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Axial Ligands and (Acido) (Phthalocyaninato) Lanthanides(III) Stability on Examples of Erbium and Lutetium

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Abstract—The results of a spectrophotometric study of the dissociation kinetics of the coordination centre in (phthalocyaninato) erbium(III) and lutetium(II), (X)LnPc (X = Cl, Br, AcO) in ethanol in the presence of acetic acid are reported. The kinetic equations, the numerical values of reaction rate constants and dependences of the letter on the temperature were determined by the method of excessive concentrations. The stoichiometric mechanism of the complexes dissociation and the nature of the limiting elementary reaction were substantiated and the role of axial ligands in the reaction mechanism was revealed using spectral data and the quasiequilibrium principle to describe kinetic regularities. The resulting data can help in the use of erbium and lutetium phthalocyanines as precursors in the synthesis of higher stoichiometry complexes.

Keywords: (phthalocyaninato) lanthanides(III), axial complexes, dissociation reactions, kinetics, reaction mechanism

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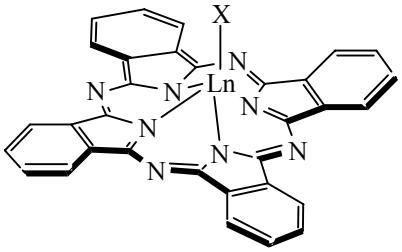
It was previously shown that the equatorial (macrocyclic) and axial ligands in metal porphyrins (MP) and metal phthalocyanines (MPc) with a mixed-ligand coordination sphere and the metal cation having the formal charge >2, not only are bound to the central atom with different strengths, but also exert a *cis* effect on each other, thereby affecting the reactivity [1–6]. Higher stoichiometry complexes, where the axial positions are occupied by one or even two porphyrin/phthalocyanine ligands, specifically, sandwich complexes are the most stable and widespread form in the case of rare earth metals having a large radius and high coordination numbers. Such complexes exhibit nonlinear optical, magnetic, electrochromic, and other practically important properties [7–16] provoking a growing interest in the synthesis of new compounds of this class. Among recent achievements, the synthesis of four- and six-membered sandwich complexes containing a flexible spacer (clamshell complexes) [17] or a cadmium ion as one of the central ions [18] are worth mentioning. Even though sandwich complexes of rare-earth metals are much more stable than 1 : 1 complexes with an axial acido ligand (X)LnP, (X)LnPc [19], the search for ways to enhance stability of the latter complexes and the study of their properties are continued. According to [20, 21], chloride and acetate axial complexes of (porphyrinato) gadolinium(III), europium(III), and thulium(III) complexes are paramagnetics, and in external magnetic fields of up to 1 T at 15–25°C they exhibit magnetocaloric properties which are much dependent on the nature of the axial ligand. (AcO)GdTPP (TPP is 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine dianion) shows a high magnetocaloric effect which compares with that of lanthanum manganite doped with silver ions [22] and implies that acidoporphyrin complexes of rare-earth metals hold promise for application in solid-state refrigerators and hyperthermia therapy.

In view of the aforesaid, it is quite obvious that the studying the influence of the nature of axial ligands on the stability of (phthalocyaninato) rare earth complexes is an urgent task. In the present work we synthesized erbium(III) and lutetium(III) phthalocyanines of the general formula (X)LnPc (X^- = Cl^-, Br^-, AcO^-) and performed a spectrophotometric study of the dissociation kinetics of their coordination centres in ethanol in the presence of acetic acid.



The UV-vis spectra of the synthesized Er and Lu complexes contain a strong band with a maximum near 670 nm, a shoulder at 640 nm, and a vibrational satellite at 603–609 nm (Fig. 1), as well as a less intense Soret band near 340 nm. Such spectral pattern is traditionally used for identification of 1 : 1 (phthalocyaninato) rare earth complexes in view of a number of features which distinguish it from the spectra of analogous complexes with another stoichiometry: MPc_2 and M_2Pc_3 [23, 24]. The spectral pattern is almost independent of the nature of the lanthanide and acido ligand. The position of the long-wave maximum appreciably varies (up to 50 nm) with the coordinating solvent, implying a hexacoordinate state of the complexes in solutions, with a molecule of the solvent in the first coordination sphere. The UV-vis spectra in the studied solvents do not vary with time. However, if the weak acid AcOH is added, both during dissolution of the complexes and already to the solution, the spectrum of the complex transforms into the spectrum of the free phthalocyanine H_2Pc (Fig. 1),

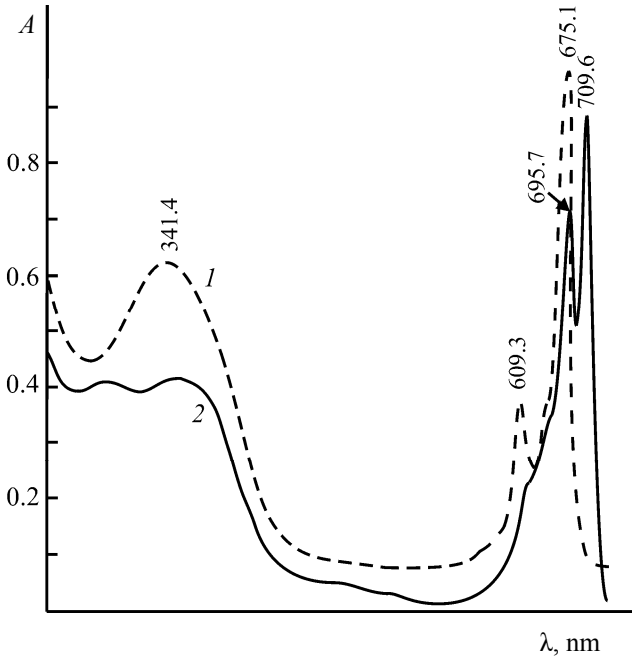


Fig. 1. UV-vis spectra of (AcO)ErPc in (*1*) DMSO and (*2*) AcOH. Spectrum *2* relates to H_2Pc.

which points to dissociation of the coordination centre in the complexes [Eq. (1)]. Noteworthy is the fact that the insoluble H_2Pc remains in the solution: no precipitate formation and the corresponding decrease in the intensity of the absorption bands are observed in this case. We showed in [25] that this phenomenon can be used to prepare dilute organic solutions of H_2Pc via its reversible coordination with an ion of one of the first members of the lanthanide series.

$$(X)LnPc + 2AcOH = Ln^{3+} + H_2Pc + X^- + 2AcO^-. \quad (1)$$

The rate of reaction (1) can be decreased by using a lower concentration of AcOH. The (X)ErPc and (X)LuPc complexes dissociate with a measurable rate (Tables 1 and 2) in ethanol in the presence of AcOH, and the lutetium complex, also in glacial AcOH. As seen from the data in Tables 1 and 2, reaction (1) is first-order with respect to (X)LnPc concentration. The dissociation rate of Er complexes increases with increasing AcOH concentration, whereas with the Lu complexes the situation is reverse. This difference is likely not associated with the dissociation mechanism and mostly relates to the replacement of a mixed solvent (EtOH–AcOH) by glacial acetic acid. As shown above, the complexes exist in solutions as coordinately saturated species having one solvent molecule in the coordination sphere. Therefore, the fact that the dissociation rate decreases almost two times in going from the 95% solution of acetic acid (16.3 M) in ethanol to glacial acetic acid (17.5 M) (Table 2) can be ascribed to a change of the solvent molecule in the coordination sphere, i.e., the transition from $(X)(C_2H_5OH)LuPc$ to (X)(AcOH)LuPc, as well as by stronger binding of AcOH.

The plotting of dependence k_{obs}–c^0_{AcOH} in log-log coordinates for the complexes (X)ErPc (Fig. 2) provides a linear correlation (the reliability of the ap-proximation R^2 is 0.968–0.999) with the slope of plots close to 2 and numerical values of the rate constants in the experimental kinetic equation (2) compiled in Table 3.

$$-dc_{(X)ErPc}/d\tau = kc_{(X)ErPc}(c^0_{AcOH})^2. \quad (2)$$

Equation (2) is successfully treated in terms of the quasiequilibrium principle.

$$(X)ErPc + HOAc \overset{K_1}{\rightleftarrows} [(AcOH)ErPc]^+ X^-, \quad (3)$$

$$[(AcOH)ErPc]^+ X^- + AcOH \xrightarrow{k_1,\ slowly} [(AcOH)ErHPc]^{2+} X^- + AcO^-, \quad (4)$$

Table 1. Dissociation rate constants of (phthalocyaninato) erbium(III) complexes in ethanol–AcOH (3.5–7.5 M)

c^0_{AcOH}, M	$k_{obs} \times 10^4$, s^{-1}			
	298.2 K	333.2 K	343.2 K	353.2 K
		(Cl)ErPc		
3.55	0.021±0.004	0.436±0.001	0.981±0.001	1.922±0.003
4.26	0.039±0.002	0.742±0.002	1.52±0.01	3.08±0.02
5.68	0.068±0.006	1.348±0.007	2.8±0.1	5.7±0.2
7.44	0.165±0.01	2.50±0.08	4.8±0.2	9.3±0.4
		(Br)ErPc		
3.55	0.020±0.002	0.401±0.001	0.868±0.001	1.698±0.002
4.26	0.036±0.003	0.648±0.001	1.306±0.002	2.65±0.02
5.68	0.076±0.003	1.364±0.001	2.839±0.003	5.5±0.2
7.44	0.108±0.002	1.928±0.003	3.96±0.08	7.3±0.4
		(AcO)ErPc		
3.55	0.015±0.003	0.31±0.02	0.704±0.04	1.38±0.025
4.26	0.026±0.001	0.516±0.005	1.07±0.01	2.175±0.03
5.68	0.051±0.004	1.043±0.009	2.17±0.02	4.5±0.1
7.44	0.113±0.001	1.715±0.01	3.33±0.07	6.415±0.03

Table 2. Dissociation rate constants of (phthalocyaninato) lutetium(III) complexes in ethanol–AcOH (16.3–17.5 M)

c^0_{AcOH}, M	$k_{obs} \times 10^4$, s^{-1}				E,[a,b] kJ/mol
	298.2 K	333.2 K	343.2 K	353.2 K	
			(Cl)LuPc		
16.3	0.180	2.97±0.04	5.9±0.5	11.7±0.5	67.0[c]
17.5	0.104	1.628±0.002	3.19±0.03	6.2±0.4	65.3
			(Br)LuPc		
16.3	0.162	2.51±0.01	4.9±0.3	9.4±0.6	64.3
17.5	0.100	1.496±0.002	2.83±0.02	5.6±0.5	64.5
			(AcO)LuPc		
16.3	0.132	2.05±0.01	4.0±0.2	7.76±0.03	65.0
17.5	0.060	1.00±0.02	2.01±0.08	4.05±0.08	68.8

[a] Approximation confidence interval 0.999–0.9999. [b]Apparent parameters found from the temperature dependence of k_{app}. [c] $-\Delta S^{\neq}$ = (119.7–133.0) ± (0.2–0.9) J mol^{-1} K^{-1}.

$$[(AcOH)ErHPc]^{2+}\,X^- + AcOH \xrightarrow{fast} (AcOH)Er^{3+} + H_2Pc + AcO^- + X^-. \quad (5)$$

As seen from the scheme, the initial mixed-ligand erbium complexes are present in equilibrium with their axially ionized form [Eq. (3)]. The dissociation of the $Er–N_{porphyrin}$ bond occurs in the cationic complex which has a coordination site available for attack of the acid molecule [Eq. (4)]. As the Ln–N bonds in the aromatic macrocyclic complex are sufficiently strong (due to the covalent contribution involving both outer *s* orbitals and partly occupied *f* orbitals [26]), this stage is slow. The following dissociation reaction of the second covalent bond in an unstable cationic $[(AcOH)ErHPc]^{2+}X^-$ is kinetically negligible. In this case, the kinetic equation for the rate-limiting stage (4) takes form (6).

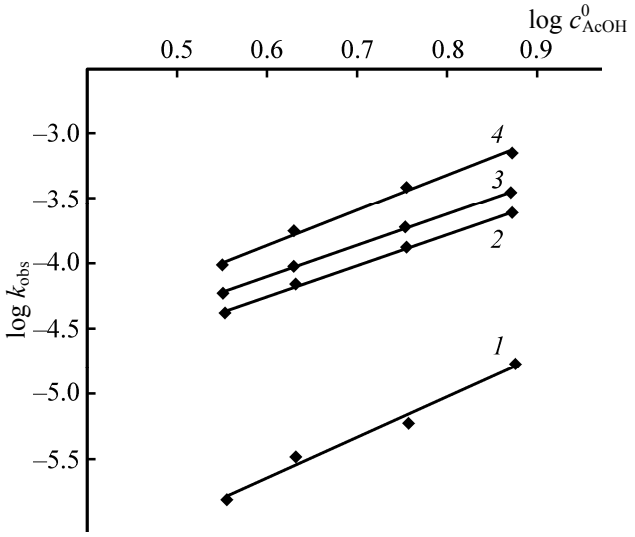


Fig. 2. Dependences log k_{obs}–log c^0_{AcOH} for the (Cl)ErPc at (*1*) 298, (*2*) 333, (*3*) 343, and (*4*) 353 K.

$$-dc_{[(AcOH)ErPc]^+X^-}/d\tau = k_1 c_{[(AcOH)ErPc]^+X^-} c^0_{AcOH}. \quad (6)$$

With accounting for equilibrium (3), Eq. (6) can be transformed to obtain Eq. (7).

$$-dc_{[(AcOH)ErPc]^+X^-}/d\tau = -dc_{(X)ErPc}/d\tau = k_1 K_1 c_{(X)ErPc}(c^0_{AcOH})^2. \quad (7)$$

Actually, Eq. (7) is consistent with the experimental equation (2), and the experimental rate constant k includes the rate constant of a slow stage (4) and the constant of a rapidly established pre-equilibrium (3): $k = k_1 K_1$.

This fact implies that the strengths of bonding of the axial ligand X^- and the equatorial macrocyclic ligand Pc^{2-} in the Eu complexes are roughly equal to each other, even though their coordination properties are quite different. The probable reason for this phenomenon is that (X)ErPcs have an unsymmetrically filled f^{11} shell, which favors π-donation not only from the aromatic macrocyclic ligand, but also from the acido ligands Cl^-, Br^-, and AcO^-.

The considered stoichiometric dissociation mechanism of (X)LnPc is based on the assumption of an integer second order of reaction (1) with respect to AcOH concentration. However, as seen from Table 3, the experimental reaction orders are not integer and, what is more, tend to decrease with temperature. This finding implies that the real dissociation mechanism is more complicated. If we include one more fast established pre-equilibrium, specifically, acid ionization of AcOH (protonation of ethanol), in the above-considered theoretical reaction scheme, we obtain a higher order of reaction (1) in the acid but acting here in the form of the solvated proton $C_2H_5OH_2^+$. Probably, when AcOH concentrations are sufficiently high (Table 1), the acid–base equilibria in the solvent-reagent mixture actually affect the kinetics of reaction (1).

Table 3. Dissociation kinetic parameters of (phthalocyaninato) erbium(III) complexes in ethanol–AcOH

Complex	T, K	$k \times 10^6$, s^{-1} mol^{-2} L^2	n, R^2	E,[a] kJ/mol	$-\Delta S^{\neq}$, J mol^{-1} K^{-1}
(Cl)ErPc	298	0.0731	2.68, 0.989	84.3	107.1±0.4
	333	2.44	2.31, 0.996		
	343	6.72	2.13, 0.999		
	353	13.7	2.12, 0.995		
(Br)ErPc	298	0.122	2.29, 0.970	78.6	123.6±0.2
	333	2.77	2.16, 0.978		
	343	6.16	2.12, 0.978		
	353	13.9	2.03, 0.968		
(AcO)ErPc	298	0.0512	2.68, 0.998	84.6	108.7±0.4
	333	1.78	2.30, 0.993		
	343	4.88	2.13, 0.991		
	353	10.0	2.12, 0.981		

[a] Approximation confidence interval 0.9993–0.9997.

The kinetic stability of both lanthanide(III) complexes was found to be sensitive to the nature of the axial ligand X^- (Tables 2 and 3). In the case of (X)LuPc, comparisons are only possible for a definite solvent composition in terms of apparent rate constants which include acid concentration. The k^{298} and k_{obs}^{298} for the Er and Lu complexes decrease, respectively, in the series: (Br)ErPc > (Cl)ErPc > (OAc)ErPc and (Cl)LuPc ≈ (Br)LuPc > (OAc)LuPc, and, therewith, the first series does not parallel the electronegativity series of the donor atoms in ligands X^-. This fact is most likely associated with a steric factor, specifically, the Er atom in (Br)ErPc stronger deviates from the plane of the coordinated nitrogen atoms of the macrocyclic ligand because of the hindrances from the bulkier Br atom. Characteristically, lanthanides with a lower atomic number (and, consequently, a larger covalent radius) do not exhibit such effect, and axial chloride complexes are less stable than bromide and, all the more, acetate ones [6, 27, 28]. This is especially related to gadolinium complexes [(X)GdPc] [6], whose stability along the series Cl > Br > > AcO varies 24.4 times.

The numerical values of k^{298} vary 2.38 times along the series (Br)ErPc > (Cl)ErPc > (OAc)Er and 1.36 and 1.73 times along the series (Cl)LuPc ≈ (Br)LuPc > (OAc)LuPc in ethanol–AcOH and glacial acetic acid, respectively. The fact that the dissociation rate constants of the erbium and lutetium complexes are less sensitive to the nature of the axial ligand, compared to the gadolinium complexes, is due to different reasons. With (X)ErPc, this is explained by the above-mentioned contribution of dative π bonds to coordination (lacking in the lutetium complexes because of the stable f^{14} configuration). The low sensitivity of the dissociation of (X)LuPc to the nature of the axial ligand provides further evidence for the significance of steric factor for the stability of the complexes in view of the small covalent radius of the central ion. The same conclusion is also valid for the erbium complexes.

These conclusions are well consistent with the dependence (Fig. 3) of the dissociation rate constants of (X)ErPc and (X)LuPc with varied axial ligands on the temperature. The low selectivity of the dissociation of (X)LuPc to ligand X^- is consistent with the close activation energies/entropies for all the studies axial complexes (Table 2). The steric effect in (Br)ErPc reveals itself in that its dissociation activation energy and entropy are lower respectively by 6 kJ/mol and ~15 J mol^{-1} K^{-1} (Table 3) compared to the respective values for the axial chloride and acetate complexes.

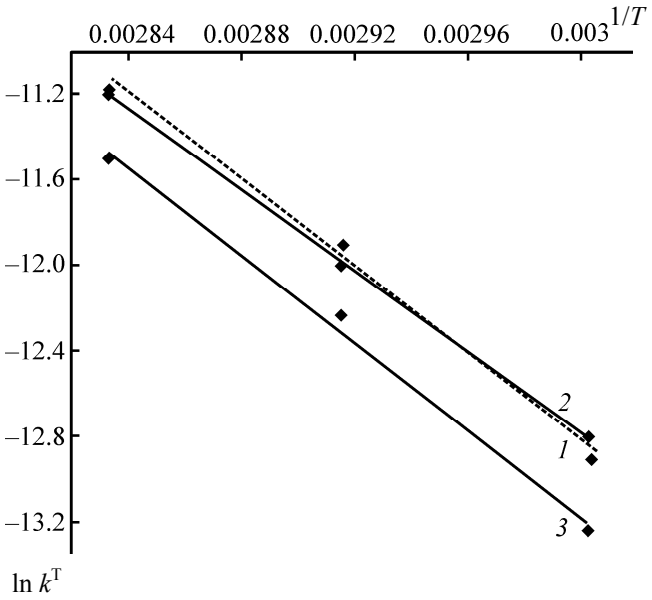


Fig. 3. Dependences ln k^T–(1/T) for complexes (X)ErPc. X: (*1*) Cl, (*2*) Br, and (*3*) AcO.

Thus, the mutual effect (Chernyaev *cis* effect) of the ligands in (phthalocyaninato) lanthanide complexes and its manifestation in the kinetic stability of the complexes is strongly dependent on the electronic structure of the lanthanide, and in the case of the rare-earth metal which is the last member of the lanthanide series, also on its covalent radius. This conclusion should be taken into account in constructing homo- and heteroleptic (phthalocyaninato) lanthanide(III) double- and triple-decker complexes based on (acido) (phthalocyaninato) lanthanide(III) complexes.

EXPERIMENTAL

The UV-vis spectra were measured on Agilent 8453 UV-Vis and Specord M400. Monitoring of the optical density at the working wavelength (672 and 709 nm for the Er and Lu complexes) in the course of kinetic experiments was performed on an SF-26 spectrophotometer with a temperature-controlled cell.

Acetic acid of chemically pure grade was dried by stepwise freezing/thawing. Ethanol was dried by a standard procedure [29]. The water content (by Fischer titration) in the dried solvents was no higher than 0.03%.

The apparent rate constants (k_{obs}), kinetic constants (k), and reaction orders with respect to AcOH

concentration (n) were determined by optimizing the functions log $[(A_0 - A_\infty)/(A_\tau - A_\infty)]$–$f(\tau)$ and log k_{obs}–$f(\log c^0_{AcOH})$, respectively, using Microsoft Excel; here A_0, A_∞, and A_τ are the optical densities of solution at the working wavelength at $\tau = 0$, current τ, and reaction completion time. The activation energies [(X)ErPc] and apparent activation energies [(X)LuPc] were obtained by optimizing the Arrhenius functions $\ln k^T$–$f(1/T)$ and $\ln k^T_{obs}$–$f(1/T)$. The activation entropies were calculated by the basic equation of the transition state theory trasformed to Eq. (8).

$$\Delta S^{\neq} = 19.1\log k^T + E/T - 19.1\log T - 205. \quad (8)$$

The mean $\Delta S^{\neq}$ value was calculated as the arithmetic mean of $\Delta S^{\neq}$ calculated for the temperatures used in the kinetic experiment.

(X)ErPcs were prepared by the template synthesis described in [23] but in solvent-free conditions. (X)LuPcs were prepared by the substitution of the metal cation in Li_2Pc [24].

Erbium(III) complexes. A mixture of $ErX_3 \cdot nH_2O$ and *o*-phthalodinitrile in a 1:8 molar ratio was heated at its melting point (~563 K) for 60 min and then cooled and dissolved in DMF. The resulting solution was subjected to column chromatography on Al_2O_3, eluent ethanol. Yield ~20%. Acetato(phthalocyaninato)erbium(III). UV-vis spectrum, λ_{max}, nm: DMSO, 675.1, 640 (shoulder), 609.3, 341.4; benzonitrile, 719.0, 691.2; chloroform, 676.8; pyridine, 674.4; benzene, 672.6; acetonitrile, 669.0; Et_2O, 667.1; acetone, 666.8.

Lutetium(III) complexes. A mixture of 1 g of H_2Pc, 1 g of LiAcO, and 1.65 g of $LuX_3 \cdot nH_2O$ in 200 mL of DMSO was heated under reflux for 15–20 min, cooled, and diluted with 5–10 mL of water. The precipitate of H_2Pc was filtered off. The filtrate was diluted with water by half, and (X)LuPc that precipitated was filtered off, washed with water, and dried in air. Yield ~90%.

Acetato(phthalocyaninato)lutetium(III). UV-vis spectrum, λ_{max}, nm: ethanol, 668.0, 640 (shoulder), 606.4, < 350.0; benzonitrile, 714.9, 691.2; chloroform, 675.3; pyridine, 674.4; benzene, 674.3; acetonitrile, 669.0; Et_2O, 667.8; acetone, 663.1; DMF, 665.3.

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