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Acid–Base Properties of Thianaphthene-Annulated Porphyrazine and Tetra(pyrazino)porphyrazine Complexes with Aluminum Group Metals

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Abstract—Acid–base properties of Al(III), Ga(III), and In(III) complexes with tert-butyl-substituted thianaphthene-annulated porphyrazine and tetra(2,3-pyrazino)porphyrazine in proton-donor medium (CH_2Cl_2–CF_3COOH) were studied by spectrophotometric titration. The concentration stability constants of the singly protonated complexes were determined. The effects of the metal nature and aromatic heterocyclic fragment on the basicity of meso-nitrogen atoms were analyzed. Negative inductive effect of the sulfur atom in the thianaphthene fragment reduces the basicity of the meso-nitrogen atoms as compared to analogous porphyrazine and phthalocyanine complexes. Acid–base transformations of the thianaphthene-annulated tetra(2,3-pyrazino)porphyrazine involve both meso-nitrogen atoms and those in the pyrazine rings.

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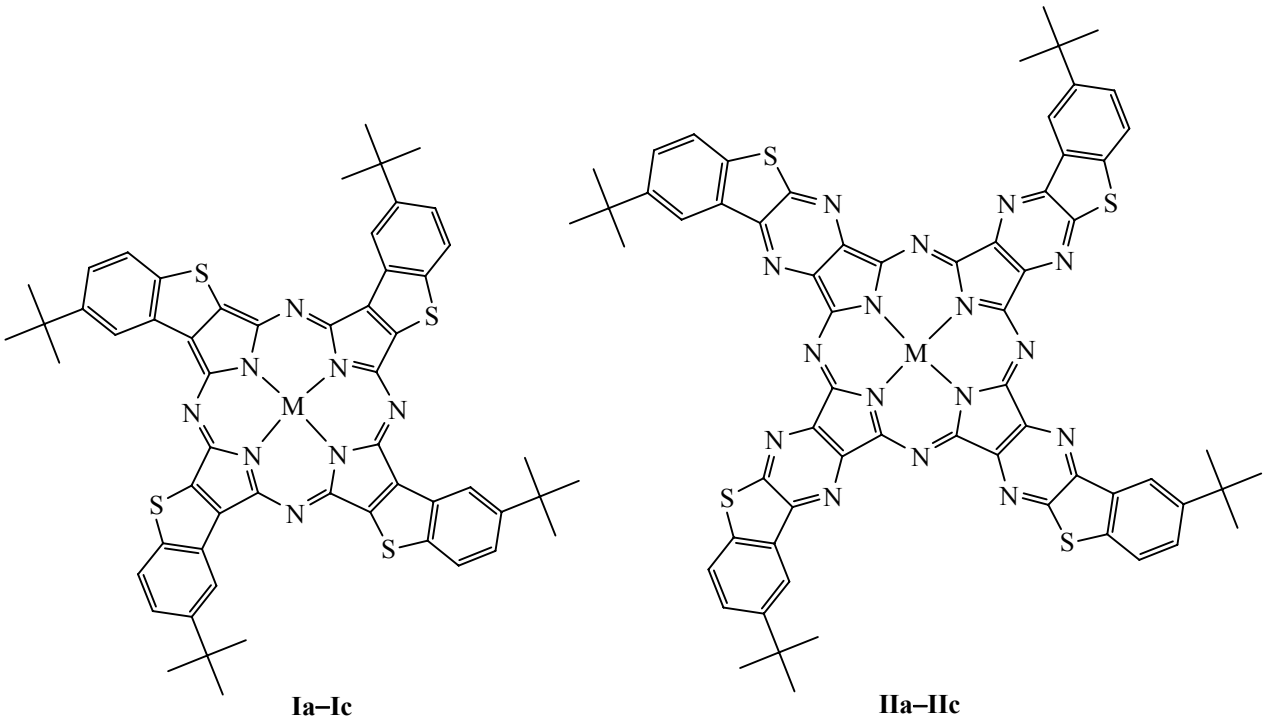
Porphyrazines (PA) and their metal complexes (MPA) are weak multicenter bases [1–3]. Acid–base interactions of porphyrazines may involve both outer (meso) and inner (in metal-free derivatives) nitrogen atoms. The acid forms differ by the degree of proton transfer from an acid molecule to the donor center. The number of donor centers in a PA molecule that participate in acid–base interaction, as well as the stability constants of acid forms, depend on the PA structure and properties of proton-donor medium. By acid–base interaction we mean a complex process which may be accompanied by formation of an H-complex, ion–ion association, or complete ionization, depending on the acidity of the medium.

Participation of donor centers in porphyrazines and their complexes in acid–base interactions leads to essential change of the aromatic conjugated π-electron system, which is reflected in their electronic absorption spectra and other optical properties, including nonlinear optical properties. For example, indium complexes of phthalocyanines (Pc) and their analogs [tetrapyrazinoporphyrazines (PAPyz), naphthalocyanines (Nc), and other porphyrazines] are efficient as optical limiters of pulsed laser radiation [4, 5]. It has recently been shown [6, 7] that acidity of the medium strongly affects optical limiting properties of such compounds.

Acid–base interactions in proton-donor media of IIIA Group metal complexes with β-octaphenylporphyrazine [8–10] and tetra-tert-butylphthalocyanine [11], as well as of indium complexes with mono- and diazaporphyrins [12], were studied previously. In addition, we reported in [13] the results of spectrophotometric titration of aluminum group metal complexes with tetra(2,3-thianaphtheno)porphyrazine (SNc). The present work continues our studies on the synthesis and properties of porphyrazines annulated with aromatic sulfur-containing heterocycles. We now report on the spectral parameters of Al(III), Ga(III), and In(III) complexes with tert-butyl-substituted thianaphthene-annulated porphyrazine [$SNc(t\text{-}Bu)_4$] (**I**) and tetra(2,3-pyrazino)porphyrazine [$PAPyzSNp(t\text{-}Bu)_4$] (**II**) in proton-donor medium (CH_2Cl_2–CF_3COOH).

Increase of the acidity of solutions of complexes **Ia**–**Ic** in methylene chloride is accompanied by red shift of the *Q*-band in their electronic absorption spectra (Fig. 1). The spectral patterns of **Ia**–**Ic** displayed distinct isosbestic points only for the first protonation step, indicating equilibrium between two forms, neutral and protonated. The red shift amounts to ~1000 cm^{-1} (see table), which is characteristic of protonation of one *meso*-nitrogen atom in the porpyrazine macroring [1–3].



Ia–Ic **IIa–IIc**

M = Al (**a**), Ga (**b**), In (**c**).

As the acid concentration rose (>1 M for **Ic**), further red shift of the *Q*-band was observed (by 69 nm; Fig. 1a) due to protonation of the second *meso*-nitrogen atom. However, no distinct isosbestic points were detected. This may be due to solvatochromic effect and/or protonation of the axial OH ligand and its elimination or replacement by trifluoroacetate anion. The same factors may be responsible for the reduction of optical density and shift of the absorption maximum toward shorter wavelengths (by 8 nm) in the spectrum of **Ib** at an acidity exceeding 3.9 M. Further red shift of the absorption maximum in concentrated sulfuric acid indicated protonation of the third and fourth *meso*-nitrogen atoms (Figs. 1, 2).

The calculated pK_1 values are given in table. It is seen that the basicity of *meso*-nitrogen atoms in Ga(III) complexes with SNc and SNc(*t*-Bu)$_4$ is lower than in analogous In(III) and Al(III) complexes. This trend is consistent with increase in electronegativity in the

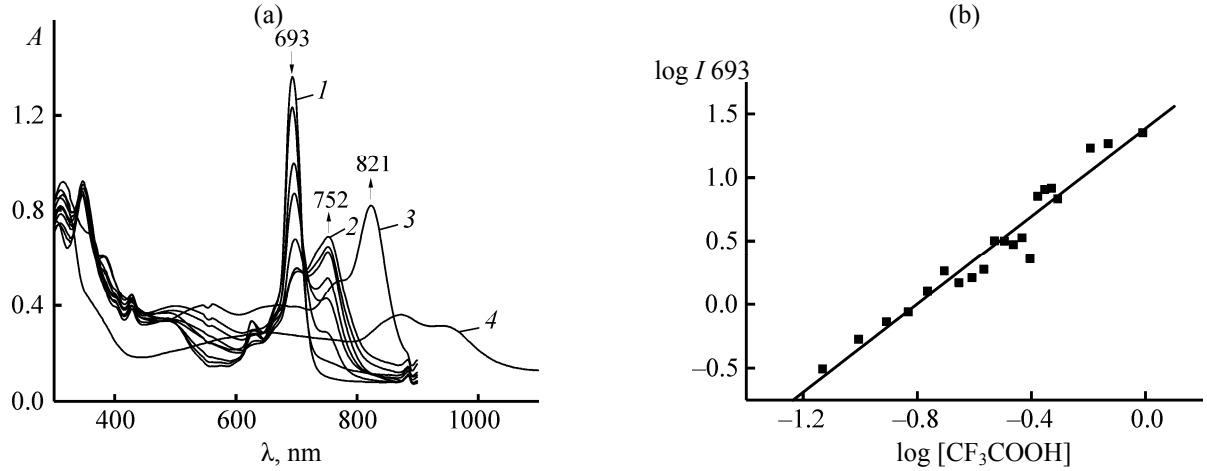


Fig. 1. (a) Variation of the electronic absorption spectra of a solution of (OH)InSNctBu$_4$ at different acidities [c_{TFA}, M: (*1*) 0, (*2*) 0.37, (*3*) 8.49, (*4*) sulfuric acid] and (b) log dependence of the indicator ratio versus acid concentration.

First step basicity constants of metal complexes **Ia**–**Ic** and **IIa**–**IIc**, (HO)MSNc, and porphyrazine and phthalocyanine derivatives

Complex		pK_1	Slope n	Absorption maximum		Red shift of the Q/B-band, cm^{-1}
				λ^0_{max}	λ^1_{max}	
SNc	(HO)Al	0.42±0.05	2.08	677	720	882
	(HO)Ga	0.04±0.01	2.4	684	742	1143
	(HO)In	0.47±0.01	3.7	684	740	1106
SNc(*t*Bu)$_4$	(HO)Al	1.44±0.16	1.54	684	735	1014
	(HO)Ga	0.50±0.06	2.15	688	770	1548
	(HO)In	0.79±0.02	1.73	693	752	1132
PAPyzSNp(*t*Bu)$_4$	(HO)Al	0.02±0.01	2.26	372	420	522/1530
	(HO)Ga	0.27±0.04	1.45	367	411	543/1680
	(HO)In	0.34±0.06	1.25	371	420	562/1180
(Cl)MTAP[a]	(HO)Al	1.71±0.02	–	–	–	–
	(HO)Ga	0.97±0.03	–	–	–	–
	(HO)In	1.44	–	–	–	–
(HO)MPc(*t*Bu)[b]	(HO)Al	2.95	–	–	–	–
	(HO)Ga	2.30	–	–	–	–
	(HO)In	2.70	–	–	–	–

[a] In $CF_3COOH–CH_2Cl_2$ [9]. [b] In $CH_3COOH–H_2SO_4$ [11].

series Al (1.61) < In (1.69) < Ga (2.01). The effect of the indium atom on the basicity of *meso*-nitrogen atoms is weakened due to its deviation from the porphyrazine ring plane. Analogous relation between the basicity of *meso*-nitrogen atoms and nature of the central metal ion [Al(III) ≥ In(III) >> Ga(III)] was observed previously for the complexes formed by β-octaphenyl-substituted porphyrazine (Cl)MTAP [9] and *tert*-butyl-substituted phthalocyanine (HO)MPc(*t*-Bu)$_4$ [11].

As follows from the pK_1 values, the *meso*-nitrogen atoms in **Ia**–**Ic** are more basic than in unsubstituted complexes (HO)MSNc due to the presence of *t*-Bu groups in the benzene rings of the thianaphthene fragments. The slope of the log I_i—log c_{acid} dependence for the first protonation step ranges from 1.5 to 2.2, which may be related to homoconjugation of the acid anion in weakly ionizing medium with low dielectric permittivity (ε = 8.9 for CH_2Cl_2): $N_{meso}H^+\cdots OC(CF_3)O\cdots HOOCCF_3$.

Complexes **IIa**–**IIc** showed a more intricate pattern of spectral variations as the acidity increased. In this case, acid–base interactions involve not only *meso*-nitrogen atoms but also those in the fused pyrazine rings. As follows from the spectral patterns and the shape of the titration curves, the range of acid concentrations up to 0.2 (**IIa**), 0.25 (**IIb**), or 0.15 M (**IIc**) comprises three consecutive acid–base interaction steps corresponding to protonation of nitrogen atoms in three pyrazine rings. The position and intensity of the long-wave *Q*-band change insignificantly, whereas variations in the Soret band region (UV range) almost could not be detected (Fig. 2). Further increase in the acid concentration above 0.65 (**IIc**), 0.4 (**IIb**), or 0.34 M (**IIa**) leads to red shift of the *Q*-band by 520–560 cm^{-1} and of the Soret band by 1180–1680 cm^{-1} due to protonation of one *meso*-nitrogen atom in the porphyrazine macroring. The smaller red shift of the *Q*-band as compared to (HO)MSNc and (HO)MSNc(*t*-Bu)$_4$ and the shape of the titration curve suggest simultaneous protonation of the 4th pyrazine ring.

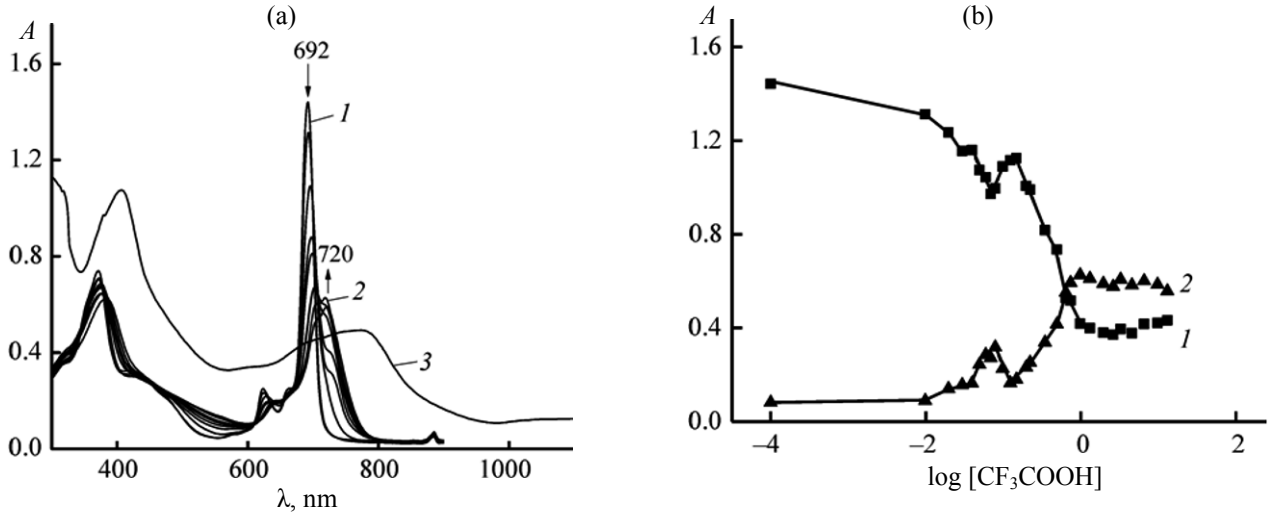


Fig. 2. (a) Variation of the electronic absorption spectra of a solution of complex **IIc** at different acidities [c_{TFA}, M: (*1*) 0, (*2*) 0.1, (*3*) sulfuric acid] and (b) titration curve.

Thus complexes **IIa**–**IIc** initially undergo protonation of pyrazine nitrogen atoms, which weakly affects the position of the Soret and *Q*-bands, and protonation of *meso*-nitrogen atoms leading to red shift of both bands is observed only under strongly acidic conditions. The red shift of the Soret band upon protonation of *meso*-nitrogen atom in **IIa**–**IIc** is 1530, 1680, and 1180 cm^{-1}, and the red shift of the *Q*-band is 522, 543, and 562 cm^{-1}, respectively. Simultaneously, the intensity of the *Q*-band decreases.

The electronic absorption spectrum of Al(III) complex **IIa** in methylene chloride differs from those of In(III) and Ga(III) complexes with PAPyzSNp(*t*-Bu)$_4$ (**IIb**, **IIc**). The reason is that complex **IIa** in CH_2Cl_2 exists as μ-oxo-dimer, as was shown for other Al(III) complexes with porphyrazine analogs [14]. Therefore, the variations observed in the spectrum of **IIa** with rise in acidity show a complicated pattern, and the series of experimental spectral curves can be divided into three families (Fig. 3). At an acid concentration of lower than 0.05 M we observed only a small change of the shape of the broadened *Q*-band from the dimer (Fig. 3a). Raising the acid concentration to 0.2 M led to the appearance of two clearly defined maxima at λ 693 and 719 nm in the *Q*-band region, which grew in intensity (Fig. 3b). The spectral pattern in the Soret band region also changed insignificantly. When the acid concentration reached 13.1 M, the Soret band moved to shorter wavelengths, the short-wave maximum on the *Q*-band (λ 693 nm) disappeared, and the intensity of the long-wave maximum (λ 719 nm) decreased (Fig. 3c). As a result, the electronic absorption spectrum of **IIa** became similar to those recorded at the same acidity for Ga(III) and In(III) complexes which do not form associates. Presumably, the first two steps of acid–base interactions involve protonation of pyrazine nitrogen atoms in the μ-oxo-dimer which is characterized by electronic absorption spectrum with the split *Q*-band. In the third step, protonation of *meso*-nitrogen atom is accompanied by decomposition of the dimer. It should be noted that we failed to observe electronic absorption spectrum typical of neutral monomeric form (λ_{max} 679 nm in pyridine) in the course of interaction of complex **IIa** with acid. Therefore, it seems reasonable to estimate the *Q*-band shift upon protonation of *meso*-nitrogen atom in **IIa** relative to the monomeric form in pyridine.

The basicity of *meso*-nitrogen atoms in **IIa**–**IIc** was calculated from variation in their absorbance in the UV region, for protonation of the pyrazine fragments does not affect absorption pattern in the Soret band region. Acid–base interaction with *meso*-nitrogen atom at an acid concentration exceeding 0.15–0.25 M induces red shift of the *Q*-band by 18 nm for the Ga(III) complex, by 25 nm for the In(III) complex, and by 33 nm for the Al(III) complex (520–560 cm^{-1}), as well as of the Soret band by 17–24 nm (1180–1680 cm^{-1}). Interestingly, the absorption at 400–500 nm, which is most likely to arise from intramolecular charge transfer from the thianaphthene fragments to the porphyrazine macroring, disappeared in acid medium. As follows from the data in table, the presence of fused pyrazine

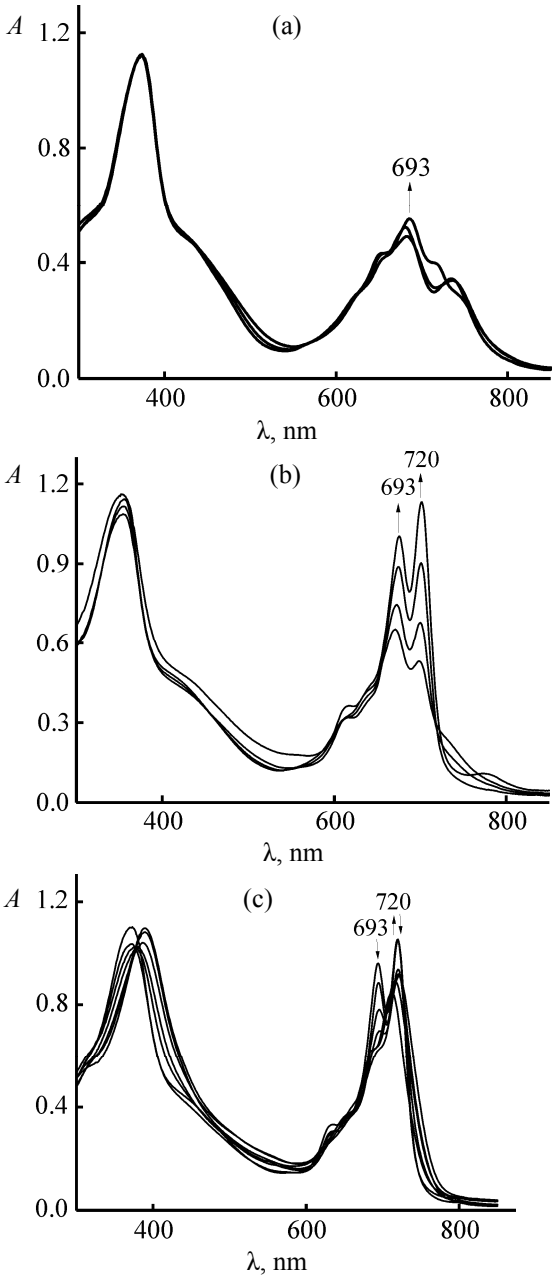


Fig. 3. Variation of the electronic absorption spectra of a solution of complex **IIc** in the trifluoroacetic acid concentration ranges (a) <0.05, (b) 0.05–0.2, and (c) 0.2–13 M.

rings in complexes **IIa**–**IIc** reduces the basicity of *meso*-nitrogen atoms as compared to (HO)MSNc and (HO)MSNc(*t*-Bu)$_4$.

Therefore, the basicity of *meso*-nitrogen atoms in Al(III) complex **IIa** is lower than in **IIc** and **IIb** (see table). Considerably contribution of the pyrazine rings in **IIa** to acid–base interactions further reduces the basicity of *meso*-nitrogen atoms therein.

Thus the basicity of *meso*-nitrogen atoms in the complexes formed by *tert*-butyl-substituted thianaphthene-annulated tetra(2,3-pyrazino)porphyrazine is considerably lower than in the corresponding (HO)MSNc and (HO)MSNc(*t*-Bu)$_4$ complexes. This is determined by electron-acceptor effect of the fused pyrazine rings on the porphyrazine macroring, which is additionally enhanced by their protonation.

EXPERIMENTAL

Complexes **Ia**–**Ic** and **IIa**–**IIc** were synthesized according to the procedures described previously [15, 16]. Their basicity was determined at 298 K in CH_2Cl_2–CF_3COOH by spectrophotometric titration using a Perkin–Elmer spectrophotometer and Lambda 20 software. The stability constants were calculated by Eq. (1):

$$\log I_i = \mathrm{p}K_i + n\log [CF_3COOH], \quad (1)$$

where n is the number of acid molecules participating in the formation of a given acid form at an ith step, pK_i is the stability constant of that form, and I_i is the indicator ratio determined by the formula

$$I_i = (A_i - A_0)/(A_\infty - A_i). \quad (2)$$

Here, A_0, A_i, and A_∞ are, respectively, the optical densities of a solution of a complex in the absence of acid, in the presence of acid at the titration step, and in the titrating agent without a solvent. Solutions for spectrophotometric titration were prepared using methylene chloride preliminarily distilled over potassium carbonate and freshly distilled trifluoroacetic acid.

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