Electrochemical investigation of lanthanide octa-*tert*-butylsubstituted diphthalocyanine complexes in solutions. Approximation of their redox transitions by semiempirical calculations for yttrium diphthalocyanine

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The electrochemical potentials of seven redox transitions for green forms and eight redox transitions for blue forms of neutral octa-*tert*-butylsubstituted diphthalocyanine complexes of lanthanides Pc^t_2Ln (Ln = Pr, Sm, Dy, and Lu) in solutions were measured by cyclic voltammetry and rotating disc electrode techniques. The spectroelectrochemical investigation of the products of two-electron oxidation and reduction of the green form of Pc^t_2Lu was performed. The frontier molecular orbitals, total charge densities, total spin densities, electrostatic potentials, and heats of ion formation for $(Pc_2Y)^{m+,n-}$ (m = 0, 1, 2, and 3; n = 1, 2, 3, and 4), which can model the products of the redox transitions of the diphthalocyanines under study, were calculated using the semiempirical ZINDO/1 method. The calculations for $(Pc_2Y)^{m+,n-}$ and absorption spectra show that the electron changes in all redox transitions of the green forms of Pc^t_2Ln are mainly localized on the ligands.

Key words: lanthanide diphthalocyanines, electrochemistry, redox transitions, yttrium diphthalocyanine, semiempirical calculations.

The importance of metal phthalocyanines is based on the fact that they are used as stable pigments[1,2] and materials for chemical sensors, and as systems for information storage.[3,4] Their unique redox properties offer great challenges for use in electrochromic devices,[5,6] as electro- and photocatalysts,[7] *etc.* Metal phthalocyanines can both donate and accept electrons to be transformed into positive or negative $(Pc_2Ln)^{n\pm}$ ions without decomposition of the complex. Due to this properties, they can be used as electrocatalysts for both reduction (of oxygen, CO_2, $SOCl_2$, SO_2Cl_2, R_2S_2, ClO_3^- ion, *etc.*) and electrooxidation (of hydrazine, glucose, and others).[7]

Although the redox properties of phthalocyanines are under intense study,[8,9] many points in this area are still unclear, and rare-earth metal diphthalocyanine complexes are least studied.

Neutral Pc_2Ln complexes can exist in two forms (green and blue), and the difference between the structures of these forms is under discussion at present. In solutions, the green and blue forms can undergo several reversible electrochemical redox transitions. For example, four reduction and two oxidation processes were observed for the green form of Pc_2Lu,[10—12] and the blue form of Pc^t_2Lu (Pc^tH_2 is tetra-*tert*-butylphthalocyanine) is characterized by four reduction and four oxidation processes.[13] Complexes of the other rare-earth metals are considerably less studied.[14—16]

A large series of green forms of Pc_2Ln has been studied[16] in *o*-dichlorobenzene (DCB) to reveal three reversible reduction process and one oxidation process. Similar results have been obtained[13] for the green form of Pc^t_2Lu, and only the first oxidation and reduction processes have been studied for the other representatives of the series of green forms of *tert*-butylsubstituted Pc^t_2Ln.[14] When DMF was used as the solvent, the range of available potentials in the cathodic area was enlarged to —2.0 V, and the fourth reversible redox transition of the green form of Pc_2Lu was observed.[11] The blue forms of diphthalocyanine complexes are considerably less studied. Only the first two oxidation processes in DCB have been studied for the whole series of rare-earth metals.[15]

Experimental data on the number of electrons participating in redox transitions are contradictory.[10—19] Based on studies by different methods, it is commonly accepted that all redox transitions occurring in solutions of lanthanide diphthalocyanine complexes are one-electron processes.[10,14,16,17,19] Nevertheless, the number of electrons (n) determined by direct electrochemical methods are often underestimated.[13,19] For example, $n < 1$ have been obtained[19] for the first oxidation and reduction processes of the green form of Pc_2Lu in a solution of CH_2Cl_2, while the dimeric structure with respect to the green form has been postulated for the blue form of Pc^t_2Lu on the basis of the experimental value $n = 0.5$.[13]

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The fourth process of reduction of the green form of Pc_2Lu in DMF (transition $(Pc_2Lu)^{3-} \rightarrow (Pc_2Lu)^{4-}$) was assumed[11] to occur with participation of two electrons. The electrochemical values of n measured by the moving boundary technique[18] for compounds in the form of films deposited onto the electrode are often close to 2 due to the more complicated mechanism of the redox process.[18]

Therefore, various nonelectrochemical methods are often used to determine the number of electrons participating in redox processes. ESR data are an objective criterion for estimating the number of electrons in electrochemical transitions of rare-earth metal diphthalocyanine complexes.[10,17] In lutetium diphthalocyanine, diamagnetic and paramagnetic forms alternate on going from one redox state to another,[10,17] which suggests[10] the one-electron character of the transitions observed:

$$(Pc_2Lu)^{+} \overset{+e}{\rightleftharpoons} (Pc_2Lu)^{0} \overset{+e}{\rightleftharpoons} (Pc_2Lu)^{-} \overset{+e}{\rightleftharpoons} (Pc_2Lu)^{2-}.$$

(red-brown diamagnetic)	(green paramagnetic)	(blue diamagnetic)	(violet paramagnetic)

The problem of localization of electronic changes in oxidation and reduction processes is also important. Based on the data of UV-VIS spectroscopy, it is considered to be reliably established that the first oxidation and reduction processes of the green forms and the first two oxidation processes of the blue forms of the complexes do not involve the metal atom but involve the electron transfer at the ligand.[10,14,15,20]

The purpose of this work is to continue the study of electrochemical properties of the green (Ln = Pr, Dy, and Lu) and blue (Ln = Sm, Dy, and Lu) forms of the $Pc^{t}_{2}Ln$ diphthalocyanines. Special attention was given to solve the problem of the localization of the redox transitions observed.

Experimental

Rare-earth metal diphthalocyanine complexes were synthesized by a known procedure.[14,15] Purity of the diphthalocyanine complexes used was confirmed by chromatography and UV-VIS spectroscopy.

Acetonitrile (pure grade, 2 L) was stirred for 24 h over CaH_2 and filtered, and KNO_3 (5 g) and H_2SO_4 (conc., 10 mL) were added. The resulting mixture was refluxed for 3 h and distilled. Then MeCN was refluxed for 2 h with P_2O_5 and distilled to collect a fraction with b.p. 81—82 °C (760 Torr).

o-Dichlorobenzene (DCB) was dried over $CaCl_2$, filtered, and distilled collecting a fraction with b.p. 65 °C (13 Torr). Prior to use, the distilled DCB was passed through a column with neutral alumina.

Methylene dichloride was purified by boiling and distillation over CaH_2 prior to use.

Electrochemical measurements were carried out on a PI-50-1.1 potentiostat, a PR-8 programmator, and a PDA1 XY-recorder using the three-electrode scheme on a Pt stationary or rotating disc electrode with a working surface of 20.7 mm^2 with 0.05 M $Bu^{n}_{4}NBF_4$ as the supporting electrolyte at 20 °C. A Pt wire served as the auxiliary electrode, and a saturated AgCl electrode was used as the reference electrode. Oxygen was removed from the cell with a dry argon flow. Voltammetric curves were obtained by cyclic voltammetry (CVA) with a scan rate of 200 mV s^{-1} and by the rotating disc electrode (RDE) method with the scan rate of 20 mV s^{-1}. After recording each curve, the electrode was thoroughly polished. The measured potential values were corrected for the IR drop. Anhydrous acetonitrile, its mixture with DCB, and methylene dichloride were used as the solvents. The concentration of solutions of the compounds under study was $8 \cdot 10^{-5}$—$8 \cdot 10^{-4}$ mol L^{-1}.

Bulk electrolysis was carried out at 20 °C in the potentiostatic regime in a special cell connected to a P-5827M potentiostat by the three-electrode scheme. A Pt plate with the surface of 200 mm^2 served as the working electrode, and 0.05 M $Bu^{n}_{4}NBF_4$ was the supporting electrolyte. Anodic and cathodic compartments were separated by a ground glass joint moistened with the solution under electrolysis. Potential values were measured *vs* a saturated Ag/AgCl electrode. Anhydrous MeCN was used as a solvent. The concentration in solutions of the compounds under study was $5 \cdot 10^{-5}$—$5 \cdot 10^{-4}$ mol L^{-1}. The solution in the cell during electrolysis was stirred and oxygen was removed during the preparation for electrolysis by the dry argon flow. UV-VIS spectra were recorded on a Hitachi 124 spectrophotometer in the 190—900 nm region using 0.05 M $Bu^{n}_{4}NBF_4$ in the same solvent as the reference solution. Experiments were carried out either directly in a quartz cell or in a 1-mm quartz cuvette.

Semiempirical calculations of neutral and ionic forms of Pc_2Y and Pc_2YH molecules were performed by the ZINDO/1 method[21,22] included into the HyperChem 4.0 program. The geometry of all molecules was optimized only by the molecular mechanics method using the MM+ force field.[23]

Ions with closed shells were calculated by the restricted Hartree—Fock method, and the nonrestricted method was used for the starting molecule and radical ion particles.

Triplet and quadruplet states of ions were not calculated.

Results and Discussion

The free phthalocyanine PcH_2 is known[24,25] to exist in the potential range from −2.3 to +1.5 V in different redox forms, from $(PcH_2)^{2+}$ to $(PcH_2)^{4-}$. To observe the pattern of redox transitions as complete as possible, the range of potentials accessible to study should be extended in both the negative and positive directions (by selection of the electrode material, solvent, supporting electrolyte, *etc.*). However, phthalocyanines, as a rule, are poorly soluble in solvents that satisfy these conditions. In the majority of the published works,[10,13—16,19,20] lanthanide diphthalocyanines have been electrochemically studied in DCB or methylene dichloride in the potential region from −1.5 to +1.5 V.

The lanthanide octa-*tert*-butylsubstituted diphthalocyanine complexes studied in this work are fairly well soluble in acetonitrile, which allowed us to study the redox processes in the potential region from −2.2 to +2.0 V. The potentials of the redox transitions obtained by CVA are presented in Table 1. The CVA curves typical of the green and blue forms of $Pc^{t}_{2}Ln$ are presented in Fig. 1. Four subsequent reversible reduction processes are observed for the green forms of $Pc^{t}_{2}Ln$, which agrees with the previous studies.[11] When the

Table 1. CVA data for green and blue forms of lanthanide octa-*tert*-butylsubstituted diphthalocyanine complexes

Compound[a]	E_p/V^b	
	Reduction	Oxidation
$Pc^t_2Lu(g)$	−0.02/0.07, −1.14/−1.07, −1.46/−1.36, −1.96/−1.75	0.39/0.29, 1.53/1.46, 1.72/1.65
$Pc^t_2Dy(g)$	0.01/0.12, −1.16/−1.08, −1.48/−1.35, −1.99/−1.75	0.44/0.36, 1.52/1.45, 1.61/1.54
$Pc^t_2Pr(g)$	0.13/0.23, −1.16/−1.09, −1.46/−1.35, −1.90/−1.75	0.55/0.45, 1.49/1.35, 1.78/1.68
$Pc^t_2Lu(b)$	−0.66/−0.58, −1.07/−0.97, −1.45/−1.35, −1.93/−1.70	0.28/0.20, 0.66/0.49, 1.23/1.13, 1.60/1.51
$Pc^t_2Dy(b)$	−0.70/−0.62, −1.03/−0.94, −1.42/−1.34, −1.94/−1.70	0.38/0.28, 0.70/0.60, 1.24/1.16, 1.60/1.53
$Pc^t_2Sm(b)$	−0.69/−0.59, −1.03/−0.96, −1.44/−1.30, −1.85/−1.60	0.41/0.32, 0.73/0.64, 1.24/1.16, 1.53/1.45

Note. Conditions of electrolysis: Pt electrode; MeCN; 0.05 *M* $Bu^n_4NBF_4$; Ag|AgCl|KCl; v = 200 mV s^{-1}; 20 °C.
[a] $Pc^t_2Ln(g)$ is the green form of the lanthanide octa-*tert*-butylsubstituted diphthalocyanine complex; $Pc^t_2Ln(b)$ is the blue form. [b] Direct peak potential/reverse peak potential.

green forms of Pc^t_2Ln were oxidized, we detected three reversible processes. The first of them is well known, and the second and third processes were observed for the first time. Eight reversible processes (four in the reduction region and four in the oxidation region) are observed on the CVA curves of the studied blue forms of Pc^t_2Ln. The potentials of four redox transitions in the reduction region and of the third and fourth transitions in the oxidation region were measured for the Sm and Dy complexes for the first time.

The data obtained agree well with the theoretical model that has been suggested recently[26] for the green forms of Pc_2Ln. Since the phthalocyanine rings make the main contribution to the energies of frontier orbitals of diphthalocyanines of rare-earth elements, the nature of the central lanthanide ion affects first of all the separation and, hence, the interaction between the phthalocyanine rings. The shorter the lanthanide radius, the stronger the interaction between the phthalocyanine rings and the higher the HOMO energy. Therefore, the oxidation potential of the diphthalocyanines should shift to the more anodic region on going from Lu to Pr, which is observed. The LUMO energy is independent of the distance between the phthalocyanine rings; therefore, the electrochemical potentials of the transitions from the monoreduced forms of the various metal diphthalocyanines to the di- and trianionic forms is almost identical for the whole series studied.

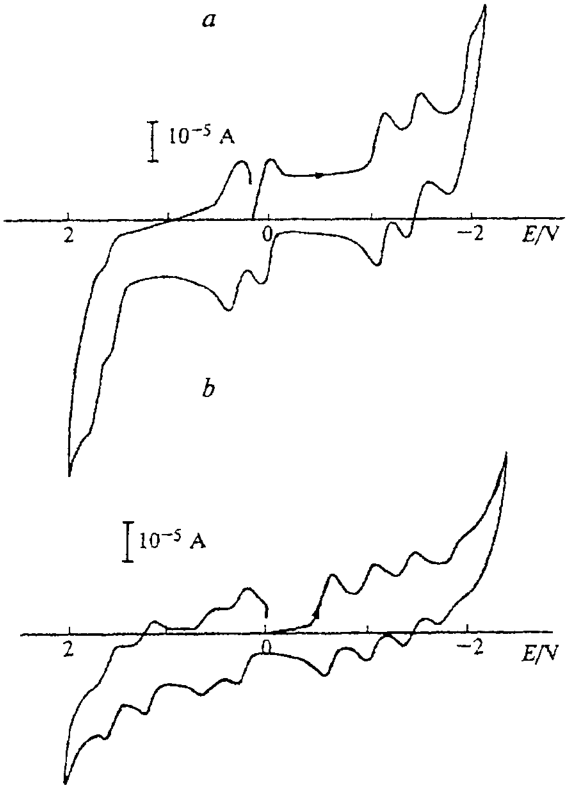

Fig. 1. Cyclic voltammograms of green (*a*) and blue (*b*) forms of Pc^t_2Lu in MeCN with the background of 0.05 *M* $Bu^n_4NBF_4$ (Pt; *vs.* Ag|AgCl|KCl; v = 200 mV s^{-1}; 20 °C).

In this work, we used the RDE method to determine the number of electrons involved in the redox transitions. The measured values of limit currents were compared to the standard value for the known one-electron process obtained on the same electrode and in the cell with the same configuration. The conventional Fc/Fc^+ (Fc is ferrocene) redox couple was chosen as the standard. As can be seen in Table 2, the *n* values obtained by this method are at best 0.5—0.6. This can be explained as follows. The magnitude of the diffusion current is known[27] to depend on the diffusion coefficient of a diffusing species:

$$I_d = 0.62(2\pi\omega)^{1/2}SnFCD^{2/3}/\nu^{1/6},$$

where ω is the rotation frequency of the electrode, *S* is the electrode surface, *n* is the number of electrons, *F* is Faraday's constant, *C* is the concentration of the species in the solution, *D* is the diffusion coefficient, and ν is the kinematic viscosity of the solution. The diffusion coefficient depends on the value of the effective Stokes radius of the molecule (r_{eff}):

$$D = kT/6r_{eff}\pi\eta,$$

where *k* is Boltzmann's constant, *T* is the absolute temperature, and h is the thermodynamic viscosity of the solution. The effective molecular radius includes the

Table 2. RDE study of green and blue forms of lanthanide octa-*tert*-butylsubstituted diphthalocyanine complexes

Compound[c]	Wave	$-E_{1/2}$/V	n[a]	n_{cor}[b]
		Reduction		
Pc^t_2Lu(g)	*1*	−0.01	0.49	0.83
	2	1.09	0.53	0.90
Pc^t_2Dy(g)	*1*	−0.04	0.57	0.97
Pc^t_2Pr(g)[d]	*1*	−0.17	0.30	0.51
	2	0.90	0.25	0.49
Pc^t_2Lu(b)	*1*	0.62	0.35	0.56
	2	1.02	0.40	0.68
	3	1.38	0.33	0.56
Pc^t_2Dy(b)	*1*	0.62	0.16	0.27
	2	0.96	0.21	0.36
		Oxidation		
Pc^t_2Lu(g)	*1*	0.35	0.50	0.85
	2	1.48	0.47	0.80
Pc^t_2Dy(g)	*1*	0.38	0.61	1.03
Pc^t_2Pr(g)[d]	*1*	0.52	0.32	0.54
Pc^t_2Lu(b)	*1*	0.24	0.30	0.51
	2	0.58	0.28	0.47
	3	1.18	0.32	0.54
Pc^t_2Dy(b)	*1*	0.31	0.16	0.27
	2	0.64	0.17	0.29
	3	1.16	0.27	0.46
	4	1.55	0.20	0.34

Note. Experimental conditions: Pt electrode; MeCN; 0.05 *M* $Bu^n_4NBF_4$; Ag|AgCl|KCl; v = 20 mV s^{-1}; ω = 2280 rpm; 20 °C.

[a] n is the number of electrons participating in the process calculated by the ferrocene/ferricinium pair.

[b] n_{cor} is the corrected number of electrons taking into account the differences in the diffusion coefficients of the diphthalocyanine complex and ferrocene (see text).

[c] Pc^t_2Ln(g) is the green form of the lanthanide octa-*tert*-butylsubstituted diphthalocyanine complex; Pc^t_2Ln(b) is the blue form. [d] MeCN—DCB (1 : 1) mixture.

Table 3. Data of calculations of molecular sizes by the molecular mechanics method (molecules approximated by cylinders)

Compound	Cylinder diagonal/Å	Cylinder height/Å	r_{eff}/Å
Pc^t_2Lu	24.7	12.8	9.4
Pc^t_2Pr	24.8	12.9	9.4
Pc^tH_2	22.7	6.4	7.3
Cp_2Fe	9.9	7.4	4.3

thickness of the solvate shell of the species. It was shown[28] that for compact species, whose central ion is well shielded from the tight interaction with solvent molecules, the van der Waals radius of the species can be used as the effective radius. The van der Waals radius for, *e.g.*, cobaltocene was calculated as the arithmetic mean between the minimum and maximum distances from the ion center to its van der Waals surface.[28] Using this approach, we calculated the theoretical n values for Pc^t_2Lu, Pc^t_2Pr, and Pc^tH_2, which could be obtained from the RDE method in the case of one-electron processes. Like ferrocene, these molecules can be approximated by cylinders, whose diagonal and height were calculated by the molecular mechanics method. The average value between the half-diagonal and half-height of the cylinder was taken as the effective radius (Table 3). The n values thus calculated are equal to 0.59 for Pc^t_2Lu and Pc^t_2Pr and 0.70 for Pc^tH_2. These values correlate fairly well with the experimental data obtained (see Table 2), including those for Pc^tH_2, whose n value for the first and second reduction processes in CH_2Cl_2 is ~0.7.

Thus, the data obtained by the RDE method support the one-electron character of the redox transitions under study. The comparison of the peak heights of different redox processes, which were obtained by the CVA method (see Fig. 1), shows that they are almost equal. This allows us to conclude that the redox transitions at high anodic and cathodic potentials, which cannot be observed directly by the RDE method, are also one-electron.

However, as can be seen in Table 2, the n values obtained for the blue forms are somewhat lower than those for the green forms of Pc^t_2Ln. These results agree with the data of previous studies,[13] according to which the number of electrons for the blue form of Pc^t_2Lu is equal to 0.5. The reason for this difference from the green forms is still unclear.

Monophthalocyanines and diphthalocyanines (more rarely) are known to be capable of forming dimers, aggregates, or associates containing solvent molecules.[29,30] For example, phthalocyanine ligands can be bound by hydrogen bonds (through a solvent molecule) or by overlapping π-systems of two rings.[29] A change in the Q band in the electronic absorption spectrum of the phthalocyanine complex[29,30] and distortion of the Lambert—Beer law can be a criterion for the occurrence of the aggregation process. When aggregates are formed, the Q band is broadened and shifted to the short-wave region as compared to the monomer.[29,30] As a rule, the phthalocyanine complexes can exist only as monomers when the concentrations are lower than 10^{-6} mol L^{-1}. When the concentration of the phthalocyanine complexes is from 10^{-6} to 10^{-4} mol L^{-1}, a mixture of the monomer, dimer, and tetramer is present in the solution, and the higher degree of aggregation is observed[29] only when the concentrations are greater than 10^{-2} mol L^{-1}. An increase in the ionic strength of the solution also increases the probability of aggregation.[29] In this work, the electrochemical properties of the diphthalocyanine complexes were studied at concentrations of the complexes of $8 \cdot 10^{-5}$—$8 \cdot 10^{-4}$ mol L^{-1} and in the presence of the supporting electrolyte $Bu^n_4NBF_4$. These conditions are favorable for the formation of associates. Nevertheless, using the green form of Pc^t_2Pr in the $MeCN-CH_2Cl_2$ (4 : 1) mixture as an example, it was shown that in the concentration range from $5 \cdot 10^{-7}$ to 10^{-4} mol L^{-1}, the electronic absorption spectra were almost identical and obey the Lambert—Beer law. Therefore, under the conditions studied, no aggregates of the starting complex are formed.

The tendency to aggregation also depends on the oxidation state of the central metal ion and the total charge of the complex. However, since the parameters of the CVA peaks (the difference between the potentials and the ratio of the heights of the anodic and cathodic peaks of the redox pair) are fairly close for all electrochemical processes observed in the complexes studied, it can be assumed that under these conditions, neither oxidized nor reduced forms of the complexes are aggregated.

Various oxidized and reduced states of the green form of Pc^t_2Lu were studied by electron absorption spectroscopy.

Reduction. The anionic blue form $(Pc^t_2Lu)^-$ was generated at the potential of −0.5 V. The electronic absorption spectrum contains the absorption at 336, 624, and 702 nm, in agreement with the published data.[14] It was rather difficult to perform the complete two-electron reduction. Nevertheless, the prolonged electrolysis at the potential of −1.3 V made it possible to detect the formation of a dark-blue solution of $(Pc^t_2Lu)^{2-}$ with absorption at 331 and 644 nm. The absorption bands observed agree well with the data obtained[11] for $(Pc_2Lu)^{2-}$. We were not able to detect the spectrum of the violet $(Pc^t_2Lu)^{3-}$ trianion after the three-electron reduction of Pc^t_2Lu because of the high sensitivity of the tricharged anion to dioxygen.

Oxidation. Absorption bands at 314, 352, 485, 617, and 697 nm are present in the electronic spectrum of the red-brown cationic $(Pc^t_2Lu)^+$ form generated at the potential of +1.0 V, which agrees with the published data.[14] We were able to obtain for the first time the electronic spectrum of the two-electron oxidation product, *i.e.*, $(Pc^t_2Lu)^{2+}$, formed during the electrolysis at high anodic potentials (Fig. 2). This yellow form observed for the first time is characterized by the absorption at 407 nm.

Subsequent electrolysis at the same potential results in the disappearance of the absorption at 407 nm and a decrease in the intensity of the color of the solution (see Fig. 2). The repeated electrolysis of the obtained solution at a potential of +0.1 V does not result, as follows from the spectrum, in the formation of the pure green form of Pc^t_2Lu. Along with Pc^t_2Lu, the solution contains a substance with absorption maximum at 673 nm. The study of the electrolysis solution by CVA showed, in addition to the peaks characteristic of the green form of Pc^t_2Lu, a new reversible pair at −1.26 V and an irreversible oxidation peak at +1.18 V.

Thus, it can be assumed that the second oxidation process is reversible only in the time scale of the CVA method (the existence of the reverse peak), but the $(Pc^t_2Lu)^{2+}$ formed in the solution enters irreversible chemical reactions.

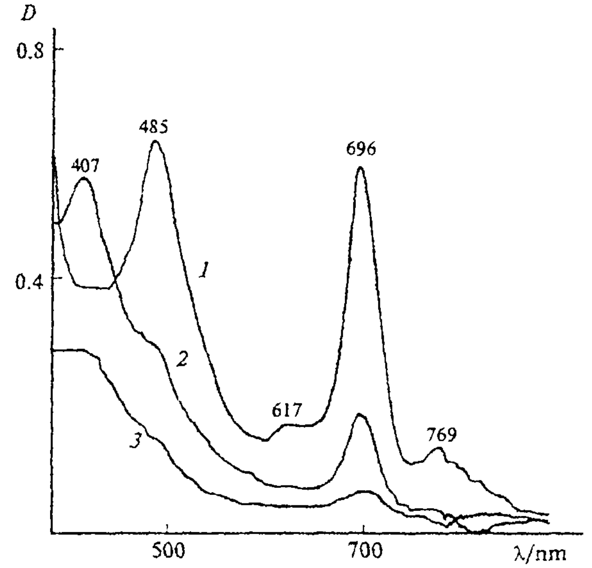

Fig. 2. Change in electronic spectra during oxidation of the red-brown form $(Pc^t_2Lu)^+$: *1*, $(Pc^t_2Lu)^+$ (red-brown); *2*, $(Pc^t_2Lu)^{2+}$ (yellow) with admixture of incompletely oxidized $(Pc^t_2Lu)^+$; *3*, continuation of electrolysis at the same potential: $(Pc^t_2Lu)^{2+}$ enters irreversible chemical reactions.

The substantial transformation of the electronic spectrum, which occurs during electrolysis at the potential of the second oxidation wave of Pc^t_2Lu, suggests that the electronic changes in this process are localized on a ligand, because their localization on a metal, *i.e.* the change in its oxidation state should lead to only slight shifts of the absorption bands.[20]

Computer simulations. The Pc_2Y molecule was calculated by the semiempirical ZINDO/1 method[21,22] to reveal the electronic structures of diphthalocyanines and their reduced and oxidized forms. Since the ZINDO/1 method was not parametrized for lanthanides, yttrium, which is close to lanthanides (especially to lutetium) in properties, was taken as the central atom. The Pc_2Y molecule consists of 113 atoms and 371 valence electrons and has 361 atomic orbitals. The structure obtained after the preliminary optimization by the molecular mechanics method is presented in Fig. 3 in two projections. It qualitatively corresponds to the results of the X-ray diffraction study performed for some lanthanide diphthalocyanine complexes [the phthalocyanine rings are nonplanar, the distance between the rings along the line passing through the metal atom is 3.05 Å (*cf.* Refs.: 3.00 Å for Pr,[31], 2.69 Å for Lu,[32] and 2.94 Å for Nd [33])] and to the data obtained using the Hückel method for the lanthanide diphthalocyanine complexes.[26] However, according to our calculations, the twisting angle of the rings relative to one another is only 22.7° (see Fig. 3), rather than 45—38° as obtained[31—33] by the X-ray diffraction study of the Pc_2Ln crystals.

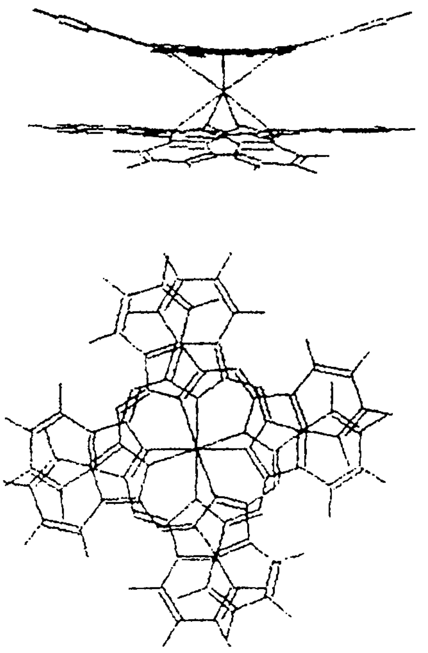

Fig. 3. Structure of the Pc_2Y molecule (in two projections) optimized by the molecular mechanics method.

Table 4. Energies of frontier orbitals and heats of formation of neutral and ionic forms of Pc_2Y, Pc_2YH, and PcH_2 calculated by the ZINDO/1 method

Compound	Charge (q)	e^{HOMO} /eV	e^{LUMO} /eV	$\Delta\Delta_fH^a$/kcal mol^{-1}
Pc_2Y	−4	10.2	15.8	608
	−3	8.5	11.1	364
	−2	5.3	8.4	156
	−1	0.4	6.4	22
	0	−2.7	3.6	0
	1	−4.6	−1.6	48
	2	−7.7	−4.7	144
	3	−14.5	−6.7	310
Pc_2YH	−4	11.3	15.2	643
	−3	7.3	12.8	356
	−2	4.9	8.9	178
	−1	1.2	6.5	45
	0	−2.1	4.8	0
	1	−5.3	0.4	30
	2	−7.7	−4.3	146
	3	−11.5	−6.7	307
PcH_2	−4	12.6	17.0	
	−3	9.3	13.9	
	−2	5.6	10.2	
	−1	1.2	7.4	
	0	−2.9	3.1	
	1	−6.3	−0.5	
	2	−13.3	−5.4	
	3	−16.8	−8.9	
	4	−20.1	−15.5	

[a] $\Delta\Delta_fH$ is the difference between the heats of formation of the complex with charge q and the neutral complex ($q = 0$).

It is of interest that when the Y^{3+} ion is removed and the rings remain at the same distance from one another as in the Pc_2Y complex, optimization of the geometry of the remaining structure leads to planar rings, which are twisted up to an angle of 45°. Thus, it is the central metal ion which determines the geometry and the twist of the rings.

The neutral molecule, mono-, di-, tri-, and tetraanions, and mono-, di-, and trications were calculated. It was assumed that the geometry of the molecule remained unchanged on going to the oxidized and reduced ionic forms. This is evident from the fact that in the cyclic voltammograms of the Lu, Dy, Sm, and Pr complexes studied, all observed redox transitions are reversible, and the distance between the anodic and cathodic peaks has either the theoretical or close to theoretical value (not greater than 100 mV), *i.e.*, structural changes occurring during ionization are not great.

The results of the calculations are presented in Table 4. As the negative charge of the complex increases or the positive charge decreases, the energies of the frontier HOMO ad LUMO orbitals regularly increase, which corresponds to the conclusions of the MO theory.

As should be expected, the heat of formation of the ions increases as the charge increases.

The electron density for the neutral molecule is maximum near the pyrrole N atoms, the spin density is distributed over the both rings, and the pattern of the electrostatic potential corresponds to the "the Y^{3+} cation in the field of eight nitrogen atoms $(8N)^{3-}$" approximation (Fig. 4).

The results of measuring E_p presented in Table 1 show that the effect of lanthanide on the potential of the same redox transition is considerably lower than the difference between the potentials of subsequent redox transitions of the same metal. This is supported by the assumption that the yttrium complex can serve as a model system for analysis of data obtained for lanthanide complexes.

The HOMO energies of $(Pc_2Y)^{n\pm}$ were compared to the standard redox potentials (E^0) of the $Pc^t{}_2Ln$ (Ln = Lu, Dy, Sm, and Pr) lanthanide complexes calculated as the average between the experimental potentials of the direct and reverse peaks of the given redox transitions (see Table 1).

According to Koopmans' theorem, the value of the HOMO energy (taken with the opposite sign) of the next more reduced form with the $+(n-1)$ or $-(n+1)$ charge was accepted as the electron affinity of the particle with the $\pm n$ charge, for example,

$$EA\,(Pc_2Y)^0 \equiv -e^{HOMO}\,(Pc_2Y)^{1-},$$

$$EA\,(Pc_2Y)^{1+} \equiv -e^{HOMO}\,(Pc_2Y)^0.$$

The correlation between the redox potentials of the lanthanide complexes and the calculated HOMO energies of the neutral and ionic $(Pc_2Y)^{n\pm}$ forms are pre-

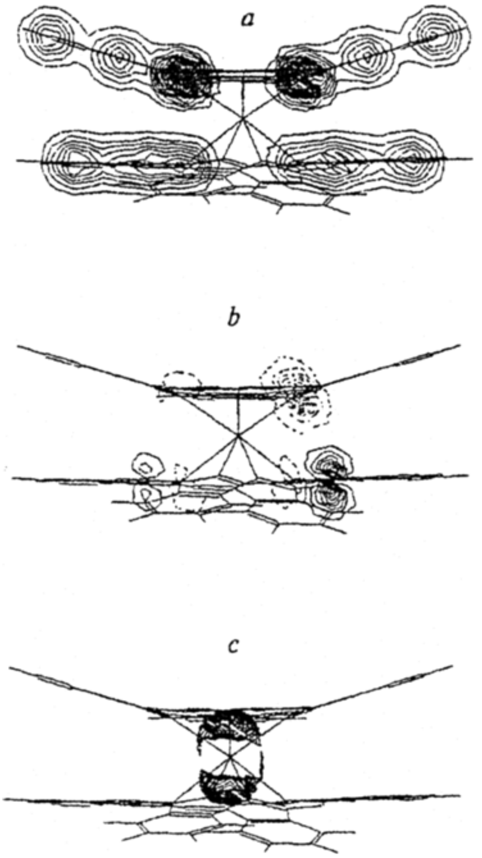

Fig. 4. Electron density (*a*), spin density (*b*) and electrostatic potential of Pc_2Y (*c*) calculated by the ZINDO/1 method.

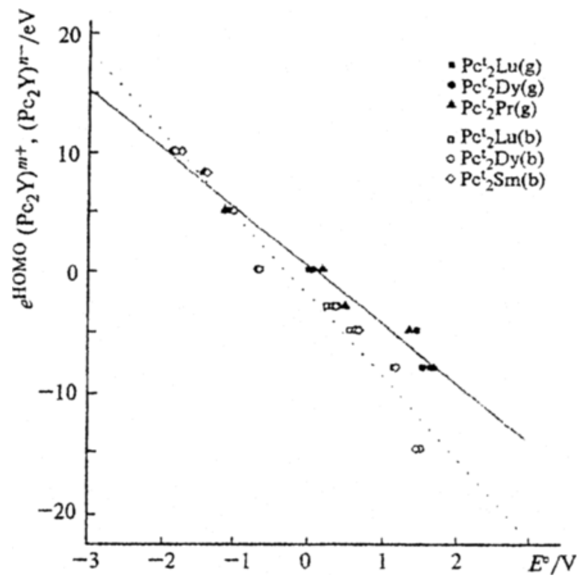

Fig. 5. Correlation between redox potentials of green and blue forms of Pc^t_2Ln and HOMO energies of neutral and ionic forms of $(Pc_2Y)^{m+,n-}$ (m = 0, 1, 2, 3; n = 1, 2, 3, 4) calculated by the ZINDO/1 method. Solid line corresponds to green forms, and the dotted line corresponds to blue forms.

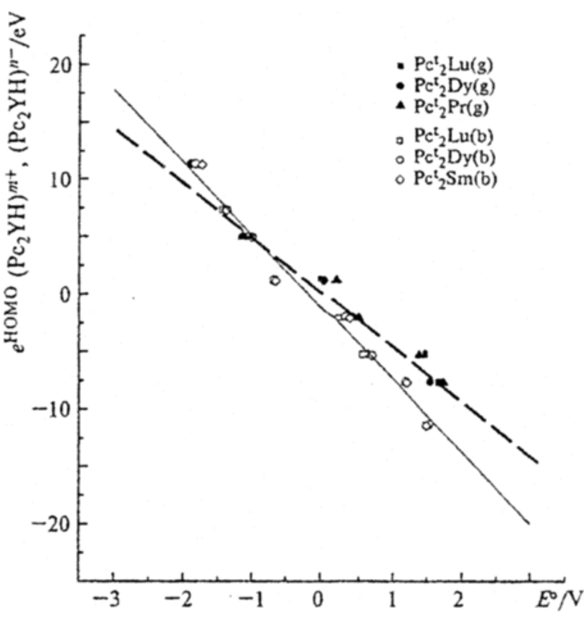

Fig. 6. Correlation between redox potentials of green and blue forms of Pc^t_2Ln and HOMO energies of neutral and ionic forms of $(Pc_2YH)^{m+,n-}$ (m = 0, 1, 2, 3; n = 1, 2, 3, 4) calculated by the ZINDO/1 method. Solid line corresponds to blue forms, and the dotted line corresponds to green forms.

sented in Fig. 5. It is seen that the linear correlation between E^0 and ε^{HOMO} is observed for both the blue and green forms with correlation coefficients of 0.9807 and 0.9873, respectively, but with a steeper slope of the line for the blue form. Thus, the Pc_2Y formula can serve as an approximation for quantum-chemical calculations of both blue and green forms of lanthanide diphthalocyanine complexes.

We also calculated the Pc_2YH yttrium complex (and its ionic forms) containing an additional hydrogen atom bound to one of the pyrrole N atoms; this structure has been proposed previously for the lanthanide diphthalocyanine complexes, (see, *e.g.*, Ref. 18). The correlation between the redox potentials of the lanthanide complexes and calculated HOMO energies of the neutral and ionic $(Pc_2YH)^{n\pm}$ forms presented in Fig. 6 is similar to that presented in Fig. 5. As is seen in Fig. 6, a linear correlation between E^0 and the ε^{HOMO} energy of particles with charge, which is more negative per unit, with correlation coefficients of 0.9917 and 0.9880, respectively, is also observed for the blue and green forms of the complexes.

Thus, the use of the Pc_2Y and Pc_2YH formulas in quantum-chemical calculations does not allow one to distinguish and approximate unambiguously the blue and green forms of Pc^t_2Ln.

Calculations of frontier orbitals of the neutral and ionic forms of Pc_2Y showed that they are mainly localized on the ligands, *i.e.*, the contribution of the d-orbitals

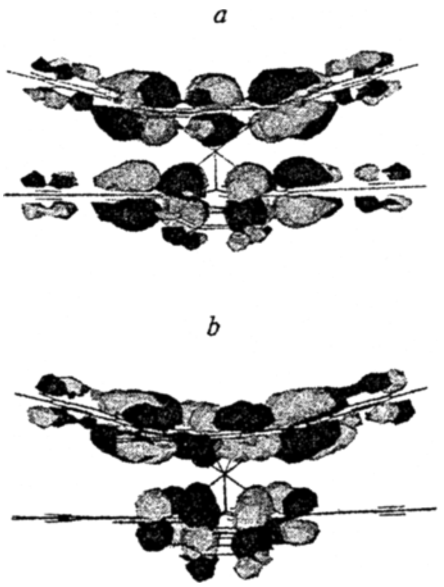

Fig. 7. Frontier orbitals of the anionic $(Pc_2Y)^-$ form calculated by the ZINDO/1 method: HOMO (*a*) and LUMO (*b*).

of a metal is very small. The frontier orbitals of the anionic $(Pc_2Y)^-$ form are shown in Fig. 7. These results are in accordance with the fact that the participation of the ligands was determining for the previously known redox processes of the lanthanide diphthalocyanine complexes[10,14,15,20] and with the data obtained previously for Pc_2Ln using the extended Hückel method.[26]

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