Correlations between electrochemical and spectral properties of alkyl-substituted diphthalocyanine lanthanide complexes

I. V. Zhukov,[a]★ V. E. Pushkarev,[a] L. G. Tomilova,[b] and N. S. Zefirov[a]

[a]Institute of Physiologically Active Compounds, Russian Academy of Sciences,
1 Severnyi proezd, 142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (095) 939 0290. E-mail: maxone@org.chem.msu.ru
[b]Department of Chemistry, M. V. Lomonosov Moscow State University,
1 Leninskie Gory, 119992 Moscow, Russian Federation.
Fax: +7 (095) 939 0290. E-mail: tom@org.chem.msu.su

The electrochemical behavior and spectral properties of a series of symmetrical 2,3,9,10,16,17,23,24,2´,3´,9´,10´,16´,17´,23´,24´-hexadecaalkyl-substituted lanthanide complexes $(R_8Pc)_2Ln$ (R = H, Me, Et, Bu^n; Ln = Eu, Dy, Lu) were studied. Regularities of changing the parameters under study were established, depending on the nature of lanthanide and substituents in the phthalocyanine macroligands. The position of the intervalence band of the complexes in the near-IR region depends on the effective distance between the macroligands and also on the electronic effect of the substituents. Correlations between the electrochemical and spectral properties of the complexes were found.

Key words: diphthalocyanine complexes, lanthanides, electrochemistry, redox transitions, electronic absorption spectra.

Practical use of lanthanide diphthalocyanine complexes is largely due to their unique redox properties.[1] Modification of the complex structure makes it possible to vary their electrochemical behavior[2] and, therefore, it seems important to study a "structure—property" relationship. It has previously been shown[3] that the nature of the central metal ion is a structural factor which determines the properties of diphthalocyanine complexes, because it specifies a certain distance and, correspondingly, the degree of π—π-interaction of two phthalocyanine macroligands. The nature of substituents in the phthalocyanine macrocycles also exerts a substantial effect on the properties of the diphthalocyanine complexes. The earlier works studied the influence of the strongly different substituents on the potentials of redox transitions for both the mono-[4] and diphthalocyanine complexes.[2] The sums of the Hammett constants of the substituents were used as quantitative characteristics describing the substituent effect. However, the properties of the diphthalocyanine complexes containing substituents similar in nature have not virtually been studied up to recently. Such complexes are exemplified by diphthalocyanines containing, in particular, substituents with different carbon chain lengths.

The purpose of this work is to study the electrochemical and spectral properties of symmetrical 2,3,9,10,16,17,23,24,2´,3´,9´,10´,16´,17´,23´,24´-hexadecaalkyl-substituted lanthanide diphthalocyanine complexes $(R_8Pc)_2Ln$ (R = Me, Et, Bu^n; Ln = Eu, Dy, Lu) and a change in the corresponding parameters, depending on the complexing lanthanide and substituents in phthalocyanine macroligands.

Results and Discussion

The electrochemical behavior of the complexes was studied by cyclic voltammetry (CV) on a graphite working electrode. The CV curve of the hexadecabutyl-substituted europium complex is presented in Fig. 1. Five redox transitions of the complexes under study are observed in the potential region accessible for measurements: two transitions in the oxidation region (*1* and *2*) and three transitions in the reduction region (*3*, *4*, and *5*). Their potentials for different complexes are presented in Table 1. The

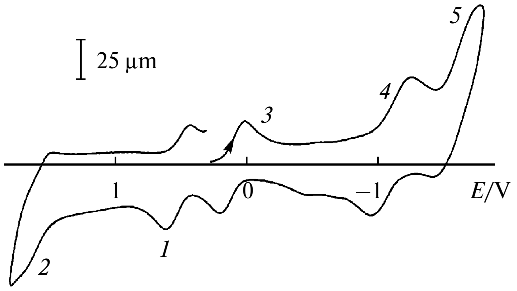


Fig. 1. Cyclic voltammogram of $(Bu^n{}_8Pc)_2Eu$ (graphite electrode, *o*-DCB; 0.15 *M* $Bu^n{}_4NBF_4$; Ag|AgCl; v = 200 mV s^{-1}; 20 °C).

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 184—189, January, 2005.

Table 1. Potentials of the redox transitions for the symmetrical alkyl-substituted lanthanide diphthalocyanine complexes[a]

Complex	R^{3+}/Å	$E_{1/2}{}^b$/V				
		Oxidation		Reduction		
		1	*2*	*3*	*4*	*5*
$(Bu^n{}_8Pc)_2Eu$	1.13	0.50	1.53	0.11	−1.06	−1.53
$(Bu^n{}_8Pc)_2Dy$	1.07	0.48	1.58	0.07	−1.06	−1.53
$(Bu^n{}_8Pc)_2Lu$	0.99	0.44	1.64	0.01	−1.08	−1.54
$(Et_8Pc)_2Lu$	0.99	0.43	1.63	0.01	−1.08	−1.54
$(Me_8Pc)_2Lu$	0.99	0.45	1.63	0.04	−1.08	−1.50
Pc_2Lu[c]	0.99	0.53	1.64	0.13	−1.02	−1.37

[a] Graphite electrode; *o*-DCB; 0.15 *M* $Bu^n{}_4NBF_4$; Ag|AgCl; $v = 200$ mV s^{-1}; 20 °C.

[b] Arithmetic mean of the forward and reverse peaks. The measurement accuracy is ±0.005 V.

[c] *o*-DCB : MeCN = 1 : 1; Pt electrode.[2]

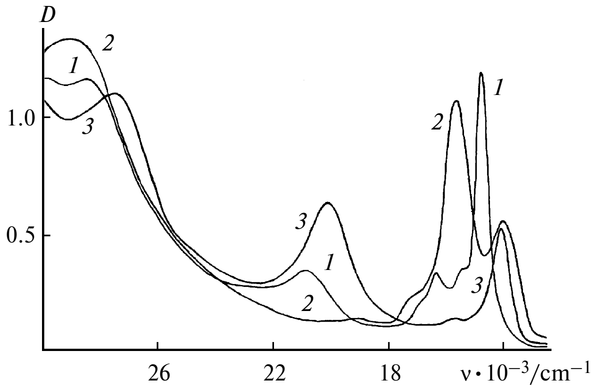
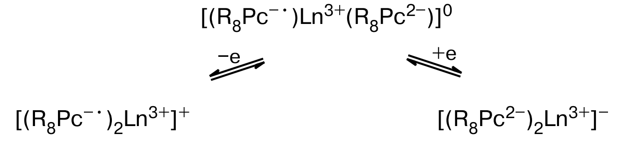


Fig. 2. Electronic absorption spectra of the neutral (*1*), reduced (*2*), and oxidized (*3*) forms of $(Bu^n{}_8Pc)_2Lu$ generated at potentials of −0.6 and +1.0 V (*vs.* Ag|AgCl) at the Pt electrode in *o*-DCB against 0.15 *M* $Bu^n{}_4NBF_4$.

redox transitions of the complexes under study are electrochemically quasi-reversible: for them the potential differences between the forward and reverse peaks in the CV curve lie within 60—130 mV. The exceptions are the second reduction process of the ethyl- and butyl-substituted complexes. The differences of the potentials between the forward and reverse peaks for these processes achieve 220 mV.

It is known[1] that the redox transitions of the diphthalocyanine complexes are accompanied by a substantial change in their electronic absorption spectra (EAS). We determined the spectral characteristics of both the complexes and their first redox forms in *o*-dichlorobenzene (Table 2). The character of the EAS of the redox forms of the complexes under study (Fig. 2) is typical of the lanthanide diphthalocyanine complexes[1,2] and indicates that one electron is involved in the first redox processes with localization of electronic changes on the phthalocyanine macrocycles[3,5—7] (Scheme 1).

Scheme 1



R = H, Me, Et, Bu^n; Ln = Eu, Dy, Lu

The nature of the central metal atom is an important structural factor affecting the electrochemical and spectral properties of the lanthanide diphthalocyanine complexes. It has previously[3] been shown that the arrangement of molecular orbitals (MOs) in the lanthanide diphthalocyanine complexes, which determines their electrochemical behavior, can be considered to a rather well approximation as a result of the interaction of the MOs of the phthalocyanine macroligands. In this case, the role of the metal ion is reduced, to a considerable extent, to the specification of a certain distance between the ligands. In fact, when the lanthanide ion radius decreases, the π—π-interaction of the macroligands increases, thus increasing the splitting of their frontier orbitals (Fig. 3). The energy of the a_2 MO of the complex, which determines

Table 2. Maxima of the electronic absorption spectra for the neutral, oxidized, and reduced forms of the symmetrical alkyl-substituted lanthanide diphthalocyanine complexes in *o*-DCB

Complex	λ_{max}*/nm		
	$(^xPc_2Ln)^+$	$(^xPc_2Ln)^0$	$(^xPc_2Ln)^-$
$(Bu^n{}_8Pc)_2Eu$	$\underline{366}$; 507; 648; 732	$\underline{357}$; 494; 602 sh; 617; 661 sh; $\underline{691}$	$\underline{347}$; 548; 587 sh; $\underline{651}$; 698 sh
$(Bu^n{}_8Pc)_2Dy$	$\underline{365}$; 504; 644; 721	$\underline{355}$; 489; 595 sh; 614; 652 sh; $\underline{684}$	$\underline{345}$; 539; 585 sh; $\underline{646}$; 707 sh
$(Bu^n{}_8Pc)_2Lu$	$\underline{361}$; 494; 636; 709	$\underline{351}$; 478; 585 sh; 608; 644 sh; $\underline{674}$	$\underline{345}$; 530; 578 sh; $\underline{637}$; 711
$(Et_8Pc)_2Lu$	$\underline{361}$; 493; 636; 707	$\underline{351}$; 479; 584 sh; 606; 644; $\underline{673}$	$\underline{344}$; 521; 575 sh; $\underline{632}$; 712
$(Me_8Pc)_2Lu$	$\underline{359}$; 493; 636; 704	$\underline{350}$; 473; 583 sh; 606; 641 sh; $\underline{672}$	$\underline{343}$; 575 sh; $\underline{632}$; 702
Pc_2Lu	$\underline{358}$; 487; 699	$\underline{344}$; 459; 576 sh; 596; 633 sh; $\underline{660}$	$\underline{336}$; 563 sh; $\underline{618}$; 702

* The most intense absorption bands are underlined.

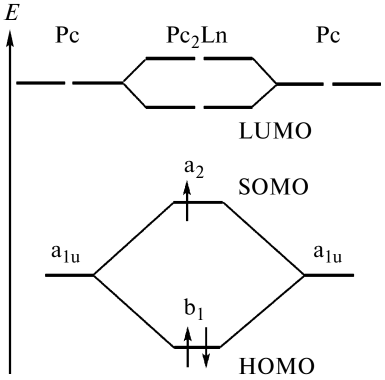


Fig. 3. Schematic correlation diagram of molecular orbitals of Pc_2Ln.

the first oxidation and reduction processes, increases and, correspondingly, the energy of the next occupied b_1 MO responsible for deeper oxidation processes decreases.[3] The influence of the lanthanide ion radius on other MOs in the complex is much weaker.[3] The plots of the redox potentials of the hexadecabutyl-substituted lanthanide diphthalocyanine complexes *vs.* radius of the central complex-forming metal ion are shown in Fig. 4. The values of the first oxidation and reduction potentials of the complexes increase linearly with an increase in the central metal ion radius with gradients of 0.43 and 0.72 V/Å, respectively (correlation coefficients R = 0.9942 and 0.9995). The resulting gradients are somewhat lower than those typical of the lanthanide diphthalocyanine complexes, usually being 0.6—1.6 V/Å.[2,8,9] The potentials of the second oxidation of the complexes also change linearly, depending on the lanthanide radius (gradient 0.78 V/Å, R = 0.9996), but with a negative slope (see Fig. 4). This agrees with a decrease in the energy of the b_1 MO with an enhancement of the interaction between the macroligands (see Fig. 3).

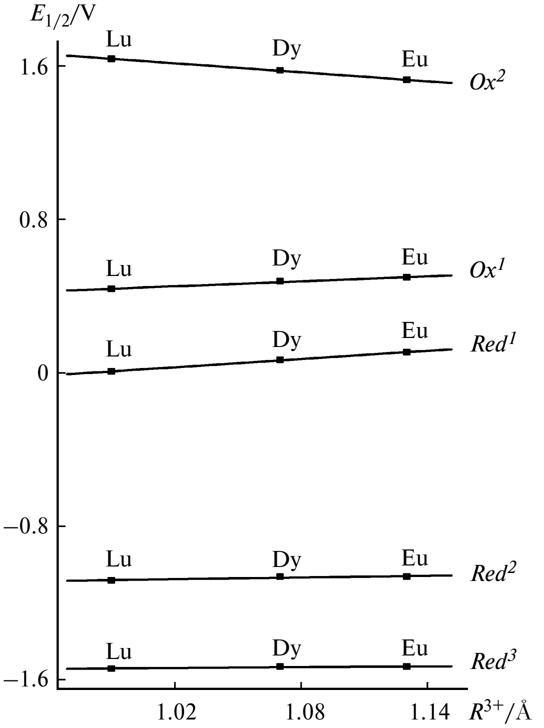


Fig. 4. Effect of the central metal ion radius on the redox transition potentials of the hexadecabutyl-substituted lanthanide diphthalocyanine complexes.

According to the spectral characteristics of the complexes, an increase in the complexing metal ion radius results in the bathochromic shift of absorption bands of both the neutral and the first oxidized and reduced redox forms (see Table 2). The exception is the long-wave component of the split Q band of the reduced forms of the complexes corresponding to the permitted state |CR+>, which appears due to the interaction between the equivalent phthalocyanine macroligands Pc^{2-}.[10,11] This absorption band exhibits a hypsochromic shift with the radius increase (see Table 2), which is in a good agreement with the earlier published data.[2,12,13]

Since both the electrochemical and spectral properties of the complexes are determined by the arrangement of their MOs, they should correlate, probably, with each other at least if they are related to the same orbitals. As already mentioned, the first oxidation and reduction processes of the diphthalocyanine complexes include the elimination and addition of an electron to the singly occupied a_2 MO. As a spectral transition involving this orbital, we can accept the absorption band of the neutral forms of the diphthalocyanine complexes at 460—490 nm (see Table 2). This absorption band is caused[3] by the electron transition from the occupied e_1 orbital to a_2. The plots of the potentials of the first redox transitions of the butyl-substituted diphthalocyanine complexes under study *vs.* wave number of this spectral band are presented in Fig. 5. These values well correlate linearly with correla-

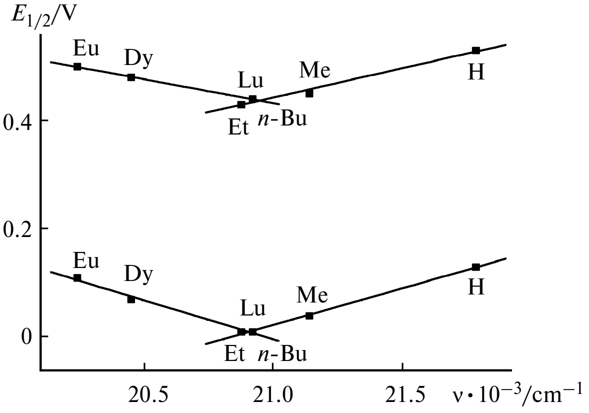


Fig. 5. Correlations between the potentials of the first redox transitions of the alkyl-substituted lanthanide diphthalocyanine complexes and the wave number of the absorption bands of the complexes at 460—490 nm.

tion coefficients of 0.9995 and 0.9944 for the oxidation and reduction processes, respectively. The slopes of the straight lines are negative and equal to –0.71 and –1.17 when both magnitudes are expressed in energy units. In fact, when the ion radius decreases on going from europium to lutetium, the redox transition potentials shift to the cathodic region simultaneously with an increase in the energy of the a_2 MO. The energy of the e_1 MO also increases due to the interaction similar to that schematically shown in Fig. 3 but lower in value. Correspondingly, the energy of the spectral transition from the e_1 to a_2 MO increases.

Thus, in the first part of the present study, we considered the regularities of changing the electrochemical parameters and spectral properties of the alkyl-substituted complexes containing lanthanides of different nature.

The second part of the study concerns the properties of the complexes of the same lanthanide, namely, lutetium, at different lengths of the alkyl substituent chain in the benzene rings of the phthalocyanine macrocycles. In the series of the studied complexes, an increase in the alkyl chain length shifts the potentials of their redox transitions to the cathodic region (see Table 1). This shift is caused by an increase in the electron-donor σ-effects of the substituents. The most substantial change in the redox potentials was observed on going from the unsubstituted to methyl-substituted complex. The potentials of the ethyl- and butyl-substituted complexes are almost the same.

The regularities of changing the spectral properties of the diphthalocyanine complexes under study with an elongation of the alkyl radical can be monitored by the data presented in Table 2. An increase in the electron density on the phthalocyanine macrocycles with an enhancement of the σ-electron-donor effect of the alkyl substituents increases the energy of the orbitals in the complexes. However, the energies of the occupied MOs increase more greatly than the energies of the free orbitals and, therefore, the energies of the spectral transitions decrease and the absorption bands undergo bathochromic shifts (see Table 2). As in the case of electrochemical parameters, the greatest change in the spectral properties is observed on going from the unsubstituted to methyl-substituted complex. The electronic spectra of the ethyl- and butyl-substituted complexes differ insignificantly.

The position of the so-called intervalence band lying in the near-IR region of the electronic absorption spectra of the neutral forms of the complexes is a characteristic that changes most remarkably with a change in the lanthanide radius. This band is usually ascribed to the electron transition between the b_1 and a_2 MOs of the complexes (see Fig. 3).[3,14] The central metal ion size exerts the most noticeable effect on the energy of precisely these orbitals,[3] and the position of the band can be considered as a quantitative characteristic of the π—π-interaction of the phthalocyanine macroligands. For example, the position of the intervalence band of the octa-*tert*-butyl-substituted lanthanide diphthalocyanine complexes for the beginning and end of the series differ by more than 700 nm.[15] The influence of the substituent nature in the phthalocyanine macrocycles on the energy of this spectral transition was not studied. It can be assumed that this energy should depend not only on the distance between the phthalocyanine macroligands but also on the electronic effects of the substituents. The spectral properties of the alkyl-substituted diphthalocyanine complexes in the near-IR region were studied. The absorption spectrum in this region of the ethyl-substituted lutetium complex is presented in Fig. 6. The absorbance at 11 000 cm^{-1} is caused by the excitation of an electron to the a_{1u} orbital inside the same oxidized phthalocyanine macroligand $Pc^{-\bullet}$ (see Fig. 3) and is characteristic of all species containing this macroligand, including the neutral forms of the lanthanide diphthalocyanine complexes.[16] The shape of the intervalence band at 6000—9000 cm^{-1} is similar for the whole series of the alkyl-substituted lutetium complexes under study. The main maximum of the intervalence band lies at 6880 ($(Bu^n{}_8Pc)_2Lu$), 6920 ($(Et_8Pc)_2Lu$), 6960 ($(Me_8Pc)_2Lu$), and 7100 cm^{-1} (Pc_2Lu). Evidently, an elongation of the alkyl chain results in the bathochromic shift of the intervalence band, whose position differs more substantially for the unsubstituted and methyl-substituted complexes. It seems improbable that this regularity can be explained by only steric hindrance for bringing together the phthalocyanine macroligands, because such a hindrance would be observed for the complexes of the series considered containing bulkier alkyl radicals. However, a similar effect was observed for changing the electrochemical parameters of the complexes and their EAS in the visible region (see Tables 1 and 2). In the general case, the enhancement of the electron-donor influence of the substituents should increase the energy of the occupied b_1 orbital more substantially than the energy of the singly occupied a_2 orbital, and the spectral transition energy should decrease. It is most likely that this energy is affected by the elec-

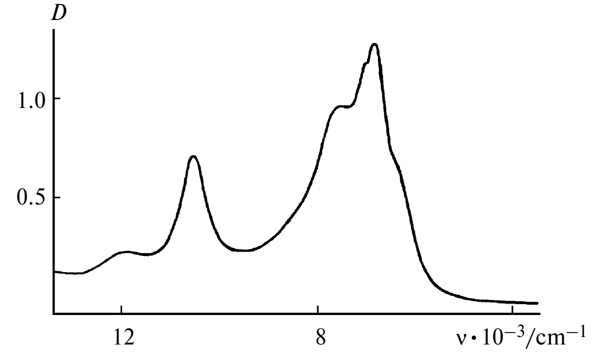


Fig. 6. Electronic absorption spectrum of $(Et_8Pc)_2Lu$ in the near-IR region ($CHCl_3$).

tronic effects of the substituents. Although it seems quite possible that the position of this band in the series of the complexes considered is additionally determined by the steric effects of the substituents too.

Let us consider the correlations between the electrochemical parameters and spectral properties of the diphthalocyanine complexes containing different alkyl substituents. The plots of the potentials of the first redox transitions for the alkyl-substituted lutetium complexes *vs.* wave number of the absorption bands of their neutral redox forms at 460—490 nm are presented in Fig. 5. We found the linear correlations with correlation coefficients of 0.9916 and 0.9988 for the oxidation and reduction processes, respectively. The slopes of the straight lines expressed in energy units are positive and equal to 0.87 and 1.09. An increase in the electron density on the phthalocyanine macrocycles due to an enhancement of the electron-donor effects of the substituents should increase, in fact, the energy of the singly occupied a_2 MO and shift the redox transitions of the complexes to the cathodic region. However, the energy of the completely occupied e_1 orbital donating an electron for the spectral transition under discussion should increase more substantially than the energy of the partially occupied a_2 orbital, and the wave number of the absorption band should decrease.

The correlations presented in Fig. 5 differ for two structural factors: the central metal ion radius and electronic effects of the substituents. If they are considered in a more general form, this implies that the influence of these two factors determining the properties of the complexes can be generalized in the same system of coordinates. Note that the factor initially considered as the lanthanide ion radius should be treated as an effective distance between the phthalocyanine macroligands, *i.e.*, it is determined by the metal ion size and also by the substituents in the phthalocyanine macrocycles creating steric hindrance.

* * *

Thus, the study of the electrochemical and spectral characteristics of the alkyl-substituted lanthanide diphthalocyanine complexes revealed the following regularities.

An increase in the central metal ion radius shifts the first oxidation and reduction processes of the complexes to the anodic direction, while the second step of their oxidation is shifted to the cathodic one. The EAS band of the complexes exhibits the bathochromic shift.

A linear correlation with a negative slope was found between the redox potentials of the complexes of different lanthanides and the energies of their spectral transition at 460—490 nm.

An increase in the electron-donor ability of the substituents shifts the redox potentials to the cathodic direction and results in the bathochromic shift of the absorption maxima of the complexes.

The intervalence band of the complexes in the near-IR region undergoes the bathochromic shift with an elongation of the alkyl substituent chain. Its position is determined by the effective distance between the phthalocyanine macroligands and also by the electronic effect of the substituents.

A linear correlation with a positive slope was observed between the redox potentials of the complexes containing different substituents and the energies of the spectral transition at 460—490 nm.

Experimental

The complexes were synthesized according to previously developed procedures.[17]

Prior to use, *o*-dichlorobenzene (*o*-DCB) (Aldrich, HPLC grade) was passed through a column with neutral Al_2O_3; and $Bu^n_4NBF_4$ (Aldrich) was twice recrystallized from Pr^iOH (special purity grade) and dried in a vacuum desiccator at 110 °C.

Electrochemical measurements were carried out on an IPC-Pro potentiostat using a three-electrode scheme on a graphite electrode (pyrolyzed polyacrylonitrile, specific surface 12 $m^2 g^{-1}$, *m* ~0.5 mg) in 0.15 *M* $Bu^n_4NBF_4$ in *o*-DCB at 20 °C. The concentration of the complexes under study was 10^{-4} mol L^{-1}. A Pt plate served as the counter electrode, and an Ag|AgCl electrode was used as the reference electrode. Oxygen was removed from the cell with a dry argon flow. Voltammetric curves were detected by the CV method at a scan rate of 200 mV s^{-1}. Measurements were carried out using the apparatus *IR* compensation. The electrolyte resistance of the *IR* compensation was calculated by the shift of the anodic and cathodic peaks of ferrocene oxidation: $(E^c - E^a) - 0.059 = IR$, where E^c and E^a are the potentials of the cathodic and anodic peaks of ferrocene oxidation, respectively (*I* is the sum of currents of the cathodic and anodic processes, and *R* is the electrolyte resistance).

The reduced and oxidized forms of the phthalocyanine complexes in solution for spectral electrochemical studies were generated using a P-5827 potentiostat in the potentiostatic regime at 20 °C in a quartz cell with anodic and cathodic spaces divided with a porous glass membrane. The cell was connected with the potentiostat by the three-electrode scheme. The working electrode was a Pt grid with a surface area of ~9.7 cm^2, and 0.15 *M* $Bu^n_4NBF_4$ in *o*-DCB served as the supporting electrolyte. A Pt plate was used as the counter electrode. Potential values were specified relatively to an Ag|AgCl electrode. The concentration of solutions of the complexes under study was 10^{-5} mol L^{-1}. A dry argon flow was used to stir a solution in the cell during electrolysis and remove oxygen. Electronic absorption spectra of the electrochemically generated redox forms of the complexes were recorded directly in the cell on a Specord UV VIS spectrophotometer (Carl Zeiss) at 30 000—12 500 cm^{-1} (333—800 nm) using 0.15 *M* $Bu^n_4NBF_4$ in the same solvent as the reference solution.

Absorption spectra of the complexes in the near-IR region were recorded on a Specord NIR-61 spectrometer (Carl Zeiss) in a range of 13 500—3500 cm^{-1} (740—2850 nm) in chloroform.

The authors thank Yu. G. Gorbunova for help in spectral studies of the complexes and useful discussion and M. O. Breusova for the synthesis of several compounds.

This work was financially supported by the Foundation of the President of the Russian Federation (Grant for Young Scientists MK-3941.2004.3) and the International Scientific Technical Center (Project No. 1526).

References

1. C. C. Leznoff and A. B. P. Lever, *Phthalocyanines: Properties and Applications*, VCH Publishers, New York, 1993.
2. T. V. Magdesieva, I. V. Zhukov, L. G. Tomilova, O. V. Korenchenko, I. P. Kalashnikova, and K. P. Butin, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 379 [*Russ. Chem. Bull.*, *Int. Ed.*, 2001, **50**, 396].
3. R. Rousseau, R. Aroca, and M. L. Rodriguez-Mendez, *J. Mol. Struct.*, 1995, **356**, 49.
4. A. B. P. Lever, *Inorg. Chim. Acta*, 1993, **203**, 171.
5. A. T. Chang and J.-C. Marchon, *Inorg. Chim. Acta*, 1981, **53**, L241.
6. G. A. Corker, B. Grant, and N. J. Clecak, *J. Electrochem. Soc.*, 1979, **126**, 1339.
7. T. V. Magdesieva, I. V. Zhukov, L. G. Tomilova, E. V. Chernykh, and K. P. Butin, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 2149 [*Russ. Chem. Bull.*, 1997, **46**, 2036 (Engl. Transl.)].
8. H. Konami, *Chem. Phys. Lett.*, 1990, **165**, 397.
9. J. Jiang, Y. Bian, F. Furuya, W. Liu, M. T. M. Choi, N. Kobayashi, H.-W. Li, Q. Yang, T. C. W. Mak, and D. K. P. Ng, *Chem. Eur. J.*, 2001, **7**, 5059.
10. N. Ishikawa, O. Ohno, Y. Kaizu, and H. Konami, *J. Phys. Chem.*, 1992, **96**, 8832.
11. N. Ishikawa and Y. Kaizu, *Chem. Phys. Lett.*, 1994, **228**, 625.
12. A. Iwase, C. Harnoode, and Y. Kameda, *J. Alloys Comp.*, 1993, **192**, 280.
13. 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.)].
14. E. Orti, J. L. Bredas, and C. Clarisse, *J. Phys. Chem.*, 1990, **92**, 1228.
15. L. G. Tomilova, E. V. Chernykh, N. A. Ovchinnikova, E. V. Bezlepko, V. M. Mizin, and E. A. Luk´yanets, *Optika i spektroskopiya* [*Optics and Spectroscopy*], 1991, **70**, 775 (in Russian).
16. D. Markovitsi, T. Tran-Thi, R. T. Even, and J. Simon, *Chem. Phys. Lett.*, 1987, **137**, 107.
17. V. E. Pushkarev, A. V. Ivanov, I. V. Zhukov, E. V. Shulishov, and Yu. V. Tomilov, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 528 [*Russ. Chem. Bull.*, *Int. Ed.*, 2004, **53**, 554].

Received October 11, 2004;
in revised form December 3, 2004