STRUCTURE OF MATTER AND QUANTUM CHEMISTRY

Stepwise Mechanism of the Rhenium(V) Porphyrin Reaction with Pyridine, and the Chemical Structure of the Donor—Acceptor Complex

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Abstract—Chemical thermodynamics and UV, visible, IR, ¹H NMR, and mass spectrometry are used to study the complex reaction of (5,15-bis(4'-methoxyphenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetraethyl-porphinato) (oxo)(chloro)rhenium(V) (O=Re(Cl)P) with pyridine (Py) and the chemical structure of the product. The nature and stoichiometry of the reaction are established and the quantitative parameters of two-way stepwise reactions are determined during a complex reaction. There is reversible replacement of Cl⁻ ions by pyridine molecules with constant K_1 of $(4.7 \pm 1.1) \times 10^2$ L/mol and the formation of cationic complex compound $[O=Re(Py)P]^+Cl^-$ in the first stage. The second stage is the reversible addition of two pyridine molecules ($[O=Re(Py)_3P]^+Cl^-$) with constant $K_2 = (0.10 \pm 0.03) L^2/mol^2$. The reaction studied is a model for processes in self-assembling systems based on metalloporphyrins and pyridyl derivatives of carbon nanoforms for the formation of active layers with photoinduced charge separation in hybrid solar cells.

Keywords: substituted rhenium(V) porphyrin, pyridine, donor–acceptor system, thermodynamics of the formation, chemical structure, spectral properties

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INTRODUCTION

Organometallic compounds with M–O and M–N bonds attract much attention as active intermediate compounds in biologically important reactions [1, 2], and have been successfully used as effective catalysts in many industrial processes [3, 4]. The high state of oxidation of the metal in the catalyst allows the reaction to be conducted under the conditions of open flasks, without the need for the strict exclusion of air and moisture [5]. The rich coordination chemistry of rhenium is used in designing radiopharmaceuticals [6– 8], since its isotopes ¹⁸⁶Re and ¹⁸⁸Re emit radiation. Rhenium is also widely used as a nonradioactive technetium model in nuclear medicine [9].

The synthesis, properties, and use of rhenium compounds with carbenes [10], heterocyclic molecules [5, 11, 12], calixarenes [6], and porphyrins [10, 13–15] are described in literature. The different possibilities of modifying rhenium compounds make them promising platforms for the formation of supramolecular [16, 17], μ -oxodimeric systems and complexes

with peroxo-coordinated oxygen [15, 16, 18]. The possibility of varying the axial group in equatorial macrocyclic rhenium complexes makes them promising for use in sensorics [19], catalysis [13], and photodynamic therapy, where rhenium compounds have already been tested and proven [20, 21]. The study of substitution and addition reactions of various groups along the axial axis of highly charged rhenium oxoporphyrin complexes considerably affects their main spectral characteristics, their stability over Re–N bonds [22], and their ability to form π -cation radicals and interact with molecular oxygen [10, 15]. Further development of the indicated areas of rhenium chemistry requires study of the physical chemistry of its compounds, particularly the reactivity to different substrates and the mechanisms of complex reactions with their participation.

The aim of this work was to study the reactions between (5,15-bis(4'-methoxyphenyl)-3,7,13,17-tetra-methyl-2,8,12,18-tetraethylporphinato)(oxo)(chloro) rhenium(V) (O=Re(Cl)P)



and pyridine (Py). The reaction between metalloporphyrin (MP) and Py is considered a simple model of self-assembly in donor-acceptor systems based on metalloporphyrins and pyridyl derivatives of such carbon nanoforms as fullerenes [23, 24]. Porphyrin– fullerene supramolecules, as confirmed by experimental studies on fluorescence quenching and calculations [25], exhibit the property of photoinduced electron transfer (PET) and can function as active layers of hybrid solar cells.

EXPERIMENTAL

(5,15-Bis(4'-methoxyphenyl)-3,7,13,17-tetramethyl-2.8.12.18-tetraethylporphinato)(oxo)(chloro)rhenium(V). O = Re(Cl)P was prepared from (5,15-bis(4'-methoxyphenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetraethylporphinato)(oxo)(phenoxy) rhenium(V) (O=Re(PhO)P), preliminarily synthesized via the reaction between H₂ReCl₆ and the corresponding porphyrin according to [26], and by passing gaseous HCl for 10 min through a solution of it in CH₂Cl₂. During this time, the color of the solution changed from green-yellow to wine red. Porphyrin was synthesized [27] and provided by Professor A.S. Semeikin. The (O=Re(Cl)P) yield was close to 100%. The UV-Vis spectrum (CH₂Cl₂): λ_{max} , nm (log ϵ) 687 (3.15), 633 (3.48), 526 (3.95), 355 (4.52). The ¹H NMR spectrum (CDCl₃), ppm, J, Hz: 10.81 (s, 2H, CH_{meso}), 8.16 (d, 2H, H_o , J = 8.3); 8.08 (d, 2H, H_o , J = 8.3); 7.73 $(q, 1H, H_m, J = 8.3); 7.55 (q, 1H, H_m, J = 7.3); 7.39$ $(m, 2H, H_m)$; 4.18 $(m, 8H, -CH_2-)$; 2.76 $(t, 12H, -CH_2-)$; 2.76 CH_{3Et}, J = 7.3); 2.20 (s, 6H, p-OCH₃); 1.96 (t, 12H, CH_3 , Me, J = 7.6). The mass spectrum (MALDI TOF), m/z 891.35 [M–Cl]⁺. The one calculated for $C_{46}H_{48}ReN_4O_3$ was 891.12.

The synthesis and properties of 1'-*N*-methyl-2'- (pyridine-4-yl)pyrrolidino[3',4':1,2][60]fullerene were described in [25].

Analytical grade Py was dried for two days over KOH granules and then distilled ($t_{\text{boil}} = 115.3^{\circ}\text{C}$). Toluene was dried with potassium hydroxide and distilled before use ($t_{\text{boil}} = 110.6^{\circ}\text{C}$). The water content was determined via Fischer titration and did not exceed 0.01%.

The reaction between O=Re(Cl)P and Py was studied in dichloromethane using the spectrophotometric method of molar ratios at 298 K. A series of solutions was prepared in CH₂Cl₂ with a constant concentration of O=Re(Cl)P (2.03×10^{-5} mol/L) and different pyridine concentrations (8.23×10^{-5} -11.17 mol/L). Equilibrium constants of reactions with Py (*K*) were determined using the equation for a threecomponent equilibrium system according to the least squares (LS) method using Microsoft Excel:

$$K = \frac{(A_{\rm i} - A_0) / (A_{\infty} - A_0)}{1 - (A_{\rm i} - A_0) / (A_{\infty} - A_0)} \times \frac{1}{\left(C_{\rm Py} - C_{\rm O=Re(Cl)P}^0 \frac{A_{\rm i} - A_0}{A_{\infty} - A_0}\right)^n},$$
(1)

where C_{Py} , $C_{O=Re(Cl)P}^{0}$ is the initial concentration of Py and O=Re(Cl)P in dichloromethane, respectively; A_0 , A_i , A_∞ are the optical densities at the working wavelength for rhenium(V) porphyrin, the equilibrium mixture at a given concentration of Py, and the reaction product. The relative error in determining K did not exceed 30%. The Py stoichiometric coefficient (*n* in Eq. (1)) was determined as slope $\log(I_i) = f(\log C_{Py})$, where I_i is the indicator ratio $(A_i - A_0)/(A_\infty - A_i)$.

UV–Vis, IR, fluorescent, ¹H NMR, and mass spectra were recorded, respectively, on an Agilent 8453 spectrophotometer, and on VERTEX 80v, Avantes AvaSpec-2048, Bruker AVANCE-500, and Shimadzu Confidence spectrometers.

RESULTS AND DISCUSSION

Dichloromethane was chosen as the solvent for studying the reactions between O=Re(Cl)P and Py, as it has good dissolving ability and chemical inertness in relation to this complex. The choice of spectrophotometry as the research method was due to the electronic absorption spectra of porphyrin rhenium(V) complexes being accurate and sensitive to the change in axial groups. In [14, 26], electronic absorption spectra were compared for rhenium(V) porphyrins of composition O=Re(Cl)P upon a change in covalently attached X ligands and a different ratio of the band intensities in the 350–460 nm range and the position



Fig. 1. Change in the UV–Vis spectrum of O=Re(Cl)P ($C_{O=Re(Cl)P} 2.03 \times 10^{-5} \text{ mol/L}$) with pyridine additives of $8.23 \times 10^{-5} - 2.23 \times 10^{-2} \text{ mol/L}$ (a) and $2.23 \times 10^{-2} - 11.17 \text{ mol/L}$ (b). Inserts show the corresponding spectrophotometric titration curves obtained at working wavelengths of (a) 526 and (b) 463 nm.

of the charge transfer band in the region of 440-550 nm were obtained.

Figure 1 shows UV–Vis spectrum of O=Re(Cl)P in dichloromethane–Pv mixtures as a function of the Pv concentration at 298 K and corresponding titration curves. A wide range of Py concentrations (8.23 \times 10^{-5} –11.17 mol/L) was used. Two families of spectral curves in which the isosbestic points are preserved are clearly present (Fig. 1). The first series of bands is observed at $C_{Pv} = 8.23 \times 10^{-5} - 2.23 \times 10^{-2} \text{ mol/L}.$ There are minor changes in the spectrum. The optical density of the charge transfer band at 526 nm is reduced, a new absorption band appears in the region of 480 nm, and the intensity of the Soret band at 355 nm falls slightly. The second series of bands at $C_{\rm Pv} = 2.23 \times 10^{-2}$ -11.17 mol/L is characterized by considerable changes in UV-Vis spectrum. Absorption in the region of 480 nm grows more intensely with a hypsochromic shift of the maximum to 463 nm, a new absorption band appears in the region of 405 nm, and the intensity of the Soret band falls from 0.7 to 0.45 optical density units.

The presence of isosbestic points in both series of curves, the titration results within each of the series, and the study of trends in UV–Vis spectra upon diluting solutions with pyridine show the reaction between O=Re(Cl)P and Py in dichloromethane proceeds in two reversible stages.

Analysis of the log *I*–log C_{Py} dependences (Fig. 2) allows us to determine the number of Py molecules that participate in equilibrium. For the first stage (at a Py concentration of 8.23×10^{-5} – 2.23×10^{-2} mol/L), the equilibrium in which is established immediately after mixing the solutions of O=Re(Cl)P and Py, a stoichiometric O=Re(Cl)P : Py ratio of 1 : 1 and an equilibrium constant K_1 of $(4.7 \pm 1.1) \times 10^2$ L/mol are determined, allowing us to write the left-hand side of equilibrium (2). The right-hand side is written in light

of the changes in UV–Vis spectrum during titration and the data in [14, 28, 29] on the effect of substituting/attaching axial ligands in oxoporphyrin complexes $O=M^{V}(X)P$, where M is W, Mo, or Re:

$$O=Re(Cl)P + Py \xleftarrow{K_{l}} O=Re(Cl)(Py)P.$$
(2)

The second stage (at a Py concentration of 2.23×10^{-2} –11.17 mol/L) is characterized by needing 10– 15 min to reach equilibrium with a much lower K_2 constant of (0.10 ± 0.03) L²/mol² and a stoichiometric O=Re(Cl)P : Py ratio of 1 : 2 (Fig. 1b):

$$O=Re(Cl)(Py)P + 2Py \xleftarrow{\Lambda_2} [O=Re(Py)_3P]^+ Cl^-. (3)$$

The (3) reaction product structure is confirmed by the IR and ¹H NMR spectroscopy data given below.

The axial bonding is known to have a considerable effect on the vibrational frequencies of metallopor-



Fig. 2. Dependences of log *I* on log C_{Py} for the reaction between O=Re(Cl)P and pyridine additives of (*I*) 8.23 × 10^{-5} -2.23 × 10^{-2} mol/L ($R^2 = 0.97$, tan $\alpha = 0.91$) and (2) 2.23 × 10^{-2} -11.17 mol/L ($R^2 = 0.98$, tan $\alpha = 2.09$) at 298 K.

Table 1. IR spectra in KBr

	Bands			
O=Re(Cl)P	Ру	$[O=Re(Py)_{3}P]^{+} \cdot Cl^{-}$	assingment	
3065			v(C-H) _{Ph}	
3030		3031		
	2956	2963	ν (C–H) _{Pv}	
	2910	2930	2	
2873		2871	ν (C–H) alkyl	
2856		2854	groups	
	1633	1637	Py ring	
	1581		vibrations	
1608		1609	v(C=C)	
1570		1571		
1512		1512		
	1482	1487	$\nu(C-N)_{Py}$	
1460		1455	ν (C=N)	
1441		1441	$\delta(C-H)$	
	1438	1398	$\nu(C-N)_{Py}$	
1379		1378	$\nu(C-N)$	
1290		1288	δ(C-H)	
1249		1245	methyne groups	
	1217	1174	ν (C–H) _{Py}	
	1147			
1104		1104	$\delta(C-H)$	
1058				
	1069		$\delta(C-H)_{Py}$	
	1031			
1026	991			
1026		0.91	$v(C_{\beta}-C)$	
982		981	alkyl groups	
963		962	V(Re=O)	
826			γ(C–H)	
840 790		790		
790 749		750		
723		720		
	748		$\delta(C-H)_{D_{V}}$	
	704	698	ve /ry	
	603			
		542	$v(Re-N_{Pv})$	
464		471	v(Re–N)	
379			v(Re-Cl)	

phyrin molecules [23]. Upon adding three Py molecules to O=Re(Cl)P, the largest changes (low-frequency shifts of 2–5 cm⁻¹) display skeletal vibrations of the macrocycle (v(C=N), δ (C–H) of methyne groups), which is logically associated with the change in the positions of metal atoms in the macrocycle plane [23]. This is also indicated by the high-frequency shift of v(Re-N) by 5 cm⁻¹. The vibrations of peripheral macrocycle substituents (phenyl and alkyl groups) are practically unchanged (Table 1).

New signals of coordinated Py at 2963, 2930, 1637, 1487, 1398, 1174, and 698 cm⁻¹ missing in the spectrum of the initial complex and shifting by 4–40 cm⁻¹ relative to the vibrations of pure Py (Table 1) are observed in the IR spectrum of the reaction (3) product, $[O=Re(Py)_3P]^+Cl^-$. The new signal at 542 cm⁻¹ presumably corresponds to Re–N_{Py} bonds [30]. The signal at 962 cm⁻¹ corresponding to v(Re=O) in the IR spectrum of the product confirms the chemical nature of $[O=Re(Py)_3P]^+Cl^-$.

O=Re(Cl)P has the ¹H NMR spectrum typical of diamagnetic MPs with clearly separated signals and is in good agreement with the literature data [26]. The introduction of Py (in the concentration leading to the formation of $[O=Re(Py)_3P]^+Cl^-)$ into the solution of O=Re(Cl)P in CDCl₃ is accompanied by the emergence of three proton signals of pyridine rings at 8.58, 7.62, and 7.24 ppm, which undergo a slight upfield shift (0.04–0.06 ppm) relative to the signals of uncoordinated pyridine [31]. The axial bonding of Py leads to an upfield shift (relative to the spectrum of O=Re(Cl)P in CDCl₃) of the signals of the *meso*-protons of the macrocycle (by 0.06 ppm) and signals of the *ortho*-protons of phenyl substituents (by ≈ 0.1 ppm), while the protons of the $-OCH_3$ group are shifted downfield (by ≈ 0.1 ppm). Such shifts of the proton signals of the macrocycle in the composition of the porphyrin-pyridine supramolecule $[O=Re(Py)_3P]^+Cl^$ can be explained by the reduced effect of the ring current of the porphyrin macrocycle due to the emergence of an additional positive charge on the Re atom upon adding Py molecules.

A comparison of equilibrium constants K_1 and K_2 shows that the presence of one Py molecule in the O=Re(Cl)(Py)P first coordination sphere prevents the subsequent bonding of Py in the second stage of the process. The displacement of Cl⁻ from the O=Re(Cl)(Py)P coordination sphere and the addition of two more Py molecules occur over time.

During the reaction between O=Re(CI)P and Py, two pyridine-containing compounds of rhenium(V) porphyrin, O=Re(CI)(Py)P and $[O=Re(Py)_3P]^+CI^$ can be separated from the solution, the electronic absorption spectra for which differ in the position of the bands and the ratio of their intensities. The UV– Vis spectrum of O=Re(CI)(Py)P in CH_2CI_2 (λ_{max} , nm) are (I) 353, 484 (shoulder) and (II) 518 (II > I). For $[O=Re(Py)_3P]^+CI^-$, (I) 409, (II) 461, and (III) 545 (II > I > III).

A comparison of the properties of the donoracceptor system obtained and analogs based on oxoporphyrin complexes with different sets of substituents

Reaction equation	K_n , L/mol	Source
$O = \operatorname{Re}(\operatorname{Cl})P + \operatorname{Py} \xleftarrow{K_1} O = \operatorname{Re}(\operatorname{Cl})(\operatorname{Py})P$	$(4.7 \pm 1.1) \times 10^2$	
$O = \operatorname{Re}(\operatorname{Cl})(\operatorname{Py})P + 2\operatorname{Py} \xleftarrow{K_2} [O = \operatorname{Re}(\operatorname{Py})_3P]^+ \operatorname{Cl}^-$	$(0.10 \pm 0.03) \text{ L}^2/\text{mol}^2$	
$O=W(OH)TPP + Py \xleftarrow{K_1} O=W(OH)(Py)TPP$	$(1.33 \pm 0.22) \times 10^4$	[25]
$O=W(OH)(Py)TPP + Py \xleftarrow{K_2} [O=W(Py)_2TPP]^+OH^-$	$(8.42 \pm 1.58) \times 10^3$	"
$[O=W(Py)_2TPP]^+OH^- + Py + H_2O \xleftarrow{K_3} [(OH)W(Py)_3TPP]^{2+} 2OH^-$	89 ± 13	"
$O=Mo(OH)TPP + Py \xleftarrow{K_1} [O=Mo(Py)TPP]^+OH^-$	$(9.1 \pm 1.2) \times 10^3$	[26]
$[O=Mo(Py)TPP]^+OH^- + Py + H_2O \xleftarrow{K_2} [(OH)Mo(Py)_2TPP]^+ 2OH^-$	39.3 ± 5.2	"
$[(OH)Mo(Py)_{2}TPP]^{+} 2OH^{-} + Py \xleftarrow{K_{3}} [Mo(Py)_{3}TPP]^{3+} 3OH^{-}$	1.0 ± 0.1	"

Fable 2.	Quantitative	parameters of th	ne reactions	between metal	oporph	vrins and	pyridine in toluene
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 K_n is a stepwise equilibrium constant.

and central metal atoms earlier studied (Table 2) shows that the porphyrin-pyridine complexes were relatively stable. It can be seen from Table 2 that the reaction between oxo-coordinated MP (M = Re, W, Mo) and Py is a complex process which ends with the formation of donor-acceptor complexes with a stoichiometric composition of 1:3 in all cases. The reaction of O = Re(Cl)P is characterized by lower values of the equilibrium constants than the similar reactions of O=W(OH)TPP and O=Mo(OH)TPP. The sequence of the change in K values repeats the series of changes in the covalent radius of W (162 pm), Mo (154 pm), and Re (151 pm) [32]. However, this correlation could be random, since the nature of the stepwise reactions between MP and Py changes dramatically. With Mo–W complexes, if the O=Re(Cl)P reaction with Py does not affect the oxo group in the molecule, the latter becomes the center of the reaction in the second and third stages of the reaction with Py, respectively. The established relationship between the stability constants of the porphyrin-pyridine supramolecules and the nature of the metal of the porphyrin component of the donor-acceptor complex can be used in developing and synthesizing donor-acceptor systems with predictable stability. This is an important factor in optimizing the chemical structures of compounds to create hybrid materials based on them (e.g., catalytic systems, sensors, and photoactive components for photovoltaic devices).

The formation of a stable donor-acceptor compound of rhenium(V) porphyrin with the first Py molecule indicates the obtained data can be used to create donor-acceptor dyads of metalloporphyrins with pyridyl derivatives of nanocarbon. In [16], the self-organization of 5-phenyl-2,3,7,8,12,13,17,18-octaethylporphinato)(oxo)(phenoxo)rhenium(V)-2'-(pyridine-4-yl)-5'-(pyridine-2-yl)-1'-(pyridine-3-ylmethyl)-2',4'dihydro-1'H-pyrrolo[3',4':1,2][C₆₀- I_h][5,6]fullerenedichloromethane systems ending in the formation of a cationic donor-acceptor 1 : 1 complex with a PhO⁻ ligand in the external coordination sphere was studied qualitatively. Such porphyrin–fullerene dyads have the property of electron transfer from a donor (macrocycle) to an acceptor (fullerene fragment) during photoexcitation. For fluorescent metalloporphyrins (manganese(III), molybdenum(V), and other complexes), PET is detected from fluorescence quenching upon the formation of the donor–acceptor complex [25, 33]. Preliminary testing of the rhenium O=Re(Cl)P complex for coordination ability with respect to acceptor 1'-*N*-methyl-2'-(pyridine-4yl)pyrrolidino[3',4':1,2][60]fullerene (PyC₆₀)



using electronic absorption and fluorescence spectroscopy had a positive result namely the formation of donor-acceptor porphyrin-fullerene in the CH_2Cl_2 medium. Despite less pronounced changes in the UV–Vis spectrum of O=Re(Cl)P with an excess of substituted fullerene instead of pyridine (i.e., a slight increase in the intensity of the band at 355 nm and a hypsochromic shift of the charge transfer band to 524 nm; Fig. 3a), the formation of a donor-acceptor complex and charge redistribution in it can be identified from the considerable drop in the fluorescence of free substituted fullerene, compared to the metalloporphyrin-bound fullerene (Fig. 3b).

The results [25, 34] from modifying titanium photoanodes with films of donor-acceptor complexes based on d-metals (including rhenium) that show an BICHAN et al.



Fig. 3. (a) Electronic absorption and (b) fluorescence spectra recorded in dichloromethane at 298 K of (1) O=Re(Cl)P, (2) its complex with PyC₆₀, and (3) PyC₆₀; (1, 2) $C_{O=Re(Cl)P} = 2.13 \times 10^{-5} \text{ mol/L}$; (2, 3) $C_{PyC_{60}} = 8.32 \times 10^{-5} \text{ mol/L}$; $\lambda_{exc} = (1, 2) 525$ and (3) 395 nm.

increase in the conversion of light energy in the presence of modifiers are an additional argument in favor of extending the possibilities of designing photoactive supramolecules using rhenium(V) porphyrins.

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