

COORDINATION
COMPOUNDS

Chemical Structure and Reactions
of Axially Coordinated Iridium(III) Porphyrins

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Abstract—Effect of modification of the axial (fifth and sixth) coordination sites on the physicochemical properties and reactivity of iridium(III) complexes with 5,10,15,20-tetraphenyl-21H,23H-porphine was studied. Oxidation reactions of (Cl)(H₂O)IrTPP in protic solvents by atmospheric oxygen (on assistance of protons at high concentration) preceded by ligand substitution at the axial position were studied. It was found that (Cl)(H₂O)IrTPP in 100% AcOH undergoes slow one-electron oxidation at the aromatic ligand to form π cation radical (CH₃COO)(CH₃COOH)IrTPP^{•+}. The reaction was studied in 100% AcOH (H₂O content 0.078%) at 288–308 K, its kinetic parameters were obtained. The (Cl)(H₂O)IrTPP reaction product in CF₃COOH was identified as complex (CF₃COO)₂Ir^{IV}TPP oxidized at the central metal cation. It was experimentally confirmed that the reaction in 99% CF₃COOH at 298 K proceeds in two stages: the substitution of axial Cl[−] and H₂O by excess CF₃COO[−] ($k_{\text{eff}} = (1.8 \pm 0.1) \times 10^{-3} \text{ s}^{-1}$) and the oxidation of iridium to Ir(IV) ($k_{\text{eff}} = (8.0 \pm 0.5) \times 10^{-5} \text{ s}^{-1}$). Data on similar Re(III) complexes (PhO)ReTPP and (Cl)ReTPP are presented for comparison.

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Variable valence in chemical compounds is one of the reasons of structure variety of iridium coordination compounds, in particular, complexes with tetrapyrrole ligands. Few Ir(I) porphyrin complexes are presented in the literature by several works. Among described compounds are intermediate [Ir^I(CO)₃]₂OEP in the course of (Cl)(CO)Ir^{III}OEP synthesis from [Ir(cod)Cl]₂ (cod is cyclooctadiene) and H₂OEP [1], tetracoordinated bis[iridium(I)] complex with N-confused porphyrin (NCTPP)Ir₂^I(CO)₄ (NCTPP is the dianion of N-confused 5,10,15,20-tetraphenyl-21H,23H-porphine) [2], and donor-acceptor SAT (sitting a top) complex μ -(5,10,15,20-tetraphenylporphyrine)-bis-chloroiridium(I) [3]. Oxidation state 3+ and CN = 6 are more typical for iridium [4]. Structures with central Ir(III) atom were studied for compounds of classes hexaphyrins [5], corroles [6, 7], porphyrins [8–11], and N-confused porphyrins [2].

According to [5–11], Ir(III) porphyrinoids display catalytic and redox activity, which depends on the state of axial coordination sites on the metal atom. Porphyrin complexes show distinct photoluminescent properties [12, 13]. There is a rapidly growing interest in the chemistry of aromatic macroheterocyclic iridium compounds in recent years due to the noted features.

The aim of this work is to study the state and reactions of 5,10,15,20-tetraphenyl-21H,23H-porphine (H₂TPP) complexes with trivalent iridium cation (for-

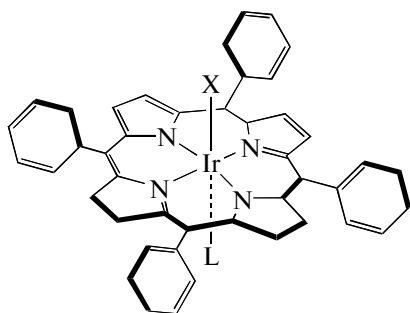
mula) in protolytic solvents AcOH and CF₃COOH and to reveal the effect of modification at the fifth and sixth axial coordination sites in molecule on the physicochemical properties and reactivity of the complexes. We also obtained data for similar Re³⁺ complexes presented for comparison. Only few works in the literature were dedicated to the physical chemistry of Re³⁺ complexes with tetrapyrrole ligands: for derivatives of *trans*-difluorophthalocyanine *trans*-[Re(F)₂pc²⁻][−] and N-confused porphyrin Re^{III}(NFP)OL (P = TPP²⁻) [14, 15].

EXPERIMENTAL

(5,10,15,20-tetraphenylporphinato)chloroaquairidium(III) (Cl)(H₂O)Ir^{III}TPP [16]. A mixture of H₂TPP (0.00360 g), (H₃O)₂IrCl₆ (0.01115 g) (molar ratio 1 : 5), and phenol (2.0 g) was heated under reflux for 3 h. Reaction completion was detected by the disappearance of H₂TPP in the reaction mixture using thin-layer chromatography (TLC) (Silufol, chloroform). The reaction mixture was cooled, dissolved in chloroform, and washed many times with warm distilled water in a separating funnel to remove phenol. The chloroform solution was concentrated and chromatographed on Brockmann activity grade II alumina using chloroform as an eluent. There were three zones. The substances of the first and the third zones were purified repeatedly. Trace amounts of compound of unknown composition from the second zone were discarded.

Table 1. ^1H NMR spectra of (L)(X)IrTPP in CDCl_3 depending on solvent used for chromatography

Solvents Product ratio	δ , ppm, J , Hz		
	H_β	$\text{H}_o, \text{H}_m, \text{H}_p$	axial ligands
Benzene– CHCl_3	9.06 (s, 8 H_β)	8.17 (d, 8 $\text{H}_o, J = 7$), 7.75 (m, 12 $\text{H}_{m,p}$)	H_2O 2.18 (s, 2H) (Cl)(H_2O)IrTPP
(Cl)(H_2O)IrTPP : (OH)(H_2O)IrTPP = 10 : 1	8.9 (s, 8 H_β)	8.58 (d, 8 $\text{H}_o, J = 7$), 7.52 (t, 8 H_p), 7.36 (t, 4 H_m)	H_2O 0.35 (s, 2H) OH –1.41 (s, 1H) (OH)(H_2O)IrTPP
EtOH– CH_3COOH	9.06 (s, 8 H_β)	8.17 (d, 8 $\text{H}_o, J = 7.3$), 7.75 (m, 12 $\text{H}_{m,p}$)	CH_3COOH 1.78 (d, 3H, $\text{CH}_3, J = 7.3$) (Cl)(CH_3COOH)IrTPP
(Cl)(CH_3COOH)IrTPP : (Cl)(EtOH)IrTPP : (OH)(EtOH)IrTPP = 3 : 1 : 1	9.02 (s, 8 H_β)	8.1 (d, 8 $\text{H}_o, J = 7.3$), 7.75 (m, 12 $\text{H}_{m,p}$)	EtOH 3.53 (m, 2H, CH_2) (Cl)(EtOH)IrTPP
	9.09 (s, 8 H_β)	8.22 (d, 8 $\text{H}_o, J = 7.3$), 7.75 (m, 12 $\text{H}_{m,p}$)	EtOH 3.63 (m, 2H, CH_2) OH –1.2 (s, 1H) (OH)(EtOH)IrTPP



$\text{X} = \text{Cl}, \text{L} = \text{H}_2\text{O}, (\text{Cl})(\text{H}_2\text{O})\text{IrTPP}$
 $\text{X} = \text{OH}, \text{L} = \text{H}_2\text{O}, (\text{OH})(\text{H}_2\text{O})\text{IrTPP}$
 $\text{X} = \text{Cl}, \text{L} = \text{CH}_3\text{COOH}, (\text{Cl})(\text{CH}_3\text{COOH})\text{IrTPP}$
 $\text{X} = \text{Cl}, \text{L} = \text{C}_2\text{H}_5\text{OH}, (\text{Cl})(\text{EtOH})\text{IrTPP}$
 $\text{X} = \text{OH}, \text{L} = \text{C}_2\text{H}_5\text{OH}, (\text{OH})(\text{EtOH})\text{IrTPP}$

The substance from the first zone was purified by chromatography on silica gel L 100/250 using chloroform and next ethanol–chloroform (1 : 1, v/v). A crimson zone containing iridium(I) complex with molecular porphyrin ligand (SAT complex) $[\text{IrCl}(\text{H}_2\text{O})_2]_2\text{H}_2\text{TPP}$ [16] was isolated. The individuality of the purified compound was confirmed by TLC on Silufol plates with the use of chloroform $R_f = 0.94$. UV-vis (benzene, λ_{max} , nm, $(\log \epsilon)$): 420 (5.11), 482 (3.27), 518 (3.73), 544 (3.73), 594 (3.25), 652 (3.1).

The compound from the third zone was repeatedly chromatographed on alumina using chloroform. The main zone was adsorbed in the upper part of the column. The substance from this zone was eluted with benzene– CHCl_3 . The obtained compound was identified by UV-vis spectrum as the complex of composition (Cl)(H_2O)Ir^{III}TPP. Yield 7%. UV-vis (CHCl_3 , λ_{max} , nm, $(\log \epsilon)$): 395 (shoulder 3.91), 418 (5.78), 476 (shoulder 3.60), 508 (shoulder 3.73), 549 (4.42), 588 (3.81), 640 (3.63).

The IR spectrum of the compound of the main zone eluted from chromatographic column with $\text{C}_2\text{H}_5\text{OH}$ –1% CH_3COOH (a solid chaotic layer, ν , cm^{-1}): phenyl substituents, 702 m, 754 s ($\gamma(\text{C}-\text{H})$); 1045, 1072 m, 1207 s ($\delta(\text{C}-\text{H})$); 1488, 1597 m, 1622 ($\nu(\text{C}=\text{C})$); 3026, 3054 ($\nu(\text{C}-\text{H})$); pyrrole fragments, 802 s ($\gamma(\text{C}-\text{H})$); 1277 ($\nu(\text{C}-\text{N})$); 1320 ($\nu(\text{C}=\text{N})$); 2853 m, 2924 s ($\nu(\text{C}-\text{H})$); 1441 m skeletal vibrations of pyrrole rings; coordination center, 465 ($\nu_s(\text{Ir}-\text{N})$) and 526 ($\nu_{as}(\text{Ir}-\text{N})$); 573 and 662 ($\nu_{as}(\text{Ir}-\text{O})$ and $\nu_s(\text{Ir}-\text{O})$); 1351 ($\delta(\text{O}-\text{H})$).

^1H NMR spectra depending on the nature of L and X^- are presented in Table 1.

(5,10,15,20-Tetraphenyl-21H,23H-porphinato)(phenoxo)rhenium(III) (PhO)ReTPP and (5,10,15,20-tetraphenyl-21H,23H-porphinato)chlororhenium(III) (Cl)ReTPP were prepared similarly to [17]. H_2TPP and H_2ReCl_6 in molar ratio 1 : 2 were heated under reflux in phenol at 454 K. The reaction completion was detected after 2 h by the termination of alterations in the UV-vis spectrum of reaction mixture sampled in

chloroform. The reaction mixture was cooled and dissolved in chloroform. The solution in CHCl_3 was washed many times with warm distilled water in a separating funnel to remove phenol, concentrated by partial removal of the solvent, and chromatographed on an Al_2O_3 column (Brockmann activity grade II) using chloroform. Two zones were obtained: green and green–brown. The substances isolated from the first and the second zones were subjected to repeated chromatography.

The chromatography of the substance from the green zone on a column with silica gel (40/100 Chemapol) using benzene as an eluent afforded an individual orange zone containing (Cl)ReTPP. The zone containing μ -oxo-dimeric form of Re^{5+} compound $[\text{O}=\text{ReTPP}]_2\text{O}$ and concentrated at the top of the column was eluted with a CHCl_3 – $\text{C}_2\text{H}_5\text{OH}$ (1 : 1).

The chromatography of substance from the green–brown zone on a silica gel column using benzene as an eluent gave a pink zone of (PhO)ReTPP. Next, $[\text{O}=\text{ReTPP}]_2\text{O}$ was eluted with a CHCl_3 – $\text{C}_2\text{H}_5\text{OH}$ (1 : 1).

Solid amorphous samples of the complexes were isolated from solutions by solvent evaporation at ambient temperature. The individuality and chromatographic purity of the products were confirmed by TLC on silica gel Silufol plates using benzene. For (Cl)ReTPP $R_f = 0.80$, for (PhO)ReTPP $R_f = 0.83$.

(Cl)ReTPP. Yield 0.5%. UV-vis (CHCl_3 , λ_{max} , nm): 555 (shoulder), 525, 495 (shoulder), 416. UV-vis (AcOH, λ_{max} , nm): 540 (shoulder), 520, 480, 437 (shoulder), 417. IR (300–2000 cm^{-1} , as KBr pellet, ν , cm^{-1}): phenyl substituents, 705, 759 ($\gamma(\text{C}-\text{H})$); 1075, 1172 ($\delta(\text{C}-\text{H})$); 1466, 1595, 1614 ($\nu(\text{C}=\text{C})$); pyrrole fragments, 799 ($\gamma(\text{C}-\text{H})$); 1029 (C_3-C_4 ($\nu(\text{C}-\text{N})$, $\delta(\text{C}-\text{H})$); 1350 ($\nu(\text{C}-\text{N})$); 1377 ($\nu(\text{C}=\text{N})$); coordination center, 408 (Re–N); 374, 392 (Re–Cl).

(PhO)ReTPP. Yield 7%. UV-vis (CHCl_3 , λ_{max} , nm, (log ϵ)): 660 (shoulder), 551 (2.3), 436 (shoulder), 425 (4.3). IR (solid chaotic layer, ν , cm^{-1}): phenyl substituents, 702, 758 ($\gamma(\text{C}-\text{H})$); 1068, 1178 ($\delta(\text{C}-\text{H})$); 1487, 1578, 1600 ($\nu(\text{C}=\text{C})$); 2956, 3060 ($\nu(\text{C}-\text{H})$); pyrrole fragments, 806 ($\gamma(\text{C}-\text{H})$); 997 (C_3-C_4 , $\nu(\text{C}-\text{N})$, $\delta(\text{C}-\text{H})$); 1340 ($\nu(\text{C}-\text{N})$); 1377 ($\nu(\text{C}=\text{N})$); coordination center, 418 (Re–N); 663 (Re–O); axial ligand, 1265, 1462, 1542 (–OPh). ^1H NMR (CDCl_3 , δ , ppm): 8.95 (d, 8 H_β), 8.25, 8.15 (d, m, 8 H_o); 7.80 (m, 8 H_m), 7.55 (m, 4 H_p), 3.63 (s, 2 H_o (OPh)), 4.71 (s, 2 H_m (OPh)), 5.37 (s, 1 H_p (OPh)).

UV-vis, IR, and NMR spectra were recorded on an Agilent 8453 UV-Vis and a Specord M-400 spectrophotometers, a VERTEX 80v spectrometer, and a Bruker AVANCE-500 radiospectrometer (using TMS as an internal reference), respectively. Solid layers of complexes for IR spectral study were prepared by evaporation of CHCl_3 solvent from a solution of complex on a silicon plate.

The reaction rates of complexes in AcOH and CF_3COOH were determined from the drop of compound concentrations monitored by spectrophotometry. The measurements were performed in 1-cm path length cells placed into a special thermostated chamber of the spectrophotometer. Accuracy of solution temperature determination was ± 0.1 K. Solutions of complexes in sulfuric acid were prepared immediately prior to thermostating. The kinetics of complexes oxidation reactions was studied by the isolation method.

Rate constants and activation energies (k_{eff} , E_{eff}) were determined using dependences $\log[(A_0 - A_\infty)/(A_\tau - A_\infty)]$ vs. T , $\ln k_{\text{eff}}$ vs. $1/T$, respectively, standard deviations were found by least squares using Microsoft Excel software. Here A_0 , A_∞ , and A_τ are the optical densities of solutions at working wavelength at time (τ) equal to 0, current τ , and the time of reaction completion; T is temperature. Activation entropy ($\Delta S_{\text{eff}}^\ddagger$) of reaction was determined by the Eyring equation in application to liquid systems for the second standard state.

100% Acetic acid was prepared by fractional defrost of glacial AcOH (water content of 0.078% was determined by the Karl Fischer titration).

RESULTS AND DISCUSSION

The prepared compounds were identified as penta-coordinated rhenium(III) complexes (X)ReTPP and hexacoordinated iridium(III) complexes (L)(X)IrTPP from the hypso-type UV-Vis spectra typical of porphyrin complexes of triply charged metal cations [18] and from the data of IR and ^1H NMR spectroscopy that agree well with those reported in [16, 17]. The results of identification of axial ligands X and L are given below.

The high reactivity of iridium(III) complexes at the axial directions was shown in the literature by the examples of $\text{Ir}(\text{CO})(\text{Cl})\text{OEP}$ reactions with pyridine, *N*-(*n*-butyl)imidazole, and (carboxy)imidazole [12] and transformation of water-soluble aqua and hydroxy derivatives of Ir(III) tetra(sulfophenyl)porphyrins in aqueous and methanolic solutions [10, 19]. The analysis of relative signal intensities in the ^1H NMR spectra of iridium complexes (Table 1) indicates the obvious dependence of axial ionic and molecular ligands in the compounds on solvents used at the complex purification stage. The solvent also affects the number of compounds present in solution. Thus, the purification of iridium complex with a benzene– CHCl_3 mixture (on repeated chromatography) leads to emergence of signals in ^1H NMR spectrum in CDCl_3 at 2.18, 0.35 ppm and –1.41 ppm related by us to the proton signals of coordinated H_2O and hydroxide ion OH^- , respectively [20, 21]. At the same time, the presence of two distinct singlets of pyrrole H_β protons at $\delta = 9.06$ and 8.9 ppm and two sets of resonances for the H_o , H_m , and H_p protons of *meso* phenyl substituents indicates the presence of $(\text{H}_2\text{O})(\text{Cl})\text{IrTPP}$ and $(\text{H}_2\text{O})(\text{OH})\text{IrTPP}$ at equilibrium in the solution in a 10 : 1 ratio.

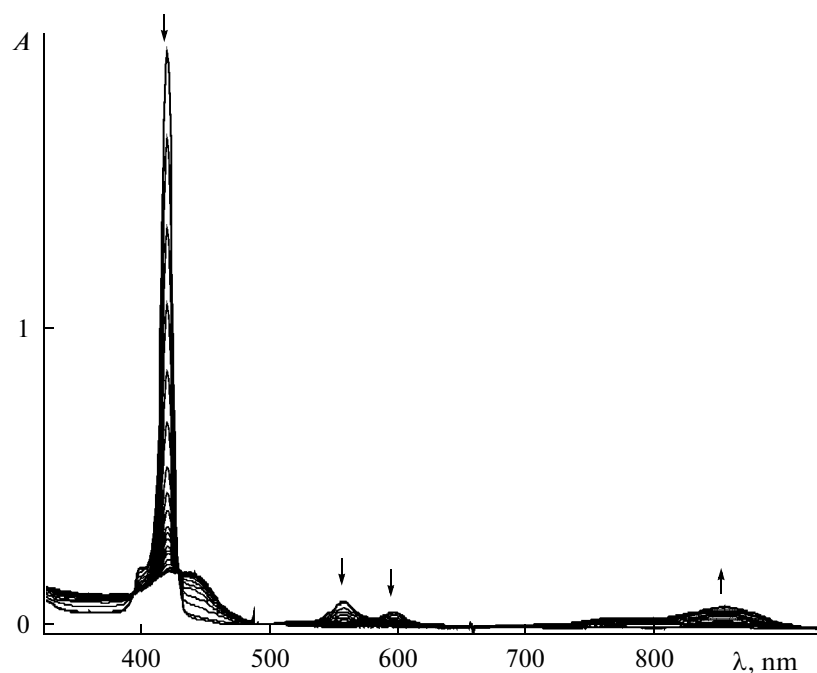


Fig. 1. UV-vis spectrum of (Cl)(H₂O)IrTPP in 100% AcOH at 298 K and τ (s) varied from 0 to 3600.

When C₂H₅OH–1% CH₃COOH was used for the chromatography of iridium(III) complex with H₂TPP, its ¹H NMR spectrum (in CDCl₃) displays new peaks of resonances of C₂H₅OH (3.53 and 3.63 ppm), CH₃COOH (1.78 ppm), and hydroxide ion OH[–] (–1.2 ppm). The IR spectrum of the compound eluted from chromatographic column with C₂H₅OH–1% CH₃COOH shows absorption with maxima at 573 and 662 cm^{–1} and a distinct peak at 1351 cm^{–1} (O–H bending vibrations), which indicate the presence of coordinated ethanol molecules in the structure of the complex.

The ¹H NMR spectrum of compound isolated by chromatography with C₂H₅OH–1% CH₃COOH exhibits three singlets (9.02, 9.06, and 9.09 ppm) related to H_β and three doublets of phenyl *ortho* protons (8.1, 8.17, and 8.22 ppm). These signals correspond to three different iridium(III) compounds. The signals of the most distant from the porphyrin macrocycle *para* and *meta* protons of the phenyl substituents display the least shift and appear as one large multiplet at $\delta = 7.75$ ppm. The computation of relative integrated intensities for the signals of protons of the same kind and the number of protons of axial ligands allows us to suppose the presence in solution of a mixture of porphyrin complexes (Cl)(CH₃COOH)IrTPP, (Cl)(EtOH)IrTPP, and (OH)(EtOH)IrTPP in 3 : 1 : 1 ratio (Table 1).

It should be noted that an upfield shift of proton signals of axial ligands in ¹H NMR spectrum (as compared with the signals of free molecules) under the action of porphyrin ligand ring current is observed for all considered iridium compounds.

The IR spectrum of (PhO)ReTPP shows absorption with maximum at 418 cm^{–1} corresponding to vibrations of Re–N bonds and the maximum for (Cl)ReTPP is shifted to 408 cm^{–1}. The latter feature probably results from the decrease in the Re–N bond force constant because of the participation of electron pairs of Cl in conjugation with Re *d* _{π} orbitals. Ligand –OPh was detected by the presence of signals of *o*-, *m*-, and *p*-protons in the ¹H NMR spectrum of complex (PhO)ReTPP, which are shifted upfield as compared with the proton signals of free phenol like in the case of iridium complexes [22]. The presence of phenoxy ligand in (PhO)ReTPP is confirmed by a new intense absorption in the IR spectrum of the compound (medium intensity bands within all spectrum) at 1285 cm^{–1} in maximum that corresponds to ν (C–O) vibrations. Furthermore, the spectrum of (PhO)ReTPP in the region of C=C bond vibrations of aromatic benzene ring (1487, 1578, and 1600 cm^{–1}) exhibits supplementary absorption bands of the same nature related to phenyl incorporated into coordinated phenoxy ligand. These are the absorption bands with frequencies 1462 and 1542 cm^{–1}. Axial ligand vibrations in (Cl)ReTPP are probably related to absorption bands at 374, 392 cm^{–1} (342 cm^{–1} in the spectrum of [ReCl₆]^{2–} [23]).

The composition of (L)(X)IrTPP at the axial position varies when the compounds are placed into solution. In glacial acetic acid, Ir(III) complexes form molecular solutions without proton transfer [24]. The spectrum of (Cl)(H₂O)IrTPP is similar to the UV-vis spectrum in chloroform but contains bathochromically shifted by ~10 nm *Q* bands (Fig. 1, $\tau = 0$). At $T \geq 288$ K, the spectrum transforms in time with retention of

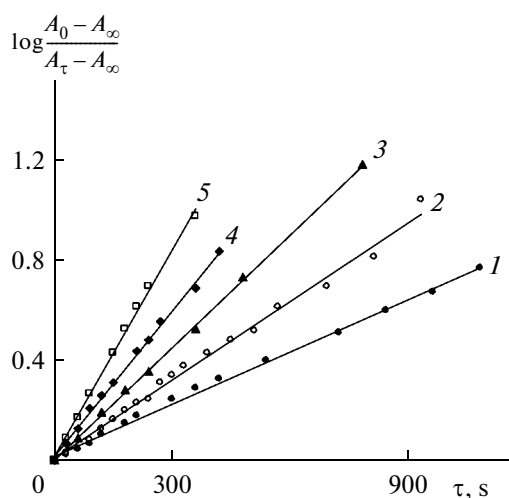
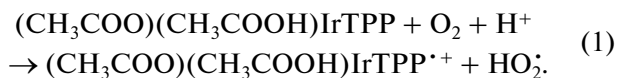


Fig. 2. Dependence $\log[(A_0 - A_\infty)/(A_\tau - A_\infty)]$ vs. τ for reaction of $(\text{Cl})(\text{H}_2\text{O})\text{IrTPP}$ in 100% AcOH at T , K: 288 (1), 293 (2), 298 (3), 303 (4), 308 (5). $\rho = 0.992\text{--}0.997$.

distinct isosbestic points (Fig. 1): the intensity of the Soret band (418 nm) and long-wavelength bands with maxima at 557 and 595 nm decreases, new bands at 438 and 770–850 nm appear and grow. The presence of isosbestic points at 392, 428, 492, and 688 nm (Fig. 1) indicates the single initial form of the complex, $(\text{CH}_3\text{COO})(\text{CH}_3\text{COOH})\text{IrTPP}$, which undergoes transformation into the second colored compound in the absence of other colored forms (with allowance made for the constant total concentration of interconverting compounds). Such changes in UV-vis spectrum are typical for the reactions of one-electron oxidation of metal porphyrins with atmospheric oxygen in the presence of acids [21, 25–28] to form their π cation radicals (equation (1)). The final spectrum of reaction product coincides with the spectrum of an oxidized form of iridium(III) complex with 5,10,15-tris-pentafluorophenylcorrole, $(\text{PPh}_3)\text{IrTPFC}^+$, prepared by electrochemical oxidation of $(\text{PPh}_3)\text{IrTPFC}$ with *t*-4BPA tris(4-bromophenylammonium) hexachloroantimonate and identified by ESR [29].



The reaction (1), which formally has first order toward metal porphyrin concentration (Fig. 2), was studied in AcOH (H_2O content 0.078%) within temperature range 288–308 K, kinetic parameters of the oxidation reaction are represented in Table 2.

On dissolution of $(\text{Cl})(\text{H}_2\text{O})\text{IrTPP}$ in CF_3COOH , the Soret band is broadened and exhibits two maxima at $\lambda_{\text{max}} = 405$ and 410 nm (Fig. 3, $\tau = 0$). At 298 K, gradually changed in time spectra produce sequentially two series of curves with isosbestic points (Fig. 3). One can suppose that the complication of spectral pattern of complex transformation in CF_3COOH is associated with the presence of slow initial stage of substi-

tution of axial ligands. Indeed, CF_3COO^- has lower affinity to metal porphyrin as compared with CH_3COO^- because of strong electron-withdrawing effect of three fluorine atoms. Therefore, the reaction of complete substitution of initial axial ligands instantly proceeds in AcOH but carries on in time in the case of trifluoroacetic acid, which is demonstrated by the presence of the complicated Soret band in UV-vis spectrum in the initial period (Fig. 3a), which becomes symmetrical band with maximum at 402 nm in the course of transformation. Rate constant k_{eff} of this process in 99% CF_3COOH at 298 K is $(1.8 \pm 0.1) \times 10^{-3} \text{ s}^{-1}$.

The second series of spectral curves (Fig. 3b) exhibits decrease in the intensity of band at 402 nm and growth of absorption at $\lambda_{\text{max}} = 355$ and 685 nm in the region of 450–500 nm. Similar hypsochromic shift of the Soret band by more than 30 nm and emergence of band at 685 nm is observed upon electrochemical

Table 2. Kinetic parameters for $(\text{Cl})(\text{H}_2\text{O})\text{IrTPP}$ oxidation in acetic acid ($C_{\text{H}_2\text{O}} = 0.078\%$)

T , K	$k_{\text{eff}} \times 10^3, \text{ s}^{-1}$
288	1.8 ± 0.1
293	2.5 ± 0.1
298	3.5 ± 0.1
303	4.8 ± 0.2
308	6.6 ± 0.2

$$E_{\text{eff}} = 48 \pm 2 \text{ kJ/mol}, \Delta S_{\text{eff}}^\ddagger = -299 \pm 5 \text{ J/(mol K)}$$

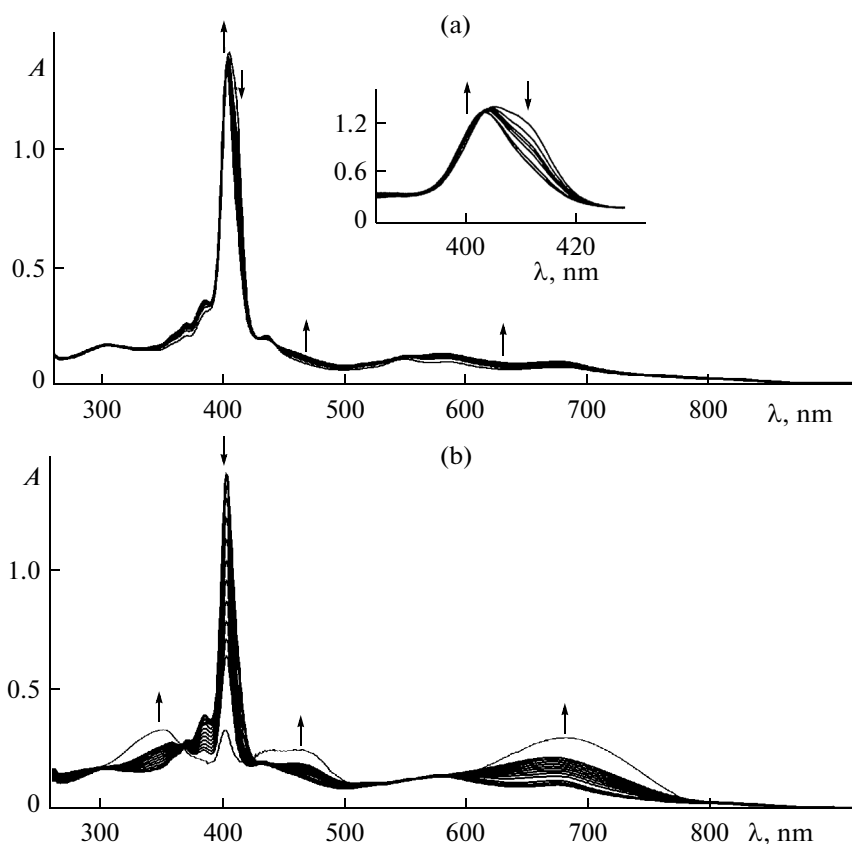
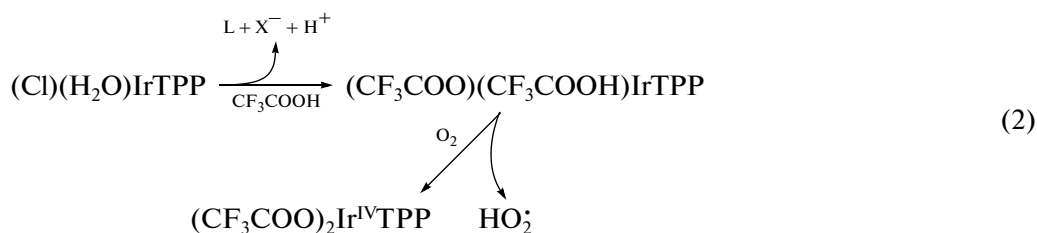


Fig. 3. UV-vis spectrum of $(\text{Cl})(\text{H}_2\text{O})\text{IrTPP}$ in 99% CF_3COOH at 298 K and τ (s) varied from 0 to 340 (a), from 341 to 7000 (b). The last spectrum was recorded after 24 h.

oxidation of $(\text{Py})_2\text{IrTPFC}$ and $(\text{TMA})_2\text{IrTPFC}$ (Py is pyridine, TMA is trimethylamine) [29] and chromium(III) porphyrinoids [30, 31] and indicates one-electron oxidation of the complex at the central metal atom. Thus, the second sequential stage of reaction of

initial $(\text{Cl})(\text{H}_2\text{O})\text{IrTPP}$ with CF_3COOH (Fig. 3b, equation (2)) is a one-electron oxidation of $(\text{CF}_3\text{COO})(\text{CF}_3\text{COOH})\text{Ir}^{\text{III}}\text{TPP}$ into $(\text{CF}_3\text{COO})_2\text{Ir}^{\text{IV}}\text{TPP}$, oxidation rate constant k_{eff} is equal to $(8.0 \pm 0.5) \times 10^{-5} \text{ s}^{-1}$ for 99% CF_3COOH at 298 K.



It is seen from the noted above that the macrocycle always remains within complex as distinct from the initial axial ligands. To confirm this statement, the compounds after completion of reaction in AcOH and CF_3COOH were isolated into chloroform, washed out from the acids, and tested spectrophotometrically: the bands of initial Ir(III) compounds in molecular form (420 and 555 nm) were detected.

The comparison of rates of the two consecutive reactions shows that the principle of quasi-stationary

state could not be employed to study kinetics of the total reaction of Ir(III) complexes in trifluoroacetic acid. Therefore, one may consider the acquisition of two separated in time series of spectral curves in experiment as a success, which allowed us to obtain kinetic constant for each of two consecutive stages of the complex reaction.

$(\text{Cl})\text{ReTPP}$ is stable in glacial AcOH , its electronic absorption spectrum in this medium is similar to that in chloroform (Experimental) and does not change on

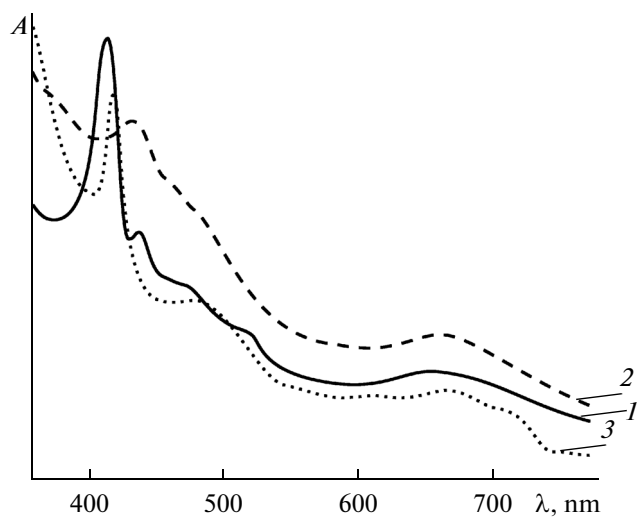


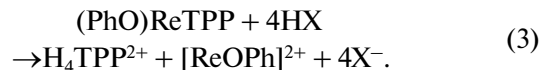
Fig. 4. UV-vis spectrum of (Cl)ReTPP in AcOH–3 M H₂SO₄ immediately after dissolution (1) and after keeping for 3 h at 298 K (2), in CHCl₃ after reprecipitation on ice (3).

heating to 328 K. The Soret and *Q* (0,0) bands are shifted hypsochromically by 5 nm relative to the spectrum in chloroform. In AcOH–3 M H₂SO₄ at 308 K, its spectrum displays bathochromic shift of *Q* band to 680 nm and that of *B* band to the region from 418 to 440 nm, as well as increase in the total background of absorption in the visible region (Fig. 4, lines 1 and 2). These changes indicate unambiguously the formation of π cation radical (Cl)ReTPP^{•+}.

The electronic absorption spectrum of the final compound transferred into chloroform and purified from protic solvents (Fig. 4, line 3) shows the presence

of the band of initial (Cl)ReTPP and its π cation radical, which is stable even in organic solvent.

(PhO)ReTPP, in contrast to (Cl)ReTPP, dissociates at the Re–N bonds to give dication H₄TPP²⁺ (equation (3), Fig. 5): slowly in 100% AcOH at 298 K and quickly, upon dissolution, in media containing sulfuric acid (AcOH–H₂SO₄, H₂SO₄–H₂O).



Different stability of two axial complexes of rhenium porphyrin indicates the strong binding of Cl[–] and –OPh in the complexes in acidic solvents, which differs rhenium from iridium in the corresponding compounds.

Variation of the central atom in the isostructural metal porphyrins is one of the factors that change reactivity upon oxidation in aerated acids. (Cl)RhTPP in mixed solvent AcOH–3–5 M H₂SO₄ produces H⁺-associated form (O₂)RhTPP^{•+}·H⁺·R containing coordinated O₂ ligand and undergoes oxidation to give π cation radical (HSO₄)RhTPP^{•+} only in media with high proton concentration, concentrated H₂SO₄ [26]. At the same time, (Cl)(H₂O)IrTPP slowly produces an oxidized at the macrocycle form even in 100% AcOH without preliminary formation of H⁺-associated form. (Cl)MnTPP is the least stable compound at the M–N bond as compared with its structural analogs and dissociates at the macrocycle without formation of stable radical forms in AcOH–3–5 M H₂SO₄ [32, 33]. The lability of manganese complex with macrocyclic ligand is explained by lower contribution of N ← M reverse dative π bond into complex stability in comparison with other noted complexes [34, 35].

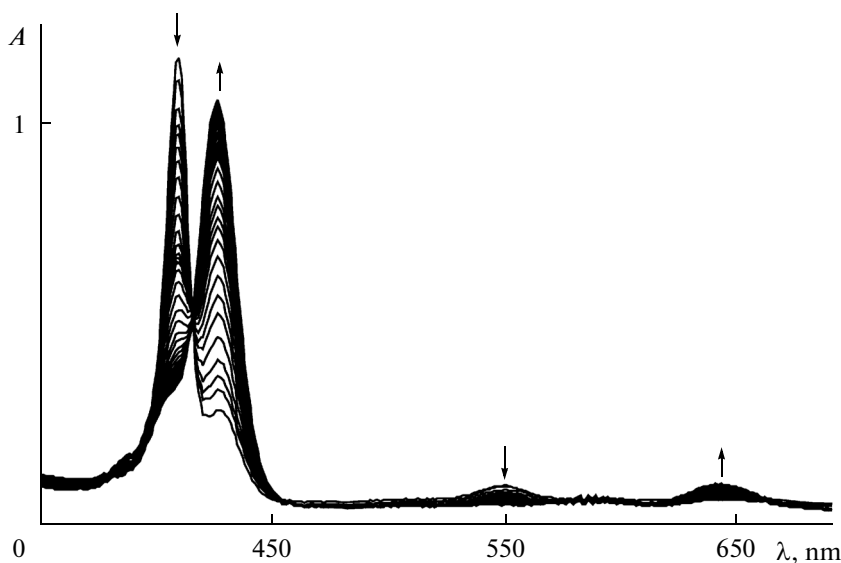
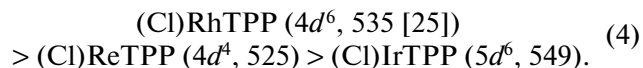


Fig. 5. UV-vis spectrum of (PhO)ReTPP in 100% AcOH at 298 K and τ (s) varied from 0 to 2280.

In the context of medium acidity necessary for oxidation reaction, the stable in protic solvents at the M–N bond (Cl)MTPP complexes with the same polyhedron (with no regard for weakly bonded molecular ligands like H₂O) can be arranged in the series (4) in agreement with their persistence toward one-electron oxidation at the macrocyclic ligand.



The electron configuration of metal ion and the position of the most intense $Q(0, 1)$ band in the visible region (λ_{max} , nm) in electronic absorption spectrum in chloroform are given in parentheses. These data show that all three complexes have electronic spectrum of hypso type indicating the contribution to coordination of the dative π interaction between HOMO (LUMO) molecular π orbitals of the macrocycle and the d_{π} orbitals of metal cation. For (Cl)IrTPP, the hypsochromic shift of $Q(0, 1)$ band as compared with its position in the spectra of normal type (~550 nm) is minimal. However, the lack of correlation between λ_{max} and the position of complexes in the series (4) indicates that the dative π interaction itself does not behave as predominant factor of persistence toward oxidation. Moreover, in the tendency to reach stable electron configuration d^5 , the considered rhodium and iridium cations produce M \rightarrow N dative π bonds, while rhenium forms N \rightarrow M dative π bonds.

In the complexes with M \rightarrow N reverse dative π bond, rhodium ion with smaller radius and higher electronegativity participates more efficiently in π interaction, which is expressed in the hypsochromic position (535 nm) of $\pi \rightarrow \pi^*$ transition band $Q(0, 1)$ as compared with Ir complex (549 nm). This is confirmed by the experimental fact that H⁺-associated form (Cl)RhTPP...H⁺...R exists (in the medium destined for oxidation reaction) [26] and there is no such a form in the case of similar iridium complex. Both these properties, to form H⁺ associate and to undergo oxidation at the macrocycle, are associated with electron-excessive state of the macrocycle in complex. And finally, the activity of axial positions in iridium(III) complexes can result in the presence of molecular ligands in the *trans* position toward anion ligand X⁻ that provides the *trans* effect by Chernyaev, which is typical for all chemistry of iridium coordination compounds. The coordination of molecular oxygen, which requires the substitution of axially coordinated ligands, is known to be one of the stages of oxidation of metal porphyrins [25].

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