ISSN 1070-3632, Russian Journal of General Chemistry, 2010, Vol. 80, No. 4, pp. 842–848. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © E.V. Motorina, T.N. Lomova, 2010, published in Zhurnal Obshchei Khimii, 2010, Vol. 80, No. 4, pp. 681–687.

Formation of Supramolecular Complex Between Imidazole and Dichloro(5,10,15,20-tetraphenylporphinato)zirconium(IV)

E. V. Motorina and T. N. Lomova

Institute of Solution Chemistry, Russian Academy of Sciences, Akademicheskaya ul. 1, Ivanovo, 153045 Russia
e-mail: tnl@isc-ras.ru

Received February 2, 2009

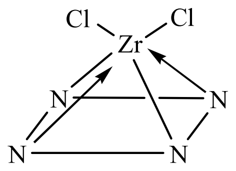
Abstract—By the reaction of 5,10,15,20-tetraphenyl-21*H*,23*H*-porphin (H_2TPP) with zirconium tetrachloride in boiling benzonitrile a complex was obtained, dichloro(5,10,15,20-tetraphenylporphinato)zirconium(IV), $(Cl)_2ZrTPP$. The equilibrium and reaction rate of stepwise reactions of $(Cl)_2ZrTPP$ with imidazole (Im) in toluene were investigated by spectrophotometry. It was established that the three steps of the complex formation include reversible processes of coordination of Im molecule and substitution of $2Cl^-$ by the second and third Im molecules. The products of the first and second stages of the reaction, $(Cl)_2(Im)ZrTPP$ and $[(Cl)(Im)_2ZrTPP]^+Cl^-$, respectively, are unstable and dissociate slowly at one Zr–Cl bond. By the analysis of the numerical values of the reactions parameters with accounting for the existence of definite spectral response to the presence of an organic base was shown a better prospect of application of $(Cl)_2ZrTPP$ in sensor systems than those of metallophtalocyianines and doubly charged cation complexes with porphyrins.

DOI: 10.1134/S1070363210040274

Mixed porphyrin-containing complexes and the phenomenon of additional coordination of ligands by metalloporphyrins (MP) with the formation of supramolecules currently attracts much attention [1–4]. Using the molecular complexation of MP promises almost unlimited possibilities of their application for transport of drugs in biological objects, molecular recognition, for the study of biochemical processes in simple models, for creation of selective receptors of ions and bases, and for the synthesis of photoactive materials. To date, it is clear that the success is determined by two factors: the composition of the first coordination sphere of the mixed complex and the state of the macrocycle, that is, by degree of its substitution, monomeric or oligomeric structure. Mixed complexes of highly charged metal cations are very specific in reactions with bases primarily due to high effective charges on the central atom. In [2–4] the reactions were studied of acetato(5,10,15,20-tetraphenylporphinato)chromium(III) and hydroxooxo(5,10,15,20-tetraphenylporphinato)tungsten(V) with nitrogen bases Im and Py. These reactions were shown to differ significantly from the simple coordination of ligand by the porphyrin complexes with doubly and some triply charged metal cations [5].

In this paper, in continuation of research in this direction the results are presented of quantitative studies of equilibria and irreversible processes of complexation and substitution of ligands in dichloro(5,10,15,20-tetraphenylporphinato)zirconium(IV) [$(Cl)_2ZrTPP$] in the reaction with organic base, imidazole (Im).

Because of the large covalent radius of the central metal atom, the porphyrin complexes of zirconium(IV) have a specific structure with the *cis*-arrangement of two acido-ligands. Thus, according to X-ray analysis [6], in $(AcO)_2ZrOEP$ (OEP is dianion 2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphin) the zirconium atom is deviated from the plane of the macrocycle by more than 1.0 Å in the direction of the two *cis*-located acetate ligands. The similarity of electron absorption spectra of Zr(IV) complexes with H_2OEP and 5,10,15,20-tetraphenylmacroporphin (H_2TPP) [7], as well as moderate kinetic stability of $(Cl)_2ZrTPP$ in proton-donor environment [8] suggest that the atom of Zr in $(Cl)_2ZrTPP$ is removed substantially from the N_4 plane (see the scheme). The *cis*-configuration of the chloride ions, as will be seen further on, becomes apparent from the specificity of ligand substitution reactions in the $(Cl)_2ZrTPP$ complex.



For the study of the reactions of $(Cl)_2ZrTPP$ with Im we selected toluene as a solvent, for it was inert with respect to both reactants. The reactions were studied in a wide range of concentrations of Im (3.58×10^{-6}–1.40×10^{-2} mol l^{-1}) at 298 K. Electron absorption spectrum of $(Cl)_2ZrTPP$ in toluene (Fig. 1) consists of a line with the maximum at 418.6 nm which is changed upon adding Im. At a gradual increase in the concentration of Im from 3.58×10^{-6} to 1.19×10^{-5} the optical density near the operating wavelength (417 nm) increases and there is a slight shift of the maximum of this band to 419.3 nm (Fig. 1, spectrum *2*). Further increase in the concentration of Im leads to a decrease in the band intensity (Fig. 1, spectrum *3*) and then the intensity increases again and the maximum is shifted to 420.7 nm (Fig. 1, spectrum *4*). At the concentrations of Im over 1.40×10^{-2} mol l^{-1} a solution is formed from which eventually precipitates Im. Regular changes in the electronic spectrum allow to determine the data for construction titration curves (Fig. 2) indicating that the reaction of $(Cl)_2ZrTPP$ with Im in toluene proceeds in three equilibrium stages.

Stepwise equilibrium constants calculated with formula (1), remain satisfactorily unchanged (see ex-

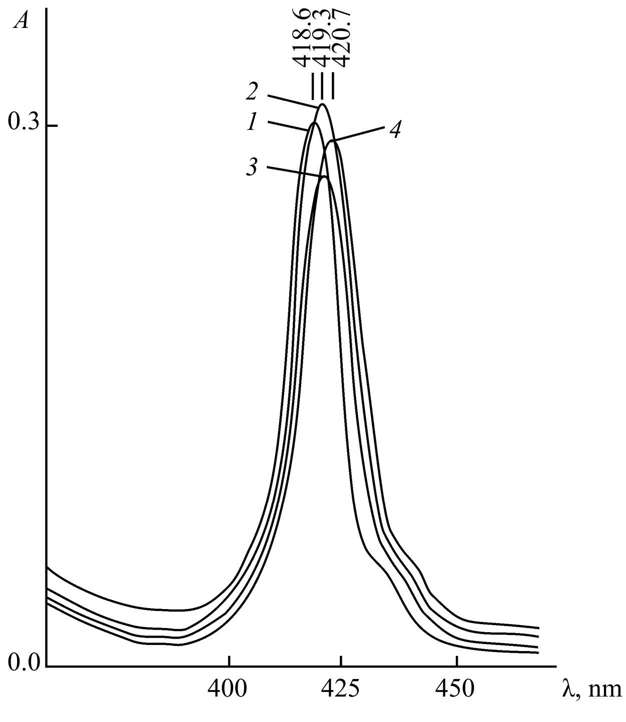


Fig. 1. Electron absorption spectra of $(Cl)_2ZrTPP$ in toluene depending on the concentration of Im. $C[(Cl)_2ZrTPP] = 2.32\times10^{-6}$ mol l^{-1}, C_{Im}, mol l^{-1}: (*1*) 0, (*2*) 1.19×10^{-5}, (*3*) 5.97×10^{-4}, and (*4*) 1.40×10^{-2}.

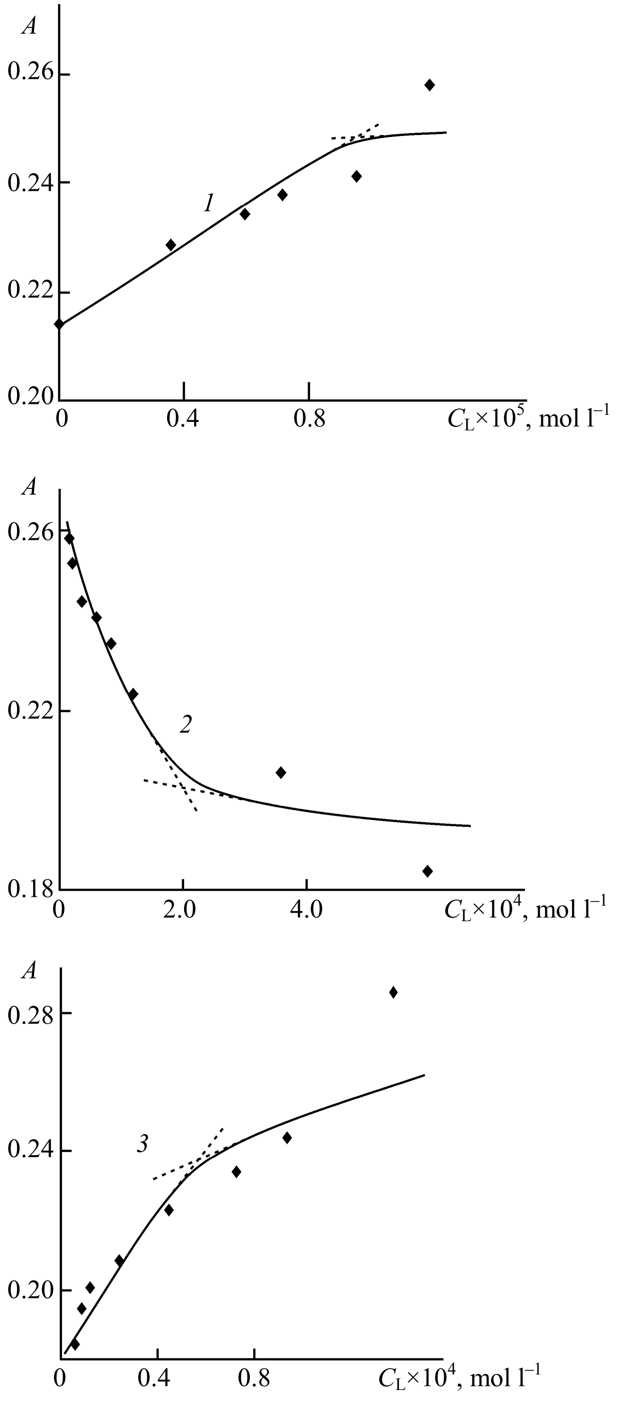


Fig. 2. The curves of spectrophotometric titration of $(Cl)_2ZrTPP$ with imidazole in toluene. C_{Im}, mol l^{-1}: (*1*) 3.58×10^{-6}–1.19×10^{-5}, (*2*) 1.19×10^{-5}–5.97×10^{-4}, and (*3*) 5.97×10^{-4}–1.40×10^{-2}.

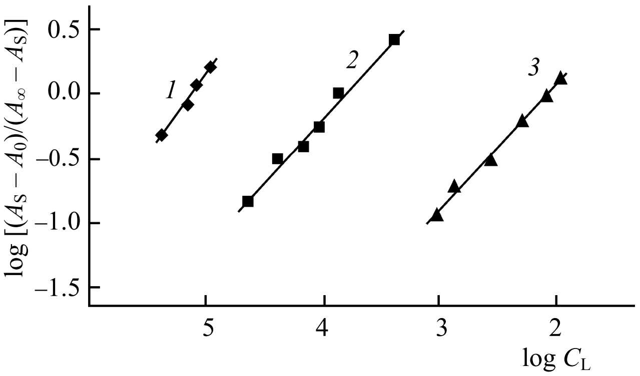


Fig. 3. Dependence log $[(A_S - A_0)/(A_\infty - A_S)]$–log C_L for the reaction of $(Cl)_2ZrTPP$ with Im in toluene at the (*1*) first, (*2*) second, and (*3*) third stages (ρ is 0.995, 0.993, and 0.997, respectively).

perimental part) for the ternary equilibrium system, that is, at $n = 1$:

$$K = \frac{(A_S - A_0)/(A_\infty - A_0)}{1 - [(A_S - A_0)/(A_\infty - A_0)]} \times \frac{1}{\{C_L - C^0_{MP}\cdot[(A_S - A_0)/(A_\infty - A_0)]\}^n}. \quad (1)$$

In Eq. (1), derived in accordance with the laws of mass action and the Bouguer–Lambert–Beer for a mixture of two colored compounds [the complex $(Cl)_2ZrTPP$ and the product of its supramolecular complexation with Im], C^0_{MP} and C_L are initial concentrations of $(Cl)_2ZrTPP$ and Im, respectively, in toluene, A_0, A_S, and A_∞ are optical densities at the working wavelength (see Experimental), respectively, solutions of $(Cl)_2ZrTPP$, equilibrium mixture at a certain concentration of Im, and supramolecular complex with Im; n is a number of added (Im) molecular ligands.

Table 1. Effective rate constants k_{eff} of the formal first-order reaction of $(Cl)_2ZrTPP$ with Im in toluene at 298 K. $C[(Cl)_2ZrTPP] = 2.32\times10^{-6}$ mol l^{-1}

Stage 1		Stage 2	
$C_{Im}\times10^6$, mol l^{-1}	$(k_{1eff}\pm\delta k_{1eff})\times10^4$, s^{-1}	$C_{Im}\times10^5$, mol l^{-1}	$(k_{2eff}\pm\delta k_{2eff})\times10^4$, s^{-1}
3.58	4.9±0.3	2.03	6.2±0.3
5.97	5.0±0.6	3.58	6.5±0.7
7.16	5.1±0.3	5.97	6.9±0.3
9.55	5.2±0.2	8.35	7.2±0.6
11.9	5.3±0.4	11.9	7.5±0.4
		35.8	8.2±0.2

The equilibrium constant in the first phase, K_1, is relatively high: $(1.85\pm0.13)\times10^5$ l mol^{-1}. It is found experimentally that the equilibrium in the first stage is reached within 5 minutes. Processing of experimental data using the dependence log $[(A_S - A_0)/(A_\infty - A_S)]$–log C_L (Fig. 3, line 1) confirms the number of Im molecules added in the first stage (tan α = 1.2). The reaction product in the first stage, which is in equilibrium with $(Cl)_2ZrTPP$, is not stable and eventually subjected to a slow and irreversible transformation into the complex spectrally identical with the product of the reversible reaction of MP with Im in the second stage (Fig. 1, curve *3*). Table 1 shows the values of the effective rate constants k_{1eff} of this transformation found for different initial concentrations of Im.

By analysis of the linear dependence (2) (Fig. 4, line *1*) we have determined the value of reaction order m_1 on C_{Im}, which amounted to the value of 0.06, and the true rate constant $k_1 = 1.09\times10^{-3}$ s^{-1}.

$$\log k_{1eff} = \log k_1 + m_1 \log C_{Im}. \quad (2)$$

From the stoichiometric ratio $(Cl)_2ZrTPP$: Im = 1:1 in the equilibrium reaction in the first stage, the spectral picture of the transformation (Fig. 1, curves *1*, *2*, and *3*), and the close to zero order of the reaction with Im in an irreversible reaction in the first stage follows the reaction equation for this stage:

$$(Cl)_2ZrTPP + Im \overset{K_1}{\rightleftarrows} (Cl)_2ZrTPP \xrightarrow{k_1} [Zr(Cl)(Im)TPP]^+Cl^-. \quad (3)$$

Obviously, the first stage includes a reversible coordination of Im molecule through the lone electron pair with the formation of a supramolecule $(Cl)_2(Im)\cdot ZrTPP$, and then a slow irreversible displacement of acido-ligand Cl^- to the second coordination sphere in the formed mixed complex. Coordination of Im, as one might expect accounting for the influence of *cis*-coordinated molecular ligand Im in the supramolecule on the Zr–$N_{porphyrin}$ bonds, leads to destabilization of the porphyrin HOMO and its growing population. In fact, this is confirmed by hyperchromic and bathochromic effects in a series of spectral curves of electron spectra in the first stage.

In each second and third stages of transformation in the system $(Cl)_2ZrTPP$–Im also react one at a time Im molecule (Fig. 3): $\tan \alpha_2 = 0.99$, $\tan \alpha_3 = 0.97$.

In the second stage of the reaction, similar to the first stage, at all Im concentrations after reaching the equilibrium a slow irreversible process occurs (Table 1), for which by the processing the linear dependence (2) (Fig. 4, line *2*) the values are determined of the reaction order on C_{Im} and the rate constant.

The product of the transformation in the third stage does not change in time, as seen from the retained pattern of the electron spectra of equilibrium mixtures at C_{Im} from 5.97×10^{-4} to 1.40×10^{-2} mol l^{-1}.

Phase of reaction	1	2
m	0.06	0.10
k, s^{-1}	1.09×10^{-3}	1.84×10^{-3}

According to Fig. 3 and above data, the reactions equations of the second and third stages should be written as follows:

$$(Cl)_2ZrTPP + Im \xrightleftharpoons{K_2} [(Cl)(Im)_2ZrTPP]^{+}Cl^{-}$$

$$\xrightarrow{k_2} [(Im)_2ZrTPP]^{2+}\cdot 2Cl^{-}, \qquad (4)$$

$$[(Cl)(Im)_2ZrTPP]^{+}Cl^{-} + Im$$

$$\rightleftharpoons [(Im)_3ZrTPP]^{2+}\cdot 2Cl^{-}. \qquad (5)$$

It is seen from the reaction Eq. (4) that in the reversible process in the second stage the molecular coordination of the ligand does not lead to a change in the coordination polyhedron and requires consumption of large energy for the replacement of covalently bound chlorine. This is well consistent with a decrease in the numerical value of the equilibrium constant ($K_2 = 7.50 \pm 0.08 \times 10^3$ l mol^{-1}) and with the spectral pattern of transformations at this stage: A reverse transformation occurs, a decrease in the absorption intensity, but the position of the absorption maximum does not change (Fig. 1, lines *2*, *3*).

The third stage (at Im concentrations 5.97×10^{-4} to 1.40×10^{-2} mol l^{-1}) of the reaction is characterized by even lower constant K_3, which is equal to $(1.4 \pm 0.1) \times 10^2$ l mol^{-1}. Here a substitution of Cl^- by Im molecule in an equilibrium process takes place, accompanied by increasing intensity of the absorption and bathochromic shift of the absorption maximum in the electronic spectrum to 420.7 nm (Fig. 1). These spectral changes may be related to the fact that heptacoordinated complexes in the left and right sides of the Eq. (5) differ only by the number of donor–acceptor and covalent bonds, and hence by different deviations of the central Zr atom from the plane of the macrocycle (see the scheme at the beginning of the article).

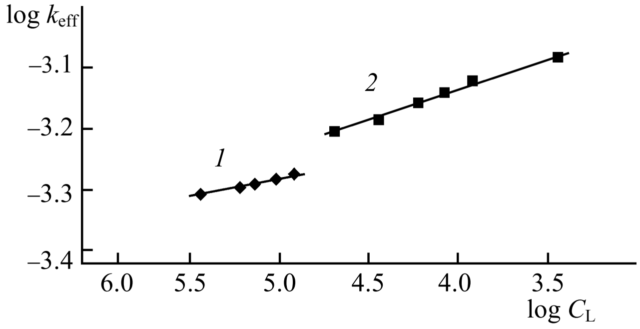


Fig. 4. Dependence log k_{eff} – log C_L for the reaction of $(Cl)_2ZrTPP$ with Im in toluene at 298 K in the (*1*) first and (*2*) second stage (ρ is 0.998 and 0.992, respectively).

We could not determine experimentally whether the reaction with Im proceeds to completion in the considered three stages, since the upper limit of the concentration of Im is defined by its solubility in toluene.

The formation of donor–acceptor complexes of the metalloporphyrin with Im in the reactions (3)–(5) is confirmed by the study of IR spectra of their mixtures with Im in toluene with Im concentrations related to the points of equivalence in the first–third stages (Fig. 2). The IR spectrum of the reaction product of the first stage, $(Cl)_2(Im)ZrTPP$, (Fig. 5a) contains a new absorption band of coordinated imidazole [9] at 721.3 cm^{-1} that is absent in the spectrum of the initial complex. In the spectrum of the reaction product of the second stage, $[(Cl)(Im)_2ZrTPP]^{+}Cl^{-}$, the frequency (728.9 cm^{-1}) and intensity of this peak increase slightly (Fig. 5b). This absorption occurs also in the IR spectrum of reaction product of the third stage, $[(Im)_3ZrTPP]^{2+}\cdot 2Cl^{-}$, and two new bands appear, with frequencies 622.1 and 521.4 cm^{-1}, which also correspond to the vibrations of the coordinated imidazole [9].

The high value of the coordination constant of the first Im molecule ($\sim 10^5$), its sharp decrease at the next stages, as well as spectral responses to the coordination of the base suggest that it is promising to use $(Cl)_2ZrTPP$ as a receptor of organic N-bases. $(Cl)_2ZrTPP$ reacts similarly [like the reactions (3)–(5)]

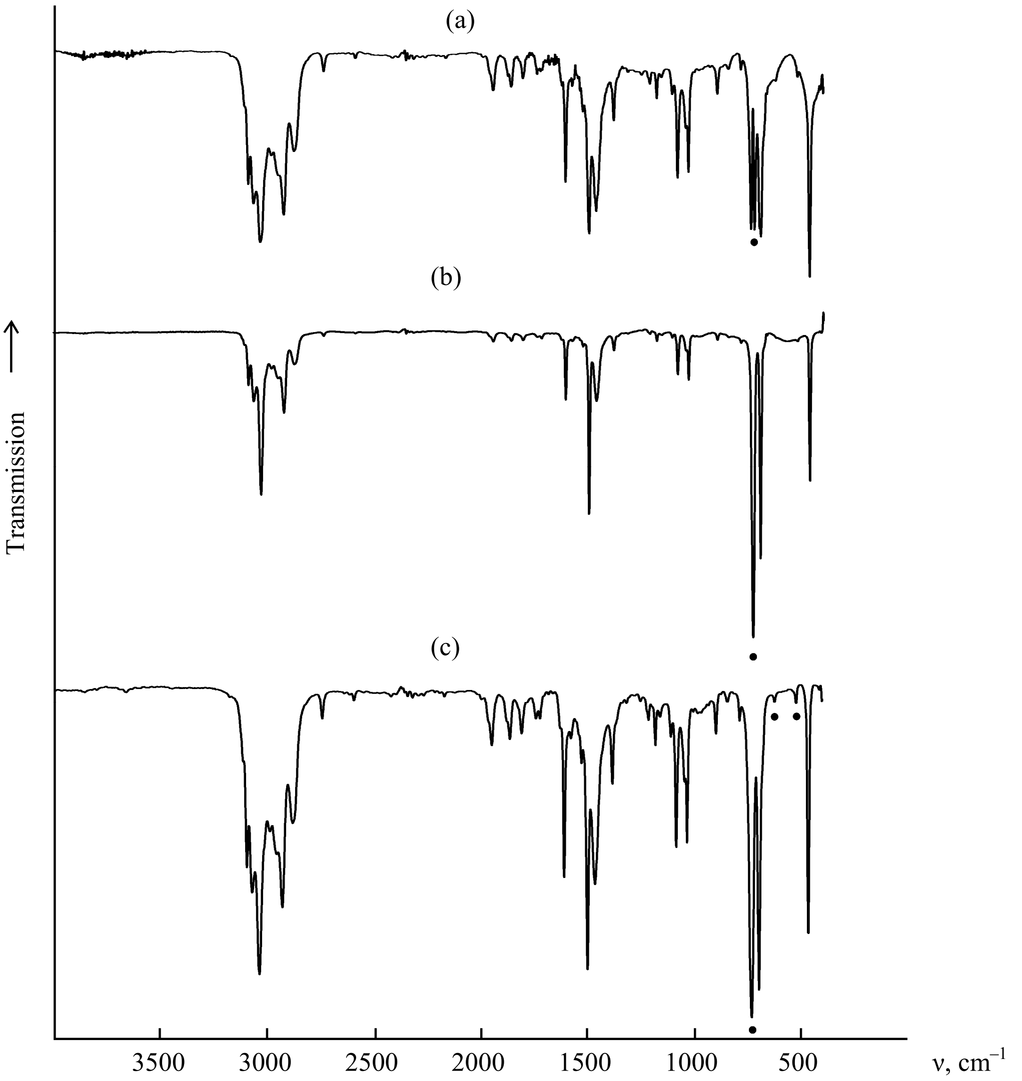


Fig. 5. IR spectra of the reaction products of $(Cl)_2ZrTPP$ with Im: (a) (Cl)(Im)ZrTPP, $C_{Im} = 1.1\times10^{-5}$ mol l^{-1}, (b) $[(Cl)(Im)_2ZrTPP]^+ Cl^-$, $C_{Im} = 2.0\times10^{-4}$ mol l^{-1}, and (c) $[(Im)_3ZrTPP]^{2+}\cdot2Cl^-$, $C_{Im} = 6.1\times10^{-3}$ mol l^{-1}.

also with the other N-base pyridine (Py). The numerical values of the constants for the reaction of Py are the following: $K_1 = 0.365 \times10^5$, $K_2 = 0.16\times10^3$ and $K_3 = 0.45$ l mol^{-1} [10], which are 5, 47 and 313 times, respectively, lower than similar constants for the reaction with Im. The values of equilibrium constants of formation of heptacoordinated complexes (K_1) correlate with the basicity of Im and Py molecules (pK_{BH^+} 6.65 and 5.15, respectively [11]). This allows, on the one hand, to conclude that the $N_{base} \rightarrow Zr$ bond in the supramolecular complexes $(Cl)_2ZrTPP$ is of σ-type, and, on the other hand, indicates the high selectivity of the reactions with bases that is important for the practical applications of $(Cl)_2ZrTPP$ as a receptor of bases. In addition, the dependence of the reaction parameters on the nature of the incoming ligand at the substitution of Cl^- in $(Cl)_2ZrTPP$ by the base points to associative mechanism of quasi-equilibrium reaction (3) (Fig. 6).

Compared to the complexes of H_2TPP with other highly charged metal cations, $(Cl)_2ZrTPP$ is one of the best reversible acceptor of Im molecules (Table 2). This complex is less than the complexes of Hf and W only in the magnitude of K_1, and less than the Hf complex in the magnitude of K_2. If we consider all MPs shown in Table 2, we have to point out one additional practically important property: a significant difference in the stepwise equilibrium constants of supramolecular complex formation of the same MP. This property makes it possible to use these complexes not only for detection of bases, but also for the quantitative determination them by consideration of direction and nature of the response in electron spectrum. Finally, the rapid reaching equilibrium and its displacement to the opposite direction at diluting the solution by the base provides another advantage of these complexes, now compared to the phthalocyanine complexes, at their application in sensor devices where the main obstacle is the long time (hours) of return [15].

EXPERIMENTAL

Dichloro (5,10,15,20-tetraphenylporphinato)-zirconium(IV) $(Cl)_2ZrTPP$ is obtained by the method [8], by the reaction of coordination of 5,10,15,20-tetraphenylporphin (H_2TPP) with zirconium(IV) chloride. 0.25 g (0.41 mmol) of H_2TPP was boiled with 0.5 g (2.64 mmol) of $ZrCl_4$ in 15 ml of benzonitrile at reflux for 1 h. The synthesis was stopped when in the electron absorption spectra of the reaction mixture disappeared the absorption bands of H_2TPP (λ_{max}, nm: 648.0, 592.0, 551.0, 516.0, 485.0, 420.0). The complex was isolated in the solid form after distilling benzonitrile off in a vacuum. Then the saturated solution of the complex in chloroform was twice subjected to chromatography on Al_2O_3 of Brockmann activity II using $CHCl_3$ as elluent. After chromatography the solution of the zirconium complex was treated additionally with gaseous HCl. Yield 60%. Electronic spectrum in chloroform [λ_{max}, nm (log ε)]: 563.0 (sh), 535.0 (4.16), 497.0 (3.67), 461.0 (3.91), 414.0 (4.64). The electronic spectra were recorded on instruments SF-26 and Specord M-40.

IR spectra of intermediate products in toluene were registered as the subtraction spectra on a VERTEX 80v instrument. As the zero line was taken the spectrum of a mixture toluene–imidazole with the same concentration of Im as in the tested solution.

Equilibrium of reaction $(Cl)_2ZrTPP$ with Im in toluene was studied by spectrophotometry by the molar ratio method. Solutions of MP in toluene were prepared just prior to use. Measurements of optical density for a series of solutions with $C[(Cl)_2ZrTPP]$ = const (2.32×10^{-6} mol l^{-1}) at different concentrations of Im were carried out at the working wavelength near the maximum of the MP absorption band (417 nm). The accuracy of the temperature control of solutions in the spectrophotometer chamber at 298 K was ±0.1 K. The numerical values of equilibrium constants K_n were determined using Eq. (1) by the least-squares method with Microsoft Excel program. The relative error did not exceed 11% (Table 3).

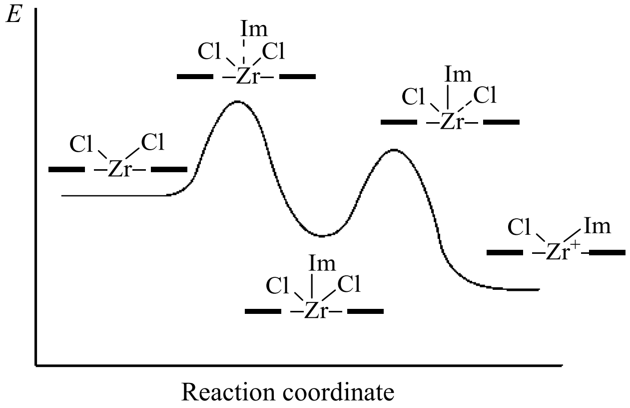


Fig. 6. Energy profile of reaction of $(Cl)_2ZrTPP$ with Im in first stage of transformation.

Reaction kinetics was studied at 298 K by the spectrophotometric method of excess concentrations using the data on changes in optical density at the working wavelength (417 nm). The rate constants of reactions $(Cl)_2ZrTPP$ with Im were calculated with the equation:

$$k_{eff} = 1/\tau \ln [(A_0 - A_\infty)/(A_\tau - A_\infty)]. \quad (6)$$

Here A_0, A_τ, and A_∞ are optical densities at the working wavelength of solutions of MP at the time 0, τ, and at the end of reaction. Optimization of the k_{eff} value and the determination of the mean-square deviations were performed using the least-squares method and Microsoft Excel program. The relative error in determining k_{eff} was 2–10%.

Table 2. The equilibrium constants of reactions of MP with imidazole at 298 K (K_n)

Complex	K_n, l mol^{-1}		
	K_1	K_2	K_3
$(Cl)_2ZrTPP$	185000	7500	140
$(Cl)_2HfTPP$ [12]	234000	14000	27.4
O=W(OH)TPP [13]	210000	750	–
O=Mo(OH)TPP [14]	1850	480	–
(AcO)CrTPP [3]	2300	820	–

Table 3. Examples of calculation of the equilibrium constants and reaction rate $(Cl)_2ZrTPP$ with idimazole in the second stage

$C_{Im}\times10^5$, mol l^{-1}	A_S	K_2^{298}, l mol^{-1}	$(K_2^{298}\pm\delta K_2)\times10^{-3}$, l mol^{-1}	$C_{Im} = 3.58\times10^{-4}$ mol l^{-1}			
				τ, min	transmission	$k_{2eff}^{298}\times10^4$, s^{-1}	$(k_{2eff}^{298}\pm\delta k_{2eff})\times10^4$, s^{-1}
1.19	0.2581		7.50±0.08	0	0.638		8.2±0.2
2.03	0.2480	7328		5	0.644	7.83	
3.58	0.2395	8735		20	0.656	8.11	
5.97	0.2358	6660		30	0.6605	8.29	
8.35	0.2300	6677		35	0.662	8.32	
11.9	0.2187	8443		45	0.664	8.29	
35.8	0.2012	7225		105	0.667	8.15	
59.7	0.1791			∞	0.6672		

ACKNOWLEDGMENTS

This work was partially supported by grants from the Presidium of Russian Academy of Sciences for Basic Research Program no. 18 and the Departmental target program of the Ministry of Education and Science, “Development of Scientific Potential of Higher Schools” (project no. 2.2.1.1/2820).

REFERENCES

1. Sanders, J.K.M., Kampos, N., Clyde-Watson, Z., et al. *The Porphyrin Handbook*, vol. 3, Kadish, K.M., Smith, K.M., and Guieard, R., Eds., London: Academic Press, 1999, p. 1.
2. Tipugina, M.Yu. and Lomova, T.N., *Zh. Neorg. Khim.*, 2002, vol. 47, no. 7, p. 1085.
3. Tipugina, M.Yu and Lomova, T.N., *Zh. Fiz. Khim.*, 2002, vol. 76, no. 4, p. 653.
4. Tipugina, M.Yu. and Lomova, T.N., *Zh. Neorg. Khim.*, 2004, vol. 49, no. 8, p. 1285.
5. Berezin, B.D. and Koifman, O.I., *Usp.Khim.*, 1980, vol. 49, no. 12, p. 2389.
6. Gouterman, M., Hanson, L.K., Khalil, G.-E., Buchler, J.W., Rohbock, K., and Dolphin, D., *J. Am. Chem. Soc.*, 1971, vol. 97, no. 11, p. 3142.
7. Buchler, J.W., Eikelmann, G., Puppe, G., Rohbock, K, Schneehage, H.H., and Weck, D., *Liebigs Ann. Chem.*, 1971, vol. 745, p. 135.
8. Berezin, B. D. and Lomova, T.N., *Zh. Neorg. Khim.*, 1981, vol. 26, no.12, p. 203.
9. Elkin, M. D., Ziganshina, O.D., Berezin, K.V., and Nechaev, V.V., *Zh. Strukt. Khim.*, 2004, vol. 45, no. 6, p. 1132.
10. Lomova, T.N., Motorina, E.V., Ovchenkova, E.N., and Klyueva, M.E., *Izv. Akad. Nauk, Ser. Khim.*, 2007, no. 4, p. 636.
11. *Tablitsy constant skorosti i ravnovesiya geterotsiklicheskikh organicheskikh reaktsii* (Tables of Rate and Equilibrium Constants of Heterocyclic Organic Reactions), Palm, V.A., Ed., vol. 2, part 1, Moscow, 1976, p. 68.
12. Tipugina, M.Yu., Motorina, E.V., and Lomova, T.N., *Zh. Fiz. Khim.*, 2005, vol. 79, no. 4, p. S39.
13. Lomova, T.N. and Motorina, E.V., J. *Porphyrins & Phthalocyanines*, 2008, vol. 12, nos. 3–6, p. 617.
14. Tipugina, M.Yu, Motorina, E.V., and Lomova, T.N., *Zh. Neorg. Khim.*, 2007, vol. 52, no. 3, p. 444.
15. Apetrei, C., Casilli, S., De Luca, M., Valli, L., Jiang, J., Rodriguez-Mendez, M.L., and De Saja, J.A., *Colloids and Surfaces, A: Physicochem. Eng. Aspects*, 2006, vols. 284–285, p. 574.