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Kinetic Stability of Indium(III) Complexes with Azaporphyrins in Aqueous Sulfuric Acid

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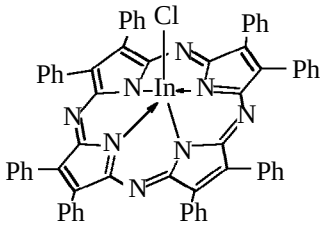
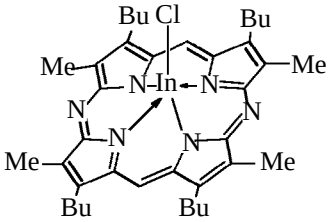
Abstract — Stability of chloro(octaphenyltetraazaporphinato)indium(III) and chloro(2,8,12,18-tetrabutyl-3,7,13,17-tetramethyl-5,15-diazaporphinato)indium(III) in 90–98 % aqueous sulfuric acid was studied. Kinetic parameters of solvoprotolytic dissociation of the complexes were determined, and a mechanism of the reaction was proposed. Diaza substitution results in more stable complexes than tetraaza substitution. The state of chloro(2,8,12,18-tetrabutyl-3,7,13,17-tetramethyl-5,15-diazaporphinato)indium(III) in a proton-donor medium was studied to show that the acid–base interaction involves one by one two *meso*-nitrogen atoms. Dissociation constants of the resulting acid forms were determined.

Presently indium(III) complexes with macrocyclic ligands attract much attention as perspective materials with nonlinear optical properties [1] and catalysts for various reactions, such as sulfination and carboxylation [2].

The ability of complexes for prolonged functioning as catalysts is determined by their stability in solutions. Therefore, in this work we studied kinetic stability of chloro(octaphenyltetraazaporphinato)-indium(III) (ClInTAP) and chloro(2,8,12,18-tetrabutyl-3,7,13,17-tetramethyl-5,15-diazaporphinato)indium(III) (ClInDAP) in 90–98% aqueous solutions of sulfuric acid.



ClInTAP



ClInDAP

Kinetic stability of metal azaporphyrins is characterized by true or apparent (for solutions with equal acidity) rate constants of the solvoprotolytic dissociation of the complexes in proton-donor media according to Eq. (1). This equation is found to be valid for most porphyrine, tetraazaporphyrine, and phthalocyanine complexes [3].

$$(L)_nMAP + 2LH^+ + 2X^- \longrightarrow M(L)_{n+2}X_2 + H_2AP. \quad (1)$$

Here MAP is a metal complex of azaporphyrin, H_2AP is an azaporphyrin ligand, LH^+ is solvated proton, and L is a solvent.

The ClInTAP complex exists in H_2SO_4 in the $[(HSO_4^-)_2InTAP]H_2^{2+}$ form with two protonated *meso*-nitrogen atoms [4]. With time the dication undergoes solvoprotolytic dissociation with expulsion of the ligand. The latter is unstable under these conditions and decomposes to give weakly colored compounds.

The ClInDAP complex has been studied by X-ray diffraction [5]. According to these data, diaza substitution in porphyrins changes bond lengths and angles formed by *meso*-nitrogen atoms in the macroring. For example, the N_{meso}-C_α bond (1.337 Å) in the complex is shorter than the same bond in chloro(tetraphenylporphinato)indium(III) ClInTPP (1.396 Å [6]), and the C_α-N_{meso}-C_α angles (124.4°) are smaller than C_α-C_{meso}-C_α (127.6° [6]). Therefore, the square coordination cavity of ClInTPP is contracted and distorted in going to ClInDAP (the diameters of the

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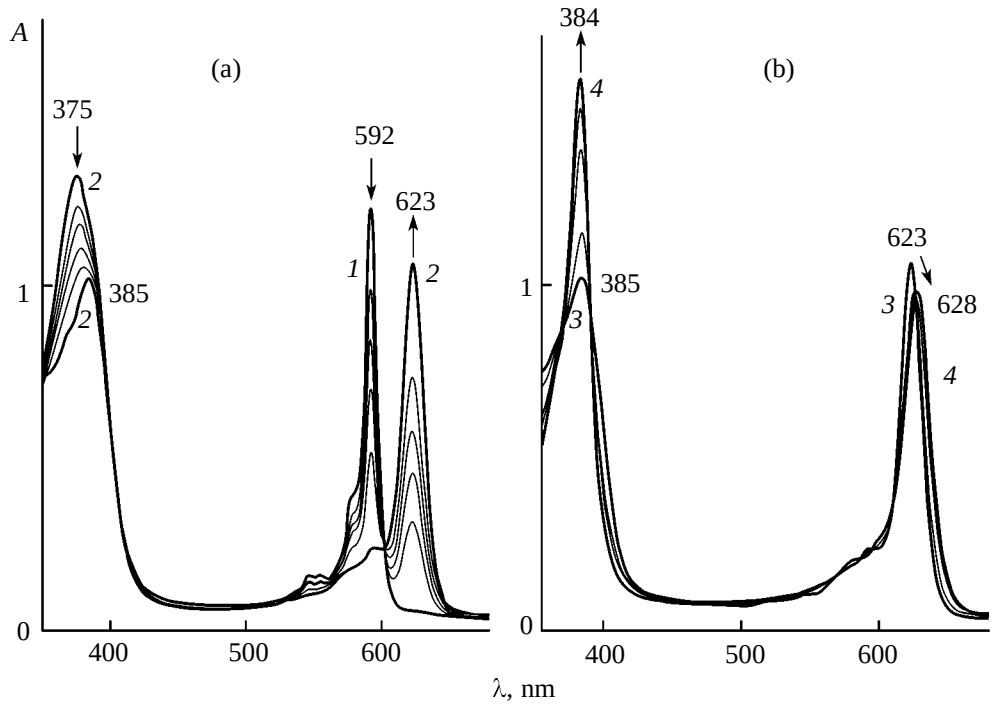

Fig. 1. Changes in the electronic absorption spectrum of 1.5×10^{-5} M solution of ClInDAP in (*1*) CH_3COOH and in a buffer solution CH_3COOH–urea–H_2SO_4 with H_0 (*2*) +0.92, (*3*) +0.54, and (*4*) –2. Thin lines denote spectral changes at intermediate solution acidities.

cavities are 4.134 and 4.049 Å, respectively). The indium atom resides above the palne of the macroring reaction center, and this deviation in ClInDAP (0.68 Å) is larger than in ClInTPP (0.61 Å) [6].

We previously studied the state of ClInDAP in a proton-donor media based on sulfuric acid. The changes observed in the electronic absorption spectra of ClInDAP solutions in CH_3COOH–urea–H_2SO_4 are shown in Fig. 1. As the acidity of the solution increases up to H_0 +1, the long-wave *Q* band shifts from 593 to 623 nm and the *B* band at 378 nm gets broader and weaker (Fig. 1a). On further acidification up to H_0 –2 the Q band undergoes a bathochromic shift to 628 nm, whereas the intensity of the *B* band at 328 nm increases, and it gets narrower (Fig. 1b). The appearance at $+3 < H_0 < -2$ of two families of spectral curves with clear isosbestic points (Figs. 1a and 1b) suggests two successive stages of a complete acid–base reaction involving the first and second *meso*-nitrogen atoms of the ClInDAP molecule. Taking into account the low dielectric constant of acetic acid, we can assume formation of ion–ion associates [schemes (2) and (3)] rather than completely ionized protonated forms.

$$\text{ClInDAP} + \text{HA} \rightleftharpoons \text{ClInDAPH}^+\cdots\text{A}^-, \quad (2)$$

$$\text{ClInDAPH}^+\cdots\text{A}^- + \text{HA} \rightleftharpoons \text{ClInDAPH}_2^{2+}\cdots 2\text{A}^-. \quad (3)$$

The above spectral changes are similar to those observed earlier for CuDAP in the same medium [7]. The dependence of the logarithm of the indicator ratio $\log I_n$ ($I_n = c_n/c_{n-1}$ is the ratio of the equilibrium concentrations of acid–base forms of ClInDAP) on H_0 for both stage (2) and stage (3) is linear with a slope close to one. Using spectrophotometric titration data in CH_3COOH–urea–H_2SO_4 medium, we calculated stability constants for the acidic forms generated in stages (2) and (3): pK_{a1} $+2.10 \pm 0.2$ and pK_{a2} -1.45 ± 0.23. The pK_{a1} value of $+2.20 \pm 0.13$ was also obtained in a CH_3COOH–antipyrine–H_2SO_4 buffer solution. Comparison of the pK_{a1} and pK_{a2} values for the indium diazaporphyrin complex and for the previously studied copper complex (pK_{a1} +3.20 [8] in $CH_3 \cdot COOH$–antipurine–H_2SO_4 and pK_{a2} 0.58 [7] in CH_3COOH–urea–H_2SO_4) points to a lower basicity of *meso*-nitrogen atoms in the indium complex. This fact seems to result from the absence of π-back donation that plays an important role in the copper complex. Therewith, the pK_{a2} value is decresed to the gretest extent, which can be accounted for by changes in the coordination sphere of the indium ion, produced, for example, by ionization of chloride anions in ClInDAP or by their replacement by urea, yielding cationic complexes $[InDAP]^+$ or $[(urea)_2InDAP]^+$.

The acid forms generated in the buffer media under

study are sufficiently stable. However, as the acidity of the medium increases further (on transition to concentrated sulfuric acid), dissociation is observed. Therewith, the electronic absorption spectrum takes a shape characteristic of the tetraprotonated form of the macrocyclic ligand $H_3DAPH_2^{4+}$ [λ(*B*) 394 and λ(*Q*) 656 nm, Fig. 2]. This tetraprotonated form of diazaporphyrin is stable under the reaction conditions.

The kinetic experiments were carried out with a great excess of H_2SO_4, i.e. under pseudo-first-order reaction conditions. The observation of linear dependences of $\log (c^0_{compl}/c_{compl})$ on reaction duration (Figs. 3 and 4) provides evidence showing that the dissociation of the indium complexes is a first-order reaction in complex. The corresponding kinetic equation takes form (4).

$$-dc_{compl}/d\tau = k_{app} c_{compl}. \quad (4)$$

Here k_{app} is the apparent rate constant of the reaction. Tables 1 and 2 list the k_{app} values for the dissociation of the indium complexes in aqueous H_2SO_4. As seen from the tables, the more dilute is sulfuric acid (i.e. the higher the concentration of hydroxonium ions H_3O^+ [9]), the higher is k_{app}. This proves the fact established earlier [3] for the dissociation of tetraazaporphyrin complexes with double-charged metal ions in sulfuric acid that the attacking species in this reaction is H_3O^+. To determine the reaction order in H_3O^+, we plotted $\log k_{app}$ against $\log c^0(H_3O^+)$. The resulting plots appeared to be linear. The reaction order in H_3O^+, determined as the slope of the straight lines, is equal to one (Figs. 5 and 6). The corresponding kinetic equation takes form (5):

$$-dc_{compl}/d\tau = k_v c_{compl} c_{H_3O^+}. \quad (5)$$

The overall second reaction order may result from the "hidden" trimolecular dissociation mechanism established earlier for tetraazaporphyrin complexes of double-charged metal ions [3]. In this case, intramolecular proton transfer from one of the *meso*-nitrogen atoms may occur in the transition state. Thus, the scheme of the dissociation of the indium complexes can be presented as follows. A prerequisite for the reaction is preliminary cleavage of the extra ligand [scheme (6)].

$$[ClInAPH_2^{2+}] + solv \rightleftarrows [InAPH_2]^{3+}_{solv} + Cl^-_{solv}. \quad (6)$$

The solvated cations formed in this stage undergo solvoprotolytic dissociation by Eq. (7):

$$[InAPH_2]^{3+}_{solv} + H^+_{solv} \longrightarrow [InHAPH_2]^{4+}_{solv} + 3H^+_{solv} \longrightarrow H_4APH_2^{4+}{}_{solv} + In^{3+}_{solv}. \quad (7)$$

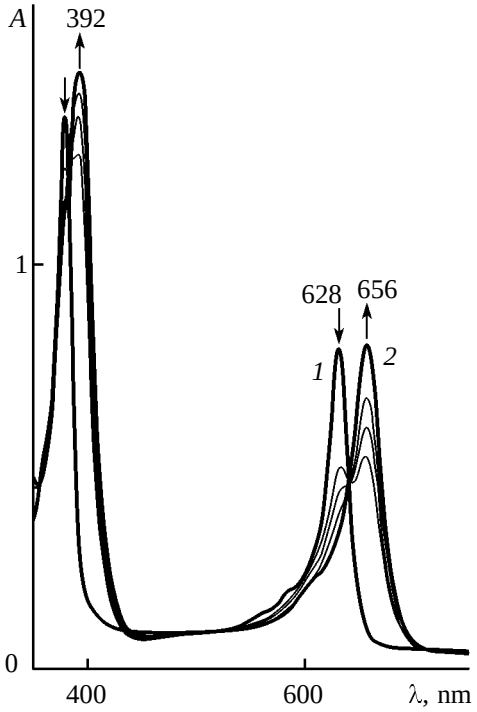

Fig. 2. Time dependence of the electronic absorption spectrum of [(Cl)InDAP] solution in 96% H_2SO_4. (*1*) Deprotonated form of the indium complex [(Cl)InDAP] and (*2*) tetracation $H_4DAPH_2^{4+}$ (after 75 min). Thin lines denote intermediate spectral curves.

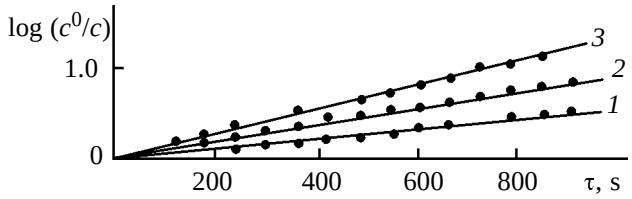

Fig. 3. Dependence of $\log (c^0/c)$ on the duration of ClInDAP dissociation in aqueous H_2SO_4 at 323 K and $c^0(H_3O^+)$, M: (*1*) 1.94, (*2*) 3.31, and (*3*) 4.04.

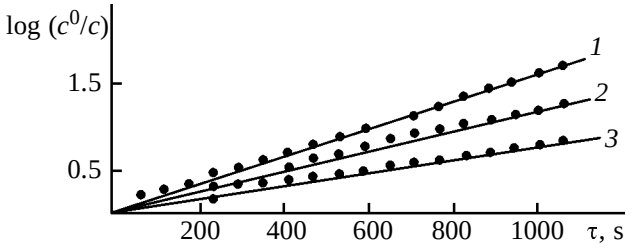

Fig. 4. Dependence of $\log (c^0/c)$ on the duration of ClInDAP dissociation in aqueous H_2SO_4 at 323 K and $c(H_3O^+)$, M: (*1*) 6.96, (*2*) 6.79, and (*3*) 6.59.

Table 1. Kinetic parameters of solvoprotolytic dissociation of ClInDAP in sulfuric acid (c^0_{compl} 1.31×10^{-6} M)

$c^0_{H_2SO_4}$, wt %	$c^0_{H_3O^+}$, M	T, K	$k_{app}\times10^4$, s^{-1}	$k_v\times10^4$, l mol^{-1} s^{-1}	E_a, kJ/mol	$\Delta S^{\neq}$ J mol^{-1} K^{-1}
94.07	5.5	298	1.65[a]	0.58	54 ± 2	–148 ± 11
		303	4.21 ± 0.11	0.76 ± 0.02		
		313	8.31 ± 0.64	1.51 ± 0.11		
		323	12.82 ± 0.52	2.33 ± 0.09		
94.84	4.96	298	2.09[a]	0.42	38 ± 4	–199 ± 12
		303	3.34 ± 0.14	0.67 ± 0.02		
		313	8.14 ± 0.24	1.64 ± 0.05		
		323	16.23 ± 1.49	3.27 ± 0.29		
96.01	4.04	298	1.53[a]	0.38	55 ± 3	–140 ± 12
		303	2.71 ± 0.20	0.67 ± 0.05		
		313	6.93 ± 0.88	1.71 ± 0.23		
		323	10.69 ± 0.82	2.65 ± 0.20		
96.89	3.31	298	1.28[a]	0.39	64 ± 4	–108 ± 11
		303	2.85 ± 0.22	0.86 ± 0.06		
		313	5.78 ± 0.36	1.75 ± 0.12		
		323	7.41 ± 0.13	2.24 ± 0.04		
97.93	1.94	298	0.81[a]	0.43	45 ± 6	–175 ± 17
		303	1.95 ± 0.11	1.01 ± 0.06		
		313	3.67 ± 0.19	1.89 ± 0.08		
		323	7.58 ± 0.38	3.91 ± 0.20		

[a] Calculated by Arrhenius' equation.

Table 2. Kinetic parameters of solvoprotolytic dissociation of ClInTAP in sulfuric acid (c^0_{compl} 9.08×10^{-6} M)

$c^0_{H_2SO_4}$, wt %	$c^0_{H_3O^+}$, M	T, K	$k_{app}\times10^4$, s^{-1}	$k_v\times10^4$, l mol^{-1} s^{-1}	E_a, kJ/mol	$\Delta S^{\neq}$ J mol^{-1} K^{-1}
96.05	4.00	298	2.31[a]	0.58	48 ± 2	–160 ± 9
		313	5.92 ± 0.26	1.48 ± 0.06		
		323	8.06 ± 0.41	2.1 ± 0.10		
		333	18.22 ± 1.03	4.55 ± 0.26		
93.95	5.59	298	2.62[a]	0.47	49 ± 1	–158 ± 4
		313	6.71 ± 0.18	1.20 ± 0.03		
		323	12.04 ± 0.50	2.15 ± 0.09		
		333	20.67 ± 1.85	3.70 ± 0.33		
92.07	6.59	298	3.79[a]	0.58	42 ± 4	–176 ± 11
		313	9.70 ± 0.88	1.47 ± 0.13		
		323	17.36 ± 0.90	2.63 ± 0.14		
		333	25.98 ± 1.21	3.94 ± 0.18		
90.89	6.79	298	3.85[a]	0.57	40 ± 1	–183 ± 4
		313	10.96 ± 0.96	1.61 ± 0.14		
		323	17.63 ± 0.89	2.59 ± 0.13		
		333	27.88 ± 2.11	4.10 ± 0.30		
90.12	6.96	298	4.44[a]	0.64	41 ± 2	–158 ± 7
		313	10.09 ± 0.96	1.45 ± 0.14		
		323	20.36 ± 1.29	2.93 ± 0.18		
		333	30.56 ± 1.27	4.39 ± 0.18		

[a] Calculated by Arrhenius' equation.

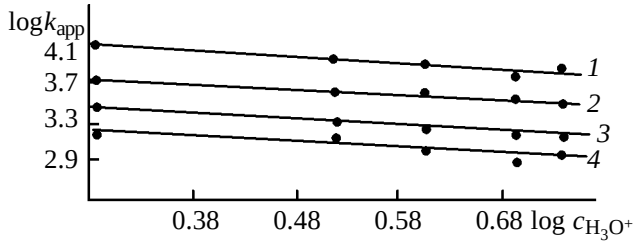

Fig. 5. Plots of log k_{app} against log $[c^0(H_3O^+)]$ for the dissociation of ClInDAP in aqueous H_2SO_4. (*1*) 298, (*2*) 303, (*3*) 313, (*4*) 323 K.

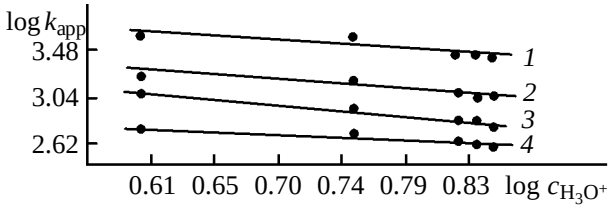

Fig. 6. Plots of log k_{app} against log $[c^0(H_3O^+)]$ for the dissociation of ClInTAP in aqueous H_2SO_4. (*1*) 298, (*2*) 303, (*3*) 313, (*4*) 323 K.

It is known that the contraction of the macroring cavity and the increased rigidity and aromaticity of the planar π ligand, produced by aza substitution, favor increased stability of complexes with cations with radii smaller than 0.6 Å. This fact is proved by the stability data for tetraazaporphyrin complexes with double-charged metal ions, reported in [3]. In contrast to porphyrin complexes, covalent complexes of tetraazaporphine either do not undergo solvoprotolytic dissociation in organic solvents in the presence of acids or dissociate extremely slowly. However, indium tetraphenylporphine studied earlier in [10] appeared to be more stable than indium octaphenyltetraazaporphine and indium diazaporphyrin. This seems to be caused by the greater deviation of the indium(III) atom from the macroring plane in the latter ligands, which was proved the above-mentioned X-ray diffraction data.

At the same time, comparison of the stabilities of the indium complexes studied shows that indium diazaporphyrin is more stable than indium octaphenyltetraazaporphine. Presumably, *trans*-diaza substitution makes possible contraction of the coordination center so that it better fits the radius of the metal ion. On the one hand, the coordination cavity in tetraazaporphyrins is smaller than in porphyrins, but, on the other, the macroring in the former is too rigid. The same we earlier observed with copper complexes [7].

EXPERIMENTAL

Chloro(octaphenyltetraazaporphinato)indium(III) was obtained by the procedure described in [4]. Chloro(2,8,12,18-Tetrabutyl-3,7,13,17-tetramethyl-5,15-diazaporphinato)indium(III) was synthesized as described in [5].

100% Sulfuric acid was prepared from 60% oleum and 96% sulfuric acid under conductometric control of concentration. Benzene was refluxed with P_2O_5 and distilled. Glacial acetic acid was frozen out several times, refluxed with a stoichiometric amount of acetic anhydride, and distilled collecting a 118°C fraction. Pharmacopoeias antipyrine was recrystallized from ethanol, and urea was recrystallized from water.

Acid–base reactions of indium(III) diazaporphyrin were studied by spectrophotometric titration on a Hitachi U-2000 spectrophotometer at 298 K by the procedure described in [11].

Kinetic measurements. Equal amounts of benzene solutions of a complex were placed in test tubes with ground-glass stoppers. The solvent was evaporated, and equal volumes of sulfuric acid solutions of required concentration were placed in the tubes. The tubes were placed in a temperature-controlled spectrophotometric cell and the optical densities of the solutions were measured at 671 (absorption maximu m of protonated indium octaphenyltetraazaporphine) and 656 nm (absorption maximum of protonated diazaporphyrin ligand). The current concentration of the complex was determined by Eq. (8).

$$c_{compl} = c^0_{compl}(A_\tau - A_\infty)/(A_0 - A_\infty). \quad (8)$$

Here A_0, A_τ, and A_∞ are the optical densities of the solution at the reaction onset, at time τ, and after the reaction completion, respectively; c_{compl} and c^0_{compl} are the current and initial concentrations of the complex.

ACKNOWLEDGMENTS

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