## Quantitative Study of the Quasiequilibrium in the System (Hydroxo)oxo-(5,10,15,20-tetraphenylporphynato)molybdenum(V)–Piperidine in Toluene Medium

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Received June 28, 2012

Abstract—The quasiequilibrium interaction of (hydroxo)oxo-(5,10,15,20-tetraphenylporphynato)molybdenum(V) and piperidine in the toluene medium has been studied by means of chemical kinetics and spectrophotometric titration. It has been revealed that the molecular complex formation proceeds as slow irreversible salt formation reaction. It is preceded by the stages of equilibrium substitution of the hydroxo group OH<sup>-</sup> with piperidine, the outer sphere cationic complex formation [ $K_1$  (2.03±0.28)×10<sup>3</sup> M<sup>-1</sup>]; and by the coordination of the second piperidine molecule to the cationic complex ( $K_2$  1.76±0.39 M<sup>-1</sup>). The complex formation has been completely kinetically described: the rate equations and rate constants have been derived, and the rate limiting stage has been identified. In addition, the physicochemical data on the intermediates and products are presented. The prospects of application of the mixed porphyrin-containing complex as piperidine receptor, alkaloids and pharmaceuticals building block, have been justified.

DOI: 10.1134/S1070363213070220

The steady interest to the molybdenum complexes is mostly due to their functions in biological systems. For example, some enzymes (nitrogenases, oxydases, or hydrogenases of varied nature [1]) contain metal atoms in the active sites. In its coordination compounds, molybdenum can exist in the oxidation states of 0 to +6, and can possess a coordination number of 4 to 8 [2]. The comparative analysis of molybdenum complexes behavior in typical chemical reactions was made in [3]. The equilibrium constants of the reaction of molybdenum oxocomplexes with ethylenediaminetetraacetate were determined in [4, 5] by means of potentiometric titration and temperature jump methods; the obtained values were consistent with other available data [6]. The coordination of porphyrin dianion to molybdenum and Mo-porphyrin reactions with organic bases were investigated using the model systems containing (hydroxo)oxo-(5,10,15,20-tetraphenylporphynato)molybdenum(V) O=Mo(OH)TPP and nitrogen bases (imidazole [7] or pyridine Py [8]), or sulfur-containing ligand H<sub>2</sub>S [9]. In that works it was demonstrated that the molybdenum complex was capable of reversible coordination of the bases; this property could be applied for construction of sensors

and other analytical devices. Still, metalloporphyrins reactions with piperidine Pip base, which is a building block of many pharmaceuticals (analgesics, anesthetics) and natural alkaloids (piperine, lobeline, morphine), have been poorly studied. For the molybdenum complexes such data is absent, to the best of our knowledge. In [10–12] the reactivity of tetraphenylporphyrin complexes with cobalt, manganese, and zinc towards piperidine coordination was studied. In the case of cobalt, in the ethanol medium the reaction resulted in the 1:1 (Pip)CoTPP complex. Zn-porphyrin formed the same 1:1 donor-acceptor complex, as well as the (Pip)<sub>2</sub>ZnTPP molecular complex in the benzene or CCl<sub>4</sub> medium. The manganese(III) complex was capable of complexing piperidine in the toluene medium, simultaneously being reduced to manganese(II) [12]. Even though the above-cited studies were performed in different media, it followed from their results that the piperidine coordination process was strongly dependent on the nature of metal contained in the metalloporphyrin.

In this work the equilibrium states and rates of elementary reactions comprising the O=Mo(OH)TPP



**Fig. 1.** Electron absorption spectra of O=Mo(OH)TPP in toluene medium in the presence of various piperidine amounts. [O=Mo(OH)TPP] =  $8.77 \times 10^{-6}$  M; [Pip] = (1) 0, (2)  $1.62 \times 10^{-2}$  M, and (3) 8.43 M;  $\lambda$ , nm: (1) 463, (2) 461, and (3) 446.

complex evolution in presence of piperidine in the toluene medium were studied, and the composition and spectral properties of the stepwise donor-acceptor complex formation were evaluated. Finally, prospects of application of the Mo-porphyrin complex as piperidine receptor were discussed.

Electron absorption spectra (in the range of Soret absorption band) of O=Mo(OH)TPP in the toluene medium upon addition of various amounts of piperidine are shown in Fig. 1. The spectral changes observed allowed to distinguish two stages of the reaction and to collect the data for the titration curves (Fig. 2) processing. In the first stage of the interaction, with organic base concentration in the toluene-piperidine mixtures increasing in the range of  $1.35 \times 10^{-4}$ –  $1.62 \times 10^{-2}$  M, in the electronic absorption spectra of O=Mo(OH)TPP an isobestic point was observed at  $\lambda$  = 475 nm (Fig. 2); this proved the existence of static equilibrium between metalloporphyrin and piperidine. The system stability was proved by the spectra shape and the invariance of the isobestic point position in time. The calculation of the equilibrium constant  $K_1$ and the titration curve are presented in Table 1 and in Fig. 2. From the slope of the log  $[(A_{eq} - A_o)/(A_{\infty} - A_{eq})] \log c_L$  plot (Fig. 3a, tan  $\alpha_1 = 1.18$ ), in the first stage of the reaction one piperidine molecule interacted with each metalloporphyrin molecule. The equilibrium constant  $K_1$  equaled (2.03±0.28)×10<sup>3</sup> M<sup>-1</sup>, thus being much larger than unity. This, in combination with



**Fig. 2.** Differential electron absorption spectra and curves of spectrophotometric titration of O=Mo(OH)TPP with piperidine in the toluene medium. [Pip] = (a)  $1.35 \times 10^{-4}$ -  $1.62 \times 10^{-2}$  M and (b) 0.27-8.43 M.

absence of drastic changes in the electron absorption spectra (new bands appearance or significant band shift) allowed concluding that the elementary reaction in the first stage of the interaction proceeded without extension of the coordination sphere, as the OH<sup>-</sup> ligand substitution.

$$O=Mo(OH)TPP + Pip \leftrightarrow [O=Mo(Pip)TPP]^+OH^-.$$
(1)

The second stage of the interaction proceeded at higher piperidine concentrations, in the range of 0.27– 8.43 M. The reaction stoichiometry was 1:1 (Fig. 3b, tan  $\alpha_2 = 1.2$ ). The equilibrium constant decreased by almost thousand times ( $K_2$  1.76±0.39 M<sup>-1</sup>) as compared with that of the first stage. The shape of the

$[Pip] = 1.35 \times 10^{-4} - 1.62 \times 10^{-2}, M^{a}$			$[Pip] = 2.70 \times 10^{-1} - 8.43, M^{b}$				
[Pip]×10 <sup>4</sup> , M	$A_{ m eq}$	$K_1, \mathrm{M}^{-1}$	[Pip], M	$A_{ m eq}$	$K_2,  \mathrm{M}^{-1}$		
0	0.7756		0.27	0.8339			
1.35	0.7993	2370	0.47	0.6529	2.22		
2.03	0.8030	1920	0.74	0.5807	1.57		
2.70	0.8149	2480	0.95	0.5199	1.52		
3.38	0.8120	1750	1.08	0.4897	1.46		
4.05	0.8191	1970	1.15	0.4617	1.62		
4.73	0.8251	2150	1.55	0.4136	1.39		
5.40	0.8248	1860	1.62	0.3861	1.74		
6.08	0.8266	1770	2.02	0.3357	2.56		
	1	1			1		

**Table 1.** Example of the equilibrium constants calculation for the first and the second stages of O=Mo(OH)TPP interaction with piperidine at 298 K

<sup>a</sup>  $K_1 \pm \delta K_1 = (2.03 \pm 0.28) \times 10^{-3}$  M. <sup>b</sup>  $K_2 \pm \delta K_2 = 1.76 \pm 0.39$  M.

electron absorption spectrum in the second stage of the reaction changed more significantly (Fig. 1, *curves 2, 3*; Fig. 2). The optical density at the absorption maximum noticeably decreased, and the band became asymmetric, with the shoulder appearing at the short wavelength range, later transforming into an intensive band. No new absorption bands appeared at long wavelength range, to the right of the maximum at  $\lambda_{max} = 462$  nm.

Thus, the second stage of the reaction of O=Mo· (OH)TPP with piperidine could be described as the coordination of the second piperidine molecule to the eighth coordination site of molybdenum [equation (2)]. The formation of molybdenum(V) complexes with the coordination number of 8 is more favorable than of seven-coordinated complexes. According to the extract [2] of ten thousand structures of the coordination



**Fig. 3.** The log  $[(A_{eq} - A_o)/(A_{\infty} - A_{eq})] - \log c_L$  dependence for the reaction of O=Mo(OH)TPP with piperidine in the toluene medium, in the piperidine concentration range of  $1.35 \times 10^{-4} - 1.62 \times 10^{-2}$  M, (a) first stage and of 0.27–8.43 M, (b) second stage.  $R^2$  were 0.942 and 0.994, respectively.

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Fig. 4. Electron absorption spectra of O=MO(OH)TPP in the system metalloporphyrin–piperidine–toluene at piperidine concentration of 1.62 M in the freshly prepared mixture (1) and after 24 hours incubation (2). Other curves correspond to intermediate times.

compounds (as deduced from the X-ray diffraction data) the population of  $Mo^V$  complexes with coordination numbers of 5, 6, 7, and 8 was 13, 32, 0, and 7, respectively. However, the stability of the eight-coordinated complex formed in the second stage is three orders of magnitude lower than that of the seven-coordinated [O=Mo(Pip)TPP]<sup>+</sup>OH<sup>-</sup> formed according to the reaction (1) in the first stage.

$$[O=Mo(Pip)TPP]^{+}OH^{-} + Pip$$
  
$$\stackrel{K_{2}}{\leftrightarrow} [O=Mo(Pip)_{2}TPP]^{+}OH^{-}.$$
(2)

In the second stage of the interaction, that is, at higher piperidine concentration, the slow reaction was observed in all the piperidine-containing mixtures. However, the absence of the isobestic point in the spectral time series at each piperidine concentration (Fig. 4) indicated the complexity of the chemical process. The fact that the absorption spectrum at  $\tau = 0$ was not consistent with the other spectra in the time series, indicated the probability of the fast irreversible stage or the fast-established pre-equilibrium; the latter possibility was confirmed by other experimental data. In Fig. 2b the reversible changes of the electronic spectra at  $\tau = 0$  with increasing piperidine concentration are shown (the reversibility was proved by tracking the spectral changes upon dilution of the mixtures). In the spectral series the isobestic point was clearly revealed at  $\lambda = 453$  nm. After the preequilibrium had been established, the slow reaction was observed at  $\tau \neq 0$ , this reaction was accompanied by changes in the electron absorption spectra with nicely revealed isobestic points (Fig. 4).

From the data presented in Table 2, the rate constants for the studied reaction were calculated (Table 3), they were almost independent of the piperidine concentration. The average rate constant  $k_{\rm ef}$  was  $(1.63\pm0.29)\times10^{-4}$  s<sup>-1</sup>, the reaction order with respect to piperidine was close to zero (0.20). Thus, the experimentally derived kinetic equation was as follows.

$$-d[O=Mo(OH)TPP]/d\tau = k[O=Mo(OH)TPP] \cdot [Pip]^{0}.$$
 (3)

In order to kinetically describe the reaction of O=Mo(OH)TPP with piperidine and to determine its mechanism, we studied the properties of the intermediates (products corresponding to the equivalence points at the titration curves) and of the irreversible reaction final product, at different piperidine concentration. The final product was the same at any piperidine concentration, this was a substance with absorption maxima at  $\lambda_{max}$  419, 514, and 548 nm [Table 4; Fig. 4 (band at  $\lambda_{max} = 548$  nm not shown)].

IR spectra were recorded separately for the initial O=Mo(OH)TPP and for products of different stages of its interaction with piperidine. In the IR spectrum of the first (reversible) stage product (Fig. 5, curve 2) new maxima were revealed with the vibration frequencies corresponding to that of piperidine [13], at 402, 548, 728, 785, 1044, 1317, 1496, 2805, 2859, and 2921  $\text{cm}^{-1}$ ; they were absent in the spectrum of the initial complex. In the IR spectrum of the second (reversible) stage product, those maxima were revealed even better. In the pure piperidine spectrum [13], the corresponding bands are observed at 429 (446), 545 (546), 741, 824, 1112, 1314, 1441, 2786, 2833, and 2898 cm<sup>-1</sup> (two values were given in [13] for the first two bands). The shift of the piperidine bands to the lower frequencies in the low-frequency part of the spectrum and to higher frequencies in its high-frequency part indicated the coordinated piperidine state.

The state of IR signals at 659 and 928 cm<sup>-1</sup> that originated from the Mo–O and Mo=O vibrations, respectively, in O=Mo(OH)TPP, reflected the changes of ligand surrounding of Mo upon interaction with piperidine. The sharp band at 659 cm<sup>-1</sup> (Fig. 5, curve 1) disappeared from the spectra of the products of the first and the second stages (Fig 5, curves 2, 3). The high-frequency absorption band (928 cm<sup>-1</sup>) was observed in all the spectra; however, its relative intensity significantly decreased in the products spectra, as so did that of many other bands. The coordination center in the initial O=Mo(OH)TPP had the  $C_{4\nu}$ 

[Pip],	τ, min											
М	0	5	10	15	20	25	30	35	40	45	50	55
0.27	0.8056	0.7889	0.7829	0.7693	0.7607	0.7571						
0.47	0.4066	0.3999	0.3918	0.3835	0.3759	0.3701	0.3636	0.3570	0.3513	0.3463	0.3408	0.3354
0.74	0.3745	0.3661	0.3582	0.3498	0.3421	0.3358	0.3301	0.3241	0.3179	0.3134	0.3076	0.3022
0.95	0.2883	0.2789	0.2712	0.2647	0.2585	0.2527	0.2468	0.2417	0.2371	0.2318	0.2271	0.2227
1.08	0.2450	0.2365	0.2296	0.2235	0.2175	0.2115	0.2056	0.2010	0.1962	0.1915	0.1869	0.1825
1.15	0.2022	0.1958	0.1886	0.1827	0.1759	0.1701	0.1650	0.1589	0.1532	0.1480	0.1430	0.1377
1.55	0.1315	0.1244	0.11682	0.1105	0.1044	0.0986	0.0932	0.0877	0.0828	0.0785	0.0745	0.0713
1.62	0.1989	0.1851	0.1749	0.1653	0.1534	0.1443	0.1367	0.1288	0.1215	0.1149	0.1077	0.1012
	τ, min											
[Pip],						τ, m	nin					
[Pip], M	60	65	70	75	80	τ, m 85	nin 90	95	100	105	110	115
[Pip], M 0.27	60	65	70	75	80	τ, m 85	iin 90	95	100	105	110	115
[Pip], M 0.27 0.47	60 0.3313	65 0.3263	70 0.3221	75 0.3178	80 0.3135	τ, m 85 0.3099	nin 90 0.3059	95 0.3022	100 0.2985	105 0.2952	110 0.2922	115 0.2899
[Pip], M 0.27 0.47 0.74	60 0.3313 0.2976	65 0.3263 0.2922	70 0.3221 0.2874	75 0.3178 0.2811	80 0.3135 0.2727	τ, m 85 0.3099 0.2664	nin 90 0.3059 0.2601	95 0.3022 0.2532	100 0.2985 0.2478	105 0.2952 0.2423	110 0.2922 0.2379	115 0.2899 0.2326
[Pip], M 0.27 0.47 0.74 0.95	60 0.3313 0.2976 0.2184	65 0.3263 0.2922 0.2141	70 0.3221 0.2874	75 0.3178 0.2811 0.2064	80 0.3135 0.2727 0.2024	τ, m 85 0.3099 0.2664 0.1985	nin 90 0.3059 0.2601 0.1953	95 0.3022 0.2532 0.1917	100 0.2985 0.2478 0.1889	105 0.2952 0.2423 0.1855	110 0.2922 0.2379 0.1814	115 0.2899 0.2326 0.1777
[Pip], M 0.27 0.47 0.74 0.95 1.08	60 0.3313 0.2976 0.2184 0.1784	65 0.3263 0.2922 0.2141	70 0.3221 0.2874	75 0.3178 0.2811 0.2064	80 0.3135 0.2727 0.2024	τ, m 85 0.3099 0.2664 0.1985	nin 90 0.3059 0.2601 0.1953	95 0.3022 0.2532 0.1917	100 0.2985 0.2478 0.1889	105 0.2952 0.2423 0.1855	110 0.2922 0.2379 0.1814	115 0.2899 0.2326 0.1777
[Pip], M 0.27 0.47 0.74 0.95 1.08 1.15	60 0.3313 0.2976 0.2184 0.1784 0.1329	65 0.3263 0.2922 0.2141 0.1283	70 0.3221 0.2874	75 0.3178 0.2811 0.2064 0.1179	80 0.3135 0.2727 0.2024 0.1132	τ, m 85 0.3099 0.2664 0.1985 0.1096	nin 90 0.3059 0.2601 0.1953 0.1053	95 0.3022 0.2532 0.1917 0.1014	100 0.2985 0.2478 0.1889 0.0982	105 0.2952 0.2423 0.1855 0.0950	110 0.2922 0.2379 0.1814 0.0924	115 0.2899 0.2326 0.1777 0.0902
[Pip], M 0.27 0.47 0.74 0.95 1.08 1.15 1.55	60 0.3313 0.2976 0.2184 0.1784 0.1329 0.0682	65 0.3263 0.2922 0.2141 0.1283 0.0661	70 0.3221 0.2874	75 0.3178 0.2811 0.2064 0.1179	80 0.3135 0.2727 0.2024 0.1132	τ, m 85 0.3099 0.2664 0.1985 0.1096	nin 90 0.3059 0.2601 0.1953 0.1053	95 0.3022 0.2532 0.1917 0.1014	100 0.2985 0.2478 0.1889 0.0982	105 0.2952 0.2423 0.1855 0.0950	110 0.2922 0.2379 0.1814 0.0924	115 0.2899 0.2326 0.1777 0.0902

**Table 2.** Optical density of the O=Mo(OH)TPP-piperidine reaction mixtures  $A_s$  as functions of piperidine concentration and time

symmetry, and the Mo atom was displaced out of the plane of four coordinated N atoms towards the double bound O atom, by approximately half of angstrom [14]. It was suggested that the resolution of the metalloporphyrin IR spectrum increased upon its interaction with piperidine, due to the formation of more planar coordination node [15]. Thus, the products

**Table 3.** Effective rate constants  $k_{ef}$  of the reactions in the system O=Mo(OH)TPP-piperidine-toluene at 298 K as function of piperidine concentration (0.27–8.43 M)

	· · · · ·
[Pip], M	$(k_{\rm ef} \pm \delta k_{\rm ef}) \times 10^4,  {\rm s}^{-1}$
0.27	$1.4{\pm}0.10$
0.47	1.5±0.10
0.74	$1.4{\pm}0.10$
0.95	$1.4{\pm}0.10$
1.08	1.5±0.10
1.15	$1.4{\pm}0.10$
1.55	2.2±0.17
1.62	2.2±0.10

of the first and the second interaction stages (those produced in the respective  $c_{Pip}$  ranges at  $\tau = 0$ ) contained coordinated piperidine molecule(s), and the stoichiometry of the metalloporphyrin–piperidine complexes was 1:1 and 1:2, respectively. Taking into account the changes in the electronic spectra in the course of the donor-acceptor complex formation (Table 4) and non-ionizing character of the solvent, the respective products could be as follows:  $[O=Mo(Pip)\cdot TPP]^+OH^-$  and  $[O=Mo(Pip)_2TPP]^+OH^-$ . Data in Table 4 demonstrate the noticeable difference in the molar absorptivity of those complexes.

In the spectra of solid molecular complexes of the 1:1 and 1:2 composition, as well as in that of the final product in the chaotic layer and in KBr (Figs. 6, 7), the shift of the maxima of the coordinated piperidine bands as compared with the free base (see above) were less significant than that in the case of the solution spectra (Fig. 5). The exception was a signal at 1412 cm<sup>-1</sup> as a sharp distinct band in the solid layer, absent in the case of the initial complex spectrum.

Compley	[]	in] M	$\lambda_{max}$ , nm (log $\varepsilon$ )				
Complex	[r	īp], īvī	I		II	III	
O=Mo(OH)TPP		-	634 (3.86)	590	(4.01)	463 (4.95)	
[O=Mo(Pip)TPP] <sup>+</sup> OH <sup>-</sup>	1.0	$62 \times 10^{-2}$	634 (3.94)	587	(4.10)	461 (4.98)	
[O=Mo(Pip) <sub>2</sub> TPP] <sup>+</sup> OH <sup>-</sup>	8.4	43	618 (3.17)	578	(3.78)	446 (5.23)	
Irreversible reaction product	8.4	43	548	514		419	
[O=Mo(Pip) <sub>2</sub> TPP] <sup>+</sup> OH <sup>-</sup> , solution	402	548	785	1317	1496	2859–2921	
Final product, KBr		618	1121	1380		2854–2929	
Final product, chaotic layer	410	619		1274	1412	2849-2926	

**Table 4.** Parameters of electron absorption spectra of O=Mo(OH)TPP and its reaction with piperidine in the toluene medium, at piperidine concentration of  $1.35 \times 10^{-4} - 1.62 \times 10^{-2}$  M and 0.27 - 8.43 M

As far as the final product of O=Mo(OH)TPPpiperidine interaction (at high concentrations of base)



**Fig. 5.** IR spectra of (1) O=Mo(OH)TPP, (2) [O=Mo(Pip)-TPP]<sup>+</sup>OH<sup>-</sup> (2) ([Pip] =  $4.73 \times 10^{-4}$  M), and (3) [O=Mo(Pip)<sub>2</sub>. TPP]<sup>+</sup>OH<sup>-</sup> ([Pip] =  $7.43 \times 10^{-1}$  M) in toluene. Signals corresponding to the coordinated piperidine vibrations are marked with vertical lines; signals partially overlapping with the porphyrin macrocycle vibration signals are marked with asterix. is concerned, the most differences from the two intermediate complexes were to be observed in the electron absorption spectra (Table 4). Upon interaction, the spectrum became similar to the absorption spectra of the Mo(+4) complexes with porphyrin



**Fig. 6.** IR spectra of (1) O=Mo(OH)TPP and molecular complexes (2)  $[O=Mo(Pip)TPP]^+OH^-$  and (3) O=Mo(Pip)<sub>2</sub>. TPP in the solid chaotic layer at the silicon plate.

 $(O=Mo^{IV}P)$  [16]. However, as piperidine is known not to be a reducer, the structure of the slow irreversible reaction product that is formed at high piperidine concentration, after the fast-established equilibriums (1) and (2), should be that of the piperidine salt of the donor-acceptor complex  $[O=Mo(Pip)_2TPP]^+OH^-$ , isoelectronic to the structure of  $Mo^{IV}(O=Mo^{IV}TPP)$ complex.



Indeed, from the system of Eqs. (1), (2), and (4) the rate equation could be deduced corresponding to the experimentally obtained kinetic equation (3).

In Eq. (5), the rate of the slow stage (2) and the concentration of  $[O=Mo(Pip)_2TPP]^+OH^-$  could be expressed taking into account equilibriums (1) and (2).

$$-dc([O=Mo(Pip)_2TPP]^+)OH^-/d\tau$$
  
=  $k_1c([O=Mo(Pip)_2TPP]^+)OH^-$ , (5)

$$c([O=Mo(Pip)_2TPP]^+)OH^- = K_2c([O=Mo(Pip)TPP])^+OH^- (Pip)$$
$$= K_2c([O=Mo(Pip)TPP]^+)OH^- \cdot const, \qquad (6)$$

$$c([O=Mo(Pip)TPP])^{+}OH^{-} = K_{1}c[O=Mo(OH)TPP] \cdot [Pip]$$
  
=  $K_{1}c[O=Mo(OH)TPP] \cdot [Pip]$   
=  $K_{1}c[O=Mo(OH)TPP] \cdot const,$  (7)  
 $-dc([O=Mo(Pip)_{2}TPP]^{+})OH^{-}/d\tau$   
=  $-dc([O=Mo(Pip)TPP]^{+})OH^{-}/dt$   
=  $-dc[O=Mo(OH)TPP]/dt = k_{1},$ 

 $K_2K_1[O=Mo(OH)TPP]$ ·const =  $k_2[O=Mo(OH)TPP]$ . (8)

In these expressions const was the concentration of piperidine which was in large excess as compared with the equilibrium one, [Pip]. From comparison of Eqs. (8) and (3) it followed that  $k = k_2 = k_1 K_2 K_1$ . Thus, the experimental rate constant k incorporated two equilibrium constants  $K_1$  and  $K_2$ ; their values determined in this work allowed to calculate the rate constant of the limiting stage  $k_1$ .

Comparative analysis of the data regarding the O=Mo(OH)TPP reactions with various bases, as well as the reactions of piperidine with various metalloporphyrins revealed that the stability of O=Mo(OH)TPP 1:1 complexes with N-bases changed only slightly in the (9) series, whereas the O=Mo(OH)TPP-piperidine complex stability was 455 times higher than that of (AcO)MnTPP [12] and 2.2 times higher than that of ZnTPP [17].

$$Py[K_{1}(9.1\pm1.2)\times10^{3} \text{ M}^{-1}] > Pip [(2.03\pm0.28)\times10^{3}]$$
  
> Im[(1.85±0.11)×10^{3}]. (9)

The (9) series did not correspond to the order of the change of the molecular ligand basicity; the ligands pK<sub>a</sub> were 5.23 [18], 11.25 [19], and 7.03 [20], respectively. Moreover, the order of the ligands in the series according to their complexes stability, similar to the (9) series, changed in the case of different complexing metal atoms (for example, change to ZnTPP), or in different medium (benzene, carbon tetrachloride) [17]. The low selectivity of complex formation [the (9) series] was compensated with the significant increase in the stability of O=Mo(OH)TPP complexes with N-bases as compared with complexes of other metals. Due to the reversibility of the processes, this could be applied to constructing of the sensors and other analytical systems. The molecular complexes thus formed were characterized by moderately high stability, distinct spectral response developing within seconds, and by high sensitivity of the reaction to the nature of base coordinating atom ( $K_1$  of the reaction with H<sub>2</sub>S was 83 M<sup>-1</sup> [21]). The noticeable optical response in the range of Soret band in the electron absorption spectra was observed at piperidine concentration of  $10^{-4}$  to 1 M. The nature of the effect (hyperchromic or hypochromic shift) was dependent on the base concentration; this might be



Fig. 7. IR spectra of O=Mo(OH)TPP in KBr tablets (1) before and (2) after the treatment with piperidine.

applied for the semi-quantitative mixture analysis. Calculation of the numerical value of the optical response [22] revealed that O=Mo(OH)TPP was effective as piperidine receptor. For instance, with piperidine concentration in the range of  $1.35 \times 10^{-4}$ –  $1.62 \times 10^{-2}$  M at 298 K the relative optical response  $A_{opt}$  equaled 0.1, comparable to the other optical sensors based on porphyrins and phthalocyanines described in the literature. At piperidine concentration of 0.27– 8.43 M,  $A_{opt}$  equaled 0.65, much higher than that of other available systems [22].

## **EXPERIMENTAL**

Electron absorption spectra of the solutions were recorded on a UV-Vis Agilent 8453 (with software for automatic metrological evaluation of the system and for quantitative analysis) and Specord M40 spectrophotometers; IR solutions spectra were recorded on a VERTEX 80v spectrometer. IR spectra (on the KBr glasses, 300–3500 cm<sup>-1</sup>) of O=Mo(OH)TPP in toluene and in toluene–piperidine mixtures ([Pip] =  $4.73 \times 10^{-4}$ ,  $7.43 \times 10^{-1}$  M) were obtained as differential spectra. The spectrum of toluene, or that of the toluenepiperidine mixture with the concentration of the latter corresponding to the equivalence point at the titration curve (with the part coordinated by metalloporphyrin subtracted) were considered as the baseline. IR spectra in the chaotic layer were obtained by the liquid evaporation from the O=Mo(OH)TPP toluene or toluene-piperidine ([Pip] =  $4.73 \times 10^{-4}$ ,  $7.43 \times 10^{-1}$  M) solutions. Final products of the reversible and irreversible reactions of O=Mo(OH)TPP with piperidine for IR spectra recording from KBr tablet were isolated in solid form from the incubated O=Mo(OH) TPP piperidine solution after distillation of the latter.

(Hydroxo)oxo-(5,10,15,20-tetraphenylporphinato)molybdenum(V) [O=Mo(OH)TPP] [23]. 0.1 g (0.16 mmol) of H<sub>2</sub>TPP was boiled with 0.076 g (0.53 mmol) of MoO<sub>3</sub> in 0.8 g of phenol at 454 K during 4 h. The complex was isolated in solid form by vacuum distillation of phenol, dissolution in CHCl<sub>3</sub>, and double elution with CHCl<sub>3</sub> through the Al<sub>2</sub>O<sub>3</sub> column. Two elution zones were obtained, of pink (unreacted porphyrin) and green (complex) colors. Yield 60%. Electron absorption spectrum (in chloroform),  $\lambda_{max}$ , nm (log  $\varepsilon$ ): 620.0 (2.94), 584.0 (2.92), 456.0 (3.78). IR spectrum (KBr), v, cm<sup>-1</sup>: 701, 752 [ $\gamma$ (C–H), benzene], 1070, 1177 [ $\delta$ (C–H), benzene], 1484, 1596 (C=C), 800 [ $\gamma$ (C–H), pyrrole], 1018 [C<sub>3</sub>–C<sub>4</sub>, C–N, δ(C–H)], 1336 (C–N), 1441 (C=N), 441 (Mo–N), 659 (Mo–O), 928 (Mo=O).

Reaction of O=Mo(OH)TPP with piperidine was studied by spectrophotometry (molar ratios and excessive concentration methods). Solutions of O=Mo (OH)TPP and piperidine in freshly distilled toluene were prepared directly before the experiment to avoid peroxides formation. Optical density of the solutions series with the constant O=Mo(OH)TPP concentration  $(8.77 \times 10^{-6} \text{ M})$  and the base concentration in the range of  $1.35 \times 10^{-4}$  to 8.43 M was measured at 462 nm at  $\tau = 0$ , and in the time series. The solutions temperature (298 K) was controlled in the special closed spectrophotometer quartz cell with the accuracy of  $\pm 0.1 \text{ K}$ .

Rate constants at different piperidine concentrations were calculated according to the formal first-order kinetic equation, at the condition of piperidine excess with respect to the metalloporphyrin (10).

$$k_{\rm ef} = \frac{1}{\tau} \ln \frac{A_0 - A_\infty}{A_\tau - A_\infty} \,. \tag{10}$$

In this expression  $A_0$ ,  $A_{\tau}$ ,  $A_{\infty}$  are the optical densities of the reaction mixture at times zero,  $\tau$ , and after reaction was complete.

Equilibrium constants of the formation reactions of the reversible donor-acceptor complexes were determined according to Eq. (11), based on the law of mass action and Bouguer–Lambert–Beer law, the latter being applied to two colored substances: O=Mo(OH) ·TPP and its molecular complex with piperidine.

$$K = \frac{\frac{A_{eq} - A_0}{A_{\infty} - A_0}}{1 - \frac{A_{eq} - A_0}{A_{\infty} - A_0}} \cdot \frac{1}{\left(c_{L} - c_{MP}^0 \frac{A_{eq} - A_0}{A_{\infty} - A_0}\right)^n}.$$
 (11)

In this equation  $c_{MP}^0$ ,  $c_L$  are initial concentrations of O=Mo(OH)TPP and piperidine, respectively;  $A_0$ ,  $A_{eq}$ ,  $A_{\infty}$  are optical densities ( $\tau = 0$ ) of the O=Mo(OH)TPP solution, of the equilibrium mixture at certain concentration of piperidine, and of the final coordination product, respectively; n was the number of the coordinated piperidine molecules.

The optimization of K and  $k_{ef}$  and the determination of the standard deviation were performed by the least squares method in Microsoft Excel software. The relative error of K and  $k_{ef}$  determination did not exceed 23 and 7%, respectively. The sample calculation of *K* at piperidine concentration in the  $1.35 \times 10^{-4} - 1.62 \times 10^{-2}$  M and 0.27 - 8.43 M ranges is given in Table 1.

## ACKNOWLEDGMENTS

This work was performed in the frames of Programs of fundamental investigations of the Presidium of the Russian Academy of Sciences no. 7 (2011) and no. 8 (2012), Federal targeted program "Scientific and scientific-pedagogical staff of innovative Russia" for 2009–2012 (State contract no. 02.740.11.0106), and of Ministry of Education and Science Program "Development of the high school scientific potential" no. 2.2.1.1/2820 (2011).

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