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Novel 2'-(Pyridin-4-yl)-5'-(pyridin-2-yl)-1'-(pyridin-2-yl)methylpyrrolidinyl[60]fullerene– Hydroxyoxo(5,10,15,20-tetraphenyl-21*H*,23*H*porphynato)molybdenum(V) Dyads

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Abstract—Interaction between hydroxyoxo(5,10,15,20-tetraphenylporphyrinato)molybdenum(V) and 2'-(pyridin-4-yl)-5'-(pyridin-2-yl)-1'-(pyridin-2-yl)methylpyrrolidinyl[60]fullerene in toluene has been studied by means of spectrophotometry. The reaction proceeds via two stages: rapidly established equilibrium between the reactants and their molecular complex 1 : 1 [$K = (1.97 \pm 0.52) \times 10^4$ L/mol] followed by slow irreversible displacement of hydroxy group into the second coordination sphere to form cationic outer sphere complex (k = 0.26 L s⁻¹ mol⁻¹). The effect of fullerene fragment on pyridine fragments coordination has been considered.

Keywords: molybdenum porphyrin complex, reaction order, dyades formation, thermodynamics, chemical kinetics

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Unsubstituted fullerenes are known as weak π electron acceptors. The electron affinity of C₆₀ in aqueous solutions is of 2.10-2.20 eV [1]. In its complexes with π -electron donors (molecular complex DA, charge transfer complex $D^{\delta^+}A^{\delta^-}$, and ion-radical salts $D^{n++}A^{n+-}$, fullerene acts as unique π -electron acceptor of spherical shape, which is important factor of the complexes stability. This is especially so in the case of planar aromatic systems acting as donor. The complexes with metal porphyrinates as electron donor are of interest, as they are capable of reducing fullerene or forming the charge transfer complexes. For instance, formation of supramolecular complexes of bisporphyrin with fullerenes C₆₀ and C₇₀ in toluene has been studied by spectrophotometric titration [2]. The interaction proceeds through formation of a charge transfer transition state (K_{C60} 2.1 \times 10⁴, K_{C70} 6.94 \times 10^4 L/mol). The most popular methods to prepare porphyrin complexes with fullerene C₆₀ have been reviewed in [3]. Such fullerene-containing complexes are of certain interest for modern science and

technology. In particular, accurate, sensitive, and selective sensor for determination of bisphenol A has been developed [4]; fullerene-encapsulated hexagonal porphyrin nanotubes, based on fullerene C_{60} or C_{70} and *meso*-tetra(pyridin-4-yl)porphynatozinc ZnP(Py)₄ have been constructed [5]; the rod-shaped electrodes built of such nanotubes can be used in light energy transformation applications [6, 7].

In order to enhance the electron affinity of fullerene, it can be chemically modified. Recently, a novel possibility to prepare the porphyrin–fullerene complexes has been recognized, via coordination binding of the electron-donor site of substituted fullerene with metal cation of porphyrin complex. In particular, axial coordination of the substituted fullerene on low-basic nitrogen atom of pyrrolidine ring on (5,10,15,20-tetraphenylporphyrinato)zinc (ZnTPP) has been confirmed by X-ray diffraction studies [7–9]. Such coordinated supramolecules form photoinduced stable (up to hundreds of μ s [10]) charge transfer states, similar to







Fig. 1. UV-vis spectra of the complex I ($c_1 1.08 \times 10^{-5} \text{ mol/L}$) in toluene (1) and of the same solution with addition of 1.38×10^{-5} – $2.02 \times 10^{-4} \text{ mol/L}$ of the substituted fullerene II.



the photosynthetic antenna. Potential application of the ZnTPP–fullerenopyrrolidine complex to develop photoactive layers of two-layered solar cells has been demonstrated [10].

Stability of such coordinated complexes has been scarcely studied so far. We have recently published quantitative data on supramolecular complex formation between *meso*-tetraphenylporphin complexes of highly charged metal cations and free pyridine [11, 12] in comparison with these of pyridinyl derivatives of pyrrodinyl[60]fullerene [13, 14]. Furthermore, a new type of free-radical complexes between molybdenum and substituted fullerene has been prepared [15–17].

In this work we used molybdenum cation surrounded by a readily polarized macrocyclic compound. In particular, we studied equilibrium state and kinetics of interaction between hydroxyoxo(5,10,15,20tetraphenylporphyrinato)molybdenum(V) [I, O=Mo(OH)· TPP] and 2'-(pyridin-4-yl)-5'-(pyridin-2-yl)-1'-(pyridin-



Fig. 2. log $[(A_s - A_0)/(A_{\infty} - A_s)]$ as function of log c_{II} for reaction of compounds I and II in toluene; $c_{II} 1.38 \times 10^{-5} - 2.02 \times 10^{-4}$ mol/L. $R^2 = 0.918$.

2-yl)methylpyrrolidinyl[60]fullerene (II, Py₃F). Toluene was used as solvent; it has been proved experimentally that fullerene C_{60} does not aggregate toluene [18] (Scheme 1).

Figure 1 displays UV-vis spectra (Soret band range) of compound I in toluene upon addition of varied amounts of compound II. In the studied range of concentrations, c_{II} of $1.38 \times 10^{-5} - 2.02 \times 10^{-4}$ mol/L), the system attained equilibrium state immediately after mixing. With increasing concentration of II, absorption at 462 nm increased, and isosbestic point was clearly revealed at 478 nm. Processing the experimental data using the log $(A_s - A_0)/(A_\infty - A_s) - \log c_{II}$ function (Fig. 2) confirmed that the equilibrium was established with participation of a single molecule of the substituted fullerene (tan $\alpha \approx 1$). Therefore, the equilibrium constant K was calculated using Eq. (1), derived for the case of three-component equilibrated system (2) taking advantage of the detailed balance and the Beer-Lambert-Bouguer law for mixture of two colored compounds. The fullerene spectrum was taken as baseline. The equilibrium constant was relatively high, $(1.97 \pm 0.59) \times 10^4$ L/mol, compared with those of other metal porphyrin complexes with bases.

$$K = \frac{(A_{\rm s} - A_0)/(A_{\infty} - A_0)}{1 - (A_{\rm s} - A_0)/(A_{\infty} - A_0)} \cdot \frac{1}{\{c_{\rm II} - c_1^0[(A_{\rm s} - A_0)/(A_{\infty} - A_0)]\}^n} \cdot (1)$$

In Eq. (1), c_{I}^{0} and c_{II} are initial concentrations of compounds I and II, respectively; A_{0} , A_{s} , A_{∞} are absorbance of at time zero of the solution of compound

I, of the equilibrium mixture at certain concentration of the fullerene **II**, and of the reaction product; n, number of the bounded molecules of the substituted fullerene **II**.



Chemical structure of the reaction product III formed via a single-stage coordination of compound II at the eighth coordination site of molybdenum was elucidated basing on the following facts: single-step shape of the titration curve (Fig. 3), stoichiometric ratio of I to II of 1 : 1, and no new electronic absorption bands appearing in the course of the interaction. IR spectrum of the reaction product contained new absorption bands assigned to the



RUSSIAN JOURNAL OF GENERAL CHEMISTRY Vol. 84 No. 5 2014



Fig. 3. Curve of spectrophotometric titration of complex I with compound II.

coordinated fullerene **II**, at 1472, 1432, 1306, 1281, 1216, 1184, 1123, 1095, 574, and 527 cm⁻¹ absent in the spectra of initial compounds.

As the UV-vis spectra did not change upon further increase of the fullerene **II** concentration up to 2.4×10^{-4} mol/L, no other equilibriums were established in the system. However, upon titration of metal porphyrin with the base, some slow ireversible process was revealed occurring after the equilibrium had been established, in the cases of all the studied concentrations of **II**. The kinetics study (see above) confirmed the monomolecular type of transformation of product **III**.

Effective rate constants determined at different initial concentrations of compound **II** are collected in Table 1. It is to be seen that the reaction rate obeyed well the first-order kinetics with respect to the initial complex **I** (the mean-squared deviation of the rate constants did not exceed 10%). The reaction rate order with respect to c_{II} equaled to unity (Fig. 4), the reaction rate constant was of $k = 0.26 \text{ L s}^{-1} \text{ mol}^{-1}$, and the rate equation was thus as follows [Eq. (4)]:

$$-dc_{\mathbf{III}}/d\tau = -dc_{\mathbf{I}}/d\tau = k \cdot c_{\mathbf{I}} \cdot c_{\mathbf{II}}.$$
 (4)

The reaction rate equation written for the quasiequilibrated system of reactions (2) and (3) coincided with the experimentally derived Eq. (4). The experimental reaction rate constant k included the rate constant k_2 of the slow irreversible reaction (3) as well as the equilibrium constant K_1 of reaction (2) [Eq. (5)].

$$-dc_{\mathbf{III}}/d\tau = -dc_{\mathbf{I}}/d\tau = k_2 \cdot c_{\mathbf{III}} = k_2 \cdot K_1 c_{\mathbf{I}} c_{\mathbf{II}}.$$
 (5)



Fig. 4. Effective rate constant as function of concentration of the substituted fullerene II in toluene at 298 K. $R^2 = 0.993$.

Hence, the rate-limiting stage (3) revealed the rate constant of $k_2 = k/K_1 = 0.132 \times 10^{-4} \text{ s}^{-1}$. It was the low rate of irreversible reaction (3) as compared with almost immediate direct reaction corresponding to equilibrium (2) that enabled experimental determination of the equilibrium constant K_1 .

The suggested scheme of quasi-stationary state was confirmed by studies of spectral changes in the course of irreversible stage (Fig. 5, c_{II}^0 of 4.16 × 10⁻⁵ mol/L). The reaction was accompanied with decreasing the absorption at 462 nm and increasing the absorption at 485 nm. The red shift of the Soret band and the slow reaction course suggested that significant changes occurred in the coordination sphere of the complex, namely, displacement of the covalently bound

 Table 1. Effective rate constants of the reaction between the complex I and the substituted fullerene II in toluene at 298 K as function of concentration of compound II

$c_{\rm II} \times 10^4$, mol/L	$(k_{\rm ef} \pm \delta k_{\rm ef}) \times 10^5, {\rm s}^{-1}$
0.66	1.1 ± 0.09
0.76	1.3 ± 0.15
0.96	1.7 ± 0.15
1.15	2.1 ± 0.18
1.44	2.4 ± 0.23
1.63	2.8 ± 0.19
2.02	3.7 ± 0.48



Fig. 5. Electronic absorption spectra of complex I in toluene, at concentration of substituted fullerene II of 4.16×10^{-5} mol/L, immediately after mixing (1) and after 24 h (2). Other curves correspond to the intermediate states.

hydroxyl to the second coordination sphere to form cationic outer sphere complex **IV**.

Thus, the mixture of metal porphyrinate I and the fullerene II could be considered a self-assembling system. A stable coordination complex formed via binding of electron-donor atom of the pyridine groups with the central metal ion existed in the solution. In the supramolecular complex, π -electronic donor (porphyrin macrocycle) and acceptor (fullerene molecule) co-existed. We elucidated that the coordination complex was formed via the only pyridinic nitrogen atoms of the three. Likely, that was the most sterically available nitrogen atom of the pyridin-4-yl fragment in the position 2' of pyrrolidine. Such complexes can form promising materials due to formation of stable charge separation systems upon photoexcitation.

A reaction similar to the above-discussed one (substitution of the covalently bound hydroxyl group with a molecular ligand) occurs in the mixture of **I** with unsubstituted pyridine (Py), revealing, however,

Table 2. Constants of stepwise equilibriums in the complex I–pyridine system (K_p) , the order of direct reactions with respect to $c_{Py}(m)$, and rate constants of direct (k) and reverse (k_{-}) reactions in toluene at 298 K

Reaction stage	т	k, L s ⁻¹ mol ⁻¹	k_{-}, s^{-1}	K _p , L/mol
1	0.96	5.25	5.75×10^{-4}	9.1×10^{3}
2	0.83	1.83×10^{-2}	$4.65\times10^{-\!4}$	39.3
3	1.03	1.19×10^{-3}	$1.20 imes 10^{-3}$	1.0

some special features. Three reversible stages of the interaction were observed. In contrast to the case of substituted fullerene II, those equilibriums were established relatively slowly, thus enabling determination of the rates of the corresponding direct and back reactions (Table 2) (see the procedure and raw experimental results in [12]). Product of the first stage of the interaction was similar to that obtained in the system containing the fullerene II: outer sphere cationic complex [O=Mo(Py)TPP]⁺·OH⁻, the equilibrium constant K_1 (Table 2) being only two times lower than that in the case of fullerene II. At the second and the third stages, successive substitution of the bidentate oxo group with two pyridine molecules occurred.

Evidently, the higher equilibrium constant in the case of reaction between compounds I and II was due to the presence of two additional pyridine and one additional pyrrolidone nitrogen atoms in molecule II, making it more basic. That the second and the third stages of interaction were not observed in the case of II, was due to steric hindrance of bulky base molecule.

Stability of coordination complexes of metal porphyrins with pyridine and pyridinyl derivatives of fullerenes (PyF) decreases in the following series.

(Cl)(PyF)InTPP ($K_1 6.92 \times 10^4$ L/mol, in CHCl ₃)	
\rightarrow O=Mo(Py ₃ F)(OH)TPP (1.97 × 10 ⁴ , in toluene)	
\rightarrow (PyF')ZnTPP (1.6 × 10 ⁴ , in cyclohexanone [19])	
\rightarrow (Py ₂ F)ZnTPP (1.2 × 10 ⁴ , in cyclohexane [19])	
\rightarrow [O=Mo(Py)TPP] ⁺ ·OH ⁻ (9.1 × 10 ³ , in toluene [12])	
\rightarrow (Cl)(Py ₃ F')InTPP (2.6 × 10 ⁵ L ⁴ /mol ⁴ ,	
4 isomers, in $CHCl_3$).	(6)

In the series (6), PyF, PyF', Py₂F, and Py₃F' represent, respectively, the following derivatives of

[60]fullerene: 2'-(pyridin-4-yl)-1'-methylpyrrolidinyl-, *cis*-2'-(pyridin-2-yl)-5'-(4-imidazolylphenyl)pyrrolidino[3',4':1,2]-, *cis*-2',5'-di(pyridin-2-yl)pyrrolidino-[3',4':1,2]-, and 2'-(pyridin-4-yl)-5'-(pyridin-2-yl)-1'-(pyridin-3-yl)methylpyrrolidinyl-.

All the pyridine derivatives of the fullerene coordinated readily at the central atom of the corresponding metal porphyrin; the complex **III** had the second high stability constant, right after the sterically not hindered (Cl)(PyF)InTPP.

To conclude, ability of the pyridinyl-substituted pyrrolodinofullerene to axial coordination was higher in the case of complexes of highly charged In^{III} and Mo^V. Significantly high charge at the central ion of metal porphyrin and the presence of additional nucleophilic sites favored the complex formation. Such complexes, in particular that of the fullerene II with the molybdenum compound I, can be promising for application as photoactive layer in organic solar cells.

EXPERIMENTAL

UV-vis spectra were registered with the UV-Vis Agilent 8453 spectrophotometer; IR spec-tra were recorded with the VERTEX 80v instrument.

Hydroxyoxo(5,10,15,20-tetraphenylporphyrinato)molybdenum(V) [I, O=Mo(OH)TPP] was prepared following the procedure published in [20]. 0.1 g (0.16 mmol) of H_2TPP was refluxed with 0.076 g (0.53 mmol) of MoO₃ in 0.8 g of phenol at 454 K during 4 h. The solid complex was isolated after phenol distillation in vacuum, dissolved in CHCl₃, and twice purified via column chromatography on Al₂O₃ (CHCl₃). The two successive zones were unreacted porphyrin (pink) and the complex (green). Yield 60%. IR spectrum (KBr), v, cm⁻¹: 701, 752 [γ (C–H)]; 1070, 1177 [δ(C–H)]; 1484, 1596 (C=C); 800 [γ(C–H)]; 1018 $[C^3-C^4, C-N, \delta(C-H)];$ 1336 (C-N); 1441 (C=N); 441 (Mo-N), 659 (Mo-O), 928 (Mo=O). UVvis spectrum (CHCl₃), λ_{max} , nm (log ε): 620.0 (2.94), 584.0 (2.92), 456.0 (3.78).

2'-(Pyridin-4-yl)-5'-(pyridin-2-yl)-1'-(pyridin-2-yl)methylpyrrolidinyl[60]fullerene (II, Py₃F) was prepared as described in [9], via interaction of C₆₀ (1 mol) and the azomethine ylide in 1,2-dichlorobenzene; the azomethine ylide was in turn prepared from (pyridin-2-yl)methyl-substituted amide of pyridine-2-carboxylic acid and pyridine-2-carbaldehyde (1.1 : 1.3 mol/mol). IR spectrum (solid chaotic layer), v, cm⁻¹: 1302 (C–N), 1463 (C=N), 1080, 1121 [δ (C–H)]; 1280,

1215 (C–N); 1432, 1184, 574, 527. UV-vis spectrum (toluene): λ_{max} , nm 285, 315, 333 sh, 432.

Equilibrium and kinetics of the reaction between compounds I and II was studied by means of spectrophotometry (the molar ratios and the excessive concentrations methods). Freshly prepared solutions of I and II in toluene were used for experiments, to avoid peroxides formation. Absorbance at 462 nm was measured for a series of solutions with $c_{\rm I}$ of 1.08×10^{-5} mol/L and $c_{\rm II}$ of 1.38×10^{-5} to 2.02×10^{-4} mol/L immediately after the preparation, and then was followed in time. UV-vis spectra of the molecular complexes were registered in the subtraction mode, using solution of compound II of the corresponding concentration as reference. Solutions temperature was maintained at 298 ± 0.1 K during the measurement.

Reaction rate constants as function of c_{II} were determined following the first-order Eq. (7) under condition of excess of the base II with respect to compound I:

$$k_{\rm ef} = 1/\tau \ln \left[(A_0 - A_\infty)/(A_\tau - A_\infty) \right],\tag{7}$$

where A_0 , A_{τ} , A_{∞} being, respectively, initial, current (time τ), and final absorbance at 462 nm.

Equilibrium constant K and rate constant k_{ef} were determined via the least squared method (Microsoft Excel).

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REFERENCES

- 1. Konarev, D.V. and Lyubovskaya, R.N., *Russ. Chem. Bull.*, 1999, vol. 68, no. 3, p. 19.
- 2. Pal, D., Ray, A., and Bhattacharya, S., *Spectrochim. Acta* (*A*), 2012, vol. 95, no. 9, p. 317.
- Mironov, A.F., *Macroheterocycles*, 2011, vol. 4, no. 3, p. 186.
- 4. Rather, J.A. and De Wael, K., *Sensors and Actuators* (*B*), 2013, vol. 176, p. 110.
- 5. Sandanayaka, A.S.D., Murakami, T., and Hasobe, T., *J. Phys. Chem. (C)*, 2009, vol. 113, no. 42, p. 18369.
- Walter, M.G., Rudine, A.B., and Wamser, C.C., J. Porphyrins and Phthalocyanines, 2010, vol. 14, no. 9, p. 759.

- Li, M., Ishihara, Sh., Ji, Q., Akada, M., Hill, J.P., and Ariga, K., *Sci. Technol. Adv. Mater.*, 2012, vol. 13, p. 1.
- Troshin, P.A. and Lyubovskaya, R.N., *Russ. Chem. Rev.*, 2008, vol. 77, no. 4, p. 323.
- Troshin, P.A., Troyanov, S.I., Boiko, G.N., Lyubovskaya, R.N., Lapshin, A.N., and Goldshleger, N.F., *Fullerenes Nanotubes and Carbon Nanostructures*, 2004, vol. 12, nos. 1–2, p. 435.
- Nanostrukturirovannye materialy dlya zapasaniya i preobrazovaniya energii (Nanostructured Materials for Energy Conversion and Storing), Razumov, V.F. and Klyuev, M.V., Eds., Ivanovo: Ivanov. Gos. Univ., 2009.
- 11. Lomova, T.N., Malov, M.E., and Klyuev, M.V., *Russ. J. Phys. Chem. A.*, 2009, vol. 83, no. 6, p. 913.
- 12. Tipugina, M.Yu., Lomova, T.N., and Motorina, E.V., *Russ. J. Coord. Chem.*, 2005, vol. 31, no. 5, p. 357.
- 13. Lomova, T.N. and Malov, M.E., *Tezisy dokl. X Mezhdunar. konf. po fiz. i koord. khimii porfirinov i ikh analogov* (X Int. Conf. of Physical and Coordination Chemistry of Porphyrins and Their Analogues), Ivanovo, 2009, p. 42.

- Motorina, E.V. and Lomova, T.N., *Tezisy dokl. VII* Mezhdunar. nauch. konf. "Kinetika i mekhanizm kristallizatsii. Kristallizatsiya i materialy novogo pokoleniya" (VII Int. Sci. Conf. "Kinetics and Mechanism of Crystallization. Crystallization and Materials of New Generation"), Ivanovo, 2012, p. 159.
- Gasanov, R.G., Lobach, A.S., Sokolov, V.I., Demenjev, A.P., Maslakov, K.I., and Obraztsova, E.D., *J. Nanosci. Nanotechnol.*, 2007, vol. 7, p. 1546.
- Bashilov, V.V., Tumanskii, B.L., Petrovskii, P.V., and Sokolov, V.I., *Russ. Chem. Bull.*, 1994, vol. 43, no. 6, p. 1069.
- Sokolov, V.I., Gasanov, R.G., Goh, L.Y., Weng, Z., Chistyakov, A.L., and Stankevich, I.V., *J. Organomet. Chem.*, 2005, vol. 690, no. 9, p. 2370.
- 18. Islamova, N.I., *Candidate Sci. (Chem.) Dissertation,* Ivanovo, 2005.
- 19. Lapshin, A.N., *Candidate Sci. (Chem.) Dissertation*, Ivanovo, 2006.
- 20. Lomova, T.N., Volkova, N.I., and Berezin, B.D., *Zh. Neorg. Khim.*, 1985, vol. 30, no. 3, p. 626.