Synthesis and Reactions of Platinum(III) Complexes with Protoporphine Ligands in Mixtures of Acetic and Sulfuric Acids

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Abstract — Unusual stable platinum complexes (Cl)Pt^{III}P were obtained by the reaction of K₂[PtCl₆] with porphyrin H₂P (full methyl ethers of proto-, meso-, deutero-, and hematoporphyrin) in a 1:2 molar ratio in boiling pyridine. The forms of existence, kinetics and mechanism of dissociation of metal porphyrins in AcOH–(0.3–2.1) M H₂SO₄ mixtures were studied at 300–330 K. The reaction has first-order with respect to metal porphyrin, low *E* values (21–48 kJ/mol), and negative ΔS^{\neq} values (–145– to –224 J mol⁻¹ K⁻¹). The dependence of the formal first-order rate constants on H₂SO₄ concentration is linear at low values of this latter (up to 1.5 M). The mechanism of the electron density redistribution produced by functional substitution in β positions of the macroring mature is determined by restricted π -electron density transfer from the metal atom to a coordinated N atom.

According to published data [1, 2], functional substitution in a porphyrin ligand incorporated in a metal porphyrin significantly affects the electronic structure and geometry of the coordination center, which shows up in changed forms of existence of the complexes in solutions and quantitative characteristics of their reactivity, in particular, dissociation under the action of acids. However, the magnitudes and directions of these changes strongly depend on the nature of the central metal atom. Therefore, studies on the properties of functional derivatives of porphine complexes with unexplored metals are topical. Of particular interest are transition metals that form either donor or dative π bonds with π ligands in addition to usual σ donor–acceptor bonds.

In this work we used the example of platinum complexes with protoporphyrin ligands [(Cl)Pt^{III}P] to study the effect of the nature of functional groups in the β positions of two pyrrole moieties on the reactivity of the complexes toward proton in H₂SO₄-AcOH mixed proton-donor solvents.

A special feature of the synthesis of (Cl)Pt^{III}P complexes is the use of a Pt(IV) compound as a complex-forming agent, which is reduced to Pt(III) during the synthesis. A similar complex-formation reaction of K₂PtCl₆ with tetraphenylporphine (H₂TPP) yields a platinum(IV) complex (Cl)₂Pt^{IV}TPP, whereas, the reaction of K₂PtCl₄ with H₂TPP in boiling PhCN for 30 h, a platinum(II) porphyrin Pt^{II}TPP [3, 4]. Ob-

viously, the stabilization of Pt(III) in protoporphyrin complexes results from intramolecular transfer of electron density onto the complex-forming atom from the macroring, the electron density in which is increased owing to the presence of eight alkyl and pseudoalkyl groups. Evidence for the composition of the (Cl)Pt^{III}P complexes comes from the electronic absorption spectra of porphyrin complexes of platinum in different oxidation states. The spectra of the complexes Pt^{II}TPP [3], (Cl)Pt^{III}P, and (Cl)₂Pt^{IV}TPP contain two visible absorption bands with $\Delta\lambda_{max} \sim 35$ nm [4, 5]. These bands undergo equidistant shifts to the longwave region along this series. Moreover, the following text shows that nonplanar (Cl)Pt^{III}P complexes with a five-coordinate platinum cation significantly differ in stability from Pt^{II} and Pt^{IV} complexes with a planar PtN₄ coordination entity.

Platinum(III) complexes with protoporphine ligands have similar absorption spectra in organic solvents, their mixtures with AcOH, and 100 % AcOH (Fig. 1), which implies that the acidity of AcOH is insufficient for protonation of donor N atoms and for dissociation of the complexes. In these media, the complexes form molecular solutions and do not form H-associated species known for (Cl)₂PtTPP and other metal porphyrins in aqueous H_2SO_4 [5, 6]. The electronic absorption spectra of Pt^{III} complexes with protoporphyrin ligands in concentrated H_2SO_4 (Figs. 1 and 2) are actually the spectra of the H_4P^{2+} cations

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formed by dissociation of platinum(III) porphyrins.

In nonaqueous acetic acid with small H_2SO_4 monohydrate additives at temperatures higher than 298 K, (Cl)Pt^{III}P complexes dissociate by Pt–N bonds [Eqs. (1) and (2); Fig. 2] at a measurable rate (see table). The constancy of the formal first-order rate constants confirms the form of kinetic equation (3) for limiting stage (1). Reaction (2) is very fast. Therefore, the unprotonated porphyrin is not accumulated in the reaction mixture, and its electronic spectrum is not observed (Fig. 2).

$$(Cl)PtP + 2H^{+} \longrightarrow H_2P + (Cl)Pt^{2+} , \qquad (1)$$

$$H_2P + 2H^+ \longrightarrow H_4P^{2+},$$
 (2)

$$V = k_{\rm app} C_{\rm (Cl)PtP}.$$
 (3)

The k_{app} - $f(C_{H_2SO_4}^0)$ dependence is linear at low H_2SO_4 concentrations at all the temperatures under study, implying that the reaction is first-order with respect to $C_{H_2SO_4}^0$.

$$V = kC_{(\text{Cl})\text{PtP}}C^0_{\text{H}_2\text{SO}_4}.$$
 (4)

However, in the AcOH medium sulfuric acid acts as a weak electrolyte [Eqs. (5) and (6)].

Fig. 2. Electronic absorption spectra of (Cl)PtDP in (1)–(8) AcOH–1.5 M H₂SO₄ mixture and (9) 17.5 M H₂SO₄ at 298 K. Time, s: (1) 0, (8) 40, (2)–(7) intermediate time moments.

$$CH_{3}COOH + H_{2}SO_{4} \xleftarrow{K_{a}} CH_{3}COOH_{2}^{+} + HSO_{4}^{-}, \quad (5)$$
$$K_{a} = [CH_{3}COOH_{2}^{+}]^{2}/C_{H_{2}SO_{4}}^{0}. \quad (6)$$

Taking into account Eqs. (4) and (6), we can draw kinetic equation (7) for dissociation of the complexes in sulfuric acid with a concentration lower than 1.5 M.

$$V = (1/K_a)kC_{(Cl)PtP}C_{[C_2H_5OH_2^+]^2}.$$
 (7)

Equation (7) allows estimation of the true (Cl)Pt^{III}P dissociation rate constants, and, from their temperature dependence, true activation parameters. With the pK_a and acidity functions of the AcOH–H₂SO₄ mixed solvent at 298 K (see [2] and references therein), by the Hammett equation we estimated the true (Cl)PtMP and (Cl)PtDP dissociation rate constants at $(5.6\pm1.6) \times 10^7$ and $(2.8\pm0.8) \times 10^8$ s⁻¹ mol⁻² l², respectively. Temperature dependences of pK_a and H_0 are absent from the literature. The dissociation of platinum(III) porphyrins in the mixed solvents under study is characterized by moderate values of E and by negative values of ΔS^{\neq} (see table).

At H₂SO₄ concentrations higher than 1.5 M, the k_{app} - $f(C_{H_2SO_4}^0)$ dependence is no longer linear (Fig. 3), which results from the fact that Eq. (6) is not valid at increased concentrations of sulfuric acid. The activa-





Concentration of N ₂ SO ₄ , M	$k_{\rm app} imes 10^3, \ {\rm s}^{-1}$				Е,	$-\Delta S^{\neq},$
	298.2 K	308.2 K	318.2 K	328.2 K	kJ/mol	J mol ⁻¹ K ⁻¹
(Cl)PtMP		1		T		
0.31	1.58 ± 0.04	2.46 ± 0.08	3.81 ± 0.09	_	34.6 ± 1	190 ± 3
0.50	1.9 ± 0.1	3.4 ± 0.16	6.3 ± 0.57	_	48 ± 3	145 ± 10
0.74	2.6 ± 0.1	4.3 ± 0.16	6.86 ± 0.3	_	37.85 ± 0.5	175 ± 2
(Cl)PtPP						
1.63	5.0 ± 0.1	7.3 ± 0.1	10.6 ± 0.8	_	30 ± 1	197 ± 3
1.91	6.15 ± 0.16	8.0 ± 0.1	10.5 ± 1.0	_	21 ± 1	224 ± 4
2.10	10.2 ± 0.8	13.45 ± 1.0	18 ± 1	_	23 ± 1.6	215 ± 5
(Cl)PtDP						
0.42	5.7 ± 0.2	8.6 ± 0.3	12.9 ± 0.7	_	32 ± 1	189 ± 3
0.81	6.3 ± 0.2	10.06 ± 0.7	16.1 ± 0.9	_	37 ± 1	170 ± 4
1.22	7.27 ± 0.4	10.2 ± 0.7	14.4 ± 0.7	_	27 ± 1	203 ± 4
1.63	7.3 ± 0.2	11.4 ± 0.6	17.8 ± 0.4	_	35 ± 1.4	176 ± 5
(Cl)PtGP						
1.49	0.87 ± 0.00	1.40 ± 0.04	2.22 ± 0.03	3.386 ± 0.01	37 ± 0	187 ± 1
2.00	1.00 ± 0.04	1.41 ± 0.02	1.90 ± 0.02	2.68 ± 0.01	27 ± 3	220 ± 10
2.55	$1.055\pm\!0.01$	1.51 ± 0.04	2.12 ± 0.05	2.97 ± 0.04	28.3 ± 1	215 ± 1
2.73	2.89	-	21 ± 2	51 ± 4	78.6	37.7
3.67	3.07	_ 	23±2	59±2	80.1	32.2

Kinetic parameters of dissociation of platinum(III) protoporphyrin complexes in the AcOH-H₂SO₄ mixed solvent

tion characteristics of the metal porphyrin–acid system (see table), the first-order dissociation kinetic equation (3), and the dependence of rate constant on $C_{\rm H_2SO_4}^0$ are similar to those for earlier studied reactions of H₂TPP complexes with double-charged 3*d*-

metal cations [7], chromium(III) [8], manganese(III) [9], and for manganese(III) protoporphyrin complexes [10].

According to data in the table and in [4, 5], the



Fig. 3. Dependence of the dissociation rate constants k_{app} of (1)–(3) (Cl)PtMP, (4) (Cl)PtPP, (5) (Cl)PtDP, and (6) (Cl)PtGP on the initial concentration of H_2SO_4 in AcOH. *T*, K: (1), (4–6) 298.2, (2) 308.2, and (3) 318.2.

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platinum(III) complexes under study are much less stable with respect to solvated protons as compared to $Pt^{II}TPP$ and $(Cl)_2Pt^{IV}TPP$ which are stable in cold concentrated H_2SO_4 . This is obviously explained by the fact that the central Pt atom in (Cl)Pt^{III}P complexes is displaced toward the Cl acido ligand, thus preventing formation of Pt \rightarrow N dative π back bonds characteristic of bi- and tetravalent platinum complexes.

As seen from the table, the kinetic stability of the complexes, measured by $k_{app}(298 \text{ K})$, decreases along series (8) for all compositions of the AcOH-H₂SO₄ mixed solvent.

The kinetic stability of platinum(III) H_2PP and H_2MP complexes varies in the same order as that described in [11–16] for similar Mg^{2+} , Cd^{2+} , Zn^{2+} , and Fe³⁺ complexes. The stability order of manganese(III) protoporphyrin complexes [10] is similar to order (8) in that meso- and deuteroporphyrin complexes are much more labile than hemato- and protoporphyrins. However, (Cl)MnPP is more stable than (Cl)MnGP. In contrast to Pt and Mn complexes, Cu²⁺ and Ni²⁺ mesoporphyrin complexes dissociate slower than protoporphyrin ones [14, 15, 17].

Thus, the above stability order is observed only for complexes in which M \rightarrow N dative π back bonding is either impossible $(Mg^{2+}, Cd^{2+}, and Zn^{2+} complexes)$ or hindered (complexes of Fe³⁺, Mn³⁺, and Pt³⁺ with a nonplanar coordination center). It should be noted that the activation of a metal porphyrin-acid reacting system involves cleavage of M-N donor-acceptor bonds and protonation of two coordinated N atoms [Eq. (1)]. We can assume that the increased kinetic stability of (Cl)PtMP compared to (Cl)PtDP results from the +*I* effect of β -CH₂–CH₃ substituents and strengthening of Pt \leftarrow N donor-acceptor σ interaction. Such interaction would prevent conjugation of nitrogen *n*-electron pairs with the macroring and thus facilitate considerably solvoprotolytic dissociation of the complexes. However, this is not the fact. This result implies prevalence of the +I effect of substituents on the electron pairs of Pt–N σ bonds. In the case of manganese(III) complexes, introduction of two ethyl radicals in the deuteroporphyrin macroring has almost no effect on the kinetic stability of the complex, i.e. the contributions into the stability of the complex of the effect of two CH₂-CH₃ substituents on the state of nitrogen *n*-electron pairs and Pt–N σ bonds mutually compensate each other.

The increased stability of the (Cl)PtGP and (Cl)PtPP complexes compared to the deuteropor-

phyrin complex can be explained in the same way, if the vinyl and methylated hyroxyalkyl groups are considered as pseudoalkyl substituents. However, in fact, an unexpected sharp increase in stability is observed [order (8)]. This probably points to electronacceptor properties of the substituents $CH(OCH_3)CH_3$ and $CH=CH_2$ with respect to nitrogen *n*-electron pairs, as the involvement of these substituents into π interaction with the macroring not compensated for by strengthened dative π bonds significantly increases stability of the metal porphine. The electron-acceptor properties of the $CH(OCH_3)CH_3$ groups can also be enhanced by their specific solvation (hydrogen bonds) in a mixture of AcOH and H_2SO_4 .

The appearance of $Pt \rightarrow N$ dative π back bonds in the PtTPP and $(Cl)_2PtTPP$ complexes with a planar coordination entity PtN_4 results in a sharp positive jump of the kinetic stability of these complexes in solutions [4, 5].

Thus, our study of the reactivity of platinum porphyrins toward proton provides, on the one hand, indirect quantitative evidence for the unusual trivalent state of platinum in monomeric complexes, and, on the other, adds to our view of the electronic effects of substituents in aromatic macrorings. It must be emphasized that the complicated electronic and geometric structure of the reaction center in platinum(III) porphyrins determines the specificity of the electronic effect of substituents as compared to that in classical substitution reactions of functional derivatives of benzene: The first-type substituents $CH(OCH_3)CH_3$ and $CH=CH_2$ become electron-acceptors.

EXPERIMENTAL

The electronic absorption spectra were recorded on SF-26, Specord M-40, and Specord M-400 instruments. The IR spectra were taken on a Specord M-80 spectrophotometer and analyzed by a comparison with the spectra of porphyrins, their complexes, and Pt complexes with acyclic ligands [18–21].

Sulfuric acid monohydrate was prepared from H_2SO_4 (chemically pure grade) and oleum (chemically pure grade), following water content by potentiometry [22]. Acetic acid (100%) was prepared from glacial AcOH by fractional unfreezing. The water contents of individual solvents were no higher than 0.02–0.03%. The mixed solvents AcOH– H_2SO_4 were prepared by the gravimetric method. The accuracy of temperature measurements in the kinetic experiments was ± 0.1 K.

The chlorine contents were determined by burning the samples in oxygen, and the Pt contents, by atomic adsorption spectroscopy on an AASIN spectrometer and by thermal analysis on a 1000D derivatograph.

(Chloro)platinum(III)porphyrins (full methyl ethers) were obtained by complex formation between H_2P and K_2PtCl_6 at a 1:2 molar ratio in boiling pyridine within 30 min. To a cooled reaction mixture, CHCl₃ and water were added until the chloroform layer separated. This layer was washed with water many times to remove excess salt and pyridine and then subjected to chromatography on an Al_2O_3 column (Brockmann activity grade II), eluent CHCl₃– EtOH (2%).

Full methyl ethers of porphyrins were obtained and purified by the standard procedure [23].

(Chloro)mesoporphyrinplatinum(III) (Cl)PtMP. IR spectrum, cm⁻¹: 456 [v(Pt–N)]; 618 [v(Pt–Cl)]; 720 (bending vibrations of pyrrole rings); 838 [γ (C_{meso}–H)]; 964, 986, 1100, 1455 (skeleton vibrations of pyrrole rings); 1122 [v(C–O)]; 1171 v[(CH₂)₂COO]; 1362, 1387 [δ (CH₃)]; 1476 [δ (CH₂)]; 1735 [v(C=O)]; 2870, 2880 [v(CH₃)]; 2935, 2970 [v(C_{meso}–H)]. Electronic absorption spectrum, λ_{max} , nm: in MeOH – 420.0, 529.7, 561.8; in AcOH 560, 528, 415. Found, %: Cl 4.84; Pt 23.6±0.1. C₃₆H₄₀ClN₄O₄Pt. Calculated, %: Cl 4.2; Pt 23.7.

(Chloro)protoporphyrinplatinum(III) (Cl)PtPP. IR spectrum, cm⁻¹: 461 [v(Pt–N)]; 630 [v(Pt–Cl)]; 726 (bending vibrations of pyrrole rings); 838 [γ (C_{meso}-H)]; 971, 992, 1100, 1460 (skeleton vibrations of pyrrole rings); 1124 [v(C–O)]; 1655 [vinyl v(C=C)]; 1370, 1388 [δ (CH₃)]; 1475 [δ (CH₂)]; 1718 [v(C=O)]; 2870, 2880 [v(CH₃)]; 2935, 2975 [v(C_{meso}-H)]; 3080 [vinyl v(C–H)]. Electronic absorption spectrum, λ_{max} , nm: in EtOH: 420, 530, 562; in AcOH: 418, 530, 560.

(Chloro)deuteroporphyrinplatinum(III) (Cl)PtDP. Electronic absorption spectrum, λ_{max} , nm: in CHCl₃: 558.9, 527.1, 417.1; in AcOH: 415.1, 526, 556.4.

(Chloro)hematoporphyrinplatinum(III) (Cl)PtGP. Electronic absorption spectrum (EtOH + 10% AcOH), λ_{max} , nm: 564.3, 531.3, 416.7.

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