Extra Coordination of Zn–Tetraphenylporphine with Pyridine, Quinoline, and Acridine N-Oxides

V. P. Andreev*, Ya. P. Nizhnik*, D. G. Bezruchko*, and A. K. Morozov**

* Petrozavodsk State University, Petrozavodsk, Russia ** Forest Research Institute, Karelian Research Center, Russian Academy of Sciences, Petrozavodsk, Russia

Received May 3, 2004

Abstract—The log *K* values of zinc tetraphenylporphine (Zn–TPhP) complexes with pyridine, quinoline, and acridine *N*-oxides and with their nonoxidized analogs, as well as the positions of absorption maxima of the complexes with respect to Zn–TPhP linearly depend on the pK_{BH^+} of the ligands in water (methanol, acetonitrile, nitromethane, and acetone) and on Hammett σ constants in the absence of steric effects.

Metal porphyrins of synthetic and natural origin show the property of extra coordination whose essence consists in that the central metal atom forms donor–acceptor bonds beyond the molecular plane with one, two, or more ligands [1, 2].

Such molecular complexes are called axial or extra complexes. They determine the biological activity *in vivo* of such peptides and enzymes as hemoglobin, cytochromes, catalase, guanylatecyclase NO-synthase, and many others containing ions of various metals [3]. It is just extra coordination that determines the biological activity of some medicinals. For example, such quinoline-based antimalarial preparations as quinine, chloroquine, amodiaquine, and mefloquine form adducts with hematin, which produce toxic effect upon malaria plasmodium [4].

At present a great number of investigations is devoted to complex formation of natural and synthetic metal porphyrins with various nitrogen-containing heterocycles and peptides, and certain extra complexes were isolated and studied in the pure state [5]. However, regarding heteroaromatic *N*-oxides we were able to find only three works reporting the study of Fe(III)Cl–TPhP (a synthetic analog of hemin; TPhP is tetraphenylporphine) complexes with pyridine *N*-oxide [6], Mn(III)–TPhP with 2,6-dimethylpyridine *N*-oxide [7], and Zn–TPhP with 3-methyl-4-nitropyridine *N*-oxide [8].

Heteroaromatic *N*-oxides, unlike their nonoxidized analogs, possess a unique combination of a high donor power of the $N\rightarrow O$ group and of its spatial accessibility. The spectrum of their biological activity is very broad: from ecologically safe agricultural plant growth stimulants [9] and medicinals to extremely powerful mutagens and carcinogens [10]. Note that heterocyclic compounds, when entering into an organism, undergo metabolic transformations into *N*-oxidized derivatives capable of reacting with various porphyrin systems of cells. For example, reduction of aliphatic and heteroaromatic *N*-oxides is often mediated by heme-containing enzymes (for example, trimethylamine *N*-oxide reductase) or even by peptide-free hemes [11]. 2-Heptyl- and 2-nonyl-4hydroxyquinoline *N*-oxides released by bacteria of the genus *Pseudomonas* being bound to heme-containing peptides are known to inhibit electron transport in the membranes of bacteria, chloroplasts, and mitochondria [12].

Previously we studied in detail molecular complexes of heteroaromatic *N*-oxides with such v-acceptors as H⁺ (Bronsted–Lowry acids), BF₃, AlCl₃, ZnCl₂, and CuCl₂ (Lewis acids) [13–15] and revealed invariable formation of n,v-type adducts involving the oxygen atom of the N→O group.

In this work we dwelt on donor-acceptor complexes of Zn–TPhP with heteroaromatic *N*-oxides of the pyridine (**I**), quinoline (**II**, **III**), acridine (**IV**), and isoquinoline (**V**) series containing such potential coordination centers as the macroring π system, metal ion, and nitrogen atoms.

In the first stage we determined the stability constants (K) of Zn–TPhP complexes with certain heterocyclic compounds in chloroform (stabilized with 1-hexene, 0.1 vol%) at 298 K by means of electronic spectroscopy. As in our previous works, we chose chloroform as solvent, since it should not compete in formation of donor–acceptor metal porphyrin com-



 $X = H (\mathbf{a}), Me (\mathbf{b}), MeO (\mathbf{c}), NO_2 (\mathbf{d}), Cl (\mathbf{e}), N_3 (\mathbf{f}), NHNH_2 (\mathbf{g}), PhCH=CH (\mathbf{h}), 4-MeOC_6H_4CH=CH (\mathbf{i}), 4-Me_2NC_6H_4 \cdot CH=CH (\mathbf{j}) PhO (\mathbf{k}).$

plexes. The initial concentration of Zn–TPhP was 2×10^{-5} M. At this concentration, metal porphyrins are not associated, which is evidenced by the fulfillment of the Bouguer–Lambert–Beer law. The stability constants of the adducts were from the difference in the optical densities of the solutions at the metal porphyrin and adduct absorption wavelengths (see Experimental). Typical changes in the electronic spectrum of Zn–TPhP in chloroform upon addition of heteroaromatic *N*-oxides are illustrated in Fig. 1.

The resulting *K* value for the adduct with pyridine (3920 ± 220) were almost coincident with the value (4100 ± 65) obtained in CHCl₃ stabilized with 2-me-thyl-2-butene [16].

We found that the dependences of $\log K$ for Zn– TPhP complexes with pyridine *N*-oxides from Hammett σ constants (and on specially introduced σ_{PyO} substituent constants for pyridine *N*-oxides [17]) and also from the basicities of the ligands in water [18], acetonitrile, nitromethane, acetone, and methanol [19] are linear (Figs. 2 and 3; Table 1). A similar phenomenon has been described by Kirksey and Hambright [22] who obtained linear dependences of the log *K* values of axial Zn–TPhP complexes in benzene with γ -substituted pyridines on the basicity of the ligands in water and on Hammett σ constants.

In the case of aprotic solvents (acetonitrile, nitromethane, and acetone), the linear dependences of log *K* on pK_{BH^+} of *N*-oxides are almost parallel to each other and locate the higher, the smaller is the general acidity (electrophilicity) parameter *E* (5.2, 5.1, and 2.1). At the same time, in the case of water and methanol, that are capable of specific interactions (H-bond formation with the N \rightarrow O group and its protonated form), the slopes of the straight lines become even larger and the higher, the smaller E (21.8 and 14.9) and the higher the general basicity (nucleophilicity) B (156 and 218) of the solvent [23]. Therefore, to predict stability of the complexes, we can use data on the basicity of the ligands in polar solvents strongly differing in the nature of their interaction with solute. This fact is of great importance, since the stability constants of many adducts of metal porphyrins are easier to determine in solvents unable to competing interactions. At the same time, to calculate the $pK_{\rm BH^+}$ values of the ligands requires use of a fairly polar medium that favors dissociation of the conjugate BH⁺ acid.

Our data show (Fig. 2) that the points for pyridine (VIa) and 4-methylpyridine (VIb) in the $\log K - pK_{BH^+}$ (H₂O) coordinates lie lower than the straight lines for *N*-oxides. Moreover, the K values calculated by Eq. (1) (Fig. 2) for the Zn-TPhP N-oxide complexes that would be expected to be as basic as compounds VIa and VIb, are 5–8 times higher than the experimental values for the corresponding pyridines. Since the macroring in Zn-TPhP is planar, it is unlikely that the easier steric accessibility of the oxygen atom in N-oxides would affect the gas-phase reaction. However, in solution, the starting pyridines and *N*-oxides, on the one hand and the intermediates and products of the donor-acceptor interaction on the other hand, should be much differently solvated. To solve this problem requires additional studies.

Along with pyridine *N*-oxides **Ia** and **Ib** capable of coordinating via the N \rightarrow O group only, we also studied compounds **Ic–Ie**, **Ii**, **Ij**, and **II**, that possess one more functional group as a second possible coordination center. In all the cases we found a good correlation between $\log K$ and Hammett σ constants, except



Fig. 1. Changes in the electronic absorption spectrum of Zn–TPhP in chloroform upon addition of 2-methylquinoline *N*-oxide (**IIIb**) $[c_{\text{Zn-TPhP}} \ 1.6 \times 10^{-6} \text{ M} \text{ (Soret band) and } 2 \times 10^{-5} \text{ M}]$. (1) Zn–TPhP and (2) Zn–TPhP·L.

for *N*-oxide **II** (Fig. 3), which may result from a certain turn of the NO₂ group out of the conjugation plane with the heteroring because of steric interaction with the neighboring CH₃ group [24]. The negative sign of the coefficient at ρ points to the fact that in



Fig. 2. Plot of the log *K* of Zn–TPhP complexes of pyridine *N*-oxides in chloroform at 298 K vs. pK_{BH^+} of ligands in (1) water (log $K = 0.33pK_{BH^+} + 2.78, r 0.986$), (2) methanol (log $K = 0.44pK_{BH^+} + 1.53, r 0.933$), (3) acetone (log $K = 0.19pK_{BH^+} + 2.04, r 0.999$), (4) nitromethane (log $K = 0.19pK_{BH^+} + 1.42, r 0.994$), and (5) acetonitrile (log $K = 0.18pK_{BH^+} + 1.23, r 0.996$) (**VIa** and **VIb** are the points corresponding to the pK_{BH^+} of pyridine and 4-methylpyridine in water).

N-oxides act as electron donors in complex formation with Zn–TPhP, and the moderate absolute value of ρ points to a moderate interaction with the reaction center.

Compound **Ij** is known to show extremely unusual properties in reaction with Broensted–Lowry acids: It takes up the first proton to the amino group (pK_{BH^+} 4.30) and the second proton, to the oxygen atom of the N \rightarrow O group (pK_{BH^+} 1.43) [20]. However, for



Fig. 3. Plot of the log *K* of Zn–TPhP complexes with pyridine *N*-oxides in chloroform at 298 K vs. (*1*) Hammett σ constants (log $K = -1.15\sigma + 3.08$, *r* 0.988) and (2) σ_{PyO} constants (log $K = -0.71\sigma_{PyO} + 3.03$, *r* 0.988) (compound **II** was excluded from correlation; **VIa** and **VIb** are the points for pyridine and 4-methylpyridine).

RUSSIAN JOURNAL OF GENERAL CHEMISTRY Vol. 75 No. 8 2005

Ligand	K, l mol ⁻¹	σ [17]	σ _{ΡyΟ} [18]	pK _{BH⁺}					
				water [18]	MeCN [19]	MeNO ₂ [19]	acetone [19]	MeOH [19]	
VIa	3920±220	0	_	5.25	_	_	_	_	
V ID Ia	6482 ± 244 1039 ± 55	_0.17 0	0	6.02 0.79	9.97	8.45	5.11	3.28	
Ib Ic	1782 ± 161 2856 ± 192	-0.17 -0.268	-0.24 -0.603	1.29 2.05	11.00 12.37	9.42 10.58	6.20	3.63 4.49	
Id	165 ± 22	+0.778	+1.19	-1.70	5.35	4.02	0.89	-	
le Ii	618 ± 18 1050 ± 20	+0.227 -0.03^{a}	+0.206 -0.10^{b}	0.36 1.00 ^c	9.06	/.68	_	-	
Ij	2110 ± 125	-0.15 ^a	-0.31 ^b	4.30 (NMe ₂) 1.43 (N \rightarrow O)	_	_	—	—	
п	346±17	+0.778	+1.19 0.069	[20] -0.97 -0.139	[21]	_	_	_	

Table 1. Stability constants (*K*) of Zn–TPhP complexes at 298 K in chloroform, Hammet σ constants and σ_{PyO} constants of substituents, and pK_{BH^+} of ligands in various solvents

^a The σ value was calculated by equations given in the legend to Fig. 4 for the absorption bands I and II. ^b The σ_{PyO} value was obtained from the correlation equation $\sigma_{PyO} = -0.48 \ pK_{BH^+} = 0.38 \ (r \ 1.000)$ we derived from data in [18] for 15 compounds. ^c Estimated by the equations given in the legend to Fig. 5 for the absorption bands I and II.

example, transfer of the dimethylcarbamoyl group between pyridine *N*-oxide [25] and this compound involves the *N*-oxide function. The fact that the point for compound **Ij** in its complex formation with Zn–TPhP falls quite well on the $\log K$ – $pK_{\rm BH^+}$ plot (Fig. 2) when using $pK_{\rm BH^+}$ 1.43 (instead of 4.30) points to the fact that the reaction with the metal porphyrin involves the oxygen rather than nitrogen atom.



Fig. 4. Plot of the shift of the Soret $(\Delta\lambda_{Soret} = -4.74\sigma + 8.65, r 0.999)$, III $(\Delta\lambda_{III} = -4.55\sigma + 11.11, r 0.995)$, II $(\Delta\lambda_{II} = -5.00\sigma + 13.80, r 0.993)$, and I $(\Delta\lambda_{I} = -4.57\sigma + 17.75, r 0.999)$ absorption bands in the electronic spectra of Zn–TPhP in chloroform vs. Hammett σ constants upon coordination with pyridine *N*-oxides.

We also showed that in the absence of steric effects the bathochromic shift of the Soret, **III**, **II**, and **I** absorption bands in the electronic spectra of Zn–TPhP in chloroform on adding heteroaromatic *N*-oxides of the pyridine, quinoline (Figs. 4 and 6), and acridine $(\Delta\lambda_{II} = 12.45 - 4.85\sigma, r 0.999; \Delta\lambda_{I} = 14.87 - 6.74\sigma,$ *r* 0.999) series linearly vary with the Hammett σ constants and basicity of the ligands. In this case, too, the coordination-induced band shifts for compound **I**



Fig. 5. Plot of the shift of the Soret $(\Delta\lambda_{\text{Soret}} = 1.33 \text{p}K_{\text{BH}^+} + 7.51, r 0.992)$, III $(\Delta\lambda_{\text{III}} = 1.34 \text{p}K_{\text{BH}^+} + 9.91, r 0.999)$, II $(\Delta\lambda_{\text{II}} = 1.42 \text{p}K_{\text{BH}^+} + 12.59, r 0.996)$, and I $(\Delta\lambda_{\text{I}} = 1.35 \text{p}K_{\text{BH}^+} + 16.45, r 0.995)$ absorption bands in the electronic spectra of Zn–TPhP in chloroform vs. pK_{BH^+} of ligands in water upon coordination with pyridine *N*-oxides.

RUSSIAN JOURNAL OF GENERAL CHEMISTRY Vol. 75 No. 8 2005

 $\Delta\lambda$, nm 20

15

IIg

IIk

IIb ____ IIa

Шf

IIe

deviate from the correlation straight lines. Comparison of the bathochromic shifts of the adducts with 2- and 4-substituted pyridine and quinoline *N*-oxides shows that those of the former change in a more complicated fashion, probably, by steric reasons. We emphasize that band III, in view of its low intensity, is the least suitable for correlation. Moreover, absorption bands of organic compounds can overlap with the Soret and III bands. However, we found (at least with heteroaromatic *N*-oxides) that the use of several bands in parallel can serve as a sufficiently reliable procedure for calculating *K* and pK_{BH^+} in various solvents and σ constants (as well as dipole moments, electrochemical oxidation half-waves, etc.).

The resulting $\Delta\lambda - \sigma$ correlation equations for the absorption bands I and II allowed us to calculate the Hammett constant for the 4-Me₂NC₆H₄CH=CH substituent (-0.15), which drastically differs from that for Me₂N (-0.84 [17]). Probably, the styryl group much attenuates direct resonance conjugation between the Me₂N and N \rightarrow O functions. Other styryl substituents, too, show a similar bridging effect. For example, our value of -0.03 for the 4-MeOC₆H₄CH=CH group is also essentially lower than the value given in [17] for the MeO group (-0.268). This fact is not very surprising. Previously, based on the pK_{BH^+} values and changes in the electronic absorption spectra, induced by protonation and complex formation with BF_3 , the authors of [26, 27] suggested a weak interaction between the nitro group and heteroring basicity center (nitrogen or oxygen atoms, respectively) in nitro derivatives of 4-trans-styryl- and 4-phenylpyridines and their N-oxides. From the $\Delta\lambda - pK_{BH^+}$ correlation straight lines (Fig. 5) we estimated the basicities of compounds Ii and Ij (1.00 and 1.46, respectively). Note that our pK_{BH^+} value for *N*-oxide **Ij** quite well agrees with the value of 1.43 in [20].

Our preliminary data show that for the coordinately unsaturated Fe^{3+} -containing metal porphyrin hemin in acetone (it is scarcely soluble in chloroform) the dependence between the shifts of bands I–III on adding an *N*-oxide and the Hammett σ constants of the substituents in the heteroring is also linear.

This fact is of utmost importance, since, with corresponding correlation equations in hand, by simply comparing the electronic absorption spectra of metal porphyrin solutions and their axial complexes with various ligands one might gain a precious information about stability of the resulting adducts and calculate hitherto unknown σ constants, basicity constants of the ligands, and stability constants of extra complexes with them.

The procedure for determining stability constants



of complexes, used in this paper, requires that their extinction coefficients are calculated under conditions of a 1000–2000 fold excess of ligand with respect to metal porphyrin. However, this is not always possible: Ligands are rather often poorly or moderately soluble in required solvents.

upon coordination with quinoline N-oxides.

The use of $\Delta\lambda$ for these purposes does not require that metal porphyrin completely passes into donoracceptor complex, but suggests that the amount of ligand is sufficient that the absorption maximum shifts distinctly and does not change position with increasing *N*-oxide concentration.

Unfortunately, the electronic absorption spectra of metal porphyrins not always show trends similar to those described above. For example, in the case of Cu–TPhP, no changes in the spectra were observed even with a 1000-fold excess of *N*-oxide, in agreement with data in [1]. Coordinately unsaturated metal porphyrins, in particular, including the Cu²⁺ ion (unlike coordinately unsaturated Zn–TPhP) are known to form unstable complexes even with ligands more basic than heteroaromatic *N*-oxides, for example, pyridine [1].

To confirm the structure of spectrally detected axial complexes, we separated 22 pure molecular complexes of Zn–TPhP with heteroaromatic *N*-oxides and with some nonoxidized analogs (Table 2) as violet (with the shades from blue to red) crystalline substances melting (decomposing) above 300° C.

According to the elemental analysis (Table 2), the Zn–TPhP:ligand ratio in all the adducts is 1:1.

Ligand	Yield, %	Found, %			Essentia	Calculated, %		
		С	Н	N	Formula	С	Н	N
Ia	61	76.09	4.36	8.62	C ₄₉ H ₃₃ N ₅ OZn	76.12	4.30	9.06
Ib	62	76.31	4.38	8.21	$C_{50}H_{35}N_5OZn$	76.28	4.48	8.90
Ic	64	74.91	4.31	8.52	$C_{50}H_{35}N_5O_2Zn$	74.77	4.39	8.72
Id	70	71.75	4.08	10.24	$C_{49}H_{32}N_6O_3Zn$	71.93	3.94	10.27
Ii	61	76.98	4.72	7.53	$C_{58}H_{41}N_5O_2Zn$	76.94	4.56	7.74
Ij	91	76.94	4.92	8.73	$C_{59}H_{44}N_6OZn$	77.16	4.83	9.15
IIa	84	77.46	4.35	8.55	C ₅₃ H ₃₅ N ₅ OZn	77.32	4.29	8.51
IIb	81	77.45	4.47	8.49	$C_{54}H_{37}N_5OZn$	77.46	4.45	8.36
IId	73	73.56	3.99	9.59	$C_{53}H_{34}N_6O_3Zn$	73.32	3.95	9.68
IIe	76	74.25	4.19	8.14	$C_{53}H_{34}CIN_5OZn$	74.22	4.00	8.17
IIf	90	73.60	4.14	12.68	$C_{53}H_{34}N_8OZn$	73.65	3.97	12.97
IIg	40	75.28	4.49	9.70	$C_{53}H_{37}N_7OZn$	74.60	4.37	11.49
IIj	74	78.23	4.95	8.47	C ₆₃ H ₄₆ N ₆ OZn	78.31	4.79	8.68
IIIb	70	77.66	4.46	8.49	$C_{54}H_{37}N_5OZn$	77.46	4.45	8.36
IIIh	66	79.14	4.53	7.42	$C_{61}H_{41}N_5OZn$	79.17	4.47	7.57
IIIi	70	77.96	4.62	7.24	$C_{62}H_{43}N_5O_2Zn$	77.94	4.54	7.33
IIIj	71	78.16	4.76	8.51	$C_{63}H_{46}N_6OZn$	78.31	4.79	8.68
IVa	32	78.35	4.60	8.38	C ₅₇ H ₃₇ N ₅ OZn	78.39	4.27	8.02
IVd	66	75.41	4.46	9.45	$C_{57}H_{36}N_6O_3Zn$	74.55	3.95	9.15
IVe	41	75.13	4.29	7.53	C ₅₇ H ₃₆ ClN ₅ OZn	75.42	4.00	7.72
\mathbf{V}	70	77.29	4.44	8.33	$C_{53}H_{35}N_5OZn$	77.32	4.29	8.51
Quinoline	54	78.30	4.57	8.95	C ₅₃ H ₃₅ N ₅ Zn	78.86	4.37	8.68

Table 2. Yields and elemental analyses of Zn-TPhP extra complexes with heteroaromatic N-oxides and quinoline

The positions of the IR absorption bands of Zn– TPhP scarcely change in going to these compounds. However, the presence of three characteristic peaks at 795–798, 749–755, and 701–704 cm⁻¹, whose position and intensity ratio are strictly individual for each complex (Table 3), as well as a noticeable attenuation of the very strong band at 1003 cm⁻¹ are worthy of special mention. The last band relates to in-plane bending δ (C-H) and stretching v[C^{β}–C^{β}] and v[C–N] vibrations of pyrrole fragments [28, 29]. The coordination of Zn–TPhP with *N*-oxides seems to result in a certain displacement of the zinc atom from the porphyrin ring plane [18], thus changing parameters of the above-noted bonds and their spectral appearance.

The IR spectra of the starting *N*-oxides contain strong stretching absorption bands in the region of 1367–1214 cm⁻¹, typical of the N \rightarrow O group (Table 3). At the same time, in the spectra of the complexes of the *N*-oxides with Zn–TPhP these bands get weaker or disappear completely. Instead of them, new bands appear in the region of 1210–1175 cm⁻¹, that overlap with metal porphyrin absorption bands (1209 and 1177 cm⁻¹). Such changes in the IR spectra of heteroaromatic *N*-oxides are caused by the decrease in double bonding between the nitrogen and oxygen atoms, induced by complex formation [15].

We noted above complex formation of heteroaromatic *N*-oxide to Zn–TPhP in chloroform gives rise to new absorption bands whose position depends on the structure of the ligand (Table 3) and intensity, in addition, on its amount. As follows from the electronic absorption spectra, in chloroform, acetone, CCl_4 , and dioxane solutions adducts are in equilibrium with their components.

Therefore, the elemental analyses and electronic absorption and IR spectra establish that the reaction of Zn–TPhP with the ligands studied gives rise to 1:1 n,v-type molecular complexes with a donor-acceptor bond between the oxygen atom of the N \rightarrow O group and the zinc atom of the metal porphyrin (as with pyridines [22]). However, we do not exclude the possibility of formation under certain conditions of other types of complexes undetectable in our experimental conditions.

Later on we are going to study the structure of our isolated extra complexes by X-ray diffraction.

EXTRA COORDINATION OF Zn-TETRAPHENYLPORPHINE

Ligand	Electronic spectrum, $\Delta \lambda_{max}$, nm $(\log \epsilon)^a$				IR spectrum, v, cm ⁻¹			
	Cope	III	Π	I	L [$\nu(N \rightarrow O)$]	ZnTFP · L ^b		
Ia	8.5 (5.67)	11.1 (3.70)	13.5 (4.39)	16.2 (4.02)	1225 v.s	798 752 701		
Ib	9.5 (5.67)	11.6(3.66)	14.5 (4.40)	18.5 (4.04)	1215 v.s	797 752 701		
Ic	10.0 (5.65)	12.6(3.61)	15.5 (4.39)	19.0(4.01)	1214 v.s	798 753 702		
Id	5.0 (5.56)	7.6 (3.68)	10.0 (4.33)	14.2 (4.00)	1517 v.s [v _{as} (NO ₂)],	1528 v.s [v _{as} (NO ₂)],		
					1272 v.s	1272 v.w, 800, 752, 704		
Ii	_	_	13.8(4.32)	18.0(3.97)	1250 v.s	1252 v.w, 800, 756, 704		
Ij	_	_	14.5 (4.36)	18.5 (4.06)	1260 v.s	800 752 704		
IIa	8.9 (5.56)	11.7 (3.85)	13.3 (4.35)	15.2 (3.92)	1309 v.s, 1265 v.s	1307 v.‡, 796, 751, 703		
IIb	9.7 (5.60)	11.7 (3.85)	13.6(4.35)	15.7 (3.92)	1314 s, 1278 s	1282 v.w, 796, 752, 702		
IId	—	8.3	8.6(4.22)	11.2 (3.76)	1522 v.s [v _{as} (NO ₂)],	1527 v.s [v _{as} (NO ₂)],		
					1307 v.s	1302 v.s, 797, 754, 703		
IIe	8.4	10.5	12.2 (4.28)	13.8 (3.90)	1305 v.s, 1253 m	1301 m, 1259 w, 796, 752, 703		
IIf	_	11.1	11.2	14.1 (3.8)	2115 v.s (N ₃), 1314 m, 1287 v.s	2117 v.s (N ₃), 1287 v.s, 796, 752, 704		
IIg	11.5	13.4	15.5 (4.24)	18.1 (3.90)	1297 s, 1211 s	796, 753, 702		
IIj	_	_	13.6	16.9 (3.88)	1264 v.s, 1236 m	1260 s, 1232 w, 794, 749, 703		
IIIb	9.2 (5.54)	12.6 (3.66)	13.5 (4.34)	15.5 (3.89)	1272 m, 1244 s	1272 v.w, 1236 w, 796, 752, 702		
IIIh	_	11.6	13.5 (4.22)	16.0(3.81)	1279 s. 1242 v.s	1240 m. 796. 754. 702		
IIIi	_	12.1	14.0 (4.23)	16.5 (3.84)	1257 v.s, 1239 v.s	1258 s, 1239 s, 796, 752, 703		
IIIi	_	_	14.5	17.5 (3.71)	1237 m	1239 w. 794, 749, 703		
IVa	_	_	12.5 (4.23)	15.0(3.75)	1330 m	798. 752. 702		
IVd	_	_	8.7 (4.28)	9.7 (3.83)	1520 v.s $[v_{ac}(NO_2)]$,	1525 v.s		
					1348 s, 1304 v.s	[v _{as} (NO ₂)], 1302 s, 798, 753, 703		
IVe	_	_	11.3 (4.30)	13.2 (3.75)	1323 s	1319 s, 797, 753, 702		
V	9.6(5.60)	11.6(3.89)	12.5 (4.26)	14.5 (3.92)	1331 v.s, 1254 s	1331 v.w, 1252 w, 798, 754, 702		
Quinoline	11.0(5.39)	12.1 (3.60)	13.5 (4.32)	17.5 (4.00)	_	797, 750, 702		
Ie	9.5 (5.66)	11.0(3.72)	12.7 (4.38)	15.5 (3.99)	_	_		
Il	6.5 (5.56)	8.6(3.78)	11.5 (4.34)	15.0 (3.96)	_	_		
IIc	10.4	13.2 (3.66)	13.8 (4.37)	15.7 (4.02)	-	_		
IIh	_	12.1 (3.74)	13.6(4.37)	15.7 (4.00)	-	_		
IIk	10.7	11.8 (3.57)	13.8(4.31)	16.8 (3.93)	-	_		

Table 3. Electronic and IR spectra of Zn-TPhP complexes with various ligands

^a $\Delta\lambda$ is the shift of Zn–TPhP absorption maxima in chloroform stabilized with 1-hexene. The absence of $\Delta\lambda$ and log ϵ at certain wavelengths is caused by the overlap with absorption bands of colored ligands. ^b We failed to detect absorption bands of the N \rightarrow O bond since they overlap with own Zn–TPhP absorption bands (1439 s, 1339 s, 1205 m, 1175 m, 1068 m, 1001 v.s, 995 v.s, 799 s, 751 s, 702 s). Compounds **Ik**, **II**, **IIb**, **IIh**, and **IIk** were not isolated pure and their IR spectral data are absent.

EXPERIMENTAL

The IR spectra were recorded in KBr on a Perkin– Elmer Paragon-1000FTIR device in the range 4000– 300 cm⁻¹. The electronic absorption spectra were obtained on a Specord UV-Vis spectrometer and on an FEK KFK-3 in the range 300–800 nm. The *N*-oxides were synthesized and purified by the procedures in [25, 27, 30-34]. Pyridine, 4-methylpyridine, and quinoline were kept over KOH and distilled. Zn–TPhP and Cu–TPhP were synthesized by the procedures in [35] and purified by column chromatography on alumina, eluent chloroform.

RUSSIAN JOURNAL OF GENERAL CHEMISTRY Vol. 75 No. 8 2005

Chloroform and other solvents we purified according to [36].

The stability constants of the complexes in chloroform stabilized with 1-hexene (0.1 vol %) were calculated using the following formulas.

$$K = [\text{Zn}-\text{TFP} \cdot \mathbf{L}_n]/([\text{Zn}-\text{TFP}][\mathbf{L}]^n),$$

$$c_1 = (D - \varepsilon_2 cl)/[(\varepsilon_1 - \varepsilon_2 c)l)].$$

Here *D* is the optical density of the solution at a specified wavelength; ε_1 and ε_2 , molar extinctions of Zn–TPhP and Zn–TPhP · L_n at a specified wavelength; c_1 , concentration of Zn–TPhP or TPhP · L_n in the solution (M); *c*, total concentration of Zn–TPhP and its TPhP · L_n in the solution, numerically equal to the starting concentration of the metal porphyrin $(2 \times 10^{-5} \text{ M})$.

The extinctions of Zn–TPhP at a specified wavelength were determined from the optical density of the reference solution of the metal porphyrin. With TPhP·L_n molecular complexes, the quantity of ligand sufficient for complete complex formation (1000– 2000-fold excess) was added to the metal porphyrin solution; complex formation was considered complete, when D no longer changed on further increase of ligand concentration. With colored ligands, we constructed a D-c calibration curve and then, by subtracting the corresponding values, calculated the total optical density defined by porphyrin absorption.

At every determination of $\Delta\lambda$ on a KFK-3 FEK we detected location of absorption bands of the starting metal porphyrin before adding ligand. The error in $\Delta\lambda$ was $\pm 0.2-0.3$ nm.

The complexes of Zn–TPhP were synthesized by mixing equimolar amounts of metal porphyrin and ligand in acetone or its mixture with hexane. The fine crystals that formed after a time were washed with acetone and dried in air.

REFERENCES

- 1. Berezin, B.D. and Enikolopyan, N.S., *Metalloporfiriny* (Metal Porphyrins), Moscow: Nauka, 1988.
- Porfiriny: struktura, svoistva, sintez (Porphyrins: Structure, Properties, and Synthesis), Enikolopyan, N.S., Ed., Moscow: Nauka, 1987.
- Uspekhi Khimii Porfirinov (Advances in Porphyrin Chemistry), Golubchikov, O.A., Ed., St. Peterburg: Nauchno-Issled. Inst. Khimii S.-Peterb. Gos. Univ., 1997, vol. 1.
- Egan, T.J., Hunter, R., Kashula, C.H., Marques, H.M., Misplon, A., and Walden, J., *J. Med. Chem.*, 2000, vol. 43, no. 2, p. 283.

- 5. Antina, E.V., Lebedeva, N.Sh., and V'yugin, A.I., *Koord. Khim.*, 2001, vol. 27, no. 10, p. 784.
- Mashiko, T., Kastner, M.E., Spartalian, K., Scheidt, W.R., and Read, C.A., J. Am. Chem. Soc., 1978, vol. 100, no. 20, p. 6354.
- Hill, C.L. and Williamson, M.M., *Inorg. Chem.*, 1985, vol. 24, no. 19, p. 3024.
- Byrn, M.P., Curtis, C.J., Hsiou, Yu., Khan, S.I., Sawin, P.A., Tendick, S.K., Terzis, A., and Strouse, C.E., *J. Am. Chem. Soc.*, 1993, vol. 115, no. 21, p. 9480.
- Regulyatory rostu roslin u zemlerobstvi: Zbirnik naukovykh prats (Plant Growth Regulators in Agriculture: Collection of Scientific Works), Shevchenko, A.O., Ed., Kiev: Agroresursy, 1998.
- Albini, A. and Pietra, S., *Heterocyclic N-oxides*, Boca Raton: CRC, 1991.
- 11. Takekawa, K., Kitamura, S., Sugihara, K., and Ohta, S., *Xenobiotica*, 2001, vol. 31, no. 1, p. 11.
- Dowson, R.M.C., Elliott, C., Elliott, W.H., and Jones, K.M., *Data for Biochemical Reasearch*, Oxford: Univ. Press, 1986.
- 13. Ryzhakov, A.V., Andreev, V.P., and Rodina, L.L., *Heterocycles*, 2003, vol. 60, no. 2, p. 419.
- Ivashevskaja, S.N., Aleshina, L.A., Andreev, V.P., Nizhnik, Y.P., Chernyshev, V.V., and Schenk, H., Acta Crystallogr., Sect. C, 2002, vol. 58, no. 5, p. 300.
- Andreev, V.P., Nizhnik, Ya.P., Tunina, S.G., and Belashev, B.Z., *Khim. Geterotsikl. Soedin.*, 2002, no. 5, p. 634.
- 16. Lebedeva, N.Sh., Mikhailovskii, K.V., and V'yugin, A.I., *Koord. Khim.*, 2001, vol. 27, no. 10, p. 795.
- 17. Becker, H., *Einfurung in die Elektronentheorie organish-chemischer Reactionen*, Berlin: Wissenschaften, 1964.
- 18. Garvey, R.G., Nelson, J.H., and Ragsdale, R.O., *Coord. Chem. Rev.*, 1968, no. 3, p. 375.
- 19. Chmurzynski, L., Wawrzyniak, G., and Warnke, Z., J. Heterocycl. Chem., 1997, vol. 34, no. 1, p. 215.
- Rybachenko, V.I., Chotii, K.Yu., Kovalenko, V.V., and Shreder, G., *Zh. Obshch. Khim.*, 2001, vol. 71, no. 5, p. 839.
- Dega-Szafran, Z., Grundwald-Wyspianska, M., Kania, A., Kosturkiewicz, Z., Tykarska, E., and Szafran, M., J. Mol. Struct., 1995, vol. 356, no. 3, p. 169.
- 22. Kirksey, C.H. and Hambright, P., *Inorg. Chem.*, 1970, vol. 9, no. 4, p. 958.
- 23. Pal'm, V.A., Osnovy kolichestvennoi teorii organicheskikh reaktsii (Principles of Quantitative Theory of Organic Reactions), Leningrad: Khimiya, 1977.
- 24. Prezhdo, V.V., Vashchenko, E.V., Prezhdo, O.V.,

Pushko, A., and Lorents, Ya., Zh. Obshch. Khim., 1997, vol. 67, no. 6, p. 1009.

- Shreder, G., Rybachenko, V.I., Chotii, K.Yu., Ko-valenko, V.V., Grebenyuk, L.V., Lenska, B., and Eitner, K., *Zh. Obshch. Khim.*, 2003, vol. 73, no. 3, p. 486.
- 26. Katritzky, A.R., Short, D.L., and Boulton, A.J., J. Chem. Soc., 1960, no. 4, p. 1516.
- 27. Andreev, V.P., Batotsyrenova, E.G., Ryzhakov, A.V., and Rodina, L.L., *Khim. Geterotsikl. Soedin.*, 1998, no. 8, p. 1093.
- 28. Lomov, T.N. and Berezin, B.D., *Koord. Khim.*, 2001, vol. 27, no. 2, p. 96.
- Zaitseva, S.V., Zdanovich, S.A., Semeikin, A.S., and Golubchikov, O.A., *Zh. Obshch. Khim.*, 2003, vol. 73, no. 3, p. 499.

- 30. Ochiai, E., Aromatic Amine Oxides, New York: Elsevier, 1967.
- 31. Itai, T. and Kamiya, S., *Chem. Pharm. Bull.*, 1961, vol. 9, no. 2, p. 87.
- 32. Kamiya, S., Sueyoshi, S., Miyahara, M., Yanagimachi, K., and Nakashima, T., *Chem. Pharm. Bull.*, 1980, vol. 28, no. 5, p. 1485.
- 33. Acheson, R.M., Adcock, B., Glover, G.M., and Sutton, L.E., J. Chem. Soc., 1960, no. 8, p. 3367.
- Nizhnik, Ya.P. and Ryzhakov, A.V., Zh. Org. Khim., 1998, vol. 34, no. 6, p. 958.
- 35. Rothemund, P. and Menotti, A.R., J. Am. Chem. Soc., 1948, vol. 70, no. 5, p. 1808.
- 36. Gordon, A.J. and Ford, R.A., *The Chemist's Com*panion, New York: Wiley, 1972.