol^{-1}) followed by the slow irreversible displacement of the acido ligand Cl^- in the resulting mixed complex $Cl)_2(Im)ZrTPP$ to the second coordination sphere. The second step involves coordination of Im as the equilibrium replacement of the acido ligand Cl^- (K_2 = 7300 L mol^{-1}) and the irreversible displacement of the second acido ligand Cl^- to the outer sphere after the establishment of equilibrium. The third step involves coordination of Im and the displacement of Cl^- to give $[(Im)_3ZrTPP]^{2+} \cdot 2Cl^-$ (K_3 = 245 L mol^{-1}).

The reactions with 1-Me—Im and Pyz were studied analogously. No irreversible steps were found in the reaction with MP. The step constants for the equilibria are given in Table 5. In spite of the simplicity of the spectral manifestation for the reaction with Pyz, which is always accompanied (as opposed to the reactions with other N-bases) by a decrease in the absorbance at the operating wavelength in the course of spectrophotometric titration, this reaction cannot be interpreted as a one-step complexation process. This is well illustrated by spectrophotometric titration curves (Fig. 7). For each reaction series, the isosbestic points were clearly found, and the corresponding wavelength changes from one series to another. In other words, the isosbestic points are not retained within the overall broad concentration range of the organic base.

Table 5. Equilibrium constants for the reactions of $(Cl)_2ZrTPP$ with nitrogen-containing molecular ligands at 298 K

Molecular ligand	Stability constants		
	K_1	K_2	K_3
Py	36500	160	0.56
Im	179000	7300	245
1-Me—Im	16000	39	0.14
Pyz	195600	4100	445

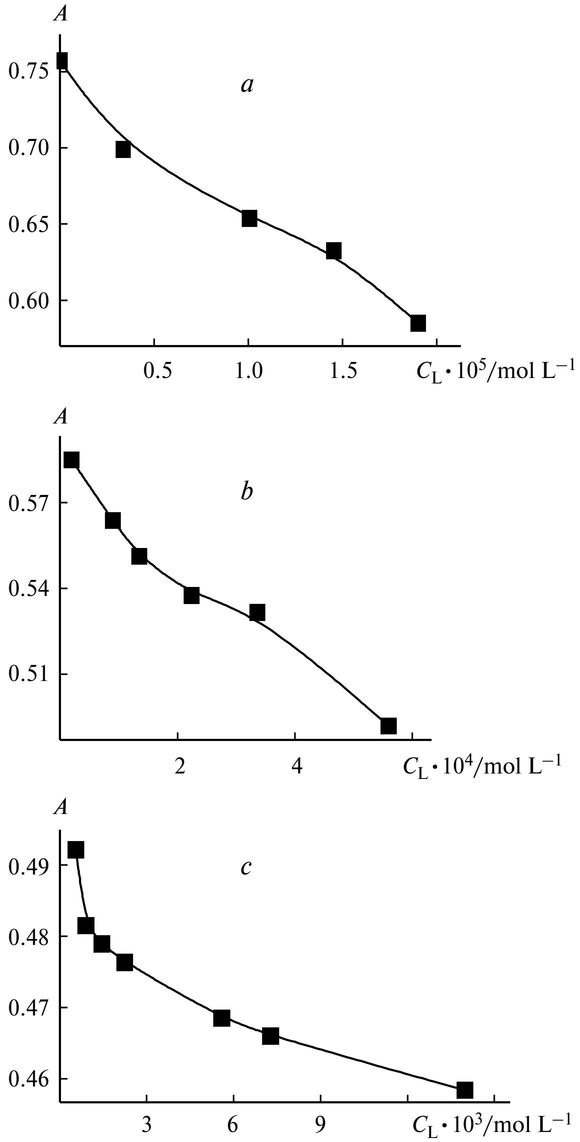


Fig. 7. Spectrophotometric titration curves for $(Cl)_2ZrTPP$ with pyrazine in toluene, C_{Pyz}/mol L^{-1}: ($3.36 \cdot 10^{-6}$)—($1.9 \cdot 10^{-5}$) (*a*), ($1.9 \cdot 10^{-5}$)—($5.6 \cdot 10^{-4}$) (*b*), ($5.6 \cdot 10^{-4}$)—($1.4 \cdot 10^{-2}$) (*c*). The operating wavelength was 417 nm.

$$(Cl)_2ZrTPP + Pyz \xrightleftharpoons{K_1} (Cl)_2(Pyz)ZrTPP, \qquad (17)$$

$$(Cl)_2(Pyz)ZrTPP + Pyz \xrightleftharpoons{K_2}$$
$$\rightleftharpoons [(Cl)(Pyz)_2ZrTPP]^+ \cdot Cl^-, \qquad (18)$$

$$[(Cl)(Pyz)_2ZrTPP]^+ \cdot Cl^- + Pyz \xrightleftharpoons{K_3}$$
$$\rightleftharpoons [(Pyz)_3ZrTPP]^{2+} \cdot 2Cl^-. \qquad (19)$$

As can be seen from Table 5 and the above-considered data for the Hf complex, the reactions of MP with N-bases are always accompanied by a decrease in the equilibrium constants from the first to the second step and from the second to the third step. The first step is characterized by the high constants, which is more indicative of the coordination of an additional ligand in the first coordination sphere rather than of the replacement of the acido ligands. In the second step, the constant sharply decreases, the constants K_1 and K_2 being noticeably dependent on the nature of the coordinated base. This is evidence of the associative reaction mechanism in the first and second steps for all the known bases. The first step involves the coordination of the nitrogen-containing base as an additional ligand, and the equilibrium reaction is completed. In the second step, the acido ligand leaves the coordination sphere of the unstable $(Cl)_2(L)ZrTPP$ complex with the expanded coordination sphere already in the course of the establishment of equilibrium.

In the reactions with Im or Py, the displacement of the acido ligand from the first coordination sphere can also be observed in a slow nonequilibrium reaction, which proceeds at a much lower rate than the establishment of equilibrium. Therefore, complexes containing no acido ligands in the coordination sphere can be achieved in two ways: by creating high concentrations of a base (third equilibrium step) or kinetically in the second step.

The following series of stability of the $(Cl)_2ZrTPP$ complexes with molecules of organic N-bases was constructed based on the constant K_1: Pyz > Im > Py > > 1-Me—Im.

For Py and Im, the stability constants of the molecular complexes are consistent with the numerical values of pK_a; the lower the acidity of a small organic base (higher its basicity), the more stable the complex. It should be noted that this is also typical of the corresponding hafnium(IV) complex. The Pyz ligand having the lowest basicity in the series of the known reactions (pK_a is 3.77)[43] forms the most stable complexes with $(Cl)_2ZrTPP$. This effect is associated with a larger number of reaction centers compared to Py. On the contrary, the 1-Me—Im ligand is weakly coordinated, at least in the second and third steps. This is attributed to steric hindrance due to the presence of the bulky Me group in the base.

As mentioned above, the stepwise equilibrium constants are highly sensitive to the nature of the base in complexation reactions. On the one hand, this allows a search for correlations between the stability of complexes and the parameters of bases and, on the other hand, this shows that $(Cl)_2ZrTPP$ complexes hold promise in the design of molecular receptors and the development of sensor, chromatographic, *etc.* devices. The use of bases of inorganic nature with an S-donor atom leads to substantial changes in both the quantitative pattern of coordination of a base by MP (stability constant sharply decreases, see above) and the nature of the elementary reaction steps.

1.2.2. Complexes with Cr^{III}, Mo^V, and W^V. Unlike MP containing doubly and triply charged metal cations, for which the ligand replacement reactions were studied in detail,[15,21,44—46] complexes with highly charged metal cations, in particular, Mo complexes, were considered in a few studies.[47—51] Below, we present our data on the thermodynamics and kinetics of the reactions of Cr^{III}, Mo^V, and W^V tetraphenylporphyrin complexes with sulfur- and nitrogen-containing bases (H_2S,[28,52,53] (Py),[54—57] and Im).

5,10,15,20-Tetraphenyl-21H,23H-porphinechromium(III) acetate (AcO)CrTPP was synthesized by the complexation reaction according to a known procedure.[31] The yield of the complex was 40%. The electronic absorption spectrum of (AcO)CrTPP (λ_{max}/nm (logε) in $CHCl_3$: 604 (3.90), 565 (3.99), 525 (3.65), 451 (5.20), 394 (4.34), 358 (4.18)) corresponds to that described earlier.[12]

5,10,15,20-Tetraphenyl-21H,23H-porphinemolybdenum(V) hydroxide oxide O=Mo(OH)TPP was synthesized by complexation of porphyrin with Mo^{VI} oxide.[31] The yield was 60%. The electronic absorption spectrum in chloroform (λ_{max}/nm (logε): 620.0 (2.94), 584.0 (2.92), 456.0 (3.78)) corresponds to the published data.[12]

5,10,15,20-Tetraphenyl-21H,23H-porphinetungsten(V) hydroxide oxide O=W(OH)TPP was prepared analogously to the Mo complex but with the use of WCl_6 as the donor of metal cations.

Chromium(III) is a typical complexing agent with respect to oxygen- and nitrogen-containing ligands.[58] In complexes with porphyrins, chromium can coordinate anionic and molecular ligands.[37] The reaction of (AcO)CrTPP with H_2S in toluene is a one-step process resulting in the replacement of the anionic ligand AcO^- by SH^-. The equilibrium constant is given in Table 6.

$$(AcO)CrTPP + H_2S \rightleftharpoons (SH)CrTPP + AcOH. \quad (20)$$

The reactions of (AcO)CrTPP with Im (21), (22), and Py (23), (24) are more complex than reaction (21).[37,54]

$$(AcO)CrTPP + Im \rightleftharpoons (AcO)(Im)CrTPP \longrightarrow [(Im)CrTPP]^+(AcO)^- \quad (21)$$

$$(AcO)(Im)CrTPP + Im \rightleftharpoons [(Im)_2CrTPP]^+(AcO)^- \quad (22)$$

$$2(AcO)CrTPP + Py \rightleftharpoons [(AcO)CrTPP]_2(Py) \quad (23)$$

$$(AcO)CrTPP + Py \rightleftharpoons (AcO)(Py)CrTPP \quad (24)$$

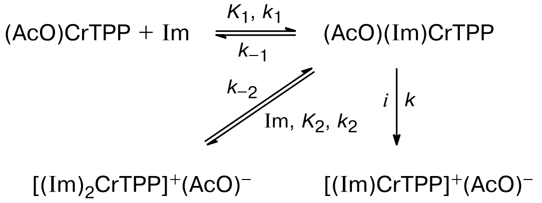
The reaction with Im involves the reversible coordination of Im (K_1 = 2300 L mol^{-1}, the forward reaction rate constant k_1 = 2.18 s^{-1} mol^{-1} L), the replacement of AcO^- in the six-coordinate (AcO)(Im)CrTPP complex with Im (K_2 = 820 L mol^{-1}), and the irreversible formation of the outer-sphere complex $[(Im)CrTPP]^+(AcO)^-$

Table 6. Equilibrium constants (K_1, K_2, and K_3/L mol^{-1}) for the reactions of metalloporphyrins with bases at 298 K

Base	K	(AcO)CrTPP	O=Mo(OH)TPP	O=W(OH)TPP
H_2S	K_1	41	83	176
	K_2			100
Py	K_1	400	9140	13300
	K_2	2.8	39.3	8400
	K_3		1.0	89
Im	K_1	2300	1850	205500
	K_2	820	480	747

(k = 2500 s^{-1} mol^{-2} L^2) after equilibration in the first reaction step (see Tables 6 and 7). The irreversible step is the rate-determining step of the overall reaction of (AcO)CrTPP with Im (Scheme 1).

Scheme 1



i. Slow.

The nature of the chemical transformations in the (AcO)CrTPP—Im system is in good agreement with the low values of $-\Delta H^0$ and ΔS^0 in the first reaction step and a change in the sign of ΔH^0 in the second step. The thermodynamic parameters of the stepwise reactions of (AcO)CrTPP with Im were determined from the temperature dependences of the equilibrium constants ($-\ln K_1$—$1/T$ and $-\ln K_2$—$1/T$) (Fig. 8). The first reaction step is exothermic ($\Delta H^0{}_1 = -10\pm1$ kJ mol^{-1}) and is characterized by low positive ΔS^0 ($\Delta S^0{}_1 = 30\pm3$ kJ mol^{-1} K^{-1}). The second step is endothermic ($\Delta H^0{}_2 = 21\pm3$ kJ mol^{-1}) and is characterized by high positive ΔS^0 ($\Delta S^0{}_2 = 126\pm10$ kJ mol^{-1} K^{-1}).

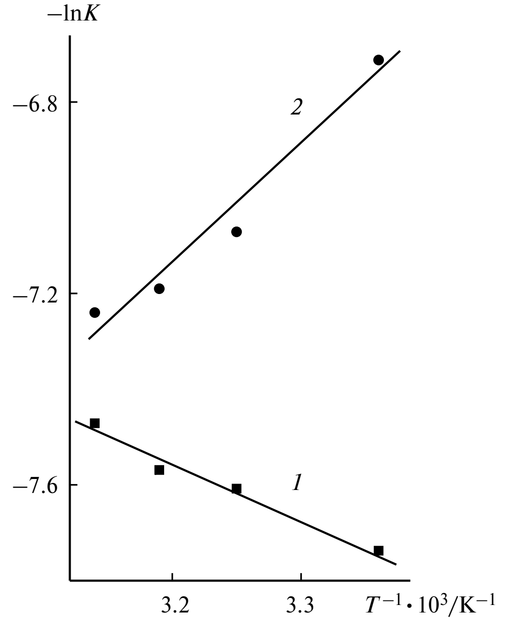


Fig. 8. Plot $-\ln K$—$1/T$ for the reaction of (AcO)CrTPP with Im in toluene in the first (*1*) and second (*2*) steps. The correlation coefficient was 0.990 and 0.981, respectively.

The specific feature of the reversible binding of Py to the (AcO)CrTPP complex (Eqs (23) and (24)) is that one Py molecule binds two MP molecules in the first step. The fact that the equilibrium system consists of three reacting compounds was experimentally confirmed. The kinetic order of the forward equilibrium reaction (23)

Table 7. Reaction order with respect to C_L and the rate constants for the forward and reverse coordination reactions of bases with metalloporphyrins

Base	Parameter	Value for (AcO)CrTPP	Parameter	Value for	
				O=Mo(OH)TPP	O=W(OH)TPP
Py	k_1/s^{-1} mol$^{-1/2}$ L$^{1/2}$	0.197	k_1/s^{-1} mol^{-1} L	5.25	1.81
	k_{-1}/s^{-1} mol$^{1/2}$ L$^{-1/2}$	$4.92\cdot10^{-4}$	k_2/s^{-1} mol^{-1} L	$1.83\cdot10^{-2}$	1.32
	m_1	0.5	k_3/s^{-1} mol^{-1} L	$1.19\cdot10^{-3}$	$4.44\cdot10^{-2}$
			k_{-1}/s^{-1}	$5.75\cdot10^{-4}$	$1.36\cdot10^{-4}$
			k_{-2}/s^{-1}	$4.65\cdot10^{-4}$	$1.57\cdot10^{-4}$
			k_{-3}/s^{-1}	$1.20\cdot10^{-3}$	$5.01\cdot10^{-3}$
			$m_{1,2,3}$	1	1
Im	k_1/s^{-1} mol^{-1} L	2.18			
	k_{-1}/s^{-1}	$9.47\cdot10^{-4}$			
	m_1	1			
	$k_{(1-2)}$/s^{-1} mol^{-2} L^2	2500			
	$m_{(1-2)}$	2			

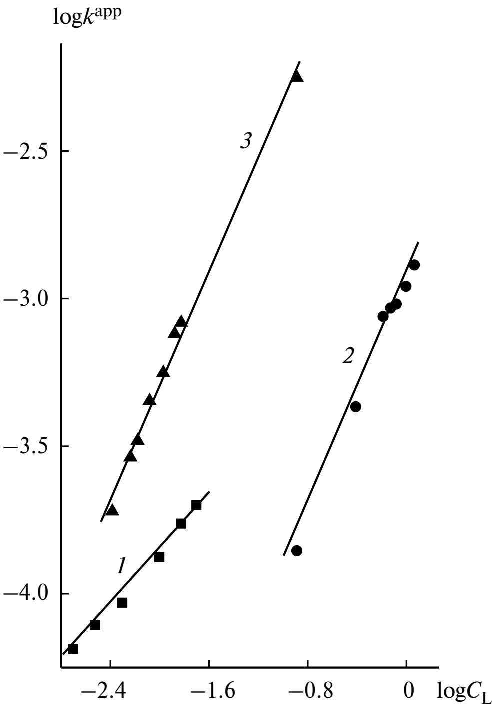


Fig. 9. Plot $\log k^{\rm app}$—$\log C_{\rm L}$ for the reaction of Py with (AcO)CrTPP (*1*) (step 1, tanα = 0.5, ρ = 0.996), O=Mo(OH)TPP (*2*) (step 3, tanα = 1, ρ = 0.995), and O=W(OH)TPP (*3*) (step 3, tanα = 1, ρ = 0.996).

(Fig. 9) is 0.5. Based on the thermodynamic and kinetic properties of the reacting system, the reaction product that is formed in the first step can be represented as the $[(\rm AcO)CrTPP]_2(Py)$ dimer. However, since only the complete transformation product (reaction (24)) can be isolated in the solid state, the dimer existing exclusively in solution in the presence of a particular excess of Py was characterized by spectroscopic data in solution.[59]

The stability of the (AcO)CrTPP complexes with bases, which is characterized by the equilibrium constants of their formation (K_1), changes in the series

$$\text{Im (2300)} > \text{Py (400)} > \text{H}_2\text{S (41)}. \qquad (25)$$

This series is consistent with the series of increasing energy of protonation of molecular ligands (E/kJ mol^{-1} is 398, 438, and 520 for Im, Py, and H_2S, respectively[60]). An analysis of the numerical values of K_1 and E shows that the K_1—E dependence is nearly proportional. In the electronic absorption spectra, the band, which is belongs to the B(0,0)—π→π* transition from the highest occupied molecular orbital to the antibonding orbitals with higher energy than the lowest unoccupied molecular orbital, is always bathochromically shifted upon coordination of L. The bathochromic shift of this band upon coordination of nitrogen-containing bases is much larger compared to H_2S. This suggests that stability of the molecular complexes (AcO)(L)CrTPP in series (25) changes in accordance with an increase in the strength of the metalloporphyrin—molecular ligand σ bond.

An analogous series was obtained for the O=W(OH)TPP complex. For O=Mo(OH)TPP, in spite of the structurally identical coordination spheres in the W and Mo complexes, the sequence of bases in an analogous series is violated because of the different (compared to the W complex) stoichiometric mechanism of the reactions with bases associated with the different strength of the bond with the bidentate O^{2-} ligand. Nevertheless, the reaction with the first H_2S molecules proceeds identically for both complexes:

$$\text{O=M(OH)TPP} + \text{H}_2\text{S} \rightleftarrows \text{O=M(SH)TPP} + \text{H}_2\text{O}. \qquad (26)$$

The equilibrium constants are given in Table 6. The reaction with the Mo complex stops at this step, whereas the reaction with the W complex involves the second equilibrium step with the constant of 100 L mol^{-1}.

$$\text{O=W(SH)TPP} + \text{H}_2\text{S} \rightleftarrows \text{W(OH)(SH)}_2\text{TPP} \qquad (27)$$

The reactions of the Mo and W complexes with Im involve the stepwise and reversible coordination of two molecules of bases (Table 6) accompanied by the displacement of the anionic ligand to the outer sphere in the second step:

$$\text{O=M(OH)TPP} + \text{Im} \rightleftarrows \text{O=M(OH)(Im)TPP}, \qquad (28)$$

$$\text{O=M(OH)(Im)TPP} + \text{Im} \rightleftarrows [\text{O=M(Im)}_2\text{TPP}]^+\text{OH}^-. \qquad (29)$$

The bidentate coordinated O^{2-} ligand in the reactions of both complexes remains intact. To the contrary, the reaction with Py involves all coordinated small anionic ligands O=M(OH)TPP. However, the different degree of binding of the O^{2-} ligand determines the reaction pathway (reactions (30)—(32) and (33)—(35) for the Mo and W complexes, respectively).

$$\text{O=Mo(OH)TPP} + \text{Py} \rightleftarrows [\text{O=Mo(Py)TPP}]^+\text{OH}^- \qquad (30)$$

$$[\text{O=Mo(Py)TPP}]^+\text{OH}^- + \text{Py} + \text{H}_2\text{O} \rightleftarrows [\text{Mo(OH)(Py)}_2\text{TPP}]^{2+}\cdot 2\text{OH}^- \qquad (31)$$

$$[\text{Mo(OH)(Py)}_2\text{TPP}]^{2+}\cdot 2\text{OH}^- + \text{Py} \rightleftarrows [\text{Mo(Py)}_3\text{TPP}]^{3+}\cdot 3\text{OH}^- \qquad (32)$$

$$\text{O=W(OH)TPP} + \text{Py} \rightleftarrows \text{O=W(OH)(Py)TPP} \qquad (33)$$

$$\text{O=W(OH)(Py)TPP} + \text{Py} \rightleftarrows [\text{O=W(Py)}_2\text{TPP}]^+\text{OH}^- \qquad (34)$$

$$[\text{O=W(Py)}_2\text{TPP}]^+\text{OH}^- + \text{Py} + \text{H}_2\text{O} \rightleftarrows [(\text{OH})\text{W(Py)}_3\text{TPP}]^{2+}\cdot 2\text{OH}^- \qquad (35)$$

The equilibrium constant for the replacement of OH^- by Im in the Mo complex does not follow the general tendency (see the stability series for molecular complexes (25)). This can be attributed to the fact that the corresponding molecular $[O{=}Mo(Im)_2TPP]^+$ complex contains an additional Im molecule, which is coordinated in the previous step.

An increase in the formal charge of the metal atom from Cr^{III} to W^V leads to an increase in the affinity of molecular ligands for the metal atom in MP; among Mo complexes, the complex with Im is an exception (see Table 6). The series of changes in K for the reactions of the known MP with the same molecular ligand are consistent with the series of kinetic stability of the bonds between the metal atom and the nitrogen atom of the macrocycle in the complexes in a strong acidic medium:[62]

$$O{=}W(OH)TPP > O{=}Mo(OH)TPP > (AcO)CrTPP. \quad (36)$$

It can be concluded that the nature of the mixed coordination sphere in the complexes under consideration hinders the *cis* effect of ligands characteristic of metal complexes with ligands more simple than aromatic porphine.

2. Coordination by metalloporphyrins as a route to the activation of molecules

Due to the above-considered ability of metal cations in MP to reversibly bind various ligands (even weak-field ligands), *i.e.*, the ability of these cations to serve as carriers of these ligands, the involvement of MP in catalytic redox reactions holds considerable promise. The coordination of anions and small and large molecules to MP determines their role in enzymatic and catalytic reactions.[15,62,63] The higher the formal charge of the metal atom in MP, the higher the necessary coordinative unsaturation of the metal. Hence, metal complexes in an oxidation state higher than two are of most interest. In this case, manganese(III) porphyrins are appropriate models. In the case of complexes with highly charged cations, axial coordination processes are complicated due to possible redox transformations of the central atom, which refers in full measure to Mn complexes as well.[42,64–66] The properties of molecular complexes differ from those of uncoordinated metalloporphyrins. For example, solutions of the $(L)Mn^{II}P$ complexes (L is methylimidazole or pyridine) are much less sensitive to the action of oxygen in the presence of a small excess of the axial ligand L. Irreversible oxidation of manganese(III) porphyrins proceeds at a low rate and is completed in several hours, whereas $Mn^{II}P$ is immediately oxidized.[67]

The equilibrium constants for the coordination reaction of molecular ligands with the $(OClO_3)Mn^{III}TPP$ complex in dichloromethane were measured. For Im, Py, and DMSO, $\log K_1$ are 4.35, 4.08, and 3.49, respectively.[66] For the reaction of $(Cl)Mn^{III}TPP$ with Im, $\log K_1 = 2.9$.[66] Therefore, the equilibrium constant depends on the nature of the acido ligand in MP. Strong bases, *viz.*, piperidine, diethylamine, triethylamine, and 3-oxypiperidine, reduce $(X)Mn^{III}TPP$ in toluene to give manganese(II) complexes.[45,68] Reduction is apparently preceded by complexation.[45] For the reaction of $(OH)Mn^{III}TPP$ with CN^- in methanol, the equilibrium constants of the first and second steps are $7.0 \cdot 10^2$ and 5.3 mol^{-1} L, respectively.[69] Since the former constant is substantially larger than the latter, it became possible to isolate the (CN)MnTPP complex.

The reaction of (AcO)MnOPTAP with THF in toluene was documented:[70]

$$(AcO)MnOPTAP + THF \xrightleftharpoons{k_1,\ K_1} (AcO)(THF)MnOPTAP, \quad (37)$$

$$(AcO)(THF)MnOPTAP + THF \xrightleftharpoons{k_2,\ K_2} [(THF)_2MnOPTAP]^+(AcO)^-, \quad (38)$$

where $k_1 = (3.0\pm0.3)\cdot10^{-4}\ s^{-1}\ mol^{-1}\ L$, $K_1 = (44\pm6)\ L\ mol^{-1}$, and $K_2 = (2.1\pm0.5)\ L\ mol^{-1}$. In the THF concentration range of 0—0.4 mol L^{-1}, the equilibrium (with the constant K_1) is established in 5 days; in the THF concentration range of 0.5—8 mol L^{-1}, the equilibrium (K_2) is established much more rapidly (in 1 day; Fig. 10). Analogous cationic complexes are formed in the presence of $\geq$ 2 equivalents of the ligands L, which are strong electron-pair donors (DMF, dimethylacetamide, 1-MeIm, or DMSO) in solutions of $(X)Mn^{III}P$ with a weakly coordinating acido ligand in nonpolar solvents.[71] Since the N→Mn π interaction in $(X)Mn^{III}OPTAP$ is substantially weaker and the bond between the central manganese atom and the acido ligand is weaker compared to analogous complexes of classical porphyrins,[72] the acetate acido ligand is displaced to the second coordination sphere even in the presence of a weak base (THF) but in the case of its large excess.

To elucidate the role of additional coordination processes in the catalytic action of MP with respect to redox reactions, the reactions of $(Cl)Mn^{III}TPP$ and $(Cl)Mn^{III}OEP$ with hydrogen peroxide in an aqueous organic medium ($DMF—H_2O$) at 288—308 K were studied by spectrophotometric and kinetic methods.[73–75] Porphyrin complexes with manganese(III) were synthesized by the reactions of porphyrin with metal salts according to Adler's method.[76] For the reaction of $(Cl)Mn^{III}TPP$ with hydrogen peroxide, three concentration ranges of peroxide were found (0.017—0.5, 0.67—1.0, and 1.26—3.98 mol L^{-1}), in which specific spectroscopic evidence of the transformation with retention of isosbestic points was observed (Fig. 11, *a*—*c*). The experimental

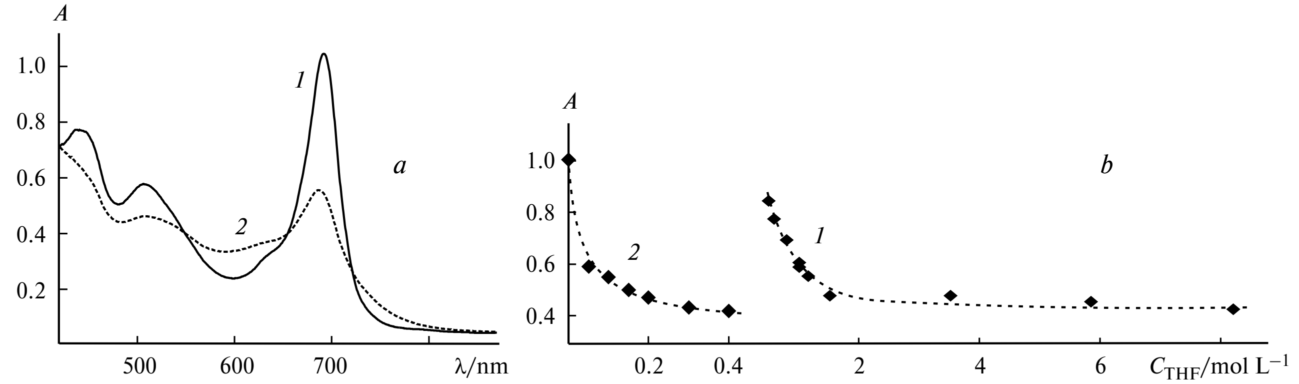


Fig. 10. *a*. Electronic absorption spectra of (AcO)MnOPTAP in toluene (*1*) and THF (*2*); $C_{(\mathrm{AcO})\mathrm{MnOPTAP}} = 2.54 \cdot 10^{-5}$ mol L^{-1}. *b*. The plot of the absorbance of a solution of (AcO)MnOPTAP in toluene *vs* the THF concentration at a wavelength of 667 nm within 1 day (*1*) and 5 days (*2*) after the preparation of the solutions.

complete kinetic equations for three concentration ranges of H_2O_2 were substantiated:[73,74]

$$-dC_{(\mathrm{Cl})\mathrm{Mn^{III}TPP}}/d\tau = k_{v1}C_{(\mathrm{Cl})\mathrm{Mn^{III}TPP}}C_{\mathrm{H_2O_2}}, \quad (39)$$

$$-dC_{(\mathrm{Cl})\mathrm{Mn^{III}TPP}}/d\tau = k_{v2}C_{(\mathrm{Cl})\mathrm{Mn^{III}TPP}}C_{\mathrm{H_2O_2}}{}^{0}, \quad (40)$$

$$-dC_{(\mathrm{Cl})\mathrm{Mn^{III}TPP}}/d\tau = k_{v3}C_{(\mathrm{Cl})\mathrm{Mn^{III}TPP}}C_{\mathrm{H_2O_2}}{}^{-1/2}, \quad (41)$$

where k_{v1}, k_{v2}, and k_{v3} are the rate constants, respectively, for the reaction with hydrogen peroxide for the first, second, and third concentration ranges of the latter compound. The numerical values of k_{v1} and k_{v3} are given in Table 8. These constants were determined from the data presented in Fig. 12.

The kinetic equation (39) corresponds to the reactions[74]

$$(\mathrm{Cl})\mathrm{Mn^{III}TPP} + \mathrm{H_2O_2} \overset{K_1}{\rightleftarrows} (\mathrm{Cl})(\mathrm{H_2O_2})\mathrm{Mn^{III}TPP}, \quad (42)$$

$$(\mathrm{Cl})(\mathrm{H_2O_2})\mathrm{Mn^{III}TPP} \xrightarrow{k_2} \mathrm{O{=}Mn^{III}(TPP^{+\bullet})} + \mathrm{H_2O} + \mathrm{Cl^-}. \quad (43)$$

The spectrophotometric titration of a solution of $(\mathrm{Cl})\mathrm{Mn^{III}TPP}$ in DMF with hydrogen peroxide at 298 K (Fig. 13) gave the concentration equilibrium constant K_1 = (20±3) L mol^{-1} for reaction (42).

Table 8. Kinetic parameters of the reactions of (X)MnP with H_2O_2 in the DMF—H_2O_2 system

Complex	$C_{\mathrm{H_2O_2}}$/mol L^{-1}	T/K	$k_v \cdot 10^2$	E/kJ mol^{-1}	$\Delta S^{\neq}$/J mol^{-1} K^{-1}
(Cl)MnTPP	0.017—0.10[a]	288	2.38±0.15	64±2	−61±6
		298	5.5±0.4		
		308	13.6±1.1		
	1.26—3.32[b]	288	0.70±0.06	49±1	−124±3
		298	1.3±0.1		
		308	2.6±0.2		
(AcO)MnTPP	0.013—0.05[c]	288	7.2±1.0	54±1	−87±3
		298	15.4±2.0		
		308	31±5		
(Cl)MnOEP	0.01—0.07[d]	293	0.30±0.01	63±1	−85±3
		298	0.46±0.01		
		303	0.72±0.01		
		308	1.04±0.04		
	1.00—2.22[e]	293	0.095±0.002	50±2	−140±6
		298	0.127±0.002		
		303	0.18±0.01		
		308	0.255±0.002		

[a] Kinetic equation (39).

[b] Kinetic equation (41).

[c] Kinetic equation: $-dC_{(\mathrm{AcO})\mathrm{Mn^{III}TPP}}/d\tau = k_v C_{(\mathrm{AcO})\mathrm{Mn^{III}TPP}}C_{\mathrm{H_2O_2}}$.

[d] Kinetic equation (49).

[e] Kinetic equation (51).

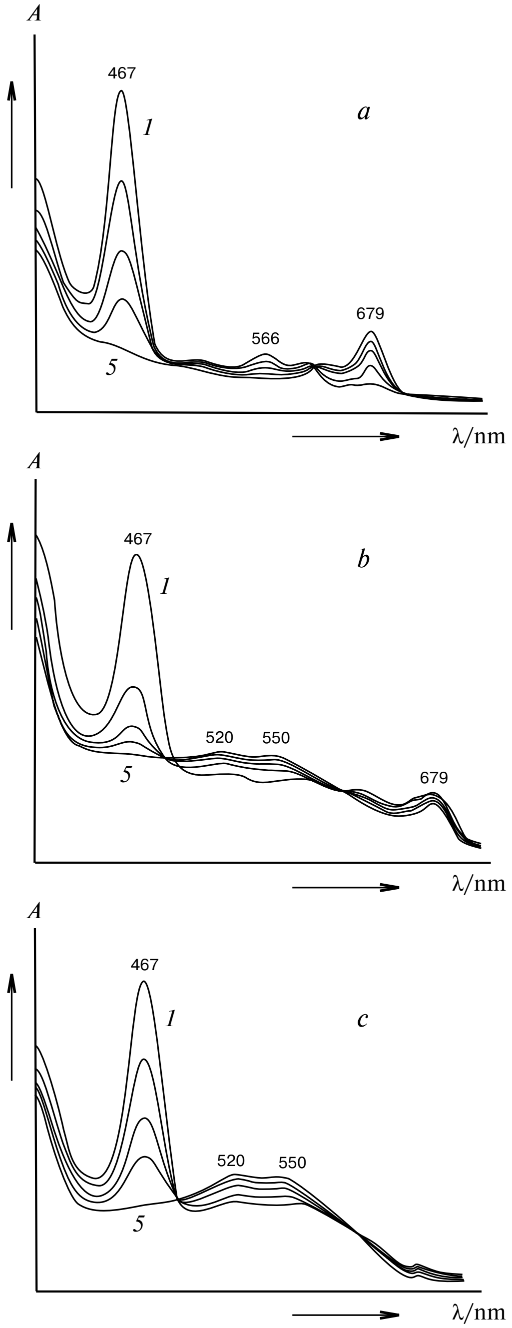


Fig. 11. Changes in the electronic absorption spectra of (Cl)Mn^{III}TPP during the reaction with H_2O_2 at 298 K at the initial instant of time (*1*), in the course of the reaction (*2—4*), and after completion of the reaction (*5*): $C_{H_2O_2}$ = 0.017 (*a*), 1.0 (*b*), 2.52 mol L^{-1} (*c*).

For the range with the highest $C_{H_2O_2}$, the system of equations is more complex:

$$H_2O_2 \overset{K_1}{\rightleftarrows} H^+ + HO_2^-, \tag{44}$$

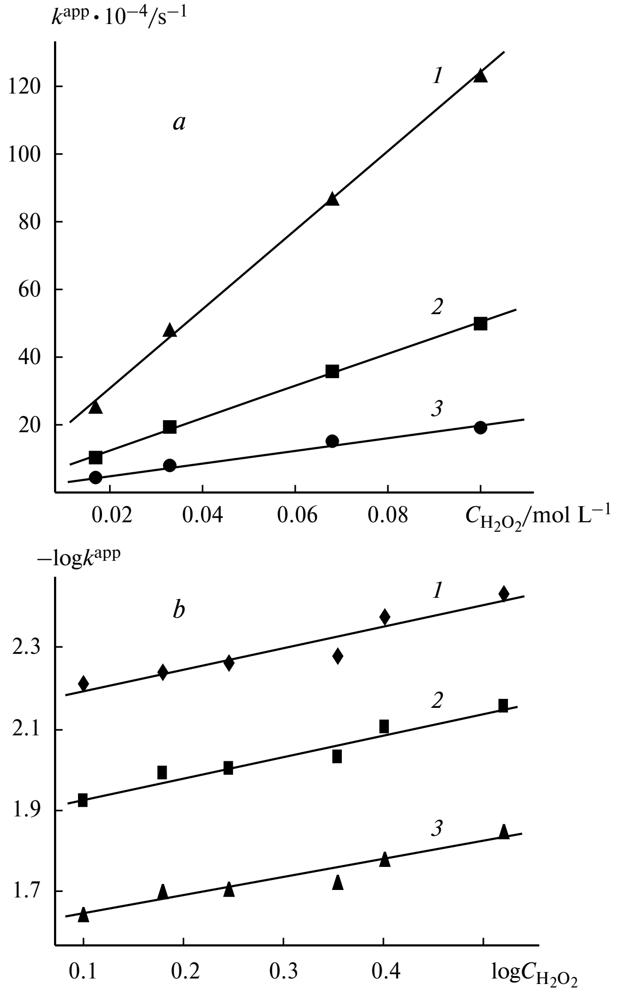


Fig. 12. *a*. Plot of the apparent rate constant for the reaction of (Cl)Mn^{III}TPP with H_2O_2 *vs* the H_2O_2 concentration, *T*/K: 308 (*1*), 298 (*2*), 288 (*3*); R^2 = 0.99 (*1*, *2*), 0.98 (3). *b*. The plot of $-\log k^{app}$ *vs* $C_{H_2O_2}$ for the reaction of (Cl)Mn^{III}TPP with H_2O_2 in the H_2O_2 concentration range of 1.26—3.32 mol L^{-1}, *T*/K: 308 (*1*), 298 (*2*), 288 (*3*); ρ = 0.91 (*1*), 0.94 (*2*), 0.92 (*3*).

$$(Cl)Mn^{III}TPP + HO_2^- \xrightarrow[i]{k_2} (Cl)(HO_2^-)Mn^{III}TPP, \tag{45}$$

$$(Cl)(HO_2^-)Mn^{III}TPP \overset{K_3}{\rightleftarrows} (Cl)O{=}Mn^{IV}(TPP^{+\bullet}) + OH^-, \tag{46}$$

$$(Cl)O{=}Mn^{IV}(TPP^{+\bullet}) + HO_2^- \xrightarrow[ii]{k_4} O{=}Mn^{IV}TPP + HCl + O_2, \tag{47}$$

$$OH^- + H_2O_2 \overset{K_5}{\rightleftarrows} HO_2^- + H_2O. \tag{48}$$

i. Rapid. *ii*. Slow.

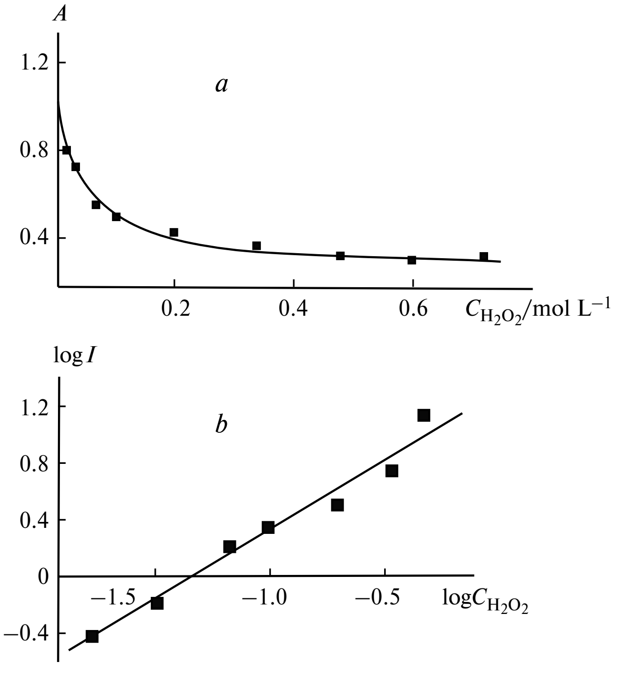


Fig. 13. Titration curve (*a*) and the plot of log*I* *vs* log$C_{H_2O_2}$ (*b*) ($\rho = 0.98$) for titration of the $\mathrm{(Cl)Mn^{III}TPP}$ complex in DMF with hydrogen peroxide.

The first reaction involving $\mathrm{(Cl)Mn^{III}TPP}$ (45), which is analogous to step (42), rapidly and irreversibly proceeds at high H_2O_2 concentrations. Peroxide is coordinated as HO_2^- to form a donor-acceptor bond. Then two electrons are transferred from the easily polarizable porphyrin macrocycle and the manganese cation to the coordinated peroxide to establish equilibrium (46). The attack of HO_2^- that is generated in the course of establishment of equilibria (44) and (48) on the coordination site of the radical-cation manganese(III) complex facilitates the slow transformation according to Eq. (47). Due to a low concentration of manganese porphyrin in the form of $\mathrm{(Cl)O{=}Mn^{IV}(TPP^{+\bullet})}$, no gas evolution was observed in the experiment, and O_2 that was formed apparently remained in solution.

In highly concentrated solutions of peroxide, the characteristic features of the reactions are different due to the appearance of HO_2^- ions in kinetically significant amounts. Because of a high affinity for metal cations, HO_2^- is coordinated instead of H_2O_2 in the first step involving metalloporphyrin. Apparently, as a result of elimination of OH^- from coordinated HO_2^- instead of H_2O (Eqs (43) and (46)), Cl^- remains in the coordination sphere of the resulting $\mathrm{Mn^{IV}}$ porphyrin π-radical cation, $\mathrm{(Cl)O{=}Mn^{IV}(TPP^{+\bullet})}$. The presence of the Cl^- anion in the coordination sphere of manganese porphyrin in the step of coordination of any form of hydrogen peroxide (Eqs (42) and (45)) is confirmed by comparing with the $\mathrm{(AcO)Mn^{III}TPP}$ complex. The data for the latter are given in Table 8 and demonstrate that the reaction rate strongly depends on the nature of the acido ligand.

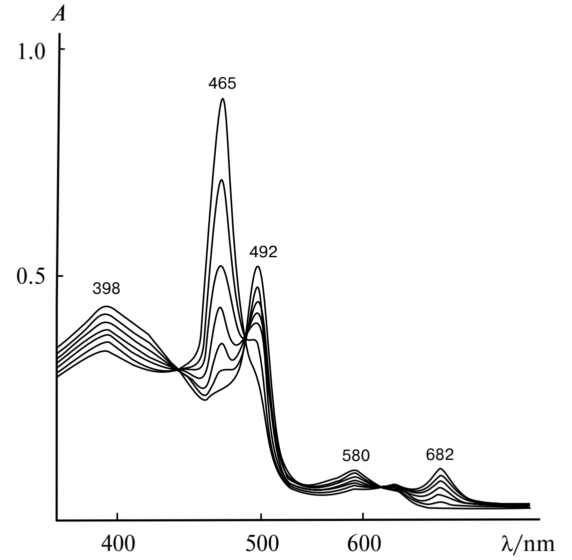


Fig. 14. Electronic absorption spectra of $\mathrm{(Cl)Mn^{III}OEP}$ in the course of the reaction with H_2O_2 at 298 K and at $C_{H_2O_2} = 1.0$ mol L^{-1}.

The spectral changes presented in Fig. 14 correspond to the reaction of $\mathrm{(Cl)Mn^{IV}OEP}$ with H_2O_2 and are characteristic for the total H_2O_2 concentration range. A kinetic study of the reaction revealed the presence of three peroxide concentration ranges of 0.01—0.07, 0.2—0.52, and 1.00—2.22 mol L^{-1}. Each range is characterized by the first order with respect to metalloporphyrin but by a variable order with respect to hydrogen peroxide and also by the corresponding rate constants (see Table 8):

$$-dC_{\mathrm{(Cl)Mn^{III}OEP}}/d\tau = k_{v1}C_{\mathrm{(Cl)Mn^{III}OEP}}C_{H_2O_2}{}^{1/2}, \qquad (49)$$

$$-dC_{\mathrm{(Cl)Mn^{III}OEP}}/d\tau = k_{v2}C_{\mathrm{(Cl)Mn^{III}OEP}}, \qquad (50)$$

$$-dC_{\mathrm{(Cl)Mn^{III}OEP}}/d\tau = k_{v3}C_{\mathrm{(Cl)Mn^{III}OEP}}C_{H_2O_2}{}^{-1/2}. \qquad (51)$$

It was demonstrated[75] that the coordination processes in the reaction under consideration also play the decisive role in the catalytic process at both low (reactions (52)—(54)) and very high H_2O_2 concentrations (reactions (55)—(59)).

$$H_2O_2 \overset{K_1}{\rightleftarrows} H^+ + HO_2^- \qquad (52)$$

$$\mathrm{(Cl)Mn^{III}OEP} + HO_2^- \overset{K_2}{\rightleftarrows} \mathrm{(Cl)(HO_2^-)Mn^{III}OEP} \qquad (53)$$

$$\mathrm{(Cl)(HO_2^-)Mn^{III}OEP} \xrightarrow[i]{k_3} \mathrm{O{=}Mn^{III}(OEP^{+\bullet})} + OH^- + Cl^- \qquad (54)$$

$$H_2O_2 \xrightleftharpoons{K_1} H^+ + HO_2^- \tag{55}$$

$$(Cl)Mn^{III}OEP + HO_2^- \xrightarrow[ii]{k_2} (Cl)(HO_2^-)Mn^{III}OEP \tag{56}$$

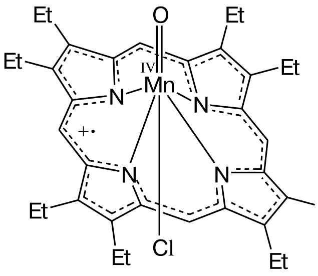
$$(Cl)(HO_2^-)Mn^{III}OEP \xrightleftharpoons{K_3} (Cl)O{=}Mn^{IV}(OEP^{+\bullet}) + OH^- \tag{57}$$

$$OH^- + H_2O_2 \xrightleftharpoons{K_4} HO_2^- + H_2O \tag{58}$$

$$2(Cl)O{=}Mn^{IV}(OEP^{+\bullet}) + HO_2^- \xrightarrow[i]{k_5} 2O{=}Mn^{III}(OEP^{+\bullet}) + HCl + O_2 + Cl^- \tag{59}$$

i. Slow. *ii*. Rapid.

The first reaction involving (Cl)Mn^{III}OEP (Eq. (56)), *viz*., coordination of hydrogen peroxide as HO_2^- at the sixth coordination site of the manganese atom, rapidly and irreversibly proceeds at high H_2O_2 concentrations. Then two electrons are transferred from the easily polarizable porphyrin macrocycle and the metal cation to the coordinated H_2O_2 molecule with establishment of equilibrium (57). Apparently, this reaction is equilibrium because of low stability of the π-radical cation (Cl)O=Mn^{IV}(OEP$^{+\bullet}$) compared to O=Mn^{III}(OEP$^{+\bullet}$) (Eq. (54)) and higher concentrations of the HO_2^- and OH^- anions hindering ionization of the acido ligand Cl^-. The latter remains in the coordination sphere of the radical cation.



Finally, the reaction with the second mole of H_2O_2 (as HO_2^-) becomes possible. This reaction proceeds more slowly than reaction (56) and is the rate-determining step. However, in the latter case, by contrast to (Cl)Mn^{III}TPP, reduction of the manganese(IV) porphyrin radical cation does not give rise to the relatively stable O=Mn^{IV}P complex (P is the porphyrin dianion) but stops at the formation of the one-electron reduced (compared to (Cl)O=Mn^{IV}(OEP$^{+\bullet}$) O=Mn^{III}(OEP$^{+\bullet}$) species, which is detected in experiments as a relatively stable final product. This is yet another difference from the (Cl)Mn^{III}TPP—H_2O_2 system, where the two-electron reduced species is generated as the final product.

The fact that the reaction mechanism of Mn porphyrin complexes with H_2O_2 changes in going from H_2TPP to H_2OEP is associated with the difference in the electronic state of the aromatic ligand, which is manifested in the quantitative characteristics of the reaction. The (Cl)Mn^{III}TPP complex reacts with H_2O_2 much more rapidly than (Cl)Mn^{III}OEP. The true reaction rate constant is an order of magnitude higher in the case of (Cl)Mn^{III}TPP both at low and high H_2O_2 concentrations, and the reaction of (Cl)Mn^{III}TPP with H_2O_2 is characterized by more negative $\Delta S^{\neq}$. In the case of (Cl)Mn^{III}TPP, the radical-cation species is generated only at low H_2O_2 concentrations, whereas the O=Mn^{IV}TPP complex oxidized at the Mn atom is the final reaction product at $C_{H_2O_2} > 0.1$ mol L^{-1}. In the case of (Cl)Mn^{III}OEP, the O=Mn^{III}(OEP$^{+\bullet}$) radical cation is the final reaction product in the total H_2O_2 concentration range. Hence it follows that the optimal parameters for coordination of H_2O_2 molecules and HO_2^- ions in different steps of the reaction with peroxide can be achieved by changing the electronic state of both the macrocycle and the Mn—N bonds, and then these parameters can be used for the design of synthetic catalases.

3. Prospects of the use of mixed porphyrin-containing complexes in membrane transfer processes and technical catalysis

Activators of membranes for separation of gas mixtures containing hydrogen sulfide. Taking into account the above-considered data on the spectroscopic evidence and the thermodynamic constants of the equilibrium coordination reactions of H_2S, the (AcO)CrTPP, $(Cl)_2$HfTPP, O=Mo(OH)TPP, and O=W(OH)TPP complexes were recommended[77,78] for use as active additives for the preparation of gas-separation membranes with high selectivity to hydrogen sulfide. Owing to the ability of metalloporphyrins to perform reversible transfer of hydrogen sulfide, the moderately high equilibrium constants for their reactions with H_2S, and very high stability of complexes with highly charged cations, these compounds can be used for activation of membranes. A membrane based on a polymeric matrix, *viz*., polyvinyltrimethylsilane, activated by Hf or Mo complexes, has a permeability with respect to H_2S in the separation of natural H_2S—CH_4—CO_2 gas mixtures no lower than that of (AcO)CrTPP studied earlier[78,79] (3000 L m^{-2} h^{-1} at.$^{-1}$). The $(Cl)_2$HfTPP and O=W(OH)TPP complexes act as reversible carriers with the highest constants of coordination of H_2S and can be used for the construction of hydrogen sulfide detectors for the high-speed highly sensitive analysis of natural gas mixtures and their processing products.[28,78]

Porphyrin catalysts. Moderate-highly coordinatively unsaturated compounds, in which coordination bonds with the macrocycle and small anionic ligands are sufficiently stable, can be prepared by the directed synthesis of MP with a mixed coordination sphere. The optimal combination of the above-mentioned properties of the complexes allows the synthesis of catalytically active compounds, in which the coordination site serves as the reaction center but in which the aromatic system of the macrocycle plays the major role in the formation of the electronic state of the latter and in the formation of intermediate compounds. Mixed porphyrin-containing complexes show high stability to an oxidant of H_2O_2, the ability to perform reversible coordination of the latter in the molecular or ionic form, and the activating action on the coordinated oxidant. As a result, efficient catalysts for disproportionation of hydrogen peroxide have been already synthesized based on these complexes.[74]

Porphyrin receptors for bases. In mixed acido porphyrin complexes with relatively weak coordination of the acido ligand, the coordination unit can act as a reversible acceptor of small organic bases, due to which these complexes can be used for the preparation of analytical reagents and chemosensors. Complexes of Zr^{IV} and Hf^{IV} with porphyrin and two Cl^- ions, like Mo^V and W^V complexes with anionic O-ligands, bind small molecules of N-bases in the reversible stepwise process characterized by the practically important moderately high equilibrium constants. The (AcO)CrTPP complex exhibits weaker affinity for small base molecules. However, due to the presence of a pronounced spectral response for the reversible coordination reaction and the several order of magnitude differences in the stability constants of molecular complexes for difference bases, all known mixed complexes with highly charged metal cations are more efficient receptors and carriers of bases compared to simple M^{2+} porphyrin complexes.

This study was financially supported by the Russian Academy of Sciences (Grants of the Presidium of the Russian Academy of Sciences, Program No. 8 "Directed Synthesis of Compounds with Desired Properties and Construction of Functional Materials on Their Basis") and the Ministry of Education and Science of the Russian Federation (Analytical Federal Target Program "Development of the Research Potential of Higher Education, RNP 2.2.1.1.7181").

References

1. M. O. Senge, in *The Porphyrin Handbook*, Eds K. M. Kadish, K. M. Smith, and R. Guilard, Academic Press, San Diego, 2000, **10**, p. 1.
2. T. N. Lomova and B. D. Berezin, *Koord. Khim.*, 1993, **19**, 171 [*Russ. J. Coord. Chem.*, 1993, **19** (Engl. Transl.)].
3. J. K. M. Sanders, N. Bampos, Z. Clyde-Watson, S. Darling, J. C. Hawley, H. J. Kim, C. C. Mak, and S. J. Webb, in *The Porphyrin Handbook*, Eds K. M. Kadish, K. M. Smith, and R. Guilard, Academic Press, San Diego, 2000, **3**, p. 2.
4. P. N. Moskalev, *Koord. Khim.*, 1990, **16**, 147 [*Sov. J. Coord. Chem.*, 1990, **16** (Engl. Transl.)].
5. T. N. Lomova and M. E. Klyueva, in *Encyclopedia of Nanoscience and Nanotechnology*, Ed. S. H. Nalwa, American Scientific Publishers, Valencia, California, USA, 2004, **2**, 565.
6. S. I. Troyanov, L. A. Lapkina, V. E. Larchenko, and A. Yu. Tsivadze, *Dokl. Chem*, 1999, **367**, 192.
7. B. D. Berezin and O. I. Koifman, *Usp. Khim.*, 1980, **49**, 2389 [*Russ. Chem. Rev.*, 1980, **49** (Engl. Transl.)].
8. V. S. Sharma and J. Schubert, *J. Chem. Edu.*, 1969, **46**, 506.
9. V. A. Borodin, V. P. Vasil´ev, and E. V. Kozlovskii, in *Matematicheskie zadachi khimicheskoi termodinamiki* [*Mathematical Problems of Chemical Thermodynamics*], Nauka, Novosibirsk, 1985, p. 219 (in Russian).
10. V. P. Vasil´ev, E. V. Kozlovskii, and V. A. Borodin, *Zh. Neorg. Khim.*, 1988, **33**, 1047 [*J. Inorg. Chem. USSR*, 1988, **33** (Engl. Transl.)].
11. V. P. Vasil´ev, V. A. Borodin, and E. V. Kozlovskii, *Primenenie EVM v khimiko-analiticheskikh raschetakh* [*Application of Computers in Chemical Analytical Calculations*], Vysshaya shkola, Moscow, 1993, 112 pp. (in Russian).
12. T. N. Lomova, N. I. Volkova, and B. D. Berezin, *Zh. Neorg. Khim.*, 1985, **30**, 626 [*J. Inorg. Chem. USSR*, 1985, **30** (Engl. Transl.)].
13. T. N. Lomova, N. I. Volkova, and B. D. Berezin, *Koord. Khim.*, 1985, **11**, 1094 [*Sov. J. Coord. Chem.*, 1985, **11** (Engl. Transl.)].
14. T. N. Lomova and L. G. Andrianova, *Koord. Khim.*, 2004, **30**, 700 [*Russ. J. Coord. Chem.*, 2004, **30** (Engl. Transl.)].
15. B. D. Berezin and O. I. Koifman, *Usp. Khim.*, 1980, **49**, 2389 [*Russ. Chem. Rev.*, 1980, **49** (Engl. Transl.)].
16. J. W. Buchler, in *Porphyrins and Metalloporphyrins*, Ed. K. M. Smith, Elsevier, Amsterdam, 1975, p. 160.
17. E. B. Fleischer, J. M. Palmer, T. S. Srivastava, and A. Chatterjee, *J. Am. Chem. Soc.*, 1971, **93**, 3162.
18. J. W. Buchler and K. L. Lay, *Z. Naturforsch.*, 1975, **30**, 385.
19. G. R. Miller and G. D. Dorough, *J. Am. Chem. Soc.*, 1952, **74**, 3977.
20. O. I. Koifman, T. A. Koroleva, and B. D. Berezin, *Koord. Khim.*, 1977, **3**, 1811 [*Sov. J. Coord. Chem.*, 1977, **3** (Engl. Transl.)].
21. J. Falk, *Porphyrins and Metalloporphyrins*, Elsevier, Amsterdam, 1964, 266 p.
22. C. B. Storm, A. H. Corwin, N. K. Arelano, and M. Martz, *J. Am. Chem. Soc.*, 1966, **88**, 2525.
23. C. H. Kirksey and P. Hambright, *Inorg. Chem.*, 1970, **10**, 958.
24. S. J. Cole, G. C. Curthous, and E. A. Magnusson, *Inorg. Chem.*, 1972, **11**, 1024.
25. D. V. Stynes, H. C. Stynes, B. K. James, and J. A. Ibers, *J. Am. Chem. Soc.*, 1973, **95**, 1796.
26. I. S. Migalova, Ph. D. (Chem.) Thesis, Ivanovo State University of Chemistry and Technology, Ivanovo, 1993, 120 pp. (in Russian).
27. S. I. Vagin, Ph. D. (Chem.) Thesis, Ivanovo State University of Chemistry and Technology, Ivanovo, 2000, 153 pp. (in Russian).

28. M. Yu. Tipugina and T. N. Lomova, *Zh. Neorg. Khim.*, 2004, **49**, 1051 [*Russ. J. Inorg. Chem.*, 2004, **49** (Engl. Transl.)].
29. M. Yu. Tipugina, E. V. Motorina, and T. N. Lomova, *Zh. Fiz. Khim.*, 2005, **79**, S39 [*Russ. J. Phys. Chem.*, 2005, **79** (Engl. Transl.)].
30. M. Yu. Tipugina, E. V. Motorina, and T. N. Lomova, *Abstrs. of Papers, IXth Intern. Conf. "The Problems of Solvatation and Complex Formation Solutions*," Plyos, Russia, 2004, p. 284.
31. J. W. Buchler and K. Rohbock, *Inorg. Nucl. Chem. Lett.*, 1972, **8**, 1073.
32. T. N. Lomova, N. I. Volkova, and B. D. Berezin, *Zh. Neorg. Khim.*, 1983, **28**, 2514 [*J. Inorg. Chem.*, 1983, **28** (Engl. Transl.)].
33. B. D. Berezin and T. N. Lomova, *Zh. Neorg. Khim.*, 1981, **26**, 203 [*J. Inorg. Chem.*, 1983, **28** (Engl. Transl.)].
34. M. Yu. Tipugina, E. V. Motorina, and T. N. Lomova, *Tez. dokl., XXVI Sessiya Vserossiiskogo seminara po khimii porfirinov i analogov* [*Abstrs. of Papers, XXVI Session of the All-Russian Seminar on Chemistry of Porphyrins and Analogs*], Ivanovo, 2004, p. 8 (in Russian).
35. S. S. Subbotina, M. Yu. Tipugina, and T. N. Lomova, *Tez. dokl., XXVI Sessiya Vserossiiskogo seminara po khimii porfirinov i analogov* [*Abstrs. of Papers, XXVI Session of the All-Russian Seminar on Chemistry of Porphyrins and Analogs*], Ivanovo, 2004, p. 9 (in Russian).
36. T. N. Lomova, *Tez. dokl., XXIX Nauchnaya sessiya Vserossiiskogo seminara po khimii porfirinov i analogov* [*Abstrs. of Papers, XXIX Scientific Session of the All-Russian Seminar on Chemistry of Porphyrins and Analogs*], Ivanovo, 2004, p. 9 (in Russian).
37. T. N. Lomova, M. Yu. Tipugina, and T. A. Ageeva, *Zh. Obshch. Khim.*, 1999, **69**, 459 [*Russ. J. Gen. Chem.*, 1999, **69** (Engl. Transl.)].
38. I. M. Cheremisina, *Zh. Strukt. Khim.,* 1978, **19**, 336 [*J. Struct. Chem. (USSR)*, 1978, **19** (Engl. Transl.)].
39. A. Gordon and R. Ford, *The Chemist's Companion. A Handbook of Practical Data, Thechniques, and References*, Wiley-Interschience Hubcication John and Sons, New York—London—Sydney—Toronto, 1972.
40. C. Langford and H. Cray, *Ligand Substitution Processes*, W. A. Benjamin, inc., New York—Amsterdam, 1965.
41. M. Yu. Tipugina and T. N. Lomova, *Zh. Fiz. Khim.*, 2002, **76**, 653 [*Russ. J. Phys. Chem.*, 2002, **76** (Engl. Transl.)].
42. T. N. Lomova, *J. Porphyrins Phthalocyanines*, 2006, **10**, 750.
43. *Svoistva organicheskikh soedinenii* [*Properties of Ogranic Compounds*], Ed. A. A. Potekhin, Khimiya, Leningrad, 1984, 520 pp. (in Russian).
44. T. A. Koroleva, O. I. Koifman, and B. D. Berezin, *Koord. Khim.*, 1981, **7**, 1642 [*Sov. J. Coord. Chem.*, 1981, **7** (Engl. Transl.)].
45. T. V. Karmanova, O. I. Koifman, and B. D. Berezin, *Koord. Khim.*, 1983, **9**, 919 [*Sov. J. Coord. Chem.*, 1983, **9** (Engl. Transl.)].
46. R. M. Izatt, J. S. Bradshaw, K. Pawlak, R. L. Bruening, and B. J. Tarbet, *Chem. Rev.*, 1992, **92**, 1261.
47. N. Ohta, W. Scheuermann, and K. Nakamoto, *Inorg. Chem.*, 1979, **18**, 457.
48. E. B. Fleischer and T. S. Srivastava, *Inorg. Chim. Acta*, 1971, **5**, 151.
49. H. Ledon and B. Mentzen, *Inorg. Chim. Acta*, 1978, **31**, 1393.
50. M. S. Bains and D. G. Davis, *Inorg. Chim. Acta*, 1979, **37**, 53.
51. J. Tachibana and T. Imamura, *Chem. Lett.*, 1990, **19**, 2085.
52. M. Yu. Tipugina, T. N. Lomova, and T. A. Ageeva, *Abstrs. of Papers, VIIth International Conf. "The Problems of Solvatation and Complex Formation Solutions*," Ivanovo, 1998, p. 285.
53. M. Yu. Tipugina, T. N. Lomova, and O. A. Golubchikov, *Tez. dokl., III Vseross. nauchn. konf. "Khimiya i primenenie nevodnykh rastvorov*" [*Abstrs. of Papers, III All-Russian Scientific Conf. "Chemistry and Application of Nonaqueous Solutions"*], Ivanovo, 1993, p. 224 (in Russian).
54. M. Yu. Tipugina, T. N. Lomova, and E. V. Motorina, *Koord. Khim.*, 2005, **31**, 380 [*Russ. J. Coord. Chem.*, 2005, **31** (Engl. Transl.)].
55. M. Yu. Tipugina, E. V. Motorina, and T. N. Lomova, *Tez. dokl., IX Mezhdun. nauch. konf.* "*Problemy sol´vatatsii i kompleksoobrazovaniya v rastvorakh*" [*Abstrs. of Papers, IX International Scientific Conf. "Problems of Solvation and Complexation in Solutions"*], Ples, 2004, p. 284 (in Russian).
56. M. Yu. Tipugina and T. N. Lomova, *Zh. Neorg. Khim.*, 2004, **49**, 1285 [*Russ. J. Inorg. Chem.*, 2004, **49** (Engl. Transl.)].
57. M. Yu. Tipugina and T. N. Lomova, *Zh. Neorg. Khim.*, 2002, **47**, 1085 [*Russ. J. Inorg. Chem.*, 2002, **47** (Engl. Transl.)].
58. A. A. Grinberg, *Vvedenie v khimiyu kompleksnykh soedinenii* [*Introduction to Chemistry of Complex Compounds*], Khimiya, Leningrad, 1966, 631 pp. (in Russian).
59. T. N. Lomova and M. Yu. Tipugina, *Zh. Neorg. Khim.*, 2002, **47**, 1088 [*Russ. J. Inorg. Chem.*, 2002, **47** (Engl. Transl.)].
60. S. V. Zaitseva, Ph. D. (Chem.) Thesis, Institute of Solution Chemistry of the Russian Academy of Sciences, Ivanovo, 1999, 155 pp. (in Russian).
61. T. N. Lomova, E. Yu. Tyulyaeva, and M. Yu. Tipugina, in *Uspekhi khimii porfirinov* [*Advances in Porphyrin Chemistry*], 2004, **4**, 152 (in Russian).
62. O. A. Golubchikov, O. I. Koifman, and G. V. Ponomarev, in *Porfiriny: spektroskopiya, elektrokhimiya, primenenie* [*Porphyrins: Spectroscopy, Electrochemistry, and Application*], Ed. N. S. Enikolopyan, Nauka, Moscow, 1987, p. 214 (in Russian).
63. A. B. Solov´eva and T. N. Rumyantseva, in *Uspekhi khimii porfirinov* [*Advances in Porphyrin Chemistry*], Ed. O. A. Golubchikov, NII khimii SpbGU, St. Petersburg, 2001, **3**, p. 245 (in Russian).
64. S. V. Zaitseva, S. A. Zdanovich, and O. A. Golubchikov, *Koord. Khim.*, 2002, **28**, 843 [*Russ. J. Coord. Chem.*, 2002, **28** (Engl. Transl.)].
65. S. V. Zaitseva, S. A. Zdanovich, T. A. Ageeva, and O. A. Golubchikov, *Zh. Obshch. Khim.*, 2003, **73**, 153 [*Russ. J. Gen. Chem.*, 2003, **73** (Engl. Transl.)].
66. W. R. Scheidt, in *The Porphyrin Handbook*, Eds K. M. Kadish, K. M. Smith, and R. Guilard, Academic Press, San Diego, 2000, **3**, 50.
67. B. Gonzalez, J. Kouba, S. Yee, J. F. Kirner, and W. R. Scheidt, *J. Am. Chem. Soc.*, 1975, **97**, 3247.
68. T. V. Gromova, Ph. D. (Chem.) Thesis, Ivanovo State University of Chemistry and Technology, Ivanovo, 2001, 166 pp. (in Russian).
69. W. R. Scheidt, Y. J. Lee, W. Luangdilok, K. J. Haller, K. Anzai, and K. Hatano, *Inorg. Chem.*, 1983, **22**, 1516.
70. M. E. Klyueva, N. V. Repina, and B. D. Berezin, *Zh. Neorg. Khim.*, 2005, **50**, 510 [*Russ. J. Inorg. Chem.*, 2005, **50** (Engl. Transl.)].

71. C. L. Hill and M. M. Williamson, *Inorg. Chem.*, 1985, **24**, 2836.
72. M. E. Klyueva, N. V. Repina, and B. D. Berezin, *Tez. dokl. IX Mezhdun. konf. po khimii porfirinov i ikh analogov* [*Abstrs. of Papers, IXth International Conf. on Chemitry of Porphyrins and Their Analogs*], Ivanovo, 2003, p. 33 (in Russian).
73. T. N. Lomova, E. N. Kiseleva, and M. E. Klyueva, *Zh. Neorg. Khim.*, 2006, **51**, 1931 [*Russ. J. Inorg. Chem.*, 2006, **51** (Engl. Transl.)].
74. T. N. Lomova, M. V. Klyuev, M. E. Klyueva, E. N. Kiseleva, and O. V. Kosareva, *Ross. Khim. Zh. (Zh. Vsesoyuz. Khim. Obshch. im. D. I. Mendeleeva* 2004, **48**, 35 [*Mendeleev Chem. J.*, 2004, **48** (Engl. Transl.)].
75. M. E. Klyueva, O. V. Kosareva, T. N. Lomova, and M. V. Klyuev, *J. Porphyrins Phthalocyanines*, 2006, **10**, 714.
76. A. D. Adler, F. R. Longo, F. Kampas, and J. Kim, *J. Inorg. Nucl. Chem.*, 1970, **32**, 2443.
77. O. A. Golubchikov, T. N. Lomova, and M. Yu. Tipugina, *Tez. dokl. Vsesoyuz. simp. "Biotekhnologicheskie i khimicheskie metody okhrany okruzhayushchei sredy"* [*Abstrs. of Papers, All-Russian Symp. "Biotechnological and Chemical Methods of Environmental Protection"*], Samarkand, 1988, p. 112 (in Russian).
78. T. N. Lomova, O. A. Golubchikov, and M. Yu. Tipugina, *Tez. dokl. I Vsesoyuz. soveshchaniya po khimii i prakticheskomu primeneniyu metallokompleksov s kraun-ligandami* [*Abstrs. of Papers, I All-Russian Conf. on Chemistry and Practical Application of Metal Complexes with Crown Ligands*], Batumi, 1989, p. 54 (in Russian).
79. M. Yu. Tipugina, Ph. D. (Chem.) Thesis, Institute of Solution Chemistry of the Russian Academy of Sciences, Ivanovo, 2000, 115 pp. (in Russian).

Received January 30, 2007;
in revised form March 12, 2007