Variations in Functional Substitution of the Macroheterocycle and Structure of Stable Rhenium(V) Porphyrins

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Received December 20, 2013

Abstract—Rhenium(V) porphyrin complexes with different natures of substituents and substitution patterns in the organic fragment (5,10,15,20-tetraphenylporphyrin, 2,3,7,8,12,13,17,18-octaethylporphyrin, 2,3,7,8,12,13,17,18-octaethyl-5-phenylporphyrin, and 2,3,7,8,12,13,17,18-octaethyl-5,15-diphenylporphyrin dianions) and different axial ligands {phenoxide and chloride ions, 2'-(pyridin-4-yl)-5'-(pyridin-2-yl)-1'-(pyridin-3-ylmethyl)pyrrolidino[3',4':1,9](C₆₀- I_h)[5,6]fullerene} have been synthesized, and their principal properties (spectral parameters and reactivity toward fullerene-containing base) have been studied.

DOI: 10.1134/S1070428014090218

Interest in purposeful structural modification of aromatic macroheterocyclic porphyrin molecules equally applies to both free bases (H₂P) and metal complexes. In some cases, of primary interest are just metal porphyrins, e.g., in catalysis. The presence of a metal atom is responsible for a useful property of an organic compound, whereas functional substitution in the aromatic fragment allows control over that property. Rhenium porphyrins are not an exception; there are published data on their use in radiopharmacology [1] and catalysis [2]. According to [3], a very promising property of rhenium porphyrins is their ability to form in acids various oxidized and protonated species whose stability is an important factor determining their catalytic activity in specific reactions in aggressive media [4]. Modification of porphyrin complexes, in particular with rhenium(V), via variation of axial ligands makes it possible to obtain such active photovoltaic systems as porphyrin-fullerenes. Porphyrin-fullerene composite materials are now used as organic thin-film [5] and bulk [6] solar cells, which are more advantageous than inorganic analogs due to their flexibility and lower cost.

Taking into account the above stated, the goal of the present work was to synthesize and examine principal properties (spectral parameters and reactivity toward a fullerene-containing base) of rhenium(V) porphyrins **I–VII** with different substitution patterns in the organic

fragment and different axial ligands. Compounds II, IV, and VII were previously unknown.

Rhenium(V) porphyrin complexes I, II, IV, and V were synthesized by reaction of the corresponding porphyrin as free base with H_2ReCl_6 in boiling phenol (Scheme 1) according to the procedure developed for the preparation of complex I [7]. Although the reactions were carried out under the same conditions, complexes I, IV and II, V had different compositions. Octaethylporphyrins gave rise to mononuclear complexes in 70–75% yield. Bridged dinuclear complex I





II, $R^1 = Ph$, $R^2 = H$, X = PhO; III, $R^1 = Ph$, $R^2 = H$, X = Cl; IV, $R^1 = R^2 = Ph$, X = Cl; V, $R^1 = R^2 = H$, X = PhO; VI, $R^1 = R^2 = H$, X = Cl; VII, $R^1 = Ph$, $R^2 = H$, X = 2'-(pyridin-4-yl)-5'-(pyridin-2-yl)-1'-(pyridin-3-ylmethyl)pyrrolidino-[3',4':1,9](C₆₀-I_h)[5,6]fullerene.

was isolated in a good yield (75%) from the product mixture containing minor rhenium(III) complexes, (chloro)(5,10,15,20-tetraphenylporphyrinato)rhenium(III) (VIII, 0.5%) and (phenoxo)(5,10,15,20-tetraphenylporphyrinato)rhenium(III) (IX, 7%), and the results of this reaction were well reproducible. Obviously, in this case a mixture of three stable organic complexes is obtained in a one-pot mode. The formation of rhenium(V) porphyrin I from rhenium(IV) compound is likely to be accompanied by disproportionation of rhenium(IV) into Re³⁺ and Re⁵⁺ within the complexes [7]. Presumably, in the presence of HCl liberated during the process, rhenium(III) complexes only with 5,10,15,20-tetraphenylporphyrin are stable. For the same reason, the μ -oxo bridge in I does not undergo protonation and rupture with formation of mononuclear rhenium(V) complexes. Such complexes were obtained only from 2,3,7,8,12,13,17,18-octaethylporphyrin (compounds II, IV, V).

It should also be noted that octaethylporphyrins gave rise to rhenium(V) complexes containing either phenoxide or chloride ion as axial ligand. Presumably, both these types of complexes are formed in reactions with all the examined porphyrins, but only one of them can be isolated because of their different stabilities. Chloride-containing complexes can be obtained in quantitative yield from the corresponding phenoxide derivative. Compounds **III** and **VI** were synthesized by passing gaseous hydrogen chloride over a period of 10 min through a solution of compound **II** or **V**, respectively, in methylene chloride.

The optimal reaction time for the synthesis of **II** and **IV** was 5–6 h, and of **V**, 9 h. Introduction of one or two *meso*-phenyl substituents into 2,3,7,8,12,13,17,18-octaethylporphyrin molecule facilitates coordination with rhenium(V); however, 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrin failed to react with H_2ReCl_6 despite variation of the reactant ratio and solvent nature (benzonitrile, pyridine, DMF). Presumably, the reason is steric hindrances.

Stoichiometry and charge of the metal cation in rhenium porphyrins. Both μ -oxo dinuclear complex I and mononuclear complexes II–VII isolated by chromatography (see Experimental) displayed hyper-type electronic absorption spectra typical of rhenium(V) porphyrins (Fig. 1), which contained an additional band in the region 300–800 nm. These spectra can readily be distinguished from those of hypso-type commonly observed for rhenium(III) porphyrins and complexes with other d^0 and d^n (n > 6) metal cations



H₂TPP is 5,10,15,20-tetraphenylporpphyrin, H₂OEP is 2,3,7,8,12,13,17,18-octaethylporphyrin, H₂POEP is 2,3,7,8,12,13,17,18-octaethyl-5,15-diphenylporphyrin, and H₂DPOEP is 2,3,7,8,12,13,17,18-octaethyl-5,15-diphenylporphyrin.

[7–10]. Thus, compounds **I–VI**, and hence **VII**, are rhenium(V) derivatives.

The electronic absorption spectrum of dinuclear complex I essentially differs from the spectra of mononuclear complexes II–VI. The latter showed strong absorption in the region $\lambda \sim 350$ nm, while the absorption of I in that region was very weak (Fig. 1). Spectral variations accompanying mutual transformations of the mononuclear and μ -oxo dinuclear complexes and the composition of the equilibrium mixture were studied in [3] using the reaction of I with acetic acid in benzene as an example.

The structure of the isolated rhenium complexes was also studied by NMR spectroscopy. The number of signals and their intensities in the ¹H NMR spectra of **III** and **IV** indicated 1:1 composition of these complexes. Their purity and the absence of dinuclear complexes were confirmed by the ¹H–¹H 2D DOSY data (Fig. 2).

Compound V in C₆D₆ displayed in the ¹H NMR spectrum two signals from protons in the *meso* positions at δ 10.77 and 9.51 ppm. The lack of correlation between these signals in the ¹H–¹H 2D COSY and ¹H–¹H 2D ROESY spectra in C₆D₆, as well as signal separation by the diffusion coefficients in the ¹H–¹H 2D DOSY spectrum, indicated the presence of two compounds in solution. With account taken of pub-



Fig. 1. Electronic absorption spectra of complexes (1) I, (2, 3) V, and (4) VI in (1, 2) benzene and (3, 4) methylene chloride.

lished data [11] and our ¹H NMR data for compound I, the signal at δ 10.77 ppm can be assigned to a mononuclear complex of rhenium(V) with octaethylporphyrin, and the upfield signal at δ 9.51 ppm, to the μ -oxo dinuclear complex. Insofar as compound V was homogeneous (see Experimental), we presumed that it exists in benzene solution as an equilibrium mixture of mononuclear and dinuclear complexes. The electronic absorption spectrum of V in methylene chloride (Fig. 1, 3) shows prevalence of the mononuclear complex since the intensity of the Soret band (λ_{max} 343 nm) is higher than the intensity of the charge transfer band (λ_{max} 469 nm). The difference in the intensities of these bands decreases in going to benzene solution (Fig. 1, 2). Taking into account that benzene favors formation



Fig. 2. ¹H–¹H 2D DOSY spectra of complexes (a) III and (b) IV.

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of μ -oxo dinuclear complexes [12], decrease of the above difference may be related to the presence of traces of dinuclear complex, in keeping with the NMR data.

The ${}^{1}\text{H}{-}^{1}\text{H}$ 2D COSY spectrum of **VI** in CDCl₃ contained cross-peaks corresponding to only interaction between CH₂ and CH₃ protons. Compounds **III** and **IV** displayed correlations between protons in the *meso*-phenyl substituents (see Experimental).

Axial ligand nature. Rhenium complexes of octaethyl-substituted porphyrins contain an axial oxo ligand in the coordination sphere, which is confirmed by the presence in their IR spectra of a Re=O stretching vibration band at 950 cm⁻¹. Strong bands corresponding to phenoxy group (1451, 1589, 1486 cm⁻¹) and Re–O bond (670, 668 cm⁻¹) in the IR spectra of II and V (Fig. 3a) proved the presence of an axial PhO⁻ ligand. No such bands were observed in the IR spectrum of IV (Fig. 3b).



Fig. 3. IR spectra of complexes (a) **V** and (b) **IV** in KBr. The Re–O vibration band is marked with an asterisk (*), and vibration bands of the axial phenoxo ligand are marked with a bullet (\bullet).

No bands assignable to PhO⁻ were observed in the IR spectra of chlorine-containing complexes III and VI. The Re–N stretching vibration frequency remains almost the same, which suggests major contribution of the macrocyle to the force constant of that bond as opposed to the contribution of axial ligands. The presence of a *meso*-phenyl substituent (weak electron acceptor) in II and III leads to a small low-frequency shift of the Re-N vibration band relative to the corresponding band in the spectra of meso-unsubstituted compounds V and VI (see Experimental). A probable reason is the contribution of dative π -bonds involving aromatic system of the macrocycle. The IR spectrum of V contained an additional band at 454 cm^{-1} in the region of Re-N vibrations and a weak absorption band at 619 cm^{-1} (Fig. 3a), the latter being analogous to that observed for compound I and absent in the spectrum of **VI**. Strong absorption in the region $650-550 \text{ cm}^{-1}$ was assigned [12] to Mo-O-Mo vibrations in the u-oxo dinuclear molybdenum(V) complex with 5,10,15,20tetraphenylporphyrin. We can conclude that complex V in KBr, as well as in C₆D₆ (see above), is represented by an equilibrium mixture with a small amount of the corresponding u-oxo dinuclear complex.

The presence of PhO⁻ ligand in **II** and **V** was also confirmed by the ¹H–¹H 2D COSY and ¹H–¹H 2D ROESY spectra (see experimental) where the chemical shifts of aromatic protons were similar to those typical of phenol (δ 6.68, 7.15, and 6.82 ppm for *o*-H, *m*-H, and *p*-H, respectively [13]). No additional signals that could be assigned to protons in axial ligands were detected in the spectra of **III**, **IV**, and **VI**.

The presence of aromatic macroheterocycle. As noted above, the electronic absorption spectra of mononuclear complexes II-VI belong to the hyper type which is characterized by the presence of additional bands in the region λ 300–800 nm (Fig. 1). These are charge transfer bands, λ_{max} 440–480 nm [14]. The position of absorption bands in the electronic spectra of II-VI changes depending on the macrocyclic and axial ligand nature. The absorption maxima of II appear are located at longer wavelengths than those of V by 5-8 nm. Introduction of meso-phenyl substituents induces red shift of most absorption maxima in the spectra of chlorine-containing analogs III, IV, and VI. The Soret band therein is located at λ 351, 354, and 347 nm, and the charge transfer band, at λ 520, 525, and 518 nm, respectively. Analogous relation between the positions of absorption maxima and degree of meso-phenyl substitution was reported for manganese(III) octaethylporphyrin complexes [15]. The change in the position of the Soret band upon replacement of the PhO⁻ axial ligand by Cl⁻ is ~5 nm, whereas the charge transfer band shifts more significantly, by 45–50 nm red. The same tendency is observed in the electronic absorption spectra of molybdenum(V) oxo complexes with 5,10,15,20-tetraphenyl-porphyrin in going from axial hydroxo ligand to chloride [12].

Regardless of the singly charge axial ligand, compounds **II–VI** displayed in the IR spectra main absorption bands corresponding to vibrations of bonds in the macrocyclic ligands.

Kinetics of formation of porphyrin-fullerene. The high reactivity of the axial positions, which was revealed in the synthesis of I-VI, opens new prospects in the modification of rhenium(V) porphyrins. We have found that axial ligand in rhenium(V) porphyrin can be replaced by the action of not only other anion but also excess neutral organic base. We examined the kinetics of the reaction of complex II with 2'-(pyridin-4-yl)-5'-(pyridin-2-yl)-1'-(pyridin-3-ylmethyl)pyrrolidino[3',4':1,9](C₆₀-I_h)[5,6]fullerene (Py₃F) at 298 K using Ostwald's isolation method. This reaction leads to the formation of donor-acceptor porphyrin-fullerene dyad (VII) which is promising from the practical viewpoint. The ratio II-Py₃F was minimum admissible for the selected method due to low molar absorption coefficient of II and limited solubility of Py₃F in methylene chloride.

Figure 4 shows variation of the electronic absorption spectrum of a mixture of complex II and Py₃F in CH₂Cl₂ with time; analogous variations were observed at all the examined Py₃F concentrations. The reaction kinetics follow common pseudofirst-order equation with respect to porphyrin II (see Experimental). The order of the reaction with respect to Py₃F (~1) was determined from the linear dependence of the first-order rate constant on Py₃F concentration: $\log k_{ef} = 0.892 \log[Py_3F] + 0.152$; r = 0.933.

 $\begin{bmatrix} Py_3F \end{bmatrix} \times 10^5, \quad 6.0 \quad 6.6 \quad 7.2 \quad 7.8 \quad 8.4 \quad 9.0 \\ M \\ k_{ef} \times 10^4, \, s^{-1} \quad 2.4 \pm 0.2 \ 2.7 \pm 0.1 \ 2.9 \pm 0.1 \ 3.0 \pm 0.3 \ 3.3 \pm 0.1 \ 3.5 \pm 0.2$

Consequently, the reaction is of overall second order and first in each reactant. The true rate constant at 298 K is $k = 1.42 \text{ L mol}^{-1} \text{ s}^{-1}$ (r = 0.985).

As seen from Fig. 4, the electronic absorption spectrum of the product is almost similar to that of initial compound II; only characteristic shift of absorption bands is observed. Therefore, we can conclude



Fig. 4. Variation of the electronic absorption spectrum of complex **II** in methylene chloride in the presence of Py_3F ; $[Py_3F] = 6.6 \times 10^{-5}$ M, observation time 0 to 9240 s, 298 K.

that at all Py_3F concentrations the axial phenoxide ion in **II** is replaced by Py_3F molecule (Scheme 2).

Scheme 2.

$$I + Py_3F \xrightarrow{k} [II \cdot Py_3F]^+ PhO^-$$

I

The absence of the reverse reaction was determined experimentally by dilution of the reaction mixtures after reaction completion. The stability of the porphyrin–fullerene dyad is also confirmed by the high rate constant for its formation. Such donor–acceptor porphyrin–fullerenes attract strong interest. First, their photoexcitation gives rise to long-lived states with charge separation like natural photosynthetic antennas; second, they are soluble in organic solvents and therefore can be successfully studied as soluble analogs of coordinately-bound phthalocyanine–fullerene dyads. The latter are nowadays extensively used as photoactive materials in organic solar cells [6, 16–18].

EXPERIMENTAL

The electronic absorption spectra were recorded on an Agilent 8453 UV-Vis spectrophotometer. The IR spectra were measured on a Bruker Vertex 80v spectrometer. The ¹H NMR spectra were obtained on a Bruker Avance III-500 instrument. The mass spectra were taken on a Bruker Autoflex spectrometer. The elemental compositions were determined on a Euro EA 3000 elemental analyzer.

The kinetics of the reaction of complex II with Py_3F were studied by spectrophotometry at 298 ± 0.1 K in closed quartz cells using a special compartment. Solutions of II and Py_3F in methylene chloride were prepared just before use. The optical density of a series of solutions with a constant concentration of rheni-

um(V) porphyrin ($c = 1.7 \times 10^{-5}$ M) was measured at λ 481 and 515 nm at definite time intervals; during the reaction, the color changed from yellow-green to light red.

The effective rate constants k_{ef} were determined using first-order equation for complex II with leastsquares optimization. The relative error in the determination of k_{ef} was less than 10%.

$$k_{\rm ef} = 1/\tau \ln[(A_0 - A_\infty)/(A_\tau - A_\infty)].$$

Here, A_0 , A_{τ} , and A_{∞} are the optical densities of the reaction mixture at λ 515 nm (where Py₃F does not absorb) at the initial moment, time τ , and by the end of the reaction, respectively. To obtain a clear spectral pattern, the spectrum of fullerene with the same concentration as in the kinetic experiment was subtracted from the spectrum of the reaction.

μ-Oxobis[(oxo)(5,10,15,20-tetraphenylporphyrinato)]rhenium(V) (I). A mixture of 5,10,15,20-tetraphenylporphyrin and H₂ReCl₆ at a ratio of 1:2 was heated in boiling phenol at 454 K as described in [7]. The reaction was assumed to be complete when absorption bands belonging to the initial porphyrin disappeared from the spectrum of a sample of the reaction mixture dissolved in chloroform and the spectrum no longer changed. The mixture was cooled, treated with water, and extracted with chloroform. The extract was repeatedly washed with warm water to remove phenol and concentrated, and the residue was subjected to column chromatography on alumina (Brockmann activity grade II) using chloroform as eluent to obtain two zones, diffuse green and sharp green-brown. The product isolated from the green zone was chromatographed on a column charged with silica gel (40-100 µm, Chemapol) using first benzene and then chloroform-ethanol (1:1) as eluents to isolate complex **VIII** (orange zone), initial porphyrin (light violet zone) and complex I (green zone). Silica gel column chromatography of the product isolated from the green-brown zone (benzene, CHCl₃-EtOH, 1:1) gave compound IX (light red) and complex I (green). The purity of the isolated amorphous solids was checked by TLC on Silufol plates using CHCl3-EtOH (50:1) as eluent for complex I ($R_{\rm f}$ 0.42) and benzene for compounds VIII $(R_{\rm f}\,0.80)$ and **IX** $(R_{\rm f}\,0.83)$.

Complex I. Yield 75%. Electronic absorption spectrum (CHCl₃), λ_{max} , nm (log ϵ): 620 sh, 582 (4.51), 461 (5.34), 333 (4.88). IR spectrum (random solid film), v, cm⁻¹: 3056, 3022 (C-H_{arom}); 1597, 1575, 1485 (C=C_{arom}); 1179, 1072 (δ C-H_{arom}); 754, 702

(γ C–H_{arom}); 1440 (C=N), 1341 (C–N), 1018 (C³–C⁴, C-N, &C-H_{pyrrole}), 801 (γC-H_{pyrrole}), 463 (Re-N); 854, 723 (Re–O–Re); 961 (Re=O). ¹H NMR spectrum (CDCl₃), δ , ppm: 7.04 t and 6.87 t (8H, *m*'-H, *J* = 7.6 Hz),* 7.47 d (8H, o'-H, J = 7.6 Hz), 7.60 t (8H, *p*-H, *J* = 7.6 Hz), 8.01 t (8H, *m*-H, *J* = 7.6 Hz), 8.79 s (16H, β -H), 9.07 d (8H, o-H, J = 7.6 Hz). ¹H–¹H 2D COSY NMR spectrum, δ , ppm: in C₆D₆: 6.67 t (2H, m''-H, J = 7.3 Hz)-6.32 d (2H, p''-H, J = 8.6 Hz), 6.85 t (2H, m'-H, J = 7.3 Hz)-6.42 d (2H, p'-H, J = 8.3 Hz), 8.00 t (8H, m-H, J = 7.1 Hz)-7.47 m (16H, *m*-H, *p*-H), 8.10 d (8H, *o*-H, J = 7.1 Hz)–7.47 m (16H, *m*-H, *p*-H); in CD₃COOD: 8.51 d (4H, *o*-H, J =7.32 Hz)-7.93 m (12H, m-H, p-H), 8.37 d (4H, o'-H, J = 7.3 Hz)-7.93 m (12H, *m*-H, *p*-H). Found, %: C 63.14; H 3.52; N 5.59. C₈₈H₅₆N₈O₃Re₂. Calculated, %: C 64.22; H 3.41; N 6.81.

(2,3,7,8,12,13,17,18-Octaethyl-5-phenylporphyrinato)(oxo)(phenoxo)rhenium(V) (II). A mixture of 2,3,7,8,12,13,17,18-octaethyl-5-phenylporphyrin and H₂ReCl₆ at a molar ratio of 1:5 was heated for 5 h in boiling phenol (454 K) under reflux. The progress of the reaction was monitored by spectrophotometry following disappearance of absorption bands belonging to the initial porphyrin. The mixture was diluted with water and extracted with methylene chloride. The extract was repeatedly washed with warm water to remove phenol and concentrated, and the residue was subjected to column chromatography on alumina (Brockmann activity grade II) using methylene chloride as eluent to obtain two zones, light red (unreacted porphyrin) and diffuse green-brown. The product isolated from the green-brown zone was chromatographed on silica gel (40-100 µm, Chemapol) using benzene as eluent to obtain two zones, orange and green-brown. The product was washed off from the latter zone with CH₂Cl₂-EtOH (1:1) and chromatographed again on a column charged with silica gel (40–100 µm, Chemapol) using methylene chloride as eluent to isolate compound II. Yield 75%. Electronic absorption spectrum (CH₂Cl₂), λ_{max} , nm (log ϵ): 595 (3.64), 477 (4.02), 348 (4.38). IR spectrum (KBr), v, cm⁻¹: 3024, 3059 (C-H_{arom}); 1546, 1600, 1631 (C=C_{arom}); 1074, 1101 (δC-H_{arom}); 707, 741 $(\gamma C-H_{arom})$; 1464 (C=N), 1378 (C-N), 1058 (C³-C⁴), (C-N); 1401, 1340 (δC-H_{aliph}); 1253, 1269 (δC-H_{meso}); 842, 853 (γC-H_{meso}); 1486 (PhO⁻), 946 (Re=O), 668 (Re–O), 464 (Re–N). ¹H NMR spectrum, δ, ppm: in CDCl₃: 1.57 s, 1.28 s, and 0.90 m (24H, CH₃); 4.28 m,

^{*} Primed and double-primed locants refer to aromatic rings attached to different porphyrin macrocycles.

3.84 s, 3.74 s, 3.67 s, and 3.58 s (16H, CH₂); 7.79 m (2H, *m*-H, PhO⁻), 7.95 d (1H, *p*-H, PhO⁻, J = 7.3 Hz), 8.35 d (1H, *o*-H, PhO⁻, J = 7.3 Hz), 8.45 d (1H, *o*-H, PhO⁻, J = 6.7 Hz), 10.70 m (3H, *meso*-H); in CD₃COOD: 1.32 m and 0.92 m (24H, CH₃); 3.51 m, 3.71 m, 3.87 s, 3.95 s, 4.26 s, and 4.41 s (16H, CH₂); 7.62 t (1H, *p*-H), 7.88 m (2H, *m*-H), 8.31 t (1H, *o*-H, J = 7.31 Hz), 8.50 t (1H, *o*-H, J = 6.7 Hz), 11.06 m (3H, *meso*-H), 7.07 s (2H, *o*-H, PhO⁻), 6.93 s (2H, *m*-H, PhO⁻), 6.83 s (1H, *p*-H, PhO⁻). Found, %: C 64.57; H 6.14; N 5.84. C₄₈H₅₃N₄O₂Re. Calculated, %: C 63.79; H 5.87; N 6.20.

(Chloro)(2,3,7,8,12,13,17,18-octaethyl-5-phenylporphyrinato)rhenium(V) (III). Gaseous hydrogen chloride was passed over a period of 10 min through a solution of complex II in methylene chloride. During that time, the originally green-yellow solution changed to dark red. Yield 100%. Electronic absorption spectrum (CH₂Cl₂), λ_{max}, nm (logε): 620 (3.67), 520 (4.13), 351 (4.73). IR spectrum (KBr), v, cm⁻¹: 3060, 3024 (C-H_{arom}); 1630, 1599, 1547 (C=C_{arom}); 1097, 1059 (δC-H_{arom}); 740, 705 (γC-H_{arom}); 1464 (C=N), 1383 (C–N), 1059 (C³–C⁴, (C–N); 1401, 1340 (δ C–H_{aliph}); 1261 (δ C–H_{meso}); 865, 908 (γ C–H_{meso}); 946 (Re=O), 464 (Re–N). ¹H NMR spectrum (CDCl₃), δ, ppm: 0.93 t, 1.34 m, and 2.08 m (24H, CH₃); 2.94 m, 3.79 m, 3.87 m, and 4.27 m (16H, CH₂); 7.55 q (1H, p-H, J = 7.3 Hz), 7.76 m (2H, m-H), 7.92 t (1H, o-H, J = 7.6 Hz), 8.36 t (1H, o-H, J = 7.0 Hz), 10.88 m (3H, *meso*-H). ¹H⁻¹H 2D COSY NMR spectrum (CDCl₃), δ ppm: 4.27 m (CH₂)–2.08 t (CH₃), 3,87 m (CH₂)– 1.34 m (CH₃), 3.79 m (CH₂)–1.34 m (CH₃), 2.94 m (CH₂)–1.34 m (CH₃), 7.76 m (2H, *m*-H)–7.55 q (1H, p-H, J = 7.3 Hz), 8.36 t (1H, o-H, J = 7.0 Hz)–7.76 m (2H, *m*-H).

(Chloro)(2,3,7,8,12,13,17,18-octaethyl-5,15-diphenylporphyrinato)(oxo)rhenium(V) (IV) was synthesized as described above for complex II; reaction time 6 h, eluent chloroform. Yield 75%. Electronic absorption spectrum (CH₂Cl₂), λ_{max} , nm (log ϵ): 625 (3.70), 525 (4.15), 354 (4.75). IR spectrum (KBr), v, cm⁻¹: 3059, 3022 (C-H_{arom}); 1600, 1532, 1491 (C=C_{arom}); 1125, 1073 (δC-H_{arom}); 702, 742 $(\gamma C-H_{arom});$ 1465 (C=N)], (C-N), 1062 (C³-C⁴, C-N); 1400, 1341 (δC-H_{aliph}); 1274 (δC-H_{meso}); 838, 861 $(\gamma C-H_{meso})$; 962 (Re=O), 467 (Re–N). ¹H NMR spectrum (CDCl₃), δ, ppm: 0.93 t, 1.56 s, and 1.95 s (24H, CH₃); 2.70 m and 4.20 s (16H, CH₂); 7.55 g (1H, p-H, J = 7.3 Hz); 7.73 q (1H, p-H, J = 7.3 Hz), 7.85 m (2H, *m*-H), 7.91 m (2H, *m*-H), 8.20 d (2H, *o*-H, J = 8.1 Hz), 8.29 d (2H, o-H, J = 8.1 Hz), 10.82 m (2H, meso-H). ¹H–¹H 2D COSY NMR spectrum (CDCl₃), δ , ppm: 2.70 s (CH₂)–1.95 t (CH₃), 4.20 s (CH₂)–1.56 t (CH₃), 4.20 s (CH₂)–1.95 t (CH₃), 7.85 m (2H, *m*-H)–7.55 q (1H, *p*-H, *J* = 7.3 Hz), 7.91 m (2H, *m*-H)–7.73 q (1H, *p*-H, *J* = 7.3 Hz), 8.20 d (2H, *o*-H, *J* = 8.0 Hz)–7.85 d (2H, *m*-H), 8.29 d (2H, *o*-H, *J* = 8.1 Hz)–7.91 m (2H, *m*-H). Found, %: C 61.05; H 5.45; N 5.41. C₃₆H₄₄N₄OClRe. Calculated, %: C 62.51; H 5.64; N 6.08.

(2,3,7,8,12,13,17,18-Octaethylporphyrinato)-(oxo)(phenoxo)rhenium(V) (V) was synthesized as described above for complex II; reaction time 9 h. Yield 70%. Electronic absorption spectrum (CH_2Cl_2) , λ_{max} , nm: 613, 580, 469, 343. IR spectrum (KBr), v, cm⁻¹: 1468 (C=N), 1376 (C-N), 1057 (C³-C⁴, C-N), 1317 (δC-H); 873, 844 (γC-H_{meso}); 1223, 1273 (δC-H_{meso}); 1589, 1451 (PhO⁻); 959 (Re=O), 670 (Re–O); 454, 466 (Re–N). ¹H NMR spectrum (C_6D_6), δ, ppm: 0.38 m, 0.91 m, 1.31 m, and 1.83 s (24H, CH₃); 4.03 m and 4.43 m (16H, CH₂), 6.85 s (1H, *p*-H, PhO⁻), 6.95 s (2H, *m*-H, PhO⁻), 7.04 s (2H, *o*-H, PhO⁻), 10.77 m and 9.51 m (4H, meso-H). ¹H-¹H 2D COSY NMR spectrum (C_6D_6), δ , ppm: 4.43 m (CH₂)– 1.83 s (CH₃), 4.03 m (CH₂)–1.83 s (CH₃). Found, %: C 62.17; H 6.31; N 7.15. C₄₂H₄₉N₄O₂Re. Calculated, %: C 60.94; H 5.93; N 6.77.

(Chloro)(2,3,7,8,12,13,17,18-octaethylporphyrinato)(oxo)rhenium(V) (VI). Gaseous hydrogen chloride was passed over a period of 10 min through a solution of complex V in methylene chloride. The originally green–yellow solution turned light red. Yield 100%. Electronic absorption spectrum (CH₂Cl₂), λ_{max} , nm (logɛ): 620 (3.90), 518 (4.30), 347 (4.92). IR spectrum (KBr), v, cm⁻¹: 1468 (C=N), 1376 (C–N), 1057 (C³–C⁴, C–N); 1316 (δ C–H_{aliph}); 1271, 1223 (δ C–H_{meso}); 871, 854, 846 (γ C–H_{meso}); 965 (Re=O), 467 (Re–N). ¹H NMR spectrum (CDCl₃), δ , ppm: 0.88 m, 1.28 m, 1.56 m, and 2.13 s (24H, CH₃); 4.38 m and 4.30 m (16H, CH₂), 10.94 m (4H, *meso*-H). ¹H–¹H 2D COSY NMR spectrum (CDCl₃), δ , ppm: 2.02 m (CH₂)–1.19 m (CH₃), 4.36 m (CH₂)–2.17 s (CH₃).

Solid amorphous complexes were isolated from the eluates by evaporation of the solvent at room temperature.

Complex **VII** was synthesized by reaction of compound **II** with 2'-(pyridin-4-yl)-5'-(pyridin-2-yl)-1'-(pyridin-3-ylmethyl)pyrrolidino $[3',4':1,9](C_{60}-I_h)[5,6]$ fullerene (Py₃F) in methylene chloride at 298 K; Py₃F was synthesized by P.A. Troshin [19] at the Institute of Chemical Physics Problems, Russian Academy of Sciences, by reaction of C_{60} with azomethine ylide prepared from *N*-(pyridin-3-ylmethyl)pyridin-2-ylmethanamine and pyridine-4-carbaldehyde at a molar ratio of 1.1:1.3 in 1,2-dichlorobenzene. Electronic absorption spectrum (CH₂Cl₂), λ_{max} , nm: 294, 313, 434. The electronic absorption spectrum of Py₃F coincided with that given in [19]: λ_{max} , nm: 294, 313, 434 (CH₂Cl₂).

This study was performed under financial support by the Council for Grants at the President of the Russian Federation (project no. NSh-3993.2012.3). The authors thank P.A. Troshin for providing a sample of substituted fullerene. The spectral studies were carried out using the equipment of the Upper Volga Region Center of Physicochemical Research.

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