# Mutual Influence of Ligands and Reactivity of Gd and Dy Acidophthalocyaninate Complexes

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**Abstract**—The results of the kinetic study of dissociation of Gd(III) and Dy(III) complexes with phthalocyanine of the composition (X)LnPc (X is single-charged acido ligand) with isolation of macrocyclic ligand depending on the temperature, composition of mixed ethanol–acetic acid solvent, and the nature of acido ligand are presented. The total kinetic equations, the rate constants, and activation parameters of dissociation reaction are determined. The stoichiomeric mechanism is suggested for the complex dissociation involving the limiting elementary reaction between acetic acid molecule and the complex that occurs as the chelate salt (X)LnPc or the outer-sphere complex [(HOAc)LnPc]<sup>+</sup>X<sup>-</sup>. The state of metal phthalocyaninate at the reaction slow stage is shown to be determined by the electronic structure of the metal cation, the strength of binding of the axial ligand, and by its *cis*-effect on the metal bonds with macrocycle.

The study of the properties of acidophthalocyaninate complexes of analogous Ln metal cations with composition (X)LnPc (Ln is lanthanide from Sm to Lu, Pc is phthalocyanine dianion (H<sub>2</sub>Pc), X is Cl<sup>-</sup>, Br<sup>-</sup>, and AcO<sup>-</sup>) showed that correlations can be derived between the parameter of a complex and the physicochemical parameter of a central ion and used further to determine the nature of the donor-acceptor bonds and their contribution to the complex stability [1]. However, these studies were performed with the same acido ligand X, and the data on the bond between the axially coordinated ligands and the Ln cation are absent. Using complexes of meso-tetraphenylporphine ( $H_2$ TPP) as an example, it was shown [2] that the rate of dissociation of macrocyclic complexes (X)MTPP (M is d metal) in solutions changes with the change of acido ligand in the complex composition.

This paper reports for the first time how the nature of acido ligand in the complexes (X)GdPc and (X)DyPc affects the kinetics and mechanism of their dissociation with isolation of a free macrocycle in the mixed ethanol-AcOH solvent at 313–353 K.

The axial ligands used in this study were Cl<sup>-</sup>, Br<sup>-</sup>, and AcO<sup>-</sup>:



Ln(III) acidophthalocyaninate complexes

 $Ln = Gd, Dy; X = Cl^{-}, Br^{-}, AcO^{-}.$ 

### **EXPERIMENTAL**

The (X)LnPc complexes were obtained from Li<sub>2</sub>Pc and the corresponding Ln salt using the procedure described in [3]. The mixture of Li<sub>2</sub>Pc (1.95 g, 3.7 mmol) and LnX<sub>3</sub> (11 mmol) in 50 ml of DMSO was heated and thermostatted at boiling temperature for 80 min and then cooled. Water (8 ml) was added to the reaction mixture. The precipitated H<sub>2</sub>Pc was filtered off. The filtrate was diluted with water in the volume ratio 1 : 2. The obtained precipitate of the (X)LnPc complex was filtered off, washed with water, and dried in air. The yield of the complexes was ~90%.

The rates of reactions of (X)GdPc and (X)DyPc with AcOH in ethanol were determined by spectrophotometric method. The electronic absorption spectra of the solutions were recorded on Specord M400 and SF-26 spectrophotometers in thermostatted cell. An accuracy of the temperature maintenance was  $\pm 0.1$  K. The change in the optical density of solutions of the complexes in mixed proton-donor solvent was recorded at the operating wavelength ( $\lambda = 668-672$  nm depending on the complex type) near the maximum of band *I* (*Q* band (0,0)).

The reagent grade acetic acid was dehydrated using thawing by stages, while ethanol was dehydrated according to the standard procedure [4]. The water content (titration with the Fisher reagent) in the dried solvents did not exceed 0.03%.

The effective rate constants ( $k_{\text{eff}}$ ), the true rate constants (k), and the reaction order in the concentration of the proton-donor species (n) were determined using the Microsoft Excel program of optimization of dependences  $\ln(c_{(X)\text{LnPc}}^0/c_{(X)\text{LnPc}}^\tau) - \tau$  and  $k_{\text{eff}} - c_{\text{AcOH}}^0$ , respectively, the activation energies ( $E_a$ ) were found by opti-

Complex	Absorption band, $\lambda_{max}$ , nm			Complex	Absorption band, $\lambda_{max}$ , nm		
	Q(0,0)	<i>Q</i> (0,1)	Soret	Complex	Q(0,0)	<i>Q</i> (0,1)	Soret
(Cl)GdPc	671	606	344	(Cl)DyPc	671	604	344
(Br)GdPc	671	606	344	(Br)DyPc	669	604	342
(AcO)GdPc	670	605	343	(AcO)DyPc	670	604	342

**Table 1.** Absorption bands in electronic absorption spectra of (X)LnPc in ethanol

mization of the dependences in the Arrhenius equation coordinates. The rate constants of dissociation at a standard temperature (298 K) were obtained by extrapolation of  $\log k_{\rm eff} - 1/T$  and  $\log k - 1/T$ . The activation entropy ( $\Delta S^{\#}$ ) was calculated from the fundamental equation of transient state theory that was transformed as follows [5]

$$\Delta S^{\#} = 19.1 \log k^{T} + E/T - 19.1 \log T - 205.$$
(1)

The average  $\Delta S^{\#}$  value was found as the arithmetic mean of the  $\Delta S^{\#}$  values calculated for all temperatures of the kinetic experiment.

## **RESULTS AND DISCUSSION**

The electronic absorption spectra of (X)LnPc (Ln is Gd and Dy) in the visible region (Table 1) are similar to those of Ln(III) phthalocyaninates in organic solvents reported in [6]. The spectra of complexes remain unchanged with time and on heating, while the optical density is proportional to their concentration  $(1-10) \times 10^{-5}$  mol/l, which indicates that Ln(III) phthalocyaninates do not undergo dissociation or association in ethanol.

The dissociation of the complexes begins when a 100% AcOH is added to the ethanol solutions to bring about the formation of  $H_2Pc$  that remains in dissolved state under experimental conditions (Fig. 1, 2). For all metal phthalocyaninates under study, the first order of dissociation in the complex concentration was determined. The corresponding effective dissociation rate constants are presented in Table 2. The dissociation rate for all complexes was found to increase with AcOH concentration. However, Gd and Dy complexes show different dependences of the reaction rate on the initial AcOH concentration, which can be explained by different reaction mechanisms.

The plot of the dependence

$$k_{\rm eff}^{T} = k^{T} (c_{\rm AcOH}^{0})^{n}$$
(2)

in the logarithmic coordinates (Figs. 2 and 3) gives the linear correlation (reliability of approximation  $R^2 = 0.957-0.999$ ) with a slope close to two for the (X)GdPc complexes and to unity for the (X)DyPc complexes. The true rate constants of the respective total third and

second orders, as well as the activation parameters are given in Table 3.

With account of the above data, the dissociation reactions for the complexes can be written as

$$(X)LnPc + 2HOAc = [(X)Ln]^{2+} + H_2Pc + 2OAc^{-} (3)$$

while the experimentally found rate equations for the Gd and Dy complexes, respectively, as

$$-dc_{(X)GdPc}/d\tau = kc_{(X)GdPc}(c_{ACOH}^{0})^{2}, \qquad (4)$$



**Fig. 1.** Electronic absorption spectra of (1) (AcO)DyPc and (2) product of its dissociation in ethanol–AcOH mixture  $(c_{AcOH}^0 = 3.55 \text{ mol/l})$  at 333.2 K.

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0 mo1/1	$k_{\rm eff} \times 10^3,  {\rm s}^{-1}$								
$c_{\rm HOAc}$ , mon	298.2 K	313.2 K	323.2 K	333.2 K					
(Cl)GdPc									
1.42	$0.761\pm0.002$	$1.244\pm0.008$	$1.69\pm0.03$	$2.31\pm0.09$					
2.13	$0.85\pm0.01$	$1.63\pm0.01$	$2.45\pm0.05$	$3.71\pm0.09$					
2.84	$1.67\pm0.02$	$3.19\pm0.03$	$4.79\pm0.07$	$7.2\pm0.1$					
3.55	$2.73\pm0.025$	$4.68 \pm 0.03$ $6.6 \pm 0.1$		$9.2\pm0.2$					
(Br)GdPc									
1.42	$0.472 \pm 0.001$	$1.232\pm0.004$	$2.23 \pm 0.04$	$4.10\pm0.07$					
2.13	$0.507\pm0.001$	$1.318\pm0.009$	$2.39\pm0.045$	$4.3 \pm 0.1$					
2.84	$1.101 \pm 0.002$	$2.38\pm0.07$	$3.84\pm0.06$	$6.2 \pm 0.1$					
3.55	$1.63\pm0.02$	$3.28\pm0.08$	$5.1 \pm 0.1$	$7.7 \pm 0.1$					
(AcO)GdPc									
1.42	$0.0407 \pm 0.0001$								
2.13	$0.10\pm0.08$	$0.325\pm0.004$	$0.64 \pm 0.02$	$1.35\pm0.03$					
2.84	$0.24\pm0.03$	$0.538 \pm 0.009$	$0.97\pm0.02$	$1.76\pm0.02$					
3.55	$0.44\pm0.04$	$0.99\pm0.02$	$1.55\pm0.08$	$2.63\pm0.08$					
4.26	$0.61\pm0.02$								
		(Cl)DyPc							
2.13	$0.0656 \pm 0.0007$	$0.370 \pm 0.009 *$	$0.514 \pm 0.005 **$	$0.262\pm0.006$					
2.84	$0.102 \pm 0.004$	$0.508 \pm 0.008*$	$0.73 \pm 0.01 **$	$0.384\pm0.005$					
3.55	$0.246\pm0.006$	0.618 + 0.007*	$0.74 \pm 0.01 **$	$0.516\pm0.009$					
(Br)DyPc									
2.13	$0.057 \pm 0.0055$	$0.302 \pm 0.007*$	$0.423 \pm 0.007 **$	$0.214\pm0.003$					
2.84	$0.097\pm0.002$	$0.508 \pm 0.009 *$	$0.69 \pm 0.01 **$	$0.363\pm0.006$					
3.55	$0.211\pm0.09$	$0.61 \pm 0.01*$	0.73 + 0.01**	$0.49\pm0.02$					
(AcO)DyPc									
2.13	$0.039 \pm 0.004$	$0.29 \pm 0.03*$	$0.41 \pm 0.02^{**}$	$0.188\pm0.004$					
2.84	$0.064 \pm 0.005$	$0.39\pm0.02*$	$0.55 \pm 0.01 **$	$0.270\pm0.009$					
3.55	$0.186 \pm 0.008$	$0.56\pm0.02*$	$0.69 \pm 0.04 **$	$0.450\pm0.008$					

Table 2. Rate constants of dissociation of Gd(III) and Dy(III) complexes with phthalocyanine in ethanol-acetic acid mixture

\* k<sup>343.2 K</sup>. \*\* k<sup>353.2 K</sup>.

$$-dc_{(X)DyPc}/d\tau = kc_{(X)DyPc}c_{AcOH}^{0}.$$
 (5)

Taking into consideration the spectrophotometric data, i.e., the electronic absorption spectra at the beginning and at the end of the reaction (Fig. 1), one can assume the following stepwise mechanism of transformations that adequately reflects the summary kinetic Eq. (4):

$$(X)GdPc + HOAc \stackrel{K_1}{\longleftrightarrow} [(AcOH)GdPc]^+X^-, \quad (6)$$

where  $K_1$  is the equilibrium constant of acido ligand X ionization.

$$[(AcOH)GdPc]^{+}X^{-} + AcOH$$

$$\xrightarrow{k_{1}} (AcOH)Gd^{3+} + H_{2}Pc + AcO^{-} + X^{-},$$
(7)

where  $k_1$  is the rate constant of an elementary limiting state of the complex dissociation. The kinetic equation

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**Fig. 2.** The plot of  $\log k_{\text{eff}}$  vs.  $\log c_{\text{AcOH}}^0$  for (X)GdPc complexes at 313 K: X = (1) AcO, (2) Br, and (3) Cl.

for the low stage (7) has the form

$$-dc_{[(\text{AcOH})\text{GdPc}]^{+}\text{X}^{-}}/d\tau = k_{1}c_{[(\text{AcOH})\text{GdPc}]^{+}\text{X}^{-}}c_{\text{AcOH}}.$$
 (8)

With account of equilibrium (6), Eq. (8) can be written as follows:

$$-dc_{[(AcOH)GdPc]^{\dagger}X^{-}}/d\tau = -dc_{(X)GdPc}/d\tau$$
  
=  $k_1 K_1 c_{(X)GdPc} (c_{AcOH})^2$ . (9)

Equation (9) corresponds to the experimental Eq. (4), and  $k = k_1 K_1$ . The elementary reaction for the Dy complexes has the form

(X)DyPc + AcOH 
$$\xrightarrow{k}$$
 [(X)Dy]<sup>2+</sup> + H<sub>2</sub>Pc + OAc<sup>-</sup>.(10)

The kinetic equation for the elementary reaction (10) coincides with the experimental Eq. (5).

Thus, in the course of the (X)GdPc dissociation, the outer-sphere complex [(AcOH)GdPc]<sup>+</sup>X<sup>-</sup> reacts at the limiting stage, while the (X)DyPc complexes enter the elementary slow dissociation reaction at the Dy–N bond in the initial state with the X ligand in composition of the first coordination sphere. This means that in the Dy complexes, the acido ligand X is bound more strongly than in the Gd complexes. The reason for this is likely to lie in the nonsymmetric occupation of the  $f^9$  shell in the (X)DyPc complexes, which stimulates the  $\pi$ -dative properties in acido ligands Cl<sup>-</sup>, Br<sup>-</sup>, and AcO<sup>-</sup>. The *f* shell in the (X)GdPc complexes is stable ( $f^7$  electronic configuration) and therefore, acido ligands are bonded to the Gd cation through a single  $\sigma$  bond.

The stoichiometric mechanisms of dissociation of the complexes described above are based on the assumption that the reaction orders in the AcOH concentration are integers (the first order for the Dy complex and the second order for the Gd complex). However, as seen from Table 3, the experimental reaction orders noticeably differ from the whole numbers and decrease on heating. This fact suggests more complicated real mechanism of the dissociation reaction. Evi-



**Fig. 3.** The plot of  $\log k_{\text{eff}}$  vs.  $\log c_{\text{AcOH}}^0$  for (X)DyPc complexes at (1) 333, (2, 3) 343 K; X = (1) Cl, (2) AcO, (3) Br.

dently, both reaction courses are realized to different extent, depending on the structure of coordination sphere of the complex participating in the limiting stage and temperature.

The kinetic stability of the complexes of both cations with macrocyclic ligand is sensitive to the nature of the axial acido ligand X (Table 3). The  $k^{298}$  value decreases in the series

$$(Cl)LnPc > (Br)LnPc > (OAc)LnPc,$$
(11)

i.e., in agreement with the electronegativity of the donor atom X.

However, the halogen–Ln or O–Ln (for the acetate complexes)  $\pi$ -dative bonds smooth out the above-mentioned sensitivity toward ligand X in the case of the Dy complexes: in series (11), the largest value of the dissociation rate constant is 24.4 and 2.4 times as high as the smallest dissociation rate constant for the Gd and Dy complexes, respectively. The kinetic stability of the (X)DyPc complexes ( $k^{298}$ ) is 4.30 and 44 times as high as that for the (X)GdPc complexes, where X is AcO<sup>-</sup>, Br<sup>-</sup>, and Cl<sup>-</sup>, respectively (Table 3). This is likely to occur due to the Dy–N  $\pi$ -dative bonds and to more closer arrangement of the Dy cation with respect to the macrocyclic plane as the result of the "lanthanide contraction" effect.

It should be stressed that the stability of the complex with phthalocianine ligand increases from Gd to Dy simultaneously with the sharp decrease in the activation energy of dissociation reaction (Table 3) in the case of (Br)LnPc and (AcO)LnPc (Br<sup>-</sup> and AcO<sup>-</sup> are more stronger  $\pi$ -donors than Cl [7]). With account of the different mechanisms of dissociation of the Gd and Dy complexes, one can conclude that this is associated with the steric hindrances for the reagent attack at the limiting stage (7) with the participation of the outersphere complex [(AcOH)GdPc]<sup>+</sup>X<sup>-</sup>, whose coordinated AcOH molecule lies on one side of the macrocyclic plane and the X<sup>-</sup> anion electrostatically bound in the second coordination sphere lies on the other side of this

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**Table 3.** Kinetic parameters of dissociation of Gd(III) and Dy(III) complexes with phthalocyanine in ethanol–AcOH mixture

Complex	<i>T</i> , K	$k \times 10^4$ , s <sup>-1</sup> mol <sup>-2</sup> l <sup>2</sup>	n	$E_a^*$ , kJ/mol	–ΔS≠, J/mol K
(Cl)GdPc	298	3.91		56.1	$140.2\pm0.6$
	313	3.45	2.08		
	323	5.80	1.95		
	333	12.69	1.81		
(Br)GdPc	298	2.41		71.3	$91.3 \pm 0.2$
	313	3.46	1.80		
	323	7.91	1.48		
	333	17.95	1.17		
(AcO)GdPc	298	0.160		90.4	$44.7 \pm 0.3$
	313	0.612	2.16		
	323	1.70	1.72		
	333	4.94	1.29		
(Cl)DyPc	298	0.0885		56.4	$160.8\pm0.2$
	333	0.961	1.33		
	343	1.73	1.01		
	353	3.05	0.74		
(Br)DyPc	298	0.0788		55.15	$168.1\pm0.2$
	333	0.627	1.64		
	343	1.105	1.38		
	353	1.94	1.11		
(AcO)DyPc	298	0.0362		60.0	$154.5\pm0.2$
	333	0.547	1.69		
	343	1.077	1.28		
	353	1.868	1.03		

\* Reliability of approximation  $R^2 = 0.982 - 0.999$ .

plane. It is obvious that the same reason underlies a substantial difference in the activation energies and kinetic stabilities of the Gd complexes with different X.

This conclusion agrees well with the more negative entropies of activation of the (X)DyPc dissociation as compared to the Gd complexes (Table 3). As compared to the Gd complexes, the transition states for the Dy complexes are more solvated than those of the initial reagents. Thus, the mutual effect (the Chernyaev *cis*-effect) of ligands in lanthanide acidophthalocyaninate complexes and its manifestation in the kinetic stability of the complexes significantly depends on the lanthanide electronic structure.

The rate of dissociation of the previously studied [8, 9] and less stable Ln complexes with tetraphenylporphine is either insensitive to the X nature (for the Tm complex) or only slightly changes (for the Dy complex) upon the replacement of Cl- by Br- and AcO- in composition of the coordination sphere. In turn, when the stable *d*-metal phthalocyaninate complexes are dissolved in concentrated  $H_2SO_4$  (that has the high content of the solvated protons and the high acidity), they lose their acido ligands and occur in solutions as the  $[MPc]^{(n-2)+}$  cations [10]. Thus, the replacement of acido ligands in complexes with moderate stability in solutions can be used, on the one hand, as the way to change their stability, and on the other hand, as an indirect method to study the strength and the nature of the axial ligand binding in the metal phthalocyaninates.

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