Structure of the blue forms of bisphthalocyanines of rare-earth elements

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Using electron spectroscopy, X-ray photoelectron spectroscopy, and ESR spectroscopy, the blue forms of bisphthalocyanines of rare-earth elements were found to have structures of sandwich-type complexes with isoelectronic phthalocyanine ligands linked with tetravalent metal ions, $[Pc^{2-}Ln^{4+}Pc^{2-}]^0$. A comparative spectral and electrochemical study of the blue and green forms of *tert*-butyl-substituted bisphthalocyanines was carried out for almost the whole series of rare-earth metals. Lutetium octa(perfluoro-*tert*-butyl)- and perchlorobisphthalocyanines were synthesized for the first time.

Key words: bisphthalocyanines, rare-earth elements, synthesis, absorption spectra, ESR, X-ray photoelectron spectroscopy.

In recent years, bisphthalocyanines of rare-earth elements have been intensively studied due to the discovery of their pronounced electrochromic properties.[1—3] These properties, along with their high thermal and chemical stability, enable them to be used in new fields of technology[4—7] as well as in microbiology and medicine.[8—10] However, both the structure of these complexes and their chemical and electrochemical transformations are still subjects of discussion due[11—14] to the variety of their colored forms, whose chemical structures and mutual conversions have not always been determined reliably.

In the mid 60's, Kirin and his collegues were the first to show the possibility of the formation of bisphthalocyanines of rare-earth elements and to propose their sandwich-type structure, HPc_2Lu, with a proton balancing the charge of the macrocycle.[15] Later, Korker *et al.*[16] discovered the radical nature of the so-called green form of lutetium bisphthalocyanine and proposed the structure of the salt of the cation radical $[HPc_2Lu]^{+\cdot}$ with an anion of unknown structure. However, investigations carried out by us did not confirm the presence of a counter-ion in the structure of this complex. This allowed us to propose the structure of a free stable radical, Pc_2Lu, for this compound on the basis of its ESR spectra and electroconductivity data.[17] In subsequent studies we succeeded in proving that this structure of the green form is typical of bisphthalocyanines of many rare-earth elements but not cerium. Nowadays, this structure is generally accepted.

There is no common concept of the structure of the blue form that is formed along with the green form in the syntheses of bisphthalocyanines. In one case, it was described as monophthalocyanine,[18] in other cases as bisphthalocyanines containing a proton to balance the charge of the macrocycle, $GdPc_2H$,[19] despite the fact that it has never been found in the structure of this form. It was also assumed that a binuclear complex with three phthalocyanine ligands, Pc_3Nd_2,[20,21] forms. In all of the structures proposed, the authors considered the oxidation state of the metal to be constant and equal to three.

This work presents the results of a study of the structure of the blue forms of bisphthalocyanines of rare-earth elements.

Previously[22] we have shown that the blue forms, along with the green forms of bisphthalocyanines, are formed in the reaction of 4-*tert*-butylphtalodinitrile with salts of some rare-earth elements. Using TLC, the compounds corresponding to these two forms were isolated in the individual state. According to elementary analysis data, the blue (**A**) and green (**B**) forms have identical chemical compositions corresponding to the structure of the bisphthalocyanine of a rare-earth element (Pc_2Ln). ESR data showed that, unlike the radical-type green forms, the blue forms are diamagnetic over a wide temperature range. It was suggested that the formation of the blue forms of bisphthalocyanines of rare-earth elements results from intramolecular transfer of an electron from a metal to the ligand in the green forms. In our opinion, this process leads to the formation of a structure with isoelectronic phthalocyanine ligands linked with the tetravalent metal ion.

$[Pc^{2-}Ln^{4+}Pc^{2-}]^0$ $[Pc^{-\cdot}Ln^{3+}Pc^{2-}]^0$

A **B**

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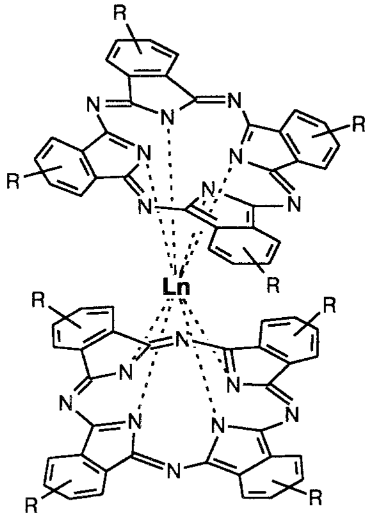


Pc^t_2Ln (R = Bu^t)

Actually, cerium bisphthalocyanine, in which the tetravalent state of the metal is more typical than for other rare-earth metals, exists only as diamagnetic blue form **A**. On the other hand, we failed to isolate the blue form in the case of lanthanum, which has only three valence electrons.

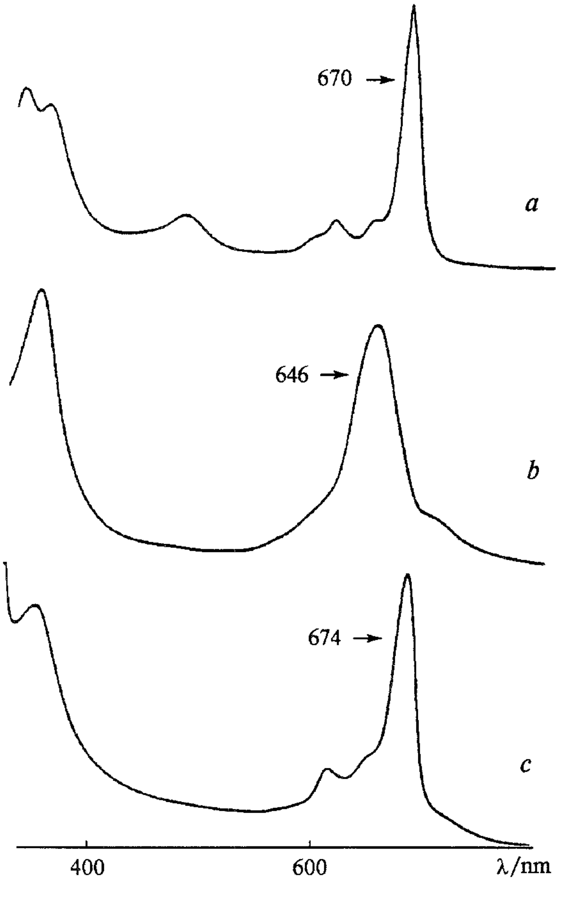


Fig. 1. Absorption spectra of dysprosium mono- and bisphthalocyanines in toluene: *a*, the green form of Pc^t_2Dy; *b*, the blue form of Pc^t_2Dy; *c*, Pc^t_2DyCl.

The electronic absorption spectra of these forms are in agreement with the structure proposed and differ substantially from monophthalocyanine. As an example, Fig. 1 shows the absorption spectra of dysprosium mono- and bisphthalocyanines.

A distinct difference between the absorption spectra of the three types of complexes under discussion can be seen in Fig. 1. These types of complexes were obtained by us for practically all of the *tert*-butyl-substituted phthalocyanines of rare-earth elements (Pc^tLn). The electronic spectra of all of the types of complexes are in good agreement with their structure. The absorption spectra of monophthalocyanines can be characterized by one main long-wave absorption maximum around 670 nm and a less intense vibrational satellite at 610 nm. The forms of the absorption spectra of bisphthalocyanines are determined by the state of the chromophores of the two ligands and by the existence or absence of resonance

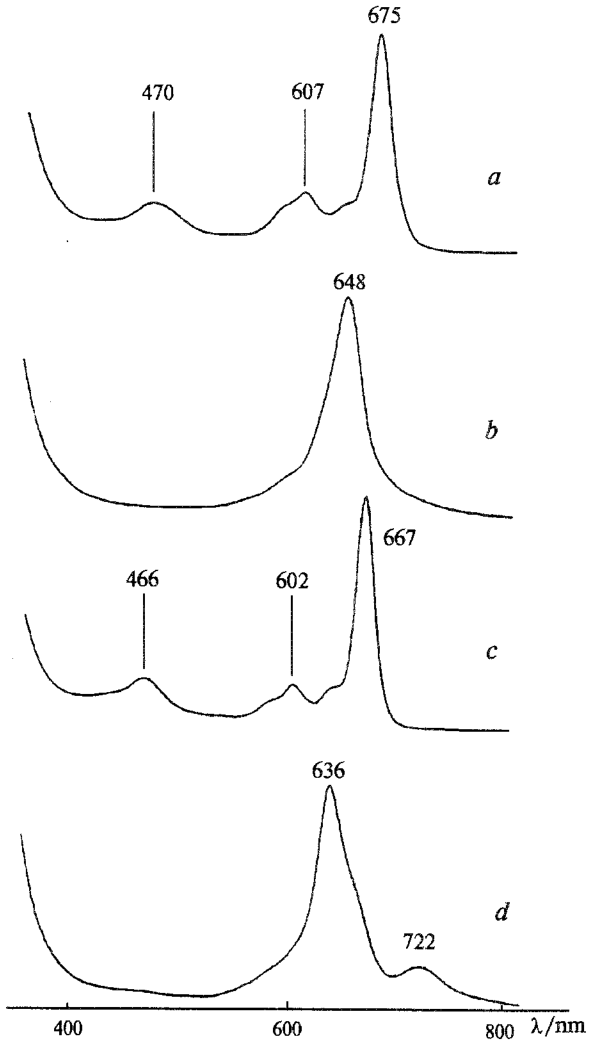
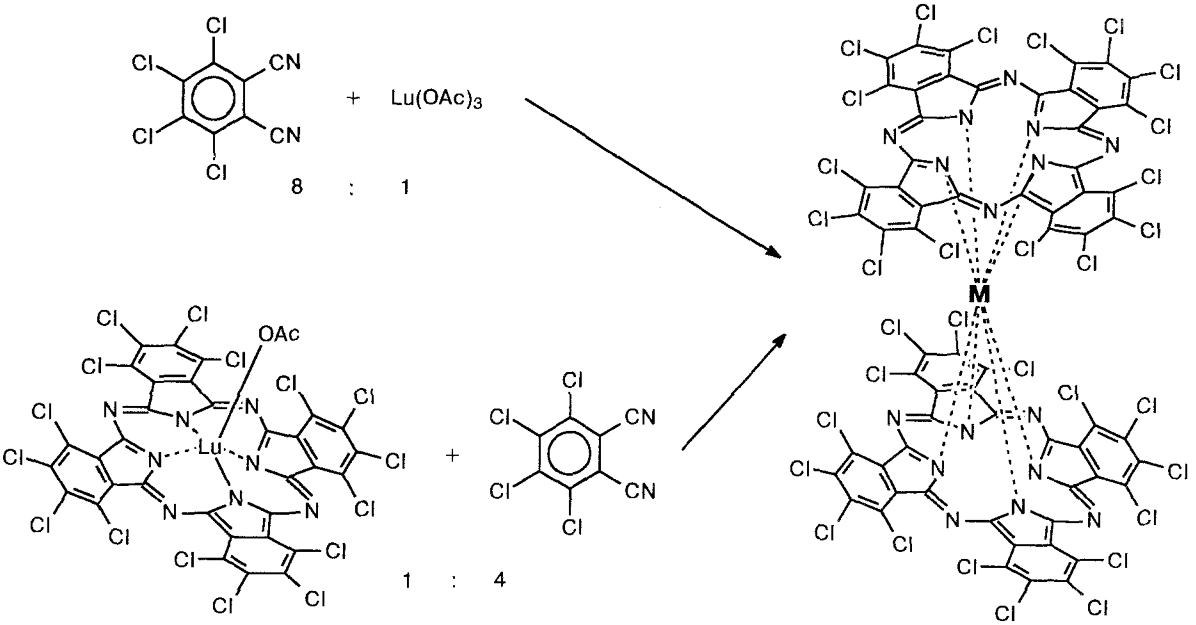


Fig. 2. Absorption spectra of neodymium and lutetium bisphthalocyanines in toluene: *a*, the green form of Pc^t_2Nd; *b*, the blue form of Pc^t_2Nd; *c*, the green form of Pc^t_2Lu; *d*, the blue form of Pc^t_2Lu.

Scheme 1



interaction between them. The absorption spectra of the blue form, which consists, in our opinion, of equivalent phthalocyanine rings $[Pc^{2-}Ln^{4+}Pc^{2-}]$ reflect resonance dipole-dipole interaction between the chromophores, which results in splitting of the Q band into two components, Q^1 and Q^2. The splitting is larger when the rings are closer to each other, *i.e.*, when the radius of the central ion is smaller. On the contrary, an increase in the ionic radius draws the bands together, gradually transforming the long-wave band at 700 nm, typical of bisphthalocyanines of Lu, Yb, Tm, and Eu, into a shoulder (Ho, Dy, Tb, Gd) and, finally, causing it to disappear completely in the case of Eu, Sm, Nd, Pr, and Ce. As an example, Fig. 1 and 2 show the absorption spectra of the blue and green forms of the bisphthalocyanines of dysprosium, neodymium, and lutetium, which are representative of the three types of spectra.

Thus, the electronic absorption spectra of the blue forms of bisphthalocyanines of rare-earth elements are also in agreement with the proposed structure. In addition, structure **A** is supported by the similarity of the electronic absorption spectra of the blue forms of $Pc^t{}_2Ln$ to the spectra of the intentionally synthesized bisphthalocyanines of Hf and Zr,[23] in which the metal is undoubtedly in the tetravalent state.

The absorption spectra of the green forms of bisphthalocyanines $[Pc^{\cdot -}Ln^{3+}Pc^{2-}]^0$, which contain both a dianion of phthalocyanine and its radical form, display a Q band around 670 nm typical of Pc^{2-} and a band around 460—480 nm, which results from the existence of the radical fragment, $Pc^{\cdot -}$, in the molecule. The absorption spectra of this form indicate the absence of resonance interaction between the ligands. The absorption of ligands is observed in different parts of the spectra, and splitting of the Q band does not occur.

It was reasonable to assume that if the conversion of the green form into the blue form results from intramolecular transfer of an electron from the metal to the ligand, then the introduction of electron-withdrawing substituents to the macrocycle molecule should favor this conversion and, therefore, lead to the formation of the blue form. In fact, the blue form of octaperfluoro-*tert*-butylbisphthalocyanines of rare-earth elements can readily be obtained in a pure state without an admixture of the green form even in the case of lutetium, which seems to be unable to form the blue form. A similar form is obtained in the synthesis of lutetium perchlorobisphthalocyanine. The synthesis was carried out by fusion of the corresponding phthalonitrile with a salt of a rare-earth element at 290—300 °C for 2—3 h.

It should be noted that the same compound can be obtained by fusion of the previously synthesized lutecium hexadecachlorophthalocyanine with perchlorophthalodinitrile (Scheme 1).

As expected, the lanthanum compounds, in which the metal has only three valence electrons, do not form structure **A** even under drastic conditions (>300 °C). The results obtained provide fairly strong, although indirect, evidence of the validity of our hypothesis.

The preparation of the blue and green forms of bisphthalocyanines for practically the entire set of rare-earth elements allowed us to carry out the first comparative spectral and electrochemical study of them. When the potential is shifted in the anodic direction, the curves of the blue forms show two reversible one-electron waves, and the electroactivated forms obtained in a potentiostatic mode are individual, as in the case with

Table 1. Data of spectral and electrochemical studies of the green forms of bisphthalocyanines of rare-earth elements in *o*-dichlorobenzene; the concentration was $2 \cdot 10^{-4}$ mol L^{-1}, with $(C_4H_9)_4NClO_4$ (0.2 mol L^{-1}) as the reference electrolyte

Ln	Pc^t_2Ln (green form)	$Pc^t_2Ln + e \rightarrow$ blue form		$[Pc^t_2Ln]^{+\cdot} - e \rightarrow$ red form	
	λ (logε)	$\varphi_{p.c.}$/V [a]	λ (logε)	$\varphi_{p.a.}$/V [b]	λ (logε)
La	686 (4.80), 646 (4.63), 462 (4.12), 318 (4.90)	0.18	686sh (4.42), 646 (5.01), 340 (5.05)	0.63	728 (4.45), 512 (4.50), 328 (5.07)
Pr	682 (4.82), 644 (4.69), 610 (4.34), 480 (4.15), 324 (4.94)	0.15	682sh (4.47), 644 (5.05), 334 (5.03)	0.60	726 (4.47), 498 (4.52), 324 (5.24)
Nd	682 (4.80), 646 (4.59), 612 (4.31), 480 (4.22), 348 (4.51), 324 (4.67)	0.14	682sh (4.67), 646 (5.02), 336 (4.84)	0.59	726 (4.50), 504 (4.61), 359 (4.55), 320 (4.59)
Sm	679 (4.86), 644 (4.60), 502 (4.16), 340 (5.02), 330 (5.04)	0.09	680sh (4.61), 644 (5.03), 340 (5.01)	0.54	718 (4.49), 498 (4.67), 354 (4.91), 320 (4.96)
Gd	674 (5.29), 644sh (4.61), 604 (4.64), 478 (4.72), 340 (5.15), 320 (5.15)	0.02	674sh (5.06), 634 (5.24), 330 (5.25)	0.47	712 (4.77), 496 (4.90), 362 (5.08), 320 (5.12)
Dy	672 (5.19), 642sh (4.60), 603 (4.55), 478 (4.72), 340 (4.91), 320 (4.97)	0.05	672sh (5.01), 632 (5.14), 334 (5.15)	0.53	706 (4.60), 492 (4.72), 358 (4.87), 320 (4.92)
Er	666 (5.05), 638sh (4.26), 600 (4.35), 464 (4.54), 342 (4.82), 318 (4.87)	0.04	696 (4.58), 626 (4.94), 333 (4.96)	0.52	702 (4.47), 486 (4.54), 352 (4.78), 318 (4.87)
Yb	664 (5.17), 636sh (4.40), 599 (4.20), 464 (4.52), 342 (4.88), 322 (4.90)	0.03	702 (4.65), 624 (5.08), 334 (5.02)	0.50	700 (4.60), 484 (4.62), 351 (4.84), 322 (4.91)
Lu	662 (5.21), 634sh (4.57), 599 (4.20), 462 (4.49), 342 (4.99), 328 (5.02)	0.02	706 (4.73), 622 (5.10), 335 (5.08)	0.48	696 (4.69), 482 (4.70), 351 (4.91), 328 (4.96)

[a] Potential of cathodic current peak. [b] Potential of anodic current peak.

the green forms. The starting complex is recovered completely when they are reduced.

$$[Pc^{2-}Ln^{4+}Pc^{2-}]^0 \overset{-e}{\rightleftharpoons} [Pc^{2-}Ln^{4+}Pc^{\bar{\cdot}}]^+ \overset{-e}{\rightleftharpoons} [Pc^{\bar{\cdot}}Ln^{4+}Pc^{\bar{\cdot}}]^{2+}$$

The results of the spectral and electrochemical studies of the green and blue forms of octa-*tert*-butylbisphthalocyanines of rare-earth elements presented in Tables 1 and 2 indicate a significant shift of the oxidation and reduction potentials into the anodic region for the blue forms as compared with the green forms (Fig. 3).

The potentials of the transition of the blue forms into cation radicals and then into dications are close to those of bisphthalocyanines of tetravalent hafnium and zirconium obtained by us.[23] This also supports the notion that the central metal ions in the blue forms of bisphthalocyanines of rare-earth elements are in the tetravalent state.

Finally, the X-ray photoelectron spectroscopy data confirmed the validity of the proposed hypothesis about the possibility of intramolecular transfer of an electron from the metal to the ligand accompanied by a change in the valent state of the ion of the rare-earth element.

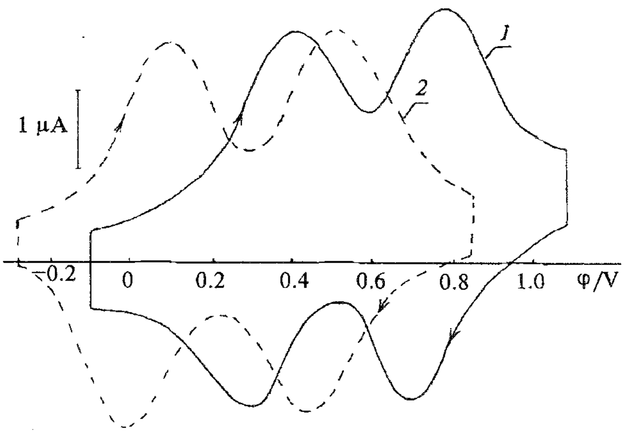


Fig. 3. Potentiodynamic curves of blue (*1*) and green (*2*) initial forms of Pc^t_2Yb in *o*-dichlorobenzene on an Au electrode.

The X-ray photoelectron spectra of Lu4d and N1s show that E_b of the Lu4d and N1s bands change inversely when passing from the blue forms of Pc^t_2Lu to the green forms, while the half widths (HW) of the Lu4d and N1s bands remain constant. The calculated atomic ratio of Lu to N is consistent with elementary analysis data (Table 3). The data obtained suggest the existence of a larger positive charge on the metal atom and a larger negative charge on the nitrogen atoms in the blue form of Pc^t_2Lu than the green form.

Thus, the evidence that the blue form of bisphthalocyanines of rare-earth elements is an isomer of the green form with isoelectronic phthalocyanine ligands and a tetravalent metal ion ($Pc^{2-}Ln^{4+}Pc^{2-}$) seems to be fairly convincing.

Experimental

Electronic absorption spectra in the visible and UV regions were obtained on SF-4A and Hitachi-356 spectrophotometers in quartz rectangular cells 0.1—10.0 mm width. The concentra-

Table 2. Results of spectral and electrochemical studies of the blue forms of bisphthalocyanines of rare-earth elements in *o*-dichlorobenzene; the concentration was $2 \cdot 10^{-4}$ mol L^{-1}, with $(C_4H_9)_4NClO_4$ (0.2 mol L^{-1}) as the reference electrolyte

Ln	Pc^t_2Ln (blue form)	$Pc^t_2Ln - e \rightarrow$ green form		$[Pc^t_2Ln]^{+\cdot} - e \rightarrow$ red form	
	λ (logε)	$\varphi^1_{p.a.}/V$ [a]	λ (logε)	$\varphi^2_{p.a.}/V$ [a]	λ (logε)
Ce	646 (4.96), 340 (4.85)	0.59	695 (4.82), 626 (4.55), 498 (4.39) 344 (4.85), 322 (4.87)	1.11	748 (4.21), 520 (4.55), 358 (4.80), 320 (4.82)
Pr	646 (4.92), 340 (4,64)	0.62	686 (4.68), 496 (4.06), 322 (4.62)	0.93	728 (4.50), 508 (4.72), 350 (4.83), 322 (4.85)
Nd	644 (4.96), 340 (4.82)	0.61	684 (4.70), 482 (4.07), 324 (4.64)	0.91	726 (4.20), 504 (4.43), 348 (4.51), 320 (4.57)
Sm	645 (4.93), 338 (4.89)	0.56	680 (4.86), 490 (4.29), 330 (4.72)	0.87	718 (4.51), 504 (4.70), 346 (4.82), 324 (4.84)
Eu	644 (4.73), 342 (4.69)	0.52	678 (4.56), 496 (4.04), 336 (4.59)	0.85	716 (4.34), 520 (4.19), 338 (4.53), 320 (4.58)
Tb	690sh (4.37), 643 (4.87), 340 (4.82)	0.50	676 (4.92), 492 (4.12), 342 (4.80)	0.84	712 (4.67), 518 (4.31), 350 (4.68), 322 (4.69)
Dy	692sh (4.30), 642 (4.82), 340 (4.78)	0.46	674 (4.90), 492 (4.14), 342 (4.82)	0.82	710 (4.65), 518 (4.30), 346 (4.70), 324 (4.58)
Ho	701sh (4.19), 640 (4.95), 342 (4.92)	0.44	674 (4.97), 490 (4.07), 342 (4.84)	0.79	712 (4.69), 520 (4.27), 350 (4.65), 326 (4.67)
Er	704 (4.17), 638 (4.92), 340 (4.87)	0.42	673 (4.92), 488 (4.12), 342 (4.82)	0.78	708 (4.69), 516 (4.31), 347 (4.65), 324 (4.62)
Yb	711 (4.07), 635 (4.90), 340 (4.80)	0.41	673 (4.93), 482 (4.20), 342 (4.76)	0.77	704 (4.62), 512 (4.32), 346 (4.72), 324 (4.68)
Lu	714 (4.05), 634 (4.84), 340 (4.81)	0.41	672 (4.89), 480 (4.18), 340 (4.77)	0.76	702 (4.67), 502 (4.33), 344 (4.72), 322 (4.71)

[a] Potential of anodic current peak.

Table 3. X-ray photoelectron spectroscopy data of Pc^t_2Ln

Sample	E_b/eV			HW*/eV		N/Lu
	$Lu4d_{3/2}$	$Lu4d_{5/2}$	N1s	$Lu4d_{5/2}$	N1s	
Blue form	207.1	195.9	397.4	4.4	1.75	19.3
Green form	206.2	194.7	398.4	4.3	1.70	15.5

* HW is the width of the band at half of its height.

tions of the solutions were between $5 \cdot 10^{-5}$ and $5 \cdot 10^{-6}$ mol L^{-1}.

ESR spectra were recorded on Radiopan SE/X-2542 (Poland) and Jeol IES ME-3X (Japan) spectrometers. Samples for ESR spectroscopy were withdrawn in an inert atmosphere at the temperature of liquid nitrogen. The stable DPPH radical was used as the standard. Freshly prepared evacuated solutions with known concentrations of the free radical, 2,2,6,6-tetramethylpiperidyl-*N*-oxyl in benzene or *o*-dichlorobenzene were used as standards for quantitative determinations.

X-ray photoelectron spectra were obtained on an AEI ES-200B spectrometer according to the reported procedure.[24] The Al K_α band ($h\nu$ = 1486.6 eV) was used as the source of X-ray irradiation. The spectra were recorded *in vacuo* at $\leq 10^{-7}$ Torr. The band from the adsorbed hydrocarbons of the diffusion oil, C1s (E_b = 285.0 eV), was used as the standard. The accuracy of bond energy measurements was ±0.2 eV. The N/Lu atomic ratio (±20 rel.%) was calculated from the ratio of the integral intensities of the bands taking into account the cross-section of photoionization and the transmission coefficients of the analyzer for electrons with various kinetic energies.

Electrochemical measurements were carried out in the usual three-electrode cells. Polarization curves in the potentiostatic mode were recorded on a P-5827M potentiostat. A gold sheet and an optically transparent In_2O_3 electrode served as working electrodes. The concentrations of the chromatographically pure complexes used were between $1 \cdot 10^{-4}$ and $5 \cdot 10^{-4}$ mol L^{-1}. The tetrabutylammonium perchlorate used as the background electrolyte was purified by double recrystallization from ethanol followed by drying at a reduced pressure.[25] The *o*-dichlorobenzene used as a solvent for spectral and electrochemical studies was also purified according to the reported procedure.[25] The potentials are given with reference to a silver chloride electrode. The oxidized and reduced forms were accumulated during the potentiostatic electrolysis of solutions of the complexes in a stream of helium on a large-square gold grid.

The blue and green forms of octa-*tert*-butylbisphthalocyanines of Ce, Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, Yb, and Lu were prepared according to the procedure previously proposed by us.[26] The electronic absorption spectra of these complexes along with the products of their one- and two-electron oxidation are presented in Tables 1 and 2.

Lutetium octa(perfluoro-*tert*-butyl)bisphthalocyanine (Pc^f_2Lu) was obtained by fusing lutecium acetate with 4-perfluoro-*tert*-butylphtalodinitrile for 1 h. Purification was carried out in a Soxlett apparatus with refluxing benzene, acetone, and heptane followed by storage *in vacuo* at 150 °C

(5 Torr). The compound was isolated as a blue powder. Found (%): C, 39.64; H, 1.12; N, 7.87. $C_{96}H_{24}F_{72}LuN_{16}$. Calculated (%): C, 39.16; H, 0.82; N, 7.61.

Lutetium perchlorobisphthalocyanine ($\mathrm{Pc^{Cl}{}_2Lu}$) was obtained by fusing lutetium acetate with tetrachlorophthalonitrile for 2 h. Purification was carried out in a Soxlett apparatus with refluxing benzene, acetone, and heptane followed by reprecipitation from H_2SO_4 and storage *in vacuo* at 150 °C (5 Torr). The compound was isolated as a blue powder. Found (%): C, 33.46; Cl, 48.92; N, 9.82. $C_{64}Cl_{32}LuN_{16}$. Calculated (%): C, 33.39; Cl, 49.28; N, 9.73.

This compound was also obtained by fusing lutetium hexadecachlorophthalocyanine, previously synthesized and characterized by elementary analysis and electronic absorption spectra, with excess tetrachlorophthalonitrile for 1 h. Purification was carried out as described above.

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References

1. P. N. Moskalev and I. S. Kirin, *Zh. Fiz. Khim.*, 1972, **46**, 1771 [*Russ. J. Phys. Chem.*, 1972, **46** (Engl. Transl.)].
2. D. Walton, B. Ely, and G. Elliott, *J. Electrochem. Soc.*, 1981, **128**, 2479.
3. D. J. Moore and T. F. Guarr, *J. Electroanal. Chem.*, 1991, **314**, 313.
4. M. Bouvet and J. Simon, *Chem. Phys. Letters*, 1990, **172**, 299.
5. P. Turek, P. Petit, J. Andre, J. Simon, R. Even, B. Boudjema, G. Guillaud, and M. Maitrot, *Mol. Crys. Liq. Crys. Bulletin*, 1988, **3**, 289.
7. C. Clarisse and M. T. Riou, *J. Appl. Phys.*, 1991, **69**, 3324.
8. M. I. Gaiduk, V. V. Grigor'yants, V. D. Menenkov, A. F. Mironov, V. D. Rumyantseva, and G. M. Sukhin, *Izv. Akad. Nauk SSSR, Ser. Fiz.*, 1990, **54**, 1904 [*Bull. Acad. Sci. USSR, Div. Phys. Sci.*, 1990, **54** (Engl. Transl.)].
9. N. Brasseur, H. Ali, R. Langlois, J. R. Wagner, J. Rousseau, and J. van Lier, *Photochem. and Photobiol.*, 1987, **45**, 581.
10. A. F. Mironov, *Itogi nauki i tekhniki. Ser. Sovr. probl. lazernoi fiziki* (*Advances in Science and Technology, Modern Problems of Laser Physics*), 1990, **3**, 5 (in Russian).
11. H. Konami and M. Hatano, *Chem. Phys. Lett.*, 1989, **160**, 163.
12. C. Piechocki and J. Simon, *Chem. Phys. Lett.*, 1985, **122**, 124.
13. F. Costaneda and V. Plichon, *J. Electroanal. Chem.* 1987, **236**, 163.
14. R. B. Daniels, J. Peterson, W. C. Porter, and Q. D. Wilson, *J. Coord. Chem.*, 1993, **30**, 357.
15 I. S. Kirin, P. N. Moskalev, and Yu. A. Makashev, *Zh. Neorg. Khim.*, 1965, **10**, 1951 [*J. Inorg. Chem. USSR*, 1965, **10** (Engl. Transl.)].
16. G. A. Corker, B. Grant, and N. J. Clecak, *J. Electrochem. Soc.*, 1979, **126**, 1339.
17. L. G. Tomilova, E. V. Chernykh, V. I. Gavrilov, I. V. Shelepin, V. M. Derkacheva, and E. A. Luk'yanets, *Zh. Obshch. Khim.*, 1982, **52**, 2606 [*J. Gen. Chem. USSR*, 1982, **52** (Engl. Transl.)].
18. S. Misumi and K. Kasuga, *Nippon Kagaku Zasshi*, 1971, **92**, 335.
19. A. G. Mackay, J. F. Boas, and G. J. Jroup, *Aust. J. Chem.* 1974, **27**, 955.
20. I. S. Kirin, P. N. Moskalev, and Yu. A. Makashev, *Zh. Neorg. Khim.*, 1967, **12**, 707 [*J. Inorg. Chem. USSR*, 1967, **12** (Engl. Transl.)].
21. I. S. Kirin, P. N. Moskalev, and N. V. Ivannikova, *Zh. Neorg. Khim.*, 1967, **12**, 944 [*J. Inorg. Chem. USSR*, 1967, **12** (Engl. Transl.)].
22. L. G. Tomilova, E. V. Chernykh, N. T. Ioffe, and E. A. Luk'yanets, *Zh. Obshch. Khim.*, 1983, **53**, 2594 [*J. Gen. Chem. USSR*, 1983, **53** (Engl. Transl.)].
23. L. G. Tomilova, N. A. Ovchinnikova, and E. A. Luk'yanets, *Zh. Obshch. Khim.*, 1987, **57**, 2100 [*J. Gen. Chem. USSR*, 1987, **57** (Engl. Transl.)].
24. Kh. M. Minachev and E. S. Shpiro, *The Catalyst Surface: Physical Methods of Analysis*, CRC Press, Boston, 1990, 375 pp.
25. V. I. Gavrilov, L. G. Tomilova, I. V. Shelepin, and E. A. Luk'yanets, *Elektrokhimiya*, 1979, **15**, 1058 [*Electrochemistry*, 1979, **15** (Engl. Transl.)].
26. L. G. Tomilova, E. V. Chernykh, and E. A. Luk'yanets, *Zh. Obshch. Khim.*, 1985, **55**, 2631 [*J. Gen. Chem. USSR*, 1985, **55** (Engl. Transl.)].

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