Russian Journal of General Chemistry, Vol. 72, No. 5, 2002, pp. 731–736. Translated from Zhurnal Obshchei Khimii, Vol. 72, No. 5, 2002, pp. 784–789.

State and Stability of Erbium(III) and Dysprosium(III) Complexes of Octaphenyltetraazaporphine in Proton-Donor Media

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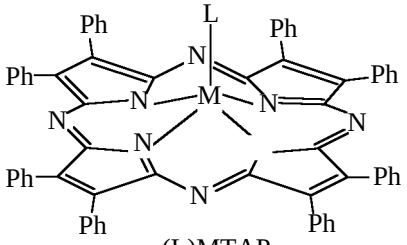
Received March 9, 2000

Abstract — The acid–base interaction of chloro(octaphenyltetraazaporphinato)erbium(III), (acetylacetonato)-(octaphenyltetraazaporphinato)erbium(III), and (acetylacetonato)(octaphenyltetraazaporphinato)dysprosium(III) in AcOH and in AcOH–benzene and AcOH–H_2SO_4 systems involves one *meso*-nitrogen atom of the complexes; the stability constants of the resulting acid forms were estimated. The solvoprotolytic dissociation of the complexes in the AcOH–H_2SO_4 system was studied, its kinetic parameters were determined, and some suggestions as to the dissociation mechanism were made.

Complexes of macrocyclic compounds with rare-earth metals attact considerable interest due to their application in electrochromic materials and sensor devices, as well as in catalysis, pharmacology, and medicine. The stability of the complexes is largely determined by their functioning as catalysts in solutions.

In the present work we studied the state and stability of the complexes of erbium(III) and dysprosium(III) octaphenyltetraazaporphyrins with an acetylacetonate extra ligand, as well as of erbium(III) octaphenyltetraazaporphine with a chloride extra ligand, in proton-donor media on the basis of acetic acid.



(L)MTAP

M = Er, Dy; L = Cl, *acac*.

Tetraazaporphyrin complexes have four donor centers (*meso*-nitrogen atoms) and are weak multicenter conjugated bases [1]. Their basicity depends on the structure of the tetraazaporphyrin and on the nature of the complex-forming metal. When analyzing acid–base interactions with tetraazaporphyrins, one should distinguish between an incomplete acid–base interaction (specific solvation of donor centers by acid molecules via hydrogen bonding to form an acid associate) and a complete acid–base interaction {formation of an H-associate, an ion–ion associate, or an ionized form [2]; scheme (1)}.

$$\mathrm{B + HA} \rightleftarrows \underset{\text{acid associate}}{\mathrm{B\cdots HA}} \rightleftarrows \underset{\text{H-associate}}{\mathrm{B\cdots H\cdots A}} \rightleftarrows \underset{\text{ion–ion associate}}{\mathrm{BH^+\cdots A^-}} \rightleftarrows \underset{\text{protonated form}}{\mathrm{BH^+ + A^-}}. \quad (1)$$

Here B is base (tetraazaporphyrin) and HA is acid.

The final result of the process depends on the properties of the base, acid, and solvent (i.e. its polarity and dielectric constant), which determines the character of solvation of cation BH^+ and anion A^- and the possibility of formation of protonated form BH^+. In the proton-donor media on the basis of acetic acid, tetraazaporphyrins behave as Hammett indicators [1–5], and one can use spectrophotometry to determine the stability constant of the acid forms formed by Eq. (2):

$$\mathrm{p}K_i = nH_0 + \log I_i. \quad (2)$$

Here K_i is the stability constant of the *i*th acid form, H_0 is the Hammett acidity function, $I_i = c_i/c_{i-1}$ is the concentration ratio of the *i*th and $(i - 1)$th equilibrial acid forms (indicator ratio), *n* is the number of donor centers involved in the complete acid–base interaction at the given stage.

The complexes of tetraazaporphyrins with double-charged metal ions in acetic acid form exclusively

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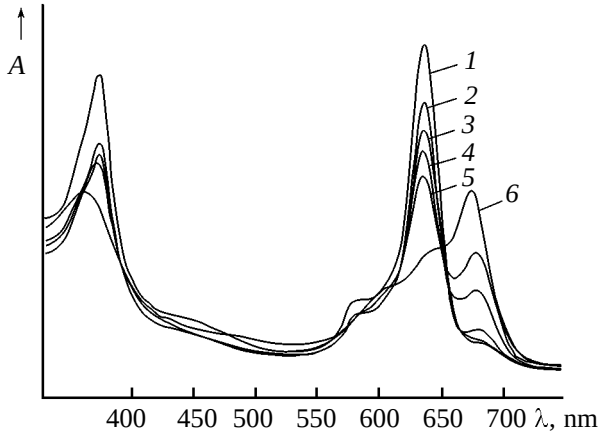

Fig. 1. Changes in the electronic absorption spectra of solutions of ClErTAP in (*1*) benzene, (*2*–*5*) AcOH–benzene system (H_0 6.4–4.5), and (*6*) AcOH–urea–H_2SO_4 buffer (H_0 4.25).

acid associates MTAP$(AcOH)_4$ which cannot be distinguished from the neutral forms which are present in aprotic solvents [1–5]. The electronic absorption spectra of ClErTAP, *acac*ErTAP, and *acac*DyTAP in benzene solutions strongly differ from those in acetic acid solutions (Fig. 1). When the concentration of AcOH in benzene is above 0.08 M, the intensity of the *Q* and *B* bands in the initial electronic spectrum (λ_{max} 635 and 375 for ClErTAP, 635 and 375 for *acac*ErTAP, and 636 and 376 nm for *acac*DyTAP, respectively) begins to weaken, and a new band apprear at λ_{max} 678 (ClErTAP), 675 (*acac*ErTAP), and 674 nm (*acac*DyTAP). In going to an AcOH–urea–H_2SO_4 buffer solution, the electronic spectrum stops to change at H_0 4.25. At higher acidities of the medium ($H_0 > 4.25$), the complexes undergo demetalation, as evidenced by the fact that the electronic spectrum acquires a pattern characteristic of the triprotonated form of the octaphenyltetraazaporphyne ligand H_4TAPH^{3+} (Fig. 2). The bathochromic shift of the *Q* band of the complexes suggests acid–base interaction with *meso*-nitrogen atoms [1]; therewith, in the AcOH–benzene system having a low dielectric constant (ε 2.28 for benzene and 6.3 for AcOH [6]), presumably, ion–ion associates are formed [scheme (3)].

$$(L)MTAP + H^+A^- \rightleftharpoons (L)MTAPH^+\cdots A^- \qquad (3)$$

The $\log I_i$–H_0 dependences are linear with a slope close to unity (0.93 for ClErTAP, 0.88 for *acac*ErTAP, and 0.83 for *acac*DyTAP) (Fig. 3). Thus, the acid–base interaction in stage (3) involves one acid molecule. Based on spectrophotometric titration data, we estimated, by the Hammett equation (2), the stability

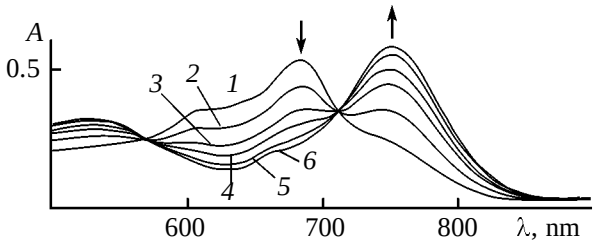

Fig. 2. Changes in the electronic absorption spectra of ClErTAP with time in the course of solvoprotolytic association in the AcOH–H_2SO_4 medium ($c^0_{H_2SO_4}$ 0.059 M, *T* 298 K). (*1*) Initial spectrum of the monoprotonated form of ClErTAP, (*2*–*5*) intermediate spectral curves, and (*6*) spectrum of triprotonated ligand H_4TAPH^{3+}.

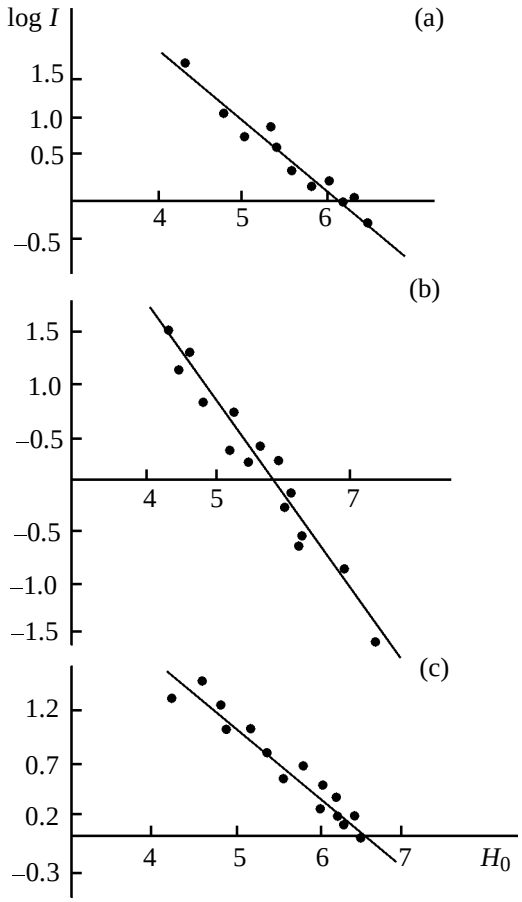

Fig. 3. Dependences of $\log I_i$ on H_0 for the equilibria of ion–ion associate formation in the AcOH–benzene and AcOH– urea–H_2SO_4 systems. Complex: (a) *acac*ErTAP, (b) ClErTAP, and (c) *acac*DyTAP.

constants of the acid forms formed: pK_1 5.93±0.03 (*acac*ErTAP), 6.02±0.02 (ClErTAP), and 6.41±0.05 (*acac*DyTAP). The pK_1 values of the erbium(III) and dysprosium(III) complexes are much higher than those

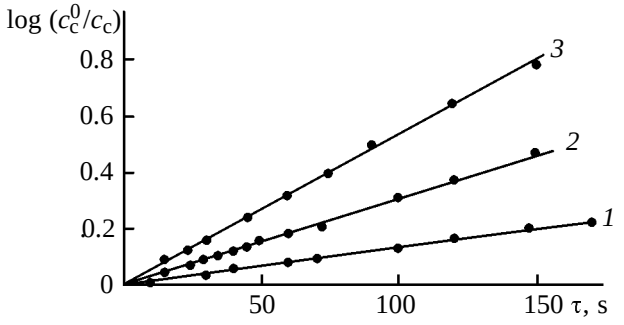

Fig. 4. Dependence of log (c_c^0/c_c) on time for the solvoprotolytic dissociation of ClErTAP in the AcOH–H_2SO_4 system ($c^0_{H_2SO_4}$ 0.074 M). *T*, K: (*1*) 288, (*2*) 298, and (*3*) 308.

of octaphenyltetraazaporphyne complexes with double-charged metal ions [4]. It can be proposed that the deviation of erbium(III) and dysprosium(III) from the macroring plane, associated with the fact that the ions (the radii of Er^{3+} and Dy^{3+} are 0.87 and 0.91 Å, respectively [7]) not perfectly fit the coordination cavity, increases the ionicity of the complexes and enhances their basicity. The experimental data show that the nature of the extra ligand only slightly affects the basicity of the complexes in the media studied. The stability constants of the ion–ion associates of ClErTAP and *acac*ErTAP are almost the same. The dysprosium(III) complex is slightly more basic than the erbium(III) complex. Probably, this is explained by the larger radius of Dy^{3+} compared with Er^{3+} and, as a result, the larger deviation of the former from the macroring plane and the higher ionicity of the M←N bond. In [8], we measured for the first time acidity functions H_0 for the AcOH–benzene system, using as Hammett indicators monoazaporphyrin (H_2MAP) and its copper complex (pK_1 5.57 for CuMAP and 3.95 for H_2MAP). The higher basicity of the erbium and dysprosium complexes allowed us to extend the scale of acidity function for the AcOH–benzene system. The new H_0 values were estimated by the Hammett equation (2) with known indicator ratios (I_i) and pK_1 values: H_0 7.75, 7.01, and 6.61 for c_{AcOH} 0.25, 0.42, and 0.83 M.

Stability of porphyrin, azaporphyrin, and phthalocyanine complexes is most commonly characterized in terms of kinetic stability [9]. It is measured by a true (or, at equal solution acidities, apparent) rate constant of solvoprotolytic dissociation of a complex in proton-donor media, according to Eq. (4) [9, 10].

$$(L)_n\text{MTAP} + 2LH^+ + 2X^- \rightarrow M(L)_{n+2}X_2 + H_2\text{TAP}. \quad (4)$$

Here MTAP is tetraazaporphyrin metal complex, H_2TAP is tetraazaporphyrin ligand, LH^+ is solvated proton, L is solvent, and X is acid anion.

The kinetic stability of the erbium and dysprosium complexes was studied at 288–309 K in the AcOH–H_2SO_4 binary system at H_2SO_4 concentrations of 0.059–0.103 M for the erbium complexes and (0.37–2.22) × 10^{-2} M for the dysprosium complex. In these media, the complexes undergo solvoprotolytic dissociation by ion–ion association to form an octaphenylazaporphine ligand protonated by a *meso*-nitrogen atom and with preservation of a strong acid–base interaction with two endocyclic nitrogen atoms (Fig. 2) [3]. Increasing H_2SO_4 concentration renders the dissociation rates so high that they are already impossible to estimate by ordinary kinetic methods. The solvoprotolytic dissociation of the complexes occurs according to Eq. (4). Kinetic experiments were performed at high H_2SO_4 : complex concentration ratios, i.e. under pseudo-first-order conditions. This is evidenced by straight-line dependences of log (c_c^0/c_c) on reaction time τ (c_c^0 and c_c are the initial and current concentrations of the complex) (Fig. 4). The kinetic equation of the solvoprotolytic dissociation of the complexes takes form (5).

$$-dc_c/d\tau = k_{app}c_c. \quad (5)$$

Here k_{app} is the apparent reaction rate constant. Tables 1 and 2 lists the k_{app} values for the complexes. These data show that the apparent rate constant increases with increasing H_2SO_4 concentration. As shown earlier, a species that drives dissociation of tetraazaporphyrin complexes is solvated proton H_s^+ [9]. In the AcOH–H_2SO_4 system, the $AcOH_s^+$ ion is such a species [Eq. (6)].

$$\text{AcOH} + H_2SO_4 \rightleftarrows AcOH_s^+ + HSO_4^-. \quad (6)$$

In this case, Eq. (7) is valid.

$$k_{app} = kc^n_{AcOH_2^+}. \quad (7)$$

Here *k* is the true reaction rate constant and *n* is the reaction order in $AcOH_2^+$. The concentrations of the $AcOH_2^+$ ion were estimated using the dissociation constant of H_2SO_4 in AcOH [Eq. (6)] (p$K_{H_2SO_4}$ 4.25 [11]). The reaction order in $AcOH_2^+$ concentration was determined from the log k_{app}–log $c_{AcOH_2^+}$ dependences (Fig. 5). These dependences are linear. The reaction order in $AcOH_2^+$, determined as the slope of the above dependences, proved equal to 2. The kinetic equation of the reaction takes form (8):

$$-dc/d\tau = kc_c c^2_{AcOH_2^+}. \quad (8)$$

Table 1. Kinetic parameters of the solvoprotolytic dissociation of the erbium(III) complexes in the $AcOH–H_2SO_4$ system[a]

$c_{H_2SO_4}$, M	$c_{AcOH_2^+} \times 10^3$, M	T, K	$k_{app} \times 10^3$, s^{-1}		$k \times 10^{-3}$, $s^{-1}\ l^2\ mol^{-2}$	
			ClErTAP	*acac*ErTAP	ClErTAP	*acac*ErTAP
0.059	1.82	288	2.40 ± 0.09	2.00 ± 0.01	0.72 ± 0.03	0.60 ± 0.03
		298	5.20 ± 0.06	4.70 ± 0.03	1.57 ± 0.03	1.42 ± 0.07
		308	11.00 ± 0.30	10.40 ± 0.20	3.32 ± 0.10	3.13 ± 0.07
0.074	2.04	288	2.80 ± 0.04	2.15 ± 0.02	0.67 ± 0.09	0.52 ± 0.05
		298	6.07 ± 0.09	5.50 ± 0.30	1.46 ± 0.02	0.53 ± 0.07
		308	12.50 ± 0.20	13.00 ± 0.40	3.01 ± 0.10	3.13 ± 0.09
0.089	2.24	288	3.70 ± 0.02	2.97 ± 0.06	0.74 ± 0.04	0.53 ± 0.02
		298	7.89 ± 0.07	6.70 ± 0.02	1.58 ± 0.02	1.40 ± 0.01
		308	16.20 ± 0.20	16.00 ± 0.20	3.24 ± 0.10	3.20 ± 0.07
0.103	2.41	288	4.40 ± 0.02	3.40 ± 0.02	0.75 ± 0.03	0.59 ± 0.01
		298	9.27 ± 0.08	8.50 ± 0.02	1.59 ± 0.03	1.39 ± 0.01
		308	18.60 ± 0.20	18.00 ± 0.70	3.20 ± 0.10	3.10 ± 0.20
For ClErTAP E_a^{av} 54 ± 1 kJ/mol, $\Delta S^{\neq}_{av}$ –110 ± 6 J mol^{-1} K^{-1}; for *acac*ErTAP E_a^{av} 62 ± 2 kJ/mol, $\Delta S^{\neq}_{av}$ –85 ± 5 J mol^{-1} K^{-1}						

[a] c_c 2.5×10^{-6} and 5.5×10^{-6} M for ClErTAP and *acac*ErTAP, respectively.

Thus, the solvoprotolytic dissociation of the complexes occurs by the trimolecular mechanism $S_{NE}3$, characteristic of most porphyrin and phthalocyanine complexes [9, 10]. Prerequisite for dissociation is elimination of an extra ligand [scheme (9)].

$$(L)MTAPH^+ \rightleftarrows [MTAPH^+]_s^+ + L_s^-. \qquad (9)$$

Here $[MTAPH^+]_s^+$ is solvated cation of protonated complex and L_s^- is solvated anion of extra ligand.

As seen from Table 1, the dissociation rate constants of ClErTAP and *acac*ErTAP are nearly equal to each other; consequently, the nature of the extra ligand has almost no rate effect in the media studied, and stage (9) is not rate-limiting, in agreement with what has been established for porphyrin complexes with rare-earth metals [12]. The complexes enter dissociation as a solvated dication. The mechanism of the solvoprotolytic dissociation of the erbium and dysprosium complexes can be represented by scheme (10).

$$[MTAPH^+]_s^+ + H_s^+ \longrightarrow [MHTAPH^+]_s^{2+} + 3H_s^+ \longrightarrow H_4TAPH_s^{3+} + M_s^{3+}. \qquad (10)$$

According to [9], at moderate concentrations of solvated proton (AcOH, AcOH + H_2SO_4), the stages of the first and second M–N bond cleavage are separated in time, and occur one after the other with comparable rates. Comparison of the dissociation rate constants of the erbium and dysprosium complexes shows that the erbium complex is slightly more stable than the dysprosium complex, which is associated with the fact that the Er–N bond is more covalent in nature than Dy–M because of the shorter ionic radius of erbium(III) compared with dysprosium(III). The solvoprotolytic dissociation of the complexes is characterized by constant activation energy and entropy, independent of the concentration of sulfuric acid in the mixed solvent.

EXPERIMENTAL

The erbium(III) and dysprosium(III) complexes were prepared according to [13, 14]. Benzene was refluxed over P_2O_5 and distilled. Glacial acetic acid was repeatedly freezed out, refluxed with required amount of acetic anhydride, and distilled, collecting a fraction at 118°C. Anhydrous 100% sulfuric acid was prepared from 60% oleum and 96% sulfuric acid with conductometric control. Urea was recrystallized three times from water.

The acid–base interactions in the AcOH–benzene system and the AcOH–urea–H_2SO_4 buffer in the H_0 range 6.4–4.25. The values of acidity function H_0 were taken from [15]. Spectrophotometric studies were perfomed with constant-concentration (0.9×10^{-4} M) solutions of the complexes in various-acidity media. The electronic absorption spectra were obtained at 298 K on a Hitachi U-2000 spectrophoto-

Table 2. Kinetic parameters of the solvoprotolytic dissociation of the dysprosium complex in the $AcOH–H_2SO_4$ system[a]

$c_{H_2SO_4} \times 10^2$, M	$c_{AcOH_2^+} \times 10^3$, M	T, K	$k_{app} \times 10^3$, s^{-1}	$k \times 10^{-3}$, $s^{-1} l^2 mol^{-2}$
0.37	0.46	289	1.01 ± 0.02	1.3 ± 0.07
		298	1.70 ± 0.04	1.81 ± 0.08
		309	3.40 ± 0.05	3.51 ± 0.10
0.74	0.64	289	2.60 ± 0.05	1.46 ± 0.01
		298	4.90 ± 0.06	2.71 ± 0.02
		309	8.90 ± 0.04	4.96 ± 0.20
1.48	0.91	289	4.40 ± 0.04	1.30 ± 0.05
		298	7.60 ± 0.09	2.25 ± 0.02
		309	14.20 ± 0.70	4.21 ± 0.08
2.22	1.12	289	5.40 ± 0.02	1.11 ± 0.01
		298	9.50 ± 0.08	1.95 ± 0.06
		309	17.20 ± 0.60	3.54 ± 0.11
E_a^{av} 44 ± 2 kJ/mol, $\Delta S_{av}^{\neq}$ –147 ± 3 J mol^{-1} K^{-1}				

[a] c_c 4.2×10^{-6} M.

meter equipped with a temperature-controlled cell. The concentration ratio of equilibrium acid–base forms $I_i = c_i/c_{i-1}$ was determined spectrophotometrically at wavelengths corresponding to their absorption maxima. The pK_i values were calculated by the least-squares method by Eq. (2) for 10–15 experimental points.

For kinetic measurements, tubes with ground-glass stoppers were charged with equal volumes of solutions of the complexes in benzene. The solvent was removed, and equal volumes of solutions of H_2SO_4 in acetic acid of a certain concentration were added. The solutions were placed in the temperature-controlled cell of the Hitachi U-2000 spectrophotometer, and their optical densities were measured at the absorption maxima of protonated complexes (678 nm for the erbium complex and 674 nm for the dysprosium complex). The current concentration of the complex was calculated by Eq. (11):

$$c_c = c_c^0(A_i - A_\infty)/(A_0 - A_\infty). \quad (11)$$

Here A_0, A_τ, and A_∞ are the initial, current (at time τ), and final optical densities of the solution; and c_c and c_c^0 are the current and initial concentration of the complex. The apparent rate constants k_{app} were calculated by Eq. (12):

$$k_{app} = 2.303/\tau[\log (c_c^0/c_c)] = 2.303/\tau\log [(A_0 - A_\infty)/(A_\tau - A_\infty)]. \quad (12)$$

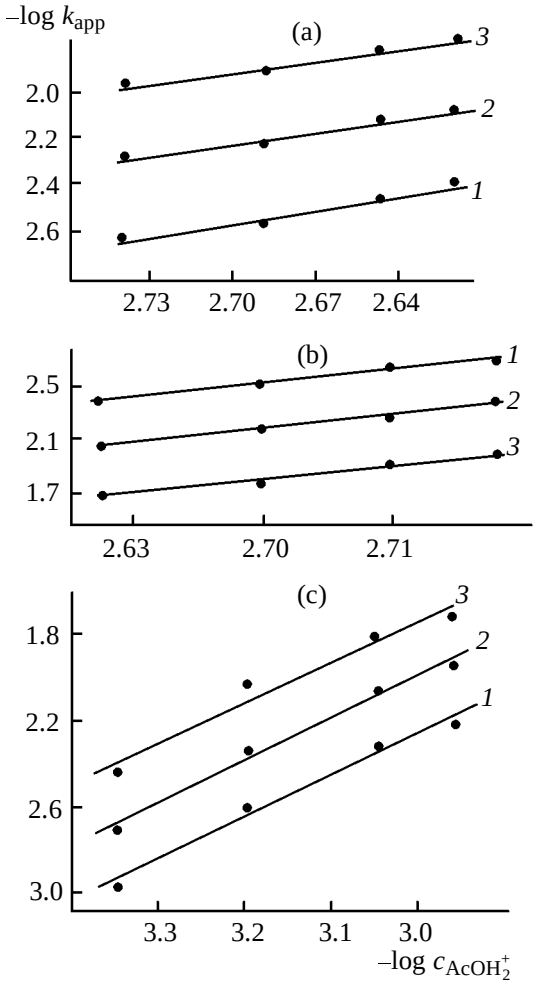

Fig. 5. Dependence of log k_{app} on log $c^0_{AcOH_2^+}$ for the dissociation of (a) ClErTAP, (b) *acac*ErTAP, and (c) *acac*DyTAP in the $AcOH–H_2SO_4$ system. T, K: (*1*) 288, (*2*) 298, and (*3*) 308.

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