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Synthesis and Reactivity of Porphyrin Complexes of Group IV *p*-Elements

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Abstract—The composition of products and the general regularities of complex formation of *meso*-tetraphenylporphine with Si(IV), Ge(IV), Sn(II), and Pb(II), as well as the kinetics and mechanism of dissociation of the resulting complexes under the action of proton-donor reagents were studied. The nature of chemical and steric factors that operate to stabilize mixed-ligand acido porphyrin *p*-metal complexes was revealed.

Pophyrin complexes of Si, Ge, and Pb are almost unexplored. The synthesis, electrochemical reactions, and modification of the complexes of Si with octaethylporphine (H_2OEP) and etioporphyrin (H_2EP) with OH, OMe, OPh, Me, Ph, or $OSi(Me)_3$ acido ligands have been reported [1–5]. The synthesis, structure, and spectral and electrochemical properties of complexes $(X)_2GeP$ [P is the dianion of porphine (H_2P), H_2OEP, or tetraphenylporphine (H_2TPP); X is Cl, OH, Et, OMe, or OEt] [2,3, 6–8] have been studied. The complexes of Pb with H_2OEP, H_2TPP, and *meso*-porphyrin (H_2MP) of the composition PbP have been synthesized in [9–11], and tetravalent Pb complexes have been described in [9, 12]. Data of different authors on the stability and spectra of such complexes are contradictory: According to [9], $[PbOEP]^{2+}$ is unstable in organic solvents in the presence of small amounts of water, which contradicts the calculation results in [12]. The structure and practical application of Sn porphyrin complexes are presently widely studied [13, 14], but no quantitative information concerning their stability is yet available.

In this work we made an attempt to reveal general regularities of the synthesis of porphyrin complexes of Group IV *p*-elements, and, on an example of H_2TPP, to detemine factors that contribute into the stability of metal porphyrins in solutions.

The experimental synthetic results for the complexes $(OH)_2SiTPP$, $(Cl)_2GeTPP$, $(Cl)_2SnTPP$, $(AcO)_2PbTPP$, and PbTPC (Table 1) show that these compound are easiest to prepare by complex formation of porphyrins with *p*-element salts in high-boiling solvents. Therewith, tetravalent silicon and germanium salts give complexes in which the formal charge of the complexing atom is +4.

Table 1. Synthesis, isolation, and purification of Si(IV), Ge(IV), Pb(IV), and Sn(IV) complexes with H_2TPP and Pb(II) complexes with H_2TPC (*meso*-tetraphenylchlorine)

Complex	Complexing agent	Solvent	*T*, K	Isolation method	Purification method	Yield, %
$(OH)_2SiTPP$	$SiCl_4$	Pyridine	458	Extraction with $CHCl_3$, washing with H_2O	Double chromatography on Al_2O_3, solvent and eluent $CHCl_3$	38
Cl_2GeTPP	$GeCl_4$	Quinoline	510	Extraction with hexane	Chromatography on Al_2O_3, solvent and eluent $CHCl_3$	93
Cl_2SnTPP	$SnCl_2$	DMF	423	Precipitation with H_2O	Double chromatography on Al_2O_3, solvent and eluent $CHCl_3$	65
PbTPC $(AcO)_2PbTPP\cdot Py$	$Pb(OAc)_2$	Pyridine	388	Extraction with $CHCl_3$, washing with H_2O	Chromatography on Al_2O_3 in $CHCl_3$, eluent $CHCl_3$–C_6H_6; chromatography on Al_2O_3 in $CHCl_3$, eluent DMF	7[a] 93[a]

[a] Relative yields of the complexes.

The reactions of H_2TPP with salts of double-charged tin(II) and lead(II) cations (Table 1) are accompanied by redox processes. The synthesis of the tin(IV) complex gives SnTPP which is readily oxidized with atmospheric oxygen to $(Cl)_2SnTPP$ [15]. Redox reactions involving metal cation, solvent, and atmospheric oxygen in the complex formation of $Pb(OAc)_2$ with H_2TPP yield two metal porphyrins, PbTPC and $(AcO)_2PbTPP$ [16]. Atomic absorption and IR spectroscopy show that the complex $(AcO)_2PbTPP$ contains Py in the coordination sphere. In solutions such species exists only in the presence of excess Py [17], and, therefore, in what follows, dealing with solutions of $(AcO)_2PbTPP$–Py in acidic media, we consider this complex as acido porphyrin $[(AcO)_2PbTPP]$. The experimental evidence for the chlorin and porphyrin structure of the complexes, respectively, is given in [16]. The spectral characteristics of the lead(II) and lead(IV) complexes coincide with those reported in [16].

As follows from the composition of the synthesized complexes, Group IV *p*-elements prefer the six-coordinate form with a mixed coordination sphere $[(X)_{n-2}MTPP]$.

The complexes $(OH)_2SiTPP$ and $(AcO)_2PbTPP$ are very stable. They undergo no dissociation in usual conditions (298 K, 1 atm) on treatment with H_2O–AcOH, H_2SO_4–AcOH, and H_2SO_4–H_2O.

The electronic absorption spectrum of the complex $(OH)_2SiTPP$ in sulfuric acid (Fig. 1) differs sharply from the spectrum in $CHCl_3$ (see Experimental). The observation of a characteristic two-band visible absorption spectrum (Fig. 1) suggests [18] formation in conc. H_2SO_4 of the ion-molecular associate $(OH)_2SiTPP\cdots H^+_{Solv}$.

Thermostating solutions of $(OH)_2SiTPP$ in 17–18 M H_2SO_4 at 340–360 K results in that the spectrum of the associate with a proton transforms, according to Eq. (1), into the spectrum of sulfonated H_4TPP^{2+} (Fig. 1) with preserved isosbestic points. This follows from Fig. 1 and the results of additional spectrophotometric study of the reaction products after their reprecipitation and extraction with an organic solvent.

$$(OH)_2SiTPP\cdots H^+_{Solv} + 3H^+_{Solv}$$
$$\xrightarrow{H_2S_2O_7} H_4TPP(SO_3H)_x^{2+} + (OH)_2Si^{2+}_{Solv}. \qquad (1)$$

The formal first-order rate constants of reaction (1) increase with increasing initial and equilibrium concentration of H_2SO_4 (Table 2, Fig. 2). Dependence (2) is fairly (*R* 0.996–0.998) fitted by a straight line with a slope ($\tan\alpha = n$) close to 2 (Fig. 2).

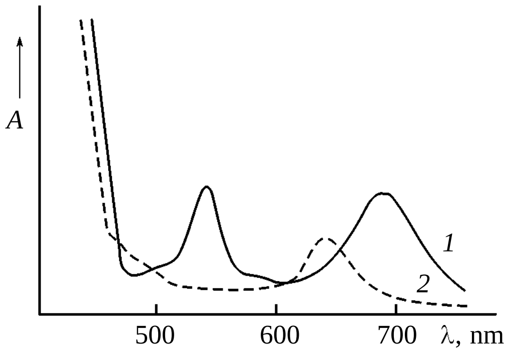

Fig. 1. Electronic absorption spectrum of $(OH)_2SiTPP$ in 17.8 M H_2SO_4 (373 K). τ: (*1*) 0 and (*2*) ∞.

$$\log k_{app} = \log k_v + n\log [H_2SO_4]. \qquad (2)$$

Here k_{app} and k_v are the apparent and true rate constants, $[H_2SO_4]$ is the concentration of unionized H_2SO_4 molecules in concentrated aqueous sulfuric acid. The $\log k_v$ values and the true activation parameters are given in Table 2. From the resulting data it follows that dissociation (1) obeys kinetic equation (3).

$$-dc_{(OH)_2SiTPP\cdots H^+_{Solv}}/d\tau$$
$$= k_v[(OH)_2SiTPP\cdots H^+_{Solv}][H_2SO_4]^2. \qquad (3)$$

The kinetic regularities of $(OH)_2SiTPP$ dissociation in H_2SO_4 are similar to those found earlier for $(Cl)_2GeTPP$ [19].

$(AcO)_2PbTPP$ is very stable. It does not dissociate in conc. H_2SO_4 and monohydrate even at high temperatures (373 K). The electronic absorption spectrum of the complex shows that it exists in conc. H_2SO_4 as the associate $(AcO)_2PbTPP\cdots H^+_{Solv}$ (Fig. 3).

Table 2. Kinetic parameters of dissociation of $(OH)_2SiTPP$ in concentrated sulfuric acid[a]

$k_{app}^{298\,K} \times 10^7$, s^{-1} [b]		$-\log k_v^T$	
$c^0_{H_2SO_4}$, M	k_{app}	T, K	$-\log k_v$
17.28	2.92	298	7.7
17.85	3.74	348	5.8
18.00	4.43	353	5.7
18.14	6.69	358	5.5
18.33	16.89		

[a] Activation parameters: *E* 78 kJ/mol, $\Delta S^{\neq}$ –140 J mol^{-1} K^{-1}.

[b] Obtained by extrapolation of the $\log k$–$1/T$ dependence.

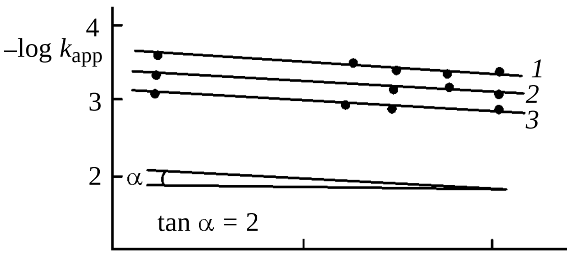

Fig. 2. Dependence of $\log k_{app}$ on $\log[H_2SO_4]$ for $(OH)_2SiTPP$ in conc. H_2SO_4. Temperature, K: (*1*) 348, (*2*) 353, and (*3*) 358 K.

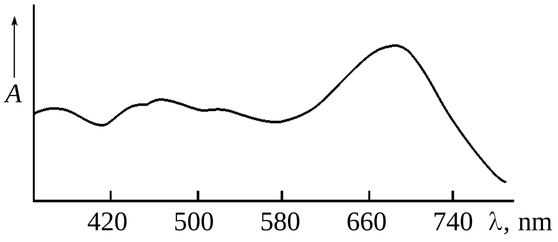

Fig. 3. Electronic absorption spectrum of $(OAc)_2PbTPP$ in 18.66 M H_2SO_4.

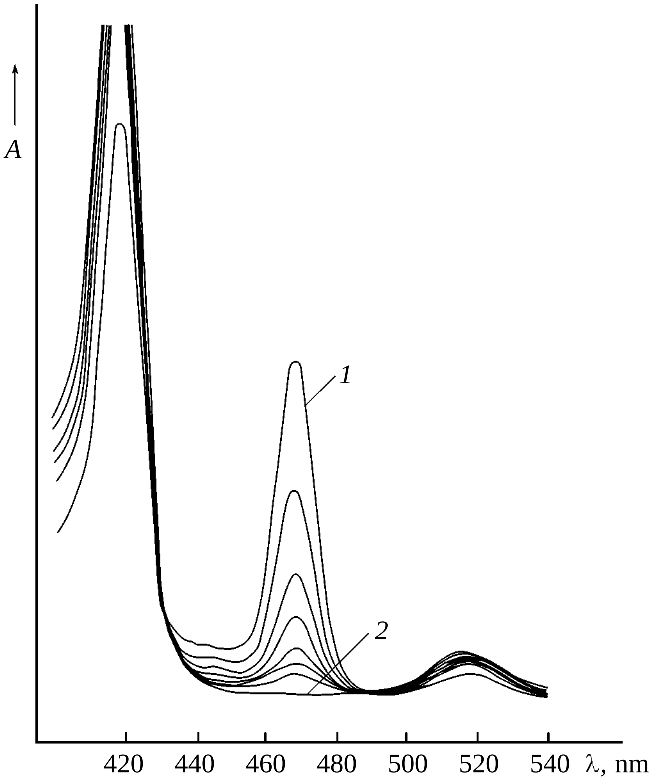

Fig. 4. Electronic absorption spectrum of PbTPC in EtOH–AcOH (c_{AcOH} 7.88×10^{-3} M, 290 K). τ: (*1*) 0 and (*2*) ∞.

The complex PbTPC, unlike the Pb(IV) complex, dissociates in usual conditions in aqueous sulfuric acid and its mixtures with AcOH at the instant of dissolution. In the system ethanol–$(3–8)\times10^{-3}$ M AcOH (Fig. 4), it dissociates at a measurable rate. Therewith, the electronic absorption spectrum of lead(II) tetraphenylchlorin transforms into the spectrum of the final product H_2TPP according to Eq. (4).

$$\mathrm{PbTPC} + 2\mathrm{H}^{+}_{\mathrm{Solv}} \xrightarrow[-\mathrm{Pb}^{2+}_{\mathrm{Solv}}]{} \mathrm{H_2TPC} \xrightarrow{[\mathrm{O}]} \mathrm{H_2TPP}. \quad (4)$$

As seen from Fig. 4, H_2TPC does not accumulate, and the electronic absorption spectrum of the reaction mixture at intermediate points definitely reveals two colored compounds, PbTPC and H_2TPP. This fact implies that the second stage of reaction (4) is not limiting.

The first-order dissociation rate constants k^{T}_{app} linearly increases with increasing initial concentration of acetic acid c^{0}_{AcOH} (Table 3, Fig. 5). The prevalence in the mixed solvent EtOH–AcOH at the specified HOAc concentrations of equilibrium (5) over the equilibria of autoprotolysis of EtOH and AcOH and the proportionality of c^{0}_{AcOH} and $[EtOH_2^+]^2$ at moderate AcOH concentrations [Eq. (6)] allow us to write the third-order reaction kinetic equation (7).

The lability, low *E* values, and the negative $\Delta S^{\neq}$ values for reaction (4) (Table 3) point to an *SEN*3 mechanism of PbTPC dissociation in EtOH–AcOH. This mechasim has been rigorously substantiated for metal porphyrins in mixed proton-donor solvents [17, 20].

$$\mathrm{EtOH} + \mathrm{AcOH} \overset{K}{\rightleftarrows} \mathrm{EtOH}_2^+ + \mathrm{AcO}^-, \quad (5)$$

$$K = [\mathrm{EtOH}_2^+]^2/[\mathrm{AcOH}] = [\mathrm{EtOH}_2^+]^2/c^{0}_{\mathrm{AcOH}}, \quad (6)$$

$$-dc_{\mathrm{PbTPC}}/d\tau = (1/K)k_v[\mathrm{PbTPC}][\mathrm{EtOH}_2^+]^2. \quad (7)$$

The above results, as well as published quantitative data [15, 19, 21] on the stability of the complexes $(Cl)_2SnTPP$ and $(Cl)_2GeTPP$ allow general regularities of the reactivity of acido porphyrin complexes of Group IVb *p*-metals in sulfuric acid solutions to be revealed. In concentrated sulfuric acid, these complexes exist as two spectrally distinguishable forms, molecular [$(Cl)_2SnTPP$ and $(Cl)_2GeTPP$] and an ion-molecular associate [$(OH)_2SiTPP\cdots H^{+}_{Solv}$ and $(AcO)_2PbTPP\cdots H^{+}_{Solv}$].

A common feature of dissociation of hexacoordinate complexes of H_2TPP with Si, Sn, and Ge is that they involve H_2SO_4 molecules as proton donors

Table 3. Kinetic parameters of dissociation of PbTPC in ethanol–acetic acid

$c^0_{\mathrm{AcOH}} \times 10^3$, M	E, kJ/mol	$-\Delta S^{\neq}$, J mol^{-1} K^{-1}	$k^{298\,\mathrm{K}}_{\mathrm{app}} \times 10^4$, s^{-1}
3.50	63±8	127±21	0.7
4.40	44±5	178±15	1.3
5.80	29±3	221±7	2.7
6.55	23±2	241±5	3.8
7.88	23±3	237±7	5.6

Table 4. Kinetic stabilities ($k^{298\,\mathrm{K}}_{\mathrm{app}}$), covalent radii ($r_{\mathrm{c}}$) of complexing atoms, and positions of the first absorption bands ($\lambda^{\mathrm{I}}_{\mathrm{max}}$) in the electronic absorption spectra

Complex	$k^{298\,\mathrm{K}}_{\mathrm{app}} \times 10^4$, s^{-1} ($c^0_{\mathrm{H_2SO_4}}$, M)	r_{c}, Å [23]	$\lambda^{\mathrm{I}}_{\mathrm{max}}$, ml
$(OH)_2SiTPP$	0.017 (18.33)	1.89	612
$(Cl)_2GeTPP$	0.200 (18.66) [19]	1.93	592 [19]
$(Cl)_2SnTPP$	0.030 (18.66) [15]	2.11	601 [15]
$(AcO)_2PbTPP$	Stable (18.66)	2.14	584

[Eqs. (3), (8), (9)] rather that H_3O^+ cations as with similar phthalocyanine complexes [22].

$$-dc_{(\mathrm{Cl})_2\mathrm{GeTPP}}/d\tau = k_v[(\mathrm{Cl})_2\mathrm{GeTPP}][\mathrm{H_2SO_4}]^2, \quad (8)$$

$$-dc_{(\mathrm{Cl})_2\mathrm{SnTPP}}/d\tau = [(\mathrm{Cl})_2\mathrm{SnTPP}](k_1[\mathrm{H_2SO_4}]^2 + k_2[\mathrm{H_2SO_4}]). \quad (9)$$

The existence of different forms of the complexes and the observation of different reaction orders in the concentration of unionized H_2SO_4 suggests that these complexes, while being similar in composition and the structure of the coordination sphere, dissociate by different mechanisms.

Complexes $X_{n-2}MTPP$ may dissociate either after *trans–cis* isomerization of acido ligands [15] or after dissociation of the acido complex by the bonds metal–acido ligand donor atom. Mixed-ligand complexes of tetravalent tin, germanium, and silicon with phthalocyanine [22] dissociate by the metal–nitrogen bond, when acido ligands have been removed from the first coordination sphere. Unlike metal phthalocyanines, the complexes $(Cl)_2SnTPP$ and $(Cl)_2GeTPP$ do not dissociate under the same conditions (aqueous H_2SO_4, Brand's region). It is only 100% H_2SO_4, i.e. an H_2SO_4–H_2O mixture with the highest dielectric constant, in which M–Cl and then M–N bonds tend to dissociate.

Since the $k^{298\,\mathrm{K}}_v$ rate constants relate to different-order reactions, the kinetic stabilities of the metal porphyrins in the series Si–Ge–Sn–Pb should be compared by the $k^{298\,\mathrm{K}}_{\mathrm{app}}$ values at the same $c^0_{\mathrm{H_2SO_4}}$ (Table 4). At H_2SO_4 concentrations close to 100% (18.66 M), the kinetic stability of the complexes decreases in series (10), in parallel with the increasing $k^{298\,\mathrm{K}}_{\mathrm{app}}$ values.

$$(\mathrm{OAc})_2\mathrm{PbTPP} < (\mathrm{Cl})_2\mathrm{SnTPP} < (\mathrm{Cl})_2\mathrm{GeTPP} < (\mathrm{OH})_2\mathrm{SiTPP}. \quad (10)$$

As known [17], chemical stabilization of metal porphyrins with σ-type donor–acceptor bonds definitely shows up in a hypsochromic shift of the first absorption band ($\lambda^{\mathrm{I}}_{\mathrm{max}}$) in the electronic absorption spectrum. The positions of the complexes in series (10) disagree with this tendency but are nicely consistent with the increasing sum of the covalent radii of the metal atom and the coordinating nitrogen atom along the silicon subgroup. Analysis of X-ray diffraction data for $(X)_2MTPP$ [24, 25] shows that all complexes of tetravalent element of the silicon subgroup are planar. Therewith, the $r_{\mathrm{M+N}}$ values for the Sn(IV) and Pb(IV) complexes (Table 4) are the most close to 2.01 Å, which corresponds to D_{4h} symmetry ideal for metal porphyrins in terms of internal strain. Coordination of the smaller Si(IV) and Ge(IV) atoms (Table 4) produces radial compression of the macroring in $(Cl)_2GeTPP$ and $(OH)_2SiTPP$ and, as a result, decreases the covalent contribution into the M–N bonds. The complex $(OH)_2SiTPP$ exhibits the lowest kinetic

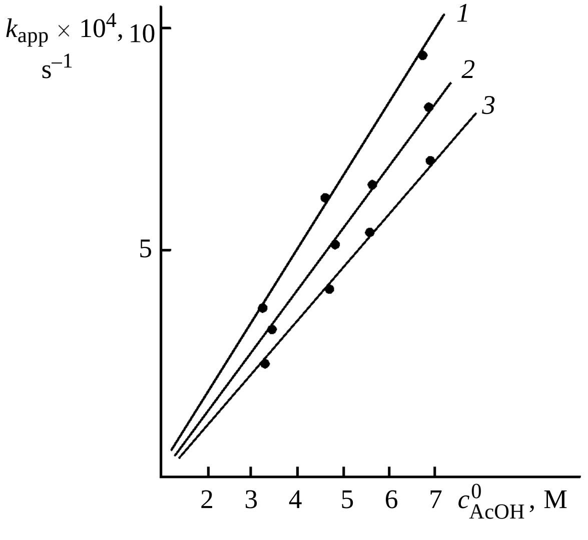

Fig. 5. Dependence of the rate constants k_{app} of dissociation of PbTPC on the initial concentration of AcOH in EtOH. Temperature, K: (*1*) 308, (*2*) 313, and (*3*) 315.

stability in series (10), probably, because of the highest ionic contribution into the Si–O and Si–N bonds. The strongest Pb–OAc and Pb–N bonding in $(AcO)_2PbTPP$ is confirmed by the largest hypsochromic shift of λ^{I}_{max} in the electronic absorption spectrum (Table 4).

Thus, the stability of tetraphenylporphyrin complexes of silicon subgroup metals is determined by the strength of their metal–nitrogen σ bonds, effects of steric shielding of the MN_4 center by acido ligands, and the tendency for ion-molecular association with solvent. The effect of radial compression on complex formation of Ge(IV) with H_2TPP destabilizes the resulting metal porphyrin. The high charge and the small radius of the Si(IV) cation ensure ionic contribution into the stability of the $(OH)_2SiN_4$ coordination entity.

In going from $(AcO)_2PbTPP$ to PbTPC, a sharp decrease in kinetic stability is observed. The destabilization of the latter complex is explained by the decreased Z_{eff} on the metal atom and electron density on the macroring (hydrogenation of one β bond), as well as the larger size of the Pb^{2+} ion [12]. These factors all prevent planar arrangement of the cation in the metal chlorine.

EXPERIMENTAL

As complexing agents for synthesis of $(OH)_2SiTPP$ and $(AcO)_2PbTPP$ were used chemical grade $SiCl_4$ and analytical grade $Pb(OAc)_2 \cdot 3H_2O$. H_2TPP (Armenian Branch, Inst. Khim. Reaktivov Osobo Chist. Khim. Veshchestv) was purified by chromatography on Al_2O_3 (Brockmann activity grade II) in chloroform. The synthesized complexes were purified on neutral Al_2O_3. Organic solvents were dried by known procedures [20].

Monohydrate of H_2SO_4 was prepared from chemical grade oleum with potentiometric control [26]. The concentration of H_2SO_4 in H_2SO_4–H_2O mixtures was determined by acid–base titration with an accuracy of no less than 0.01%.

The electronic absorption spectra were measured on Specord M-400 and SF-26 instruments. The IR spectra were obtained on a Specord M-80 instrument in KBr and assigned analytically using data in [27–29]. The ^1H NMR spectra were measured on a Tesla BS-497 spectrometer (100 MHz, internal reference TMS).

The synthesis and physicochemical characteristics of Cl_2SnTPP and Cl_2GeTPP were described earlier [15,19]. The complexes of silicon(IV) and lead(IV) with H_2TPP and of lead(II) with H_2TPC (*meso*-tetraphenylchlorine) were prepared by complex formation of porphyrins with metal salts in pyridine (Table 1).

Tetraphenylporphinesilicon dihydroxide $(OH)_2SiTPP$. IR spectrum, cm^{-1}: pyrrole rings: 800 (γ_{C-H}), 992 (ν_{C-C}, δ_{C-H}, ν_{C-N}), 1336 (ν_{C-N}), 1440 ($\nu_{C=N}$), 1520 (in-plane vibrations); benzene rings: 696 and 740 (γ_{C-H}), 1068 and 1176 (δ_{C-H}), 1496, 1595 sh and 1576 ($\nu_{C=C}$), 2920 and 3045 (ν_{C-H}); 460 ($Si-N_{porf}$); 560 and 608 (Si–O). Electronic absorption spectrum ($CHCl_3$), λ_{max}, nm (log ε): 652 (4.05), 612 (4.227), 571 (4.501), 524 (4.22), 410 (5.14).

(Pyridine)tetraphenylporphinelead diacetate $(AcO)_2PbTPP$–Py. IR spectrum, cm^{-1}: pyrrole rings: 798 (γ_{C-H}), 976 (ν_{C-C}, δ_{C-H}, ν_{C-N}), 1340 (ν_{C-N}), 1440 ($\nu_{C=N}$), 1523 (in-plane vibrations); benzene rings: 704, 778 (γ_{C-H}), 1072, 1159 (δ_{C-H}), 2860, 2920 (ν_{C-H}); pyridine: 700, 1460, 1560; 405 ($Pb-N_{pyridine}$); 450 ($Pb-N_{porf}$); 1655 and 1734 (O···C···O). Electronic absorption spectrum ($CHCl_3$), λ_{max}, nm: 584, 444, 345 sh, 310 s; intensity decreases in the series IV > III > II > I.

Tetraphenylchlorinelead PbTPC. IR spectrum, cm^{-1}: pyrrole rings: 796 (γ_{C-H}), 1000 (ν_{C-C}, δ_{C-H}, ν_{C-N}), 1328 (ν_{C-N}), 1440 ($\nu_{C=N}$), 1525 (in-plane vibrations); benzene rings: 704 i 752 (γ_{C-H}), 1072 and 1176 (δ_{C-H}), 1470, 1576 and 1592 ($\nu_{C=C}$), 2860, 2920 and 3020, 3080 (ν_{C-H}); 416 (Pb–N). ^1H NMR spectrum ($CDCl_3$, HMDS), δ, ppm: 7.73 m (12H, H_m, H_p), 8.16 m (8H, H_o), 8.77 d (4H, C_4H_2N), 8.89 t (6H, C_4H_4N). Electronic absorption spectrum ($CHCl_3$), λ_{max}, nm (log ε): 652 (3.37), 609 (3.52), 551 (3.25), 516 (3.4), 466 (4.33), 419 (4.5), 355 (3.76).

The kinetics of dissociation of PbTPC and $(OH)_2SiTPP$ in EtOH–AcOH and H_2SO_4–H_2O mixtures, respectively, were studied spectrophotometrically. The apparent rate constants k^T_{app}, activation energies E, and reaction orders in the concentrations of complex and proton-donor species were determined by least-squares treatment of the $\log (A_0 - A_\infty)/(A_\tau - A_\infty)$–τ, $\log k$–$(1/T)$, and $\log k_{app}$–$[H^+_{Solv}]$ dependences using Microsoft Excel. The activation entropies were calculated by the equation $\Delta S^{\neq} = 19.1\log k^T_{app} + (E/T) - 19.1\log T - 205$.

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