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Complexation of Zinc(II) and Ruthenium(II) Porphyrinates with Methyl Glycinate and Methyl *m*-Aminobenzoate

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Abstract—Zinc(II) and ruthenium(II) monohydroxyporphyrinates with a different arrangement of the reaction center in the *meso*-aryl moiety of the macrocycle were synthesized, and their ability of complexing with the methyl esters of glycine and *m*-aminobenzoic acid in toluene were studied using the methods of spectrophotometric titration and ^{1}H NMR spectroscopy. The stability constants of the resulting complexes and concentration ranges of their existence were determined.

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Analysis of published data shows that zinc(II) and ruthenium(II) porphyrinates can show effective complexing ability with respect to amino acids [1–7]. In the case of zinc porphyrinates [ZnP(Solv)] the main factor for linking is the coordination interaction between the reaction center of the substrate molecule and the zinc porphyrinate cation. In the case of ruthenium porphyrinates [RuP(CO)(Solv)], the metal cation can bind successively two molecules of amino acid. Moreover, if the binding of the first molecule of the substrate readily occurs at the location of solvent molecule, the binding of the second molecule of the substrate, which occurs at the location of the CO group, requires more rigid conditions [8].

The processes of selective binding of amino acids by zinc and ruthenium porphyrinates are of particular interest, when the substrate is *recognized* through coordination interaction of the metal cation of the porphyrin receptor reaction center with the simultaneous formation of H-bonds on the periphery of the macrocycle (the so-called two-center binding of the substrate molecule by the receptor molecule) [1, 2].

In continuation of our research on the creation of tetrapyrrole receptors for selective binding of amino acids [9-11], we synthesized 10-aryl-2,18-diethyl-3,17-dimethylporphyrin ligands with different arrangements of the reaction center in the *meso*-aryl moiety of the macrocycle, as well as related zinc and ruthenium complexes. The methods of spectrophotometric titration and ^{1}H NMR spectroscopy were used to investigate the complexing ability of the synthesized porphyrinates with respect to methyl glycinate and methyl *m*-aminobenzoate. The constants of stability of the resulting complexes and concentration ranges of their existence were determined.

In this paper, by the reaction of 5,5'-diformyl-4,4'-dimethyl-3,3'-diethyl-2,2'-dipyrrolylmethane (**I**) with *meso*-(2-X-phenylene)dipyrrolylmethanes [X = H (**II**), OH (**III**), OCH_2OH (**IV**)] in ethanol in the presence of hydrobromic acid followed by oxidation of the intermediate porphyrinogenes by tetrachlorbenzoquinone we synthesized 10-phenyl-2,18-diethyl-3,17-dimethylporphyrin (**V**), 10-(2-hydroxyphenylene)-2,18-diethyl-3,17-dimethylporphyrin (**VI**), and 10-(2-hydroxymethyleneoxyphenylene)-2,18-diethyl-3,17-dimethylporphyrin (**VII**) (see scheme). Average yield of the desired products was 25%. By the reaction of the porphyrin ligands (**V–VII**) with zinc acetate in DMF the corresponding zinc porphyrinates (**VIII–X**) were obtained. Ruthenium porphyrinates $RuP(CO)(H_2O)$ (**XI-XIII**) were obtained by boiling the porphyrin ligand (**V–VII**) with $Ru_3(CO)_{12}$ in phenol.

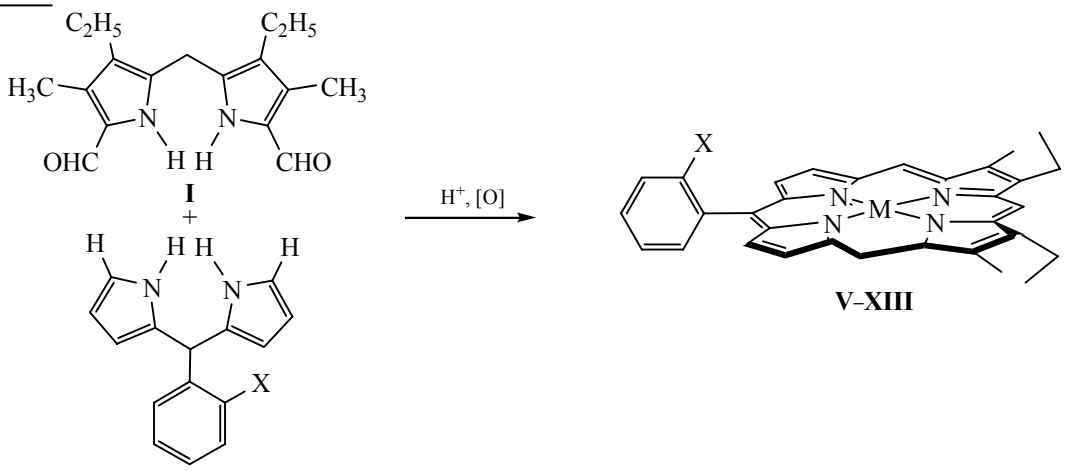
Coordinatively unsaturated zinc porphyrinates **VIII–X** coordinate amino acid molecules to the zinc cation axially to form complexes ZnP(L) according to Eq. (1):

$$ZnP + L \leftrightarrow ZnP(L). \quad (1)$$

The six-coordinated ruthenium porphyrinates RuP(CO)(Solv), where Solv = H_2O or EtOH, form stable complexes with amino acids RuP(CO)L according to Eq. (2):

$$RuP(CO)(Solv) + L \rightleftarrows RuP(CO)L + Solv. \quad (2)$$

At the axial coordination of multifunctional organic ligands on the central cation of zinc (**IX, X**) and ruthenium (**XII, XIII**) porphyrinates, when the receptor molecule and the substrate contain complementary reaction centers, the formation is possible of the porphyrinate-ligand complexes with two sites of binding.



II–IV **V–XIII**

X = H (**II, V, VIII, XI**), OH (**III, VI, IX, XII**), O(CH_2)OH (**IV, VII, X, XIII**), M = H_2 (**V–VII**), Zn (**VIII–X**), Ru(CO)(H_2O) (**XI–XIII**).

The process of the formation by ligand **I** of the axial complexes ZnP–L with one donor-acceptor bond or with multiple binding sites is accompanied by upfield shifts in ^{1}H NMR spectra of the proton signals of axial-coordinated aromatic ligands and the red shift by10–15 nm of absorption bands in the EAS of the reaction system receptor-substrate.

Complexation of ligand **II** is characterized by ever stronger upfield shifts of proton signals of the ligands (~0.6 ppm) in ^{1}H NMR spectra, but a much smaller red shift of the absorption bands (1–3 nm) in the electron absorption spectra of the reaction system.

Spectrophotometric study of complexation of zinc porphyrinate **VIII** and ruthenium porphyrinate **XI,** which have no hydroxy groups, with methyl glycinate (L1) and *methyl m*-aminobenzoare (L2) showed the formation of complexes with a donor-acceptor bond (Zn–N). The spectral changes observed during the formation of the complexes **VIII**–L1, **XI**–L1, **VIII**–L2, and **XI**–L2, and the corresponding titration curves by an example of a system of **VIII**–L1 are shown in Fig. 1. The existence of a single step in the spectrophotometric titration curve indicates that under these conditions the system forms a complex of only one type. The complex composition 1:1 follows from the graphic dependence log $[(A_o - A_d)/(A_d - A_e)]$ vs. logs of the ligand, which has a slope of ~1. As can be seen from the table, stability of the ruthenium porphyrinate-amino acid complexes with a single binding site is by about two orders of magnitude higher than that of the corresponding zinc porphyrinate complexes with the same substrate.

Spectral changes at the titration of porphyrinates **IX** and **XII** by the substrate L1 are similar to the changes shown in Fig. 1, but the saturation of the reaction system in these cases occurs at lower concentrations of the substrate. The slope of the plot log $[(A_o - A_d)/(A_d - A_e)]$ vs. log c_{ligand} for these systems also equals to unity. The increase in stability constants K_{stab} (~4-fold) in the systems of **IX**–L1 and **XII**–L1 compared with the systems of **VIII**–L1 and **XI**–L1 suggests that a complex is formed with two binding sites between the porphyrinate and methyl ester of α-amino acid (donor-acceptor M–N bond and a hydrogen bond between the carbonyl oxygen atom of the ester and hydroxy group of the porphyrinate). Probably, in the cases of the zinc and ruthenium porphyrinates **IX** and **XII** there is a good geometric correspondence between the reaction

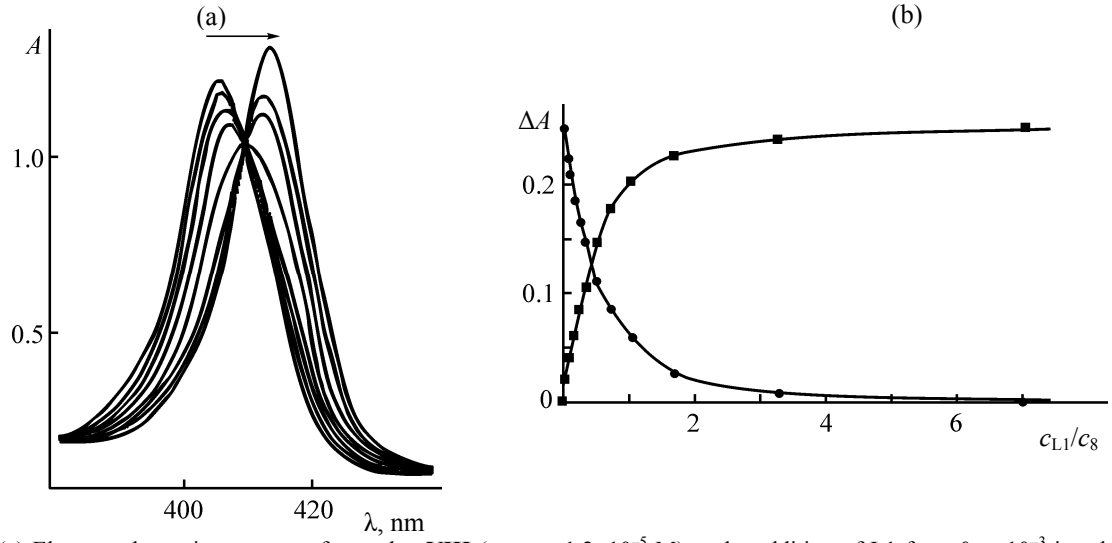
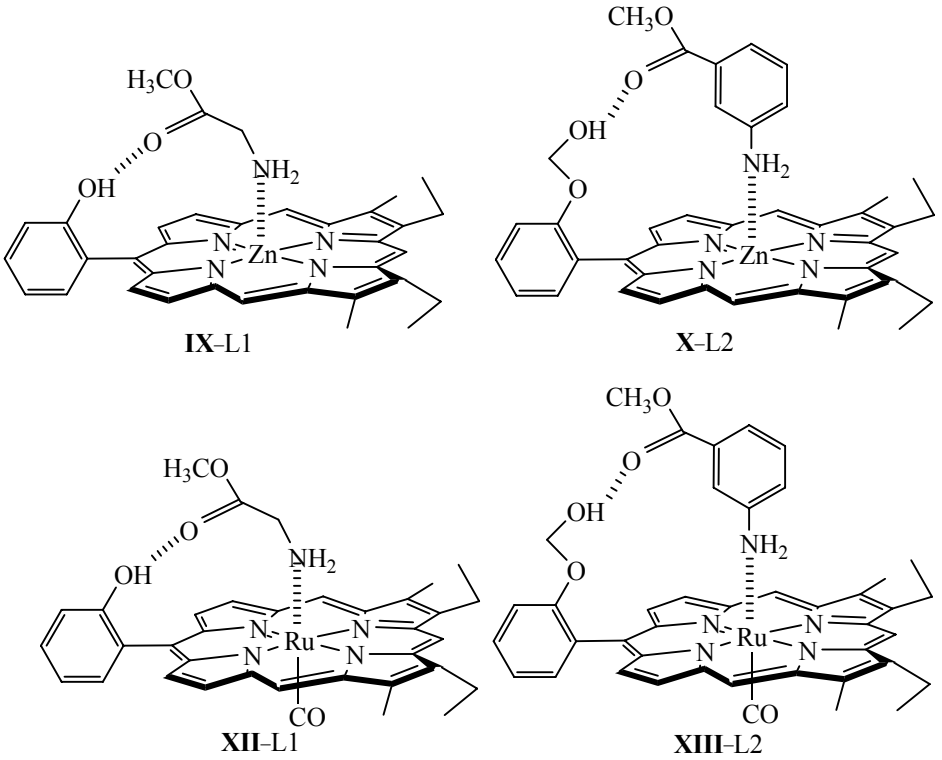


Fig. 1. (a) Electron absorption spectra of complex **VIII** (c_{porph} = 1.2×10^{-5} M) at the addition of L1 from 0 to 10^{-3} in toluene and (b) the spectrophotometric titration curves of complex **VIII** with L1 on "descending" and "growing" wavelengths (20°C), c_{porph} = 1.2×10^{-5} M , c_{L1} = 0–10^{-3} M).

centers in the receptor-substrate system and the hydroxy group in *ortho*-position of the phenyl substituent and the carboxy group of glycine, which ensures the formation of a second bond.



The corresponding ^{1}H NMR spectra of the complex provide the confirmation of the formation of porphyrinate–amino acid complexes with two sites of binding. In the presence of L1, in the spectrum of ruthenium porphyrinate **XII** in deuterochloroform the signal of the OH group proton in the aryl moiety of the tetrapyrrole macrocycle is shifted downfield by 1.35 ppm, and in the spectrum of zinc porphyrinate **IX**, by 12 ppm.

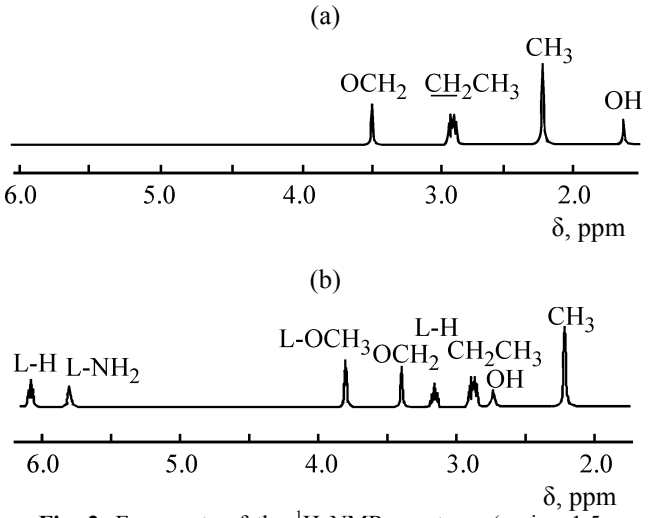


Fig. 2. Fragments of the ^{1}H NMR spectrum (region 1.5–6.1 ppm) of porphyrinate **X** (a) and its complex with L2 (b), deuterochloroform (25°C).

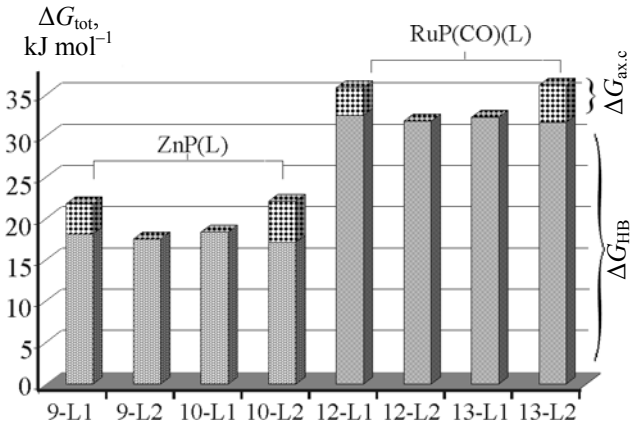


Fig. 3. Contributions to the total binding energy (ΔG_{tot}) of complexes porphyrinates–amino acid of the energy axial coordination ($\Delta G_{ax.c}$) and the hydrogen bond energy (ΔG_{HB}).

A significant increase in the stability constants $K_{stab.}$ (more than 7 times in the zinc porphyrinate **X** and more than 6 times in the ruthenium porphyrinate **XIII**) was found also for the porphyrinates with the hydroxy group in the hydroxymethyleneoxyphenylene fragment at their interaction with L2 (see the table). At the formation of these complexes, in the corresponding ^{1}H NMR spectra the signal of the proton of OH group of the porphyrinate aryl moiety is shifted downfield (by ~1.20 ppm), whereas the signals of the protons of benzene ring of the ligand are shifted upfield (by ~5.0 ppm for the *ortho*-aryl protons of the substrate) (Fig. 2).

A quantitative measure of the increasing stability of the porphyrinate-amino acid complexes due to additional hydrogen bond may be the ratio of K'_{stab}/K'_{stab}, where the K'_{stab} is the binding constant of porphyrin with the hydroxy group, K_{bind} is the binding constant of a porphyrin of similar structure, but without the hydroxy group [1] (see the table). The total binding energies ΔG_{total} of the complexes and the energies of individual bonds ΔG_{axial} and $\Delta G_{H\text{-}bond}$ calculated by standard methods [1] using the formulas (3)–(5) are shown in the diagram in Fig. 3.

The stability constants of complexes of porphyrinates **VIII–XIII**–amino acid ester (K_{st}, M^{-1}) in toluene at 25°C[a]

Porphyrinates	Complexes with L1		Complexes with L2	
	K_{st}, M^{-1}	$K_{st}/K_{st}^{compare}$	K_{st}, M^{-1}	$K_{st}/K_{st}^{compare}$
VIII	1510	–	1023	–
IX	6850	4.5[b]	1200	1.2[b]
X	1680	1.1[b]	7610	7.5[b]
XI	5.1×10^5	–	2.8×10^5	–
XII	19.5×10^5	3.8[c]	2.5×10^5	0.9[c]
XIII	4.7×10^5	1.1[c]	9.7×10^5	6.2[c]

[a] The error in estimation of K_{st} zinc porphyrinates is 3–5%, for ruthenium porphirinates, 5–7%. [b] Complex **VIII** for comparison. [c] Complex **XI** for comparison.

As is evident from these data, the strongest hydrogen bonds with amino acid esters form the zinc porphyrinates, and the strongest electron-donating bonds with amino groups of the esters form ruthenium porphyrinates.

Thus, the techniques described in this paper allowed us to synthesize zinc and ruthenium hydroxyporphyrinates showing the ability to two-center binding methyl glycinate and methyl *m*-aminobenzate. The zinc and ruthenium *o*-hydroxyphenylporphyrinates due to the formation of additional hydrogen bonds at the periphery of the macrocycle effectively bind methyl glycinate, while the zinc and ruthenium porphyrinates with the hydroxy group in the conformationally mobile *ortho*-hydroxymethyleneoxyphenylene fragment of the macrocycle form stable complexes with two sites of binding to methyl *m*-aminobenzate. In general, complexes of ruthenium porphyrinates with the amino acid esters are characterized by a higher stability, but lesser selectivity than similar complexes formed by the zinc porphyrinates.

EXPERIMENTAL

The electron absorption spectra (EAS) of porphyrinates and their complexes with amino acid esters in toluene were recorded on a spectrophotometer "Cary 100." ^{1}H NMR spectra were recorded on a spectrometer Brusker VC-500 at operating frequency 500.17 MHz in deuterochloroform, internal reference TMS.

The stability constants (K_{st}) of complexes of zinc bisporphyrinates (A) with the corresponding substrates (B) were evaluated by spectrophotometric titration:

$$K_{st} = \frac{[AB]}{[A][B]} = 1/[B] \quad \frac{\Delta A_{i,\lambda 1}}{\Delta A_{o,\lambda 1}} \cdot \frac{\Delta A_{o,\lambda 2}}{\Delta A_{i,\lambda 2}},$$

where λ_1 is the decreasing wavelength, λ_2 is the increasing wavelength [A] is the concentration of bisporphyrinate, [S] is the concentration of substrate, ΔA_o is the maximum change in optical density of the solution at a given wavelength, ΔA_i is the change in optical density solution at a given wavelength at a given concentration as described in [9–11].

10-(2-hydroxyphenylene)-2,18-diethyl-3,17-dimethylporphyrin (VI). 5,5'-Diformyl-4,4'-dimethyl-3,3'-diethyl-2,2'-dipyrrolylmethane (0.5 g, 1.5 mmol) and *meso*-(2-hydroxyphenylene)dipyrrolylmethane (0.5 g, 1.7 mmol) were dissolved in 50 ml of ethanol containing 1 ml of hydrobromic acid. The solution was stirred for 2 h, and to the reaction mixture was added tetrachloro-1,2-benzoquinone (1 g, 4.1 mmol) in 10 ml of chloroform. The solvent was evaporated and the residue was washed with 10% KOH solution, dried, and chromatographed on silica gel eluting with benzene. 3312 (NH), 3210 (OH), 2982, 2928, 2875 (CH), 1665, 1617 (C–C), 1507, 1480, 1170, 1109, 1068 (δ_{CH}), 1353, 1307 (C≡N), 1230 (δ_{OH}), 967 (δ_{NH}), 832, 753, 723 (γ_{CH}), 696 (γ_{NH}). EAS (toluene), λ, nm (log ε): 630 (3.36), 579 (3.89), 551 (3.70), 517 (4.24), 405 (5.13). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 10.12 s (2H, *ms*-H), 10.08 s (1H, *ms*-H), 8.82 d (2H, CH_{Pyr}, *J* 4.8), 8.76 d (2H, CH_{Pyr}, *J* 4.8), 7.52 t (1H, Ar, *J* 7.7), 7.36 m (2H, Ar), 7.21 d (1H, Ar, *J* 7.7), 2.97 q (4H, $\underline{CH_2}CH_3$, *J* 8.2), 5.31 s (1H, OH), 2.24 s (6H, CH_3), 1.18 t (6H, $CH_2\underline{CH_3}$, *J* 8.2), –3.53 br.s (1H, NH), –3.56 br.s (1H, NH). Found, %: C 81.23; H 6.04; N 9.94. $C_{38}H_{34}N_4O$. Calculated, %: C 81.54; H 6.08; N 10.17.

Similarly, 10-phenyl-2,18-diethyl-3,17-dimethylporphyrin (**V**) and 10-(2-hydroxymethyleneoxyphenylene)-2,18-diethyl-3,17-dimethylporphyrin (**VII**) were obtained.

10-Phenyl-2,18-diethyl-3,17-dimethylporphyrin (V). Yield: 23%. R_f 0.53, (Al_2O_3, eluent – benzene). IR spectrum (KBr), ν, cm^{-1}: 3310 (NH), 2980, 2929, 2870 (CH), 1663, 1616 (C–C), 1505, 1482, 1170, 1108, 1069 (δ_{CH}), 1350, 1306 (C≡N), 967 (δ_{NH}), 830, 752, 723, 548 (γ_{CH}), 691 (γ_{NH}). EAS (toluene), λ, nm (log ε): 631 (3.33), 579 (3.89), 550 (3.70), 517 (4.24), 404 (5.13). ^{1}H NMR spectrum, δ, ppm: 10.10 s (2H, *ms*-H), 10.06 s (1H, *ms*-H), 8.80 d (2H, CH_{Pyr}, *J* 4.6), 8.73 d (2H, CH_{Pyr}, *J* 4.6), 7.52 t (1H, Ar, *J* 7.8), 7.26 m (4H, Ar), 2.95 q (4H, $\underline{CH_2}CH_3$, *J* 8.2), 2.22 s (6H, CH_3), 1.15 t (6H, $CH_2\underline{CH_3}$, *J* 8.2), –3.50 br.s (1H, NH), –3.54 br.s (1H, NH). Found, %: C 83.50; H 6.19; N 10.23. $C_{38}H_{34}N_4O$. Calculated, %: C 83.82; H 6.26; N 10.41.

10-(2-Hydroxymethyleneoxyphenylene)-2,18-diethyl-3,17-dimethylporphyrin (VII). Yield: 21%. R_f 0.49, (Al_2O_3, eluent – benzene). IR spectrum (KBr), ν, cm^{-1}: 3310 (NH), 3215 (OH), 2989, 2930, 2878 (CH), 1677, 1620 (C–C), 1511, 1485, 1175, 1110, 1064 (δ_{CH}), 1356, 1308 (C≡N), 1245, 1030 (C–O–C), 1237, 1014 (δ_{OH}), 969 (δ_{NH}), 838, 755, 728, 520 (γ_{CH}), 697 (γ_{NH}). EAS (toluene), λ, nm (log ε): 632 (3.31), 580 (3.81), 551 (3.73), 518 (4.21), 406 (5.11). ^{1}H NMR spectrum, δ, ppm: 10.09 s (2H, *ms*-H), 10.01 s (1H, *ms*-H), 8.78 d (2H, CH_{Pyr}, *J* 4.8), 8.71 d (2H, CH_{Pyr}, *J* 4.8), 7.50 t (1H, Ar, *J* 7.7), 7.31 m (2H, Ar), 7.19 d (1H, Ar, *J* 7.7), 2.90 q (4H, $\underline{CH_2}CH_3$, *J* 8.0), 1.68 s (1H, OH), 3.53 s (2H, $O\underline{CH_2}$), 2.21 s (6H, CH_3), 1.13 t (6H, $CH_2\underline{CH_3}$, *J* 8.0), –3.57 br.s (1H, NH), –3.59 br.s (1H, NH). Found, %: C 79.19; H 6.01; N 9.42. $C_{39}H_{36}N_4O_2$. Calculated, %: C 79.41; H 6.08; N 9.76.

Zn(II) 10-(2-hydroxyphenylene)-2,18-diethyl-3,18-dimethylporphyrinate (IX). To a solution of the porphyrin ligand (30 mg) in DMF (70 ml) was added an excess (1:10 mole) of zinc acetate and the reaction mixture was boiled for 30 min. The content of the flask was cooled and diluted with water (1:1). The precipitate was filtered off, dried, and chromatographed on alumina, eluting with CH_2Cl_2–C_6H_{14}, 1–1. The solvents were distilled off in a vacuum, the residue was recrystallized from a mixture of CH_2Cl_2-CH_3OH, 1:2. Yield: 81%. R_f 0.78, (Al_2O_3, eluent – benzene). IR spectrum (KBr), ν, cm^{-1}: 3216 (OH), 3058, 2928, 2850 (NH); 1665, 1617 (C–C), 1507, 1480, 1170, 1094, 1068 (δ_{CH}), 1353, 1307 (C≡N), 1233 (δ_{OH}), 999 (Zn–N), 829, 753, 703 (γ_{CH}), 454, 404 (Zn–N). EAS (toluene), λ, nm (log ε): 579 (3.45), 540 (4.23), 405 (5.01). ^{1}H NMR spectrum, δ, ppm: 10.14 s (2H, *ms*-H), 10.11 s (1H, *ms*-H), 8.79 d (2H, CH_{Pyr}, *J* 4.8), 8.71 d

(2H, CH_{Pyr}, *J* 4.8), 7.49 t (1H, Ar, *J* 7.7), 7.32 m (2H, Ar), 7.19 d (1H, Ar, *J* 7.7), 2.94 q (4H, $\underline{CH_2}CH_3$, *J* 8.0), 5.29 s (1H, OH), 2.21 s (6H, CH_3), 1.14 t (6H, $CH_2\underline{CH_3}$, *J* 8.0).

Complex IX–L1. ^{1}H NMR spectrum, δ, ppm: 10.18 s (2H, *ms*-H), 10.06 s (1H, *ms*-H), 8.75 d (2H, CH_{Pyr}, *J* 4.6), 8.68 d (2H, CH_{Pyr}, *J* 4.6), 7.46 t (1H, Ar, *J* 7.7), 7.29 m (2H, Ar), 7.15 d (1H, Ar, *J* 7.7), 6.41 s (1H, OH), 5.02 br.s (2H, NH_2), 3.89 s (3H, OCH_3), 2.90 q (4H, $\underline{CH_2}CH_3$, *J* 8.0), 2.19 s (6H, CH_3), 1.16 t (6H, $CH_2\underline{CH_3}$, *J* 8.0), 3.05 m (2H, CH_2), 3.83 s (3H, OCH_3).

Similarly, zinc(II) 10-phenyl-2,18-diethyl-3,17-dimethylporphyrinat (**VIII**) and zinc(II) 10-(2-hydroxymethyleneoxyphenylene)-2,18-diethyl-3,17-dimethylporphyrinate (**X**) were obtained.

Zinc(II) 10-phenyl-2,18-diethyl-3,17-dimethylporphyrinate zinc (VIII). Yield: 85%. R_f 0.73, (Al_2O_3, eluent – benzene). IR spectrum (KBr), ν, cm^{-1}: 3070, 2929, 2869 (CH), 1643, 1606 (C–C), 15010, 1482, 1170, 1086, 1074 (δ_{CH}), 1350, 1306 (C≡N), 998 (Zn–N), 826, 752, 708 (γ_{CH}), 436, 403 (Zn–N). EAS (toluene), λ, nm (log ε): 578 (3.42), 541 (4.21), 404 (5.00). ^{1}H NMR spectrum, δ, ppm: 10.12 s (2H, *ms*-H), 10.08 s (1H, *ms*-H), 8.77 d (2H, CH_{Pyr}, *J* 4.6), 8.69 d (2H, CH_{Pyr}, *J* 4.6), 7.47 t (1H, Ar, *J* 7.8), 7.22 m (4H, Ar), 2.92 q (4H, $\underline{CH_2}CH_3$, *J* 8.2), 2.20 s (6H, CH_3), 1.11 t (6H, $CH_2\underline{CH_3}$, *J* 8.2).

Zinc(II) 10-(**2-hydroxymethyleneoxyphenylene)-2,18-diethyl-3,17-dimethylporphyrinate (X**). Yield: 77%. R_f 0.71, (Al_2O_3, eluent – benzene). IR spectrum (KBr), ν, cm^{-1}: 3219 (OH), 3030, 2930, 2850 (CH), 1677, 1620 (C–C), 1512, 1485, 1175, 1110, 1064 (δ_{CH}), 1356, 1308 (C≡N), 1240, 1032 (C–O–C), 12340 (δ_{OH}), 999 (Zn–N), 828, 755, 708 (γ_{CH}), 456, 403 (Zn–N). EAS (toluene), λ, nm (log ε): 580 (3.48), 541 (4.27), 407 (5.05). ^{1}H NMR spectrum, δ, ppm: 10.03 s (2H, *ms*-H), 9.99 s (1H, *ms*-H), 8.75 d (2H, CH_{Pyr}, *J* 4.8), 8.69 d (2H, CH_{Pyr}, *J* 4.8), 7.46 t (1H, Ar, *J* 7.8), 7.28 m (2H, Ar), 7.17 d (1H, Ar, *J* 7.8), 2.87 q (4H, $\underline{CH_2}CH_3$, *J* 8.0), 1.57 s (1H, OH), 3.51 s (2H, $O\underline{CH_2}$), 2.20 s (6H, CH_3), 1.18 t (6H, $CH_2\underline{CH_3}$, *J* 8.0).

Complex X–L2. ^{1}H NMR spectrum of, δ, ppm: 10.01 s (2H, *ms*-H), 9.98 s (1H, *ms*-H), 8.73 d (2H, CH_{Pyr}, *J* 4.6), 8.67 d (2H, CH_{Pyr}, *J* 4.6), 7.69 d (1H, Ar, *J* 7.6), 7.43 t (1H, Ar, *J* 7.8), 7.26 m (2H, Ar), 7.14 d (1H, Ar, *J* 7.8), 2.77 s (1H, OH), 6.07 t (1H, Ar, *J* 7.6), 5.81 s (2H, NH_2), 3.82 s (3H, OCH_3), 3.45 s (2H, OCH_2), 3.21 m (2H, Ar), 2.85 q (4H, $\underline{CH_2}CH_3$, *J* 8.0), 2.18 s (6H, CH_3), 1.16 t (6H, $CH_2\underline{CH_3}$, *J* 8.0).

Ruthenium(II) 10-(2-hydroxyphenylene)-2.18-diethyl-3,17-dimethylporphyrinate (CO)(H_2O) (XII). A mixture of porphyrin **I** (50 mg, 0.059 mmol) and $Ru_3(CO)_{12}$ (40 mg, 0.06 mmol) was boiled in 5 g of phenol for 3 min. The reaction mixture was cooled, dissolved in 20 ml of DMF, poured into water, washed with hot water, twice chromatographed on silica gel eluting with chloroform. Yield: 39%. R_f 0.67, (Al_2O_3, eluent – benzene). IR spectrum (KBr), ν, cm^{-1}: 3217 (OH), 2985, 2928, 2850 (CH), 1940 (C=O), 1665, 1617 (C–C), 1507, 1480, 1170, 1109, 1068 (δ_{CH}), 1353, 1307 (C≡N), 1230 (δ_{OH}), 1012 (Ru–N), 830, 763, 723 (γ_{CH}), 520 (Ru–CO), 464, 407 (Ru–N). EAS (toluene), λ, nm (log ε): 547 (4.57), 517 (4.01), 404 (5.12). ^{1}H NMR spectrum, δ, ppm: 10.12 s (2H, *ms*-H), 10.07 s (1H, *ms*-H), 8.77 d (2H, CH_{Pyr}, *J* 4.8), 8.69 d (2H, CH_{Pyr}, *J* 4.8), 7.44 t (1H, Ar, *J* 7.8), 7.33 m (2H, Ar), 7.17 d (1H, Ar, *J* 7.8), 2.91 q (4H, $\underline{CH_2}CH_3$, *J* 8.2), 5.30 s (1H, OH), 2.17 s (6H, CH_3), 1.11 t (6H, $CH_2\underline{CH_3}$, *J* 8.2).

Complex XII–L1. ^{1}H NMR spectrum, δ, ppm: 10.16 s (2H, *ms*-H), 10.01 s (1H, *ms*-H), 8.73 d (2H, CH_{Pyr}, *J* 4.6), 8.66 d (2H, CH_{Pyr}, *J* 4.6), 7.41 t (1H, Ar, *J* 7.7), 7.30 m (2H, Ar), 7.12 d (1H, Ar, *J* 7.7), 3.89 s (3H, OCH_3), 2.85 q (4H, $\underline{CH_2}CH_3$, *J* 8.0), 6.35 s (1H, OH), 2.15 s (6H, CH_3), 5.12 br.s (2H, NH_2), 1.13 t (6H, $CH_2\underline{CH_3}$, *J* 8.0), 0.96 s (3H, CH_3), 3.08 m (2H, CH_2), s (3H, OCH_3).

Similarly, ruthenium(II) 10-phenyl-2,18-diethyl-3,17-dimethylporphyrinate (CO)(H_2O) (**XI**) and ruthenium(II) 10-(2-hydroxymethyleneoxyphenylene)-2,18-diethyl-3,17-dimethylporphyrinate (CO)(H_2O) (**XIII**) were obtained.

Ruthenium(II) 10-phenyl-2,18-diethyl-3,17-dimethylporphyrinate (CO)(H_2O) (XI). Yield: 43%. R_f 0.61, (Al_2O_3, eluent – benzene). IR spectrum (KBr), ν, cm^{-1}: 2980, 2929, 2850 (CH), 1942 (C=O), 1663, 1616 (C–C), 15010, 1482, 1170, 1108, 1069 (δ_{CH}), 1350, 1306 (C≡N), 1010 (Ru–N), 832, 762, 723 (γ_{CH}), 548 (Ru–CO), 464, 405 (Ru–N). EAS (toluene), λ, nm (log ε): 545 (4.53), 515 (4.04), 406 (5.17). ^{1}H NMR spectrum, δ, ppm: 10.09 s (2H, *ms*-H), 10.01 s (1H, *ms*-H), 8.75 d (2H, CH_{Pyr}, *J* 4.8), 8.63 d (2H, CH_{Pyr}, *J* 4.8), 7.46 t (1H, Ar, *J* 7.7), 7.21 m (42H, Ar), 2.90 q (4H, $\underline{CH_2}CH_3$, *J* 8.2), 2.13 s (6H, CH_3), 1.07 t (6H, $CH_2\underline{CH_3}$, *J* 8.2).

Ruthenium(II) 10-(2-hydroxymethyleneoxyphenylene)-2,18-diethyl-3,17-dimethylporphyrinate (CO) · (H_2O) (XIII). Yield: 33%. R_f 0.51, (Al_2O_3, eluent – benzene). IR spectrum (KBr), ν, cm^{-1}: 3220 (OH), 2990, 2930, 2850 (CH), 1938 (C=O), 1677, 1620 (C–C), 1512, 1485, 1175, 1110, 1064 (δ_{CH}), 1356, 1308 (C≡N), 1246, 1032 (C–O–C), 1236 (δ_{OH}), 1014 (Ru–N), 833, 765, 728 (γ_{CH}), 520 (Ru–CO), 466, 408 (Ru–N). ^{1}H NMR spectrum, δ, ppm: 10.09 s (2H, *ms*-H), 10.05 s (1H, *ms*-H), 8.79 d (2H, CH_{Pyr}, *J* 4.8), 8.73 d (2H, CH_{Pyr}, *J* 4.8), 7.45 t (1H, Ar, *J* 7.7), 7.21 m (2H, Ar), 7.04 d (1H, Ar, *J* 7.7), 1.45 s (1H, OH), 3.49 s (2H, O$\underline{CH_2}$), 2.82 q (4H, $\underline{CH_2}CH_3$, *J* 8.2), 2.13 s (6H, CH_3), 1.13 t (6H, $CH_2\underline{CH_3}$, *J* 8.2).

Complex XIII–L2. ^{1}H NMR spectrum, δ, ppm: 10.07 s (2H, *ms*-H), 10.04 s (1H, *ms*-H), 8.77 d (2H, CH_{Pyr}, *J* 4.6), 8.71 d (2H, CH_{Pyr}, *J* 4.6), 7.69 d (1H, Ar, *J* 7.6), 7.42 t (1H, Ar, *J* 7.8), 7.18 m (2H, Ar), 7.00 d (1H, Ar, *J* 7.8), 6.01 t (1H, Ar, *J* 7.6), 5.12 br.s (2H, NH_2), 3.79 s (3H, OCH_3), 2.65 s (1H, OH), 3.43 s (2H, O$\underline{CH_2}$), 2.61 m (2H, Ar), 2.80 q (4H, $\underline{CH_2}CH_3$, *J* 8.0), 2.11 s (6H, CH_3), 1.10 t (6H, $CH_2\underline{CH_3}$, *J* 8.0).

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