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COORDINATION COMPOUNDS

Synthesis of Calix[4]arene-bis(tin(IV)porphyrins) and Supramolecular Complexes on Their Basis

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Abstract—Selective substitution of one of the two *trans* hydroxy groups of calix[4]arene-bis(porphyrinatotin(IV)) resulted in supramolecular tetramer assemblies based thereon with parallel and perpendicular arrangement of tetrapyrrole macrocyclic rings, which were characterized by UV spectroscopy, ^{1}H NMR, and elemental analysis data.

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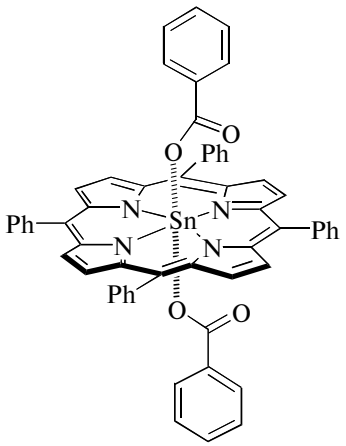
According to [1–3], zinc(II) and ruthenium(II) porphyrinates containing amino or pyridyl substituents in the macrocyclic ring are able to self-assemble. The corresponding monomeric porphyrin units are combined into dimeric, trimeric, tetrameric, and other oligomeric supramolecular assemblies. These processes are underlain by donor–acceptor interaction of the metal cation of the porphyrinate reaction site with the nitrogen atom of the amino group or pyridyl moiety of the substrate molecule. This process is controllable equilibrium since the M^{n+}–N bond is relatively labile in organic solvents (it is rapidly and reversibly broken and formed again at room temperature). As compared with the pentacoordinated Zn porphyrin complexes, Ru porphyrins have a hexacoordinated geometry and form more stable complexes.

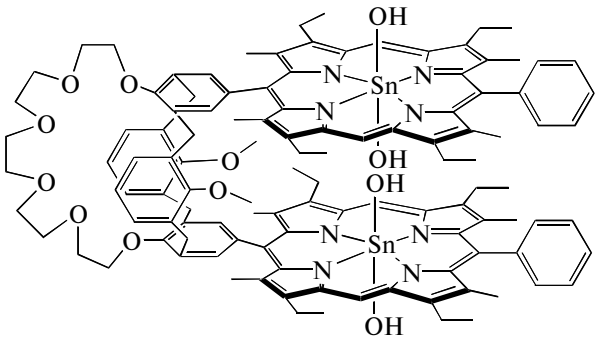
No less interesting for design of supramolecular porphyrin assemblies are tin(IV) porphyrinates. The large multicharged Sn^{4+} cation can enter the porphyrin cavity, without disturbing the planarity of the macrocyclic ligand [4]. Sn(IV) porphyrins preferably bind oxygen-containing ligands (as a rule, carboxylates and phenolates) and are hexacoordinated complexes with *trans*-diaxial coordination of anionic or neutral ligands [4–8]. The latter, as in the case of amines coordinated to zinc porphyrinates, can be selectively replaced by other substrates.

Carboxylate complexes of Sn(IV) porphyrins can be synthesized by mixing a carboxylic acid excess with dihydroxyporphyrinatotin(IV). The rate and degree of substitution (mono or di-) depend on the acidic properties of organic acids. Dicarboxylate complexes $SnP(R)_2$ (**I**) are formed by strong acids and when the acid concentration is twice as large as the porphyrinate concentration. For example, the complex with dichloroacetic acid is formed in a few seconds, whereas it takes 30 min for the complex with propionic acid to be formed [7]. Benzoic acid mainly forms dicarboxylate complexes with monomeric tin(IV) porphyrinates [7].

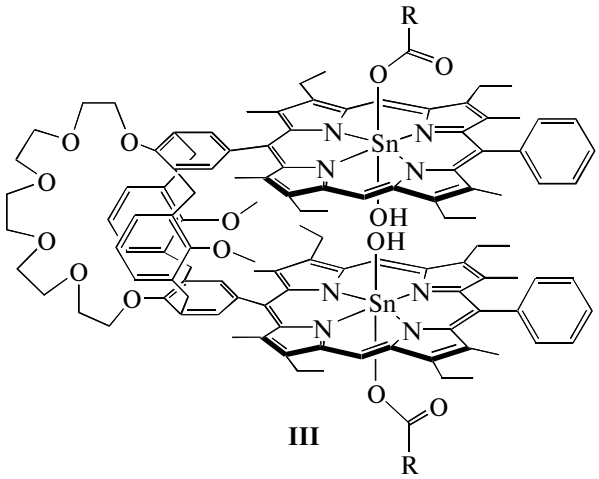


I

The stability of the carboxylate complexes of Sn(IV) porphyrinates depends not only on the acidity of the carboxylate but also on the existence of additional (π–π- or donor–acceptor) interactions that can arise in the complex and on the conformation rigidity of an oxygen-containing ligand (a ligand with a more rigid carbon skeleton forms a more stable complex). The Sn(IV) porphyrin complexes with phenols and *n*-hydroxyphenyl-substituted porphyrins are formed by refluxing that latter with *trans*-dichloroporphyrinatotin(IV) in benzene or pyridine for several hours [6].



II

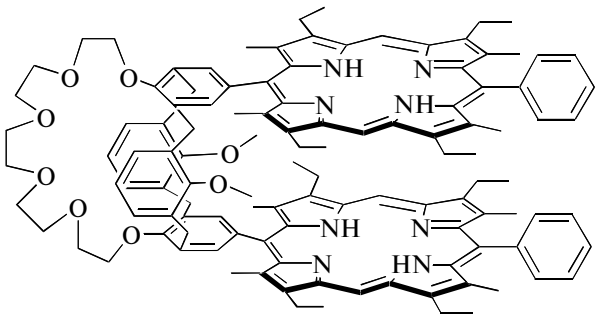


III

In the present work, selectively substituting for one of the two hydroxy groups at the Sn(IV) cation in the synthesized calix[4]arene-bis(porphyrinatotin(IV)) ($Sn_2D(OH)_4$, **II**), we obtained for the first time two new supramolecular tetrameric assemblies with parallel and perpendicular arrangement of the tetrapyrrole macrocyclic rings and characterized them by UV spectroscopy, ^1H NMR, and elemental analysis data. The approximate arrangement of the porphyrinate moieties in the $Sn_2D(OH)_4$ dimer prevents bulky substrates, such as benzoic (L^1) and 4-pyridinecarboxylic (L^2) acid molecules, from entering the interporphyrin complexing cavity of the dimer. Therefore, unlike the described methods of synthesis of supramolecular assemblies based of tin(IV) porphyrinates, the method suggested by us affords the addition of substrate molecules only on one "outer" side of the porphyrinate moieties, which results in both the $(Sn_2D(OH)_2(O_2CR)_2$ complexes (**III**) and more complex porphyrin assemblies.

EXPERIMENTAL

5-(4-Hydroxyphenyl)-10,15,20-tri-(4-methylphenyl)porphyrin (IV) was synthesized as described in [9], the calix[4]arene-bis(β-octaalkylporphyrin) ligand (**V**) was synthesized as in [10], and tin tetraphenylporphyrinate ($SnP(OH)_2$ (**VI**) was synthesized by the method [8].



V

Individual compounds were separated using column chromatography on neutral alumina. Organic solvents were purified by known procedures [11]. The course of the reaction was monitored by thin-layer chromatography (TLC) on Silufol UV-254 plates. The ^1H NMR spectra of solutions in deuterated chloroform (TMS as an internal reference) were recorded on a Bruker VC-500 spectrometer operating at 500.17 MHz. The electronic absorption spectra were recorded on a Varian Cary-100 spectrophotometer.

Calix[4]arene-bis(*trans*-dichloro-β-octaalkylporphyrinatotin(IV)). Compound **V** (0.40 g) was dissolved in pyridine, and a 1.5-fold excess of $SnCl_2 \cdot 2H_2O$ was added to the solution. The reaction mixture was refluxed for 8 h. The reaction course was monitored by observing the changes in the visible absorption spectra. After cooling, the solution was filtered, the solvent was vacuum-distilled off, and the residue was recrystallized from a dichloromethane–hexane (2 : 1) mixture. The yield was 0.44 g (92%). R_f 0.73 (Al_2O_3, elution with CH_2Cl_2–C_6H_{14}, 1 : 2).

^1H NMR ($CDCl_3$, δ, ppm): 9.95 (s, 4H, *ms*-H), 7.91 (m, 8H, Ar-$H_{porph + calixarene}$), 7.60 (m, 8H, Ar-$H_{porph + calixarene}$), 7.24 (t, 2H, Ar-H_{porph}), 7.06 (t, 2H, Ar-$H_{calixarene}$), 4.41 (s, 6H, OCH_3), 4.03 (d, 4H, $ArCH_2Ar$), 3.84 (q, 16H, $\underline{CH_2}CH_3$), 3.40 (d, 4H, $ArCH_2Ar$), 2.39 (s, 24H, CH_3), 1.35 (t, 24H, $CH_2\underline{CH_3}$). UV (CH_2Cl_2, nm (logε)): 406 (4.96), 521 (3.41), 559 (3.97), 599 (3.80).

For $C_{116}H_{122}N_8O_8Sn_2Cl_4$ anal. calcd. (%): C, 65.24; H, 5.72; N, 5.25.

Found (%): C, 65.99; H, 5.69; N, 5.33.

Calix[4]arene-bis(*trans*-dihydroxy-β-octaalkylporphyrinatotin(IV)) (II). Compound **VI** (0.30 g, 0.13 mmol) and potassium carbonate (0.21 g, 1.50 mmol) were dissolved in 100 mL of tetrahydrofuran and 25 mL of water, and the reaction mixture was refluxed for 4 h. The solution was concentrated to 30 mL by rotary evaporation and left overnight in a refrigerator. The

precipitated crystals were filtered off, washed with cold water, and vacuum-dried. The yield was 0.24 g (85%).

^{1}H NMR (DMSO, δ, ppm): 9.92 (s, 4H, *ms*-H), 7.93 (m, 8H, Ar-$H_{porph + calixarene}$), 7.63 (m, 8H, Ar-$H_{porph + calixarene}$), 7.25 (t, 2H, Ar-H_{porph}), 7.09 (t, 2H, Ar-$H_{calixarene}$), 4.44 (s, 6H, OCH_3), 4.01 (d, 4H, $ArCH_2Ar$), 3.88 (q, 16H, $\underline{CH_2}CH_3$), 3.32 (d, 4H, $ArCH_2Ar$), 2.33 (s, 24H, CH_3), 1.30 (t, 24H, $CH_2\underline{CH_3}$), –6.34 (s, 4H, OH). UV (CH_2Cl_2, nm (logε)): 408 (4.90), 522 (3.30), 558 (3.57), 598 (3.59).

For $C_{116}H_{126}N_8O_{12}Sn_2$ anal. calcd. (%): C, 67.59; H, 6.12; N, 5.44.

Found (%): C, 67.21; H, 6.18; N, 5.66.

Calix[4]arene-bis(*trans*-(hydroxy,L^1)-β-octaalkylporphyrinatotin(IV)) (IIIa). Compound **II** (0.03 g, 0.014 mmol) and benzoic acid (0.004 g, 0.028 mmol) were heated in dichloromethane for 30 min. The solution was cooled, and the solvent was slowly evaporated. The resulting crystals were washed with cold water and vacuum-dried.

^{1}H NMR (DMSO, δ, ppm): 9.95 (s, 4H, *ms*-H), 7.97 (m, 8H, Ar-$H_{porph + calixarene}$), 7.65 (m, 8H, Ar-$H_{porph + calixarene}$), 7.27 (t, 2H, Ar-H_{porph}), 7.12 (t, 2H, Ar-$H_{calixarene}$), 4.81 (d, 2H, CH_{L1}), 4.47 (s, 6H, OCH_3), 4.25 (d, 4H, CH_{L1}), 4.03 (d, 4H, $ArCH_2Ar$), 3.90 (q, 16H, $\underline{CH_2}CH_3$), 3.36 (d, 4H, $ArCH_2Ar$), 3.17 (d, 4H, CH_{L1}), 2.31 (s, 24H, CH_3), 1.33 (t, 24H, $CH_2\underline{CH_3}$), –6.30 (s, 2H, OH).

For $C_{130}H_{134}N_8O_{14}Sn_2$ anal. calcd. (%): C, 68.80; H, 5.91; N, 4.94.

Found (%): C, 68.48; H, 5.88; N, 4.66.

Calix[4]arene-bis(*trans*-(hydroxy,L^2)-β-octaalkylporphyrinatotin(IV)) (IIIb). A mixture of compound **II** (0.03 g, 0.014 mmol) and 4-pyridinecarboxylic acid (0.004 g, 0.028 mmol) was heated in dichloromethane for 30 min. The solution was cooled, and the solvent was slowly evaporated. The resulting crystals were washed with cold water and vacuum-dried.

^{1}H NMR (DMSO, δ, ppm): 9.91 (s, 4H, *ms*-H), 7.93 (m, 8H, Ar-$H_{porph + calixarene}$), 7.64 (m, 8H, Ar-$H_{porph + calixarene}$), 7.26 (t, 2H, Ar-H_{porph}), 7.11 (t, 2H, Ar-$H_{calixarene}$), 4.44 (s, 6H, OCH_3), 4.23 (d, 4H, CH_{L2}), 4.07 (d, 4H, $ArCH_2Ar$), 3.92 (q, 16H, $\underline{CH_2}CH_3$), 3.33 (d, 4H, $ArCH_2Ar$), 3.19 (d, 4H, CH_{L2}), 2.30 (s, 24H, CH_3), 1.31 (t, 24H, $CH_2\underline{CH_3}$), –6.33 (s, 2H, OH).

For $C_{128}H_{132}N_{10}O_{14}Sn_2$ anal. calcd. (%): C, 67.68; H, 5.82; N, 6.17.

Found (%): C, 69.13; H, 6.05; N, 6.39.

(5,10,15,20-Tetraphenylporphyrinato)ruthenium RuP(CO)(H_2O)) (VII). A mixture of tetraphenylporphine (0.05 g, 0.081 mmol) and $Ru_3(CO)_{12}$ (0.03 g, 0.054 mmol) was heated in 5 g of phenol for 1 h. The melt was cooled and dissolved in 20 mL of dimethylformamide, the solution was poured into water, and the precipitate was filtered off and washed with hot water. The residue was chromatographed two times on alumina with chloroform. The yield was 0.044 g (73%). R_f 0.81 (elution with chloroform–ethanol, 20 : 1).

^{1}H NMR ($CDCl_3$, δ, ppm): 8.65 (d, 8H, $CH_{pyrrole}$), 8.05 (d, 8H, Ar-H_{ortho}), 8.21 (t, 8H, Ar-H_{meta}), 7.70 (t, 4H, Ar-H_{para}). UV ($CHCl_3$, nm (logε)): 411 (5.31), 490 (3.66), 529 (4.30).

For $C_{45}H_{32}N_4O_2Ru$ anal. calcd. (%): C, 66.09; H, 3.92; N, 6.85.

Found (%): C, 66.01; H, 3.89; N, 6.81.

(5,10,15,20-Tetraphenylporphyrinato)ruthenium RuP(CO)(L^3)) (VIIIa). Compound **VII** (0.03 g, 0.045 mmol) and pyridine (0.007 g, 0.045 mmol) were kept in dichloromethane for 1 h. The solvent was evaporated, and the resulting crystals were washed with water and vacuum-dried.

^{1}H NMR ($CDCl_3$, δ, ppm): 8.67 (d, 8H, $CH_{pyrrole}$), 8.02 (d, 8H, Ar-H_{ortho}), 8.17 (t, 8H, Ar-H_{meta}), 7.69 (t, 4H, Ar-H_{para}), 4.55 (t, 1H, Py_{para}), 4.29 (d, 2H, Py_{meta}), 3.12 (d, 2H, Py_{ortho}).

For $C_{51}H_{35}N_4ORu$ anal. calcd. (%): C, 74.63; H, 4.27; N, 6.83.

Found (%): C, 74.58; H, 4.21; N, 6.78.

(5,10,15,20-Tetraphenylporphyrinato)ruthenium RuP(CO)(L^2)) (VIIIb). A mixture of compound **VII** (0.03 g, 0.045 mmol) and 4-pyridinecarboxylic acid (0.006 g, 0.045 mmol) in dichloromethane was kept for 1 h. The solvent was evaporated, and the resulting crystals were washed with water and vacuum-dried.

^{1}H NMR ($CDCl_3$, δ, ppm): 8.62 (d, 8H, $CH_{pyrrole}$), 8.07 (d, 8H, Ar-H_{ortho}), 8.19 (t, 8H, Ar-H_{meta}), 7.71 (t, 4H, Ar-H_{para}), 4.19 (d, 2H, CH_{L2}), 3.27 (d, 2H, CH_{L2}).

For $C_{50}H_{34}N_5O_3Ru$ anal. calcd. (%): C, 70.34; H, 3.98; N, 8.21.

Found (%): C, 70.28; H, 3.89; N, 8.16.

(CO)RuP-L^2-$Sn_2D(HO)_2$-L^2-RuP(CO) (IX). A mixture of compound **VIIIb** (0.03 g, 0.015 mmol) and RuP(CO)(H_2O) (0.02 g, 0.030 mmol) in dichloromethane was kept for 1 h and then slowly evaporated. The resulting crystals were washed with water and vacuum-dried.

^{1}H NMR (DMSO, δ, ppm): 9.89 (s, 4H, *ms*-H), 8.65 (d, 16H, $CH_{pyrrole}$), 8.05 (d, 16H, Ar-H_{ortho}), 8.21 (t, 16H, Ar-H_{meta}), 7.91 (m, 8H, Ar-$H_{porph + calixarene}$), 7.70 (t, 8H, Ar-H_{para}), 7.62 (m, 8H, Ar-$H_{porph + calixarene}$), 7.21 (t, 2H, Ar-H_{porph}), 7.11 (t, 2H, Ar-$H_{calixarene}$), 4.42 (s, 6H, OCH_3), 4.04 (d, 4H, $ArCH_2Ar$), 3.89 (q, 16H, $\underline{CH_2}CH_3$), 3.39 (d, 4H, CH_{L2}), 3.28 (d, 4H, $ArCH_2Ar$), 3.20 (d, 4H, CH_{L2}), 2.31 (s, 24H, CH_3), 1.33 (t, 24H, $CH_2\underline{CH_3}$), –6.30 (s, 2H, OH). UV (CH_2Cl_2, nm (logε)): 410 (4.65), 492 (4.32), 528 (4.08), 560 (3.14), 601 (3.21).

For $C_{218}H_{188}N_{16}O_{16}Sn_2Ru_2$ anal. calcd. (%): C, 70.26; H, 5.05; N, 6.02.

Found (%): C, 70.33; H, 5.12; N, 6.07.

P–O–$Sn_2D(HO)_2$–O–P (X). A mixture of compounds **II** (0.03 g, 0.014 mmol) and **IV** (0.02, 0.030 mmol) in benzene was refluxed for 3 h. The sol-

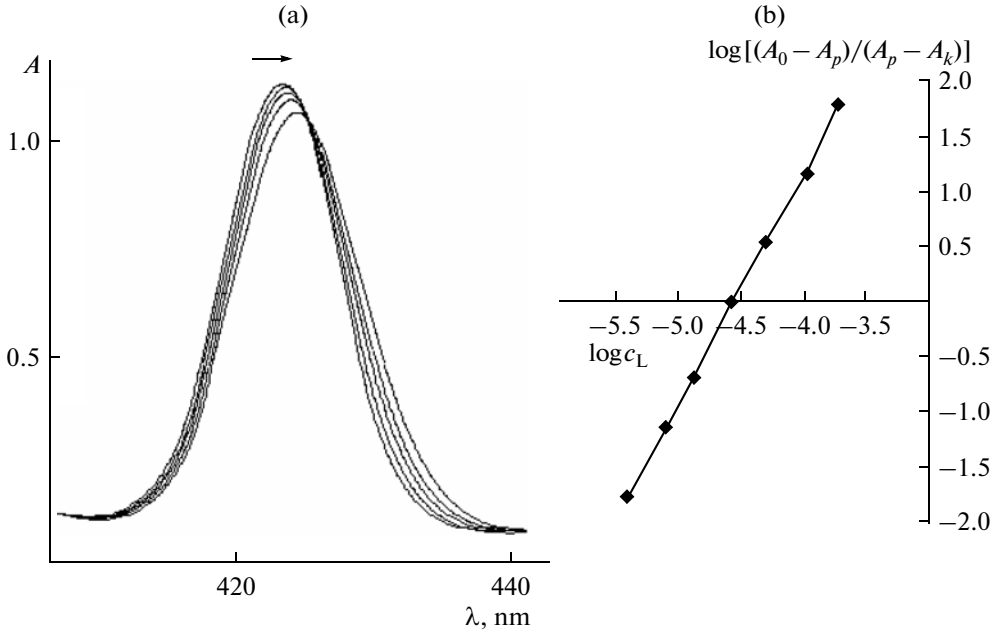


Fig. 1. (a) Absorption spectra of solutions in the region of the Soret band of compound **VI** ($c_{porph} = 8 \times 10^{-6}$ mol/L, CH_2Cl_2, 25°C) with additions of benzoic acid (L^1) from 0 to 6×10^{-3} mol/L and (b) the plot of $\log[(A_0 - A_p)/(A_p - A_k)]$ vs $\log c_{ligand}$.

vent was evaporated, and the resulting crystals were washed with water and vacuum-dried.

^{1}H NMR (DMSO, δ, ppm): 9.90 (s, 4H, *ms*-H), 9.34 (d, 16H, $CH_{pyrrole}$), 8.60 (d, 12H, Ar-H_{ortho2}), 8.21 (t, 16H, Ar-H_{meta}), 7.92 (m, 8H, Ar-$H_{porph + calixarene}$), 7.89 (d, 4H, Ar-H_{ortho1}), 7.61 (m, 8H, Ar-$H_{porph + calixarene}$), 7.26 (t, 2H, Ar-H_{porph}), 7.10 (t, 2H, Ar-$H_{calixarene}$), 4.46 (s, 6H, OCH_3), 4.03 (d, 4H, $ArCH_2Ar$), 3.90 (q, 16H, $\underline{CH_2}CH_3$), 3.30 (d, 4H, $ArCH_2Ar$), 2.74 (s, 18H, Ar-CH_3), 2.35 (s, 24H, CH_3), 1.33 (t, 24H, $CH_2\underline{CH_3}$), −2.65 (s, 4H, $NH_{pyrrole}$), −6.30 (s, 2H, OH). UV (CH_2Cl_2, nm (logε)): 409 (4.88), 414 (4.92), 521 (3.32), 559 (3.54), 599 (3.49), 650 (3.20).

For $C_{210}H_{194}N_{16}O_{12}Sn_2$ anal. calcd. (%): C, 74.83; H, 5.76; N, 6.65.

Found (%): C, 74.87; H, 5.69; N, 6.61.

The stability constants (K_s) of the 1 : 1 porphyrin receptor (A)–substrate (B) complexes were calculated by the equation

$$K_s = \frac{[AB]}{[A][B]} = 1/[B]\left(\frac{\Delta A_{i,\lambda_1}}{\Delta A_{o,\lambda_1}}\frac{\Delta A_{o,\lambda_2}}{\Delta A_{i,\lambda_2}}\right) \quad (mol/L)^{-1}, \quad (1)$$

where λ_1 is the decreasing wavelength, λ_2 is the increasing wavelength, [A] is the porphyrinate concentration, [B] is the substrate concentration, ΔA_o is the maximal change in the solution absorbance at a given wavelength, ΔA_i is the change in the solution absorbance at a given wavelength at a given concentration [12].

RESULTS AND DISCUSSION

According to the literature data [5–8], the complexation of monomeric tin(IV) porphyrinates with aromatic carboxylic acids occurs by the equation

$$SnP(OH)_2 + 2HL \rightleftarrows SnP(L)_2 + 2H_2O, \quad (2)$$

i.e., carboxylate groups are substituted for both *trans*-hydroxyl groups. This process is equilibrium established in a few minutes.

Figure 1 shows typical changes in the UV spectra caused by the formation of complex **I**. Studying the complexation of monomeric tin tetraphenylporphyrinate **VI** with L^1 showed that, in a wide ligand concentration range ($c_{ligand} = 0–5.3 \times 10^{-4}$ mol/L), spectral changes in the course of reaction occur with retention of one family of isosbestic points. The titration curve has one step, which is evidence of the formation of one type of complex; the slope of the $\log[(A_0 - A_p)/(A_p - A_k)]$ versus $\log c_{ligand}$ plot is 2, which indicates that the resulting complex has the 1 : 2 composition (Fig. 1b).

In the ^{1}H NMR spectrum of complex **I**, the proton signals of the ligand are shifted upfield with respect to the proton signals of the free ligand. The largest shift is observed for the ligand protons located closer to the porphyrin macrocyclic ring in the complex and, thus, subjected to the stronger shielding effect of its ring current.

Studying the complexation of **II** with benzoic acid by spectrophotometric titration in dichloromethane showed that spectral changes in the course of spectrophotometric titration of **II** with L^1 in a wide ligand concentration range ($c_{ligand} = 0–5.3 \times 10^{-4}$ mol/L)

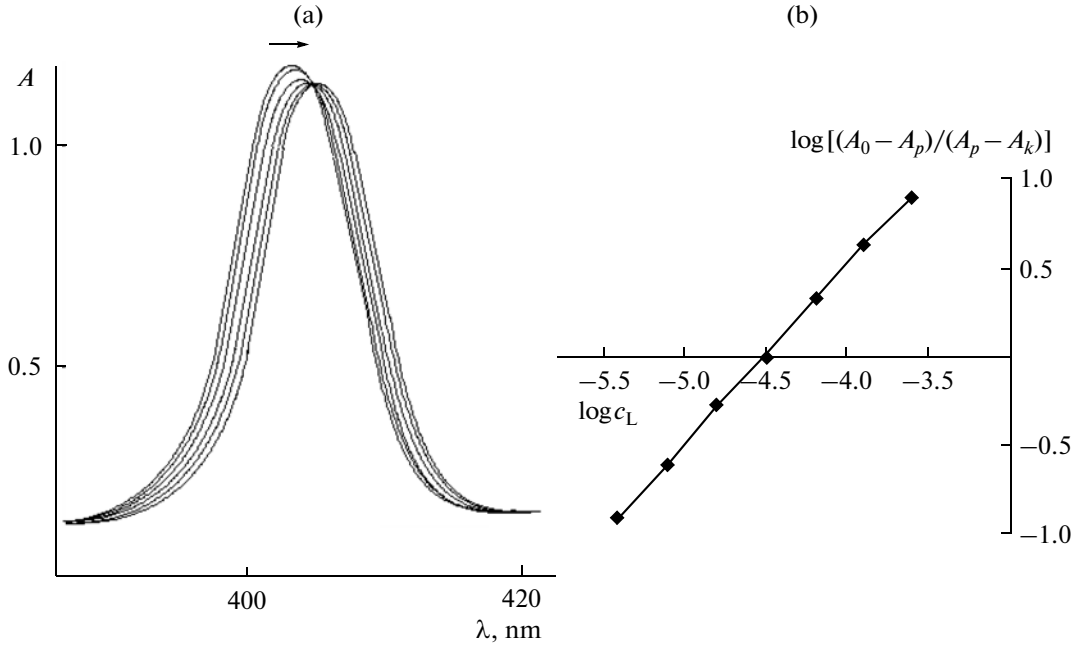


Fig. 2. (a) Absorption spectra of solutions in the region of the Soret band of compound **II** ($c_{porph} = 8 \times 10^{-6}$ mol/L, CH_2Cl_2, 25°C) with additions of benzoic acid (L^1) from 0 to 5×10^{-3} mol/L and (b) the plot of $\log[(A_0 - A_p)/(A_p - A_k)]$ vs $\log c_{ligand}$.

also occur with retention of one family of isosbestic points. The titration curve has one step; however, the slope of the $\log[(A_0 - A_p)/(A_p - A_k)]$ versus $\log c_{ligand}$ plot is 1, which is evidence that the resulting receptor–substrate complex has the 1 : 1 composition (Fig. 2). Thus, the formation of complex **III** from **II** involves two parallel independent reactions at each of the two tetrapyrrole moieties:

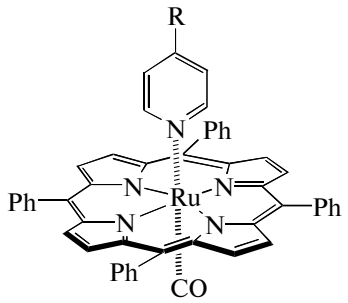
$$SnP(OH)_2 + HL \rightleftarrows SnP(OH)\text{-}L + H_2O. \quad (3)$$

The processes with 4-pyridinecarboxylic acid (L^2) are analogous. The spectrophotometric titration data enable us to calculate the stability constants of complexes **IIIa** and **IIIb** by a common procedure using Eq. (1): they are estimated at 1.2×10^4 $(mol/L)^{-1}$ for benzoic acid and 1.4×10^4 $(mol/L)^{-1}$ for 4-pyridinecarboxylic acid.

The elemental analysis data for the complexes obtained by slow crystallization of the reaction mixture from dichloromethane at the reagent molar ratio corresponding to the inflection point on the titration curve confirm that the molecular complexes contain two carboxylate moieties and two hydroxy groups. The characteristics of the ^1H NMR spectra of the complexes are consistent with these data: (1) the ligand signals are shifted upfield as compared with the signals of the free ligands; (2) the closer the ligand protons to the porphyrin macrocyclic ring, the larger the shift of the corresponding signals (i.e., each ligand in the complex is in the shielding field of one porphyrin macrocyclic ring); (3) the intensity of the OH signals in the ^1H NMR spectrum of the complex is twice as low as the intensity of the OH signals in the spectrum of **II**.

The conclusion that complex **IIIb** is the "external" one. i.e., carboxyl groups are substituted only for the hydroxy groups on the outer side of the porphyrinate moieties of dimer **II**, is supported by the splitting of the signals of the corresponding ligand protons. When "internal" complexes are formed and the ligand is in the field of two tetrapyrrole macrocyclic rings (so-called sandwich structure of the complex), the *ortho*- and *meta*-protons of the ligand become equivalent and give rise to one ^1H NMR signal [10].

Studying the complexation of ruthenium tetraphenylporphyrinate (**VII**) with pyridine (L^3) (the organic substrate molecule is substituted for one water molecule in the inner coordination sphere of ruthenium porphyrinate) by spectrophotometric titration in dichloromethane showed that the visible absorption spectrum of the reaction mixture also displays one family of spectral curves with its set of isosbestic points (Fig. 3a). The titration curve has one step, which is evidence that complexation is a one-step process resulting in the 1 : 1 receptor–substrate complex (**VIIIa**) by the equation



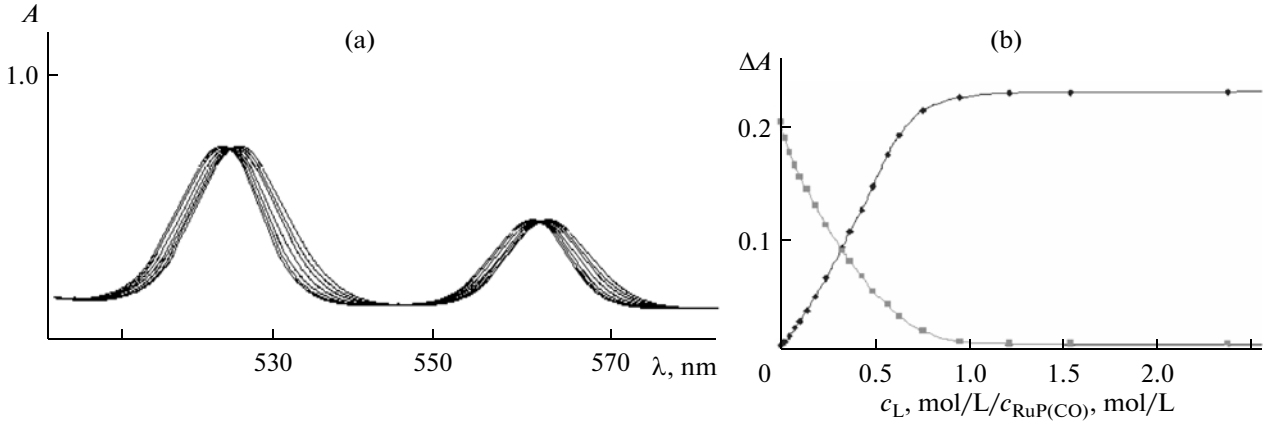


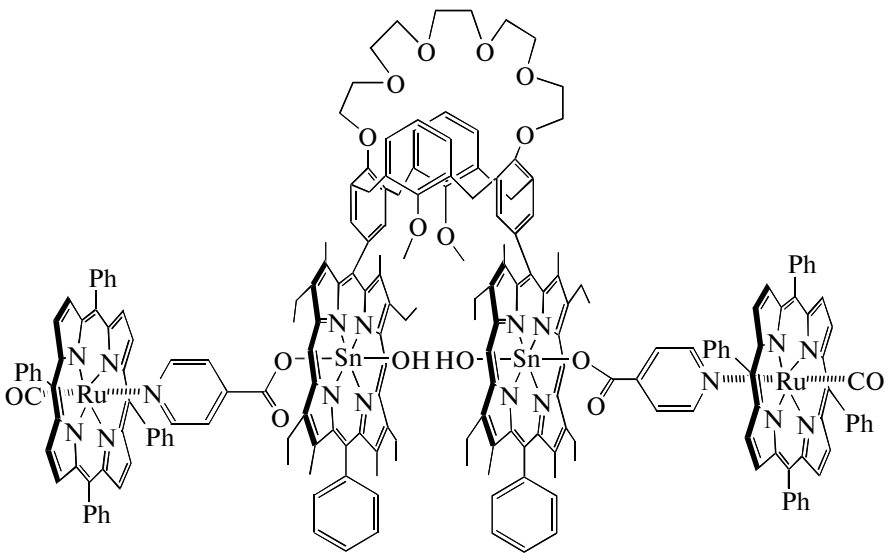
Fig. 3. (a) Changes in the visible absorption spectra of solutions of compound **VII** ($c_{porph} = 10^{-5}$ mol/L, 25°C) in dichloromethane caused by additions of pyridine (L^3) from 0 to 3×10^{-5} mol/L; (b) the titration curve of **VII** with pyridine at the "decreasing" and "increasing" wavelengths.

$$RuP(CO)(H_2O) + L \rightleftarrows RuP(CO)\text{-}L + H_2O. \quad (4)$$

The equilibrium constants characterizing process (4) calculated by a common procedure from the spectrophotometric titration data by Eq. (5) are 3.5×10^7 $(mol/L)^{-1}$ for **VIIIa** and 3.1×10^7 $(mol/L)^{-1}$ for **VIIIb**.

The elemental analysis data for the complexes obtained by slow crystallization of the reaction mixture from dichloromethane at the reagent molar ratio corresponding to the inflection point on the titration curve (Fig. 2b) indicate that the molecular complexes contain one pyridine moiety and one CO group. The characteristics of the ^1H NMR spectra of the complex are well consistent with these data: the ligand signals are shifted upfield as compared with the signals of free pyridine (by 5.5 ppm for the *ortho*-protons, 3.0 ppm for the *meta*-protons, and 1.1 ppm for the *para*-protons of the substrate molecule). Analogous shifts of the proton signals are observed for 4-pyridinecarboxylic acid.

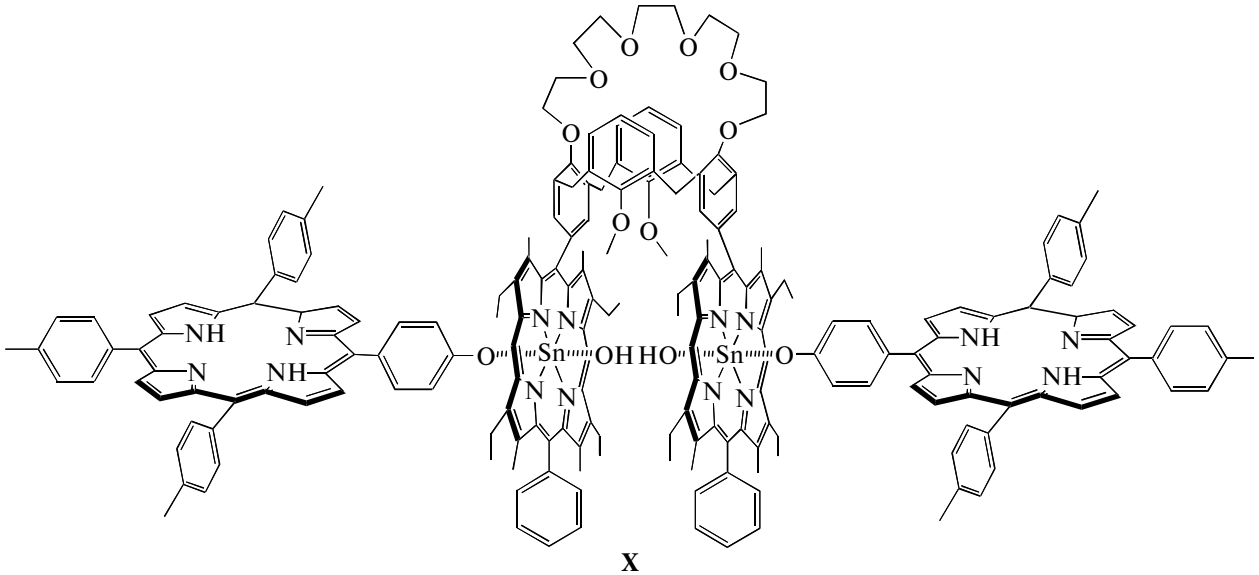
Ruthenium and tin porphyrinates in the presence of 4-pyridinecarboxylic acid are able to self-organize into different supramolecular assemblies [13, 14]. We found experimentally that the $Sn_2D(OH)_4$ and $Sn_2D(OH)_2(L^2)_2$ complexes can be used as building blocks for producing heterometallic porphyrin oligomers. In particular, slow evaporation of the reaction mixture consisting of $Sn_2D(OH)_4$ and $RuP(CO)(L^2)$ (1 : 2.5 molar ratio) or of $Sn_2D(OH)_2(L^2)_2$ and $RuP(CO)(H_2O)$ (1 : 2 molar ratio) resulted in the same complex, which, according to elemental analysis, can be represented as supramolecular assembly **IX** consisting of four porphyrin units with orientation close to the cyclophane one.



IX

In the ^{1}H NMR spectrum of complex **IX**, the signals of pyridinecarboxylic acid are equally shifted upfield from their positions for the free acid. This is evidence that the protons experience the same shielding effect of two porphyrin macrocyclic rings. The parallel arrangement of the tetrapyrrole moieties in complex **IX** is also supported by the broadening of the Soret band and the decrease in its intensity as compared with the absorption spectra of $Sn_2D(OH)_4$ and $RuP(CO)(L_2)$.

Slow evaporation of the cooled reaction mixture obtained by long-term heating under reflux of a mixture of $Sn_2D(OH)_4$ and **IV** (1 : 2.1 molar ratio) yielded a complex that, according to elemental analysis data, can be represented as supramolecular assembly **X**, in which one hydroxyporphyrin is coordinated to each porphyrinate moiety of the dimer on the outer side of the tetrapyrrole macrocyclic rings. In the ^{1}H NMR spectrum of complex **X**, the largest upfield shifts are observed for the ortho-protons of the 4-hydroxyphenyl moiety of porphyrin **IV**. These protons are located closer to the tetrapyrrole macrocyclic rings of dimer **II** than the *ortho*-protons of the tolyl moieties and, thus, experience the strongest shielding effect of the macrocycles. In the electronic absorption spectrum of complex **X**, the Soret band is split, which is typical of oligomeric porphyrin systems with non-cyclophane mutual arrangement of the porphyrin moieties.



X

Thus, we synthesized new tin(IV) porphyrinates and supramolecular complexes based thereon and characterized them by UV spectroscopy, ^{1}H NMR, and elemental analysis. The use, as the key compound, of calix[4]arene-bis(porphyrinatotin(IV)) with a fixed arrangement of the reaction sites on a macrocyclic platform enables creating tetramer assemblies with parallel and perpendicular arrangement of tetrapyrrole chromophores, which can be used in design of functional materials for optoelectronics.

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