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Sandwich Complexes of Yttrium, Neodymium, Gadolinium, and Dysprosium with *meso-trans*-Di(hexadecyl)-tetrabenzoporphyrin and Phthalocyanine Fragments. Synthesis and Spectral Properties

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Abstract— Sandwich-type asymmetric complexes of yttrium, neodymium, gadolinium, and dysprosium were synthesized by the reaction of the corresponding *meso-trans*-bis(hexadecyl)tetrabenzoporphyrinates with dilithium phthalocyianine. Spectral properties of these compounds were investigated.

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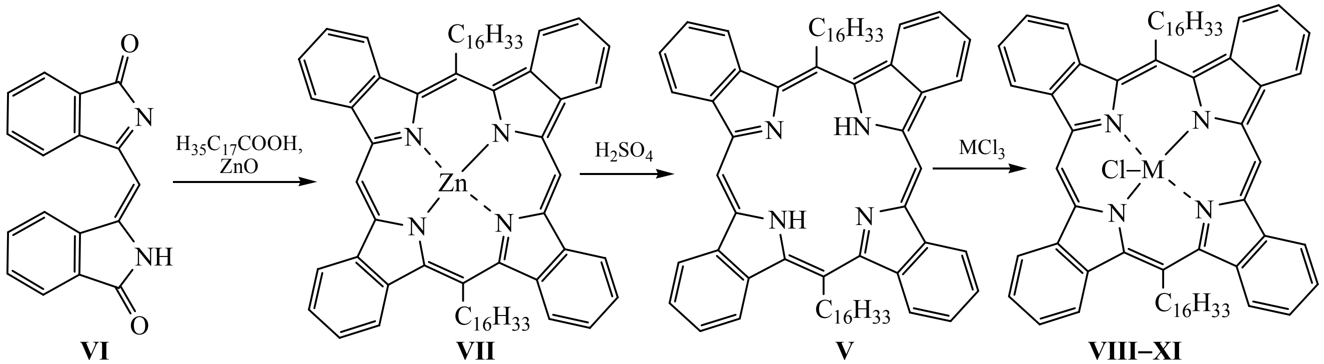
Sandwich complexes of rare earth elements with tetrapyrrole ligands are stable compounds of unique structure, attracting both theoretical and practical interest. They can be used as materials for sensor systems [1, 2], optical limiters [3], electrochromic materials [4], materials for the sensors of ionizing radiation [5] and in other areas.

At present there are numerous methods of synthesis of sandwich lanthanide complexes containing phthalocyanine and porphyrin molecules [6–10]. However, the information about the structure of such complexes containing phthalocyanine and tetrabenzoporphyrin molecules is very limited [11, 12], and the information on the structures that combine the *meso-trans*-dialkyl-tetrabenzoporphyrin and phthalocyanine fragments has not been found in the literature.

This communication concerns the synthesis and spectral properties of the sandwich complexes of yttrium (**I**), neodymium (**II**), gadolinium (**III**), and dysprosium (**IV**) containing fragments of the *meso-trans*-bis(hexadecyl)tetrabenzoporphyrin and phthalocyanine. The starting compound for their synthesis were *meso-trans*-bis(hexadecyl)tetrabenzoporphyrin (**V**) obtained by the interaction 1-[1-oxo-1*H*-isoindol-3-yl)methyl]isoindolin-3-one (**VI**) synthesized by the method [13] with stearic acid and zinc oxide, followed by demetallation of the formed zinc *meso-trans*-bis(hexadecyl)tetrabenzoporphyrinate (**VII**) with sulfuric acid. By boiling solution of the porphyrin (**V**) in DMF with an excess of yttrium, neodymium, gadolinium, or dysprosium chloride the corresponding lanthanide complexes **VIII–XI** were obtained in accordance with Scheme 1.

Scheme 1.



VI **VII** **V** **VIII–XI**

M = Y (**VIII**), Nd (**IX**), Gd (**X**), Dy (**XI**).

The formation of complexes was monitored spectrophotometrically by disappearance of the bands at 608 and 663 nm characteristic of ligand **V** in the electron absorption spectrum of the reaction mixture and the appearance of bands at 627–629 nm corresponding to the *Q*-bands of the complexes **VIII–XI**. Because of the large ionic radii of the metals the reaction proceeds relatively slowly and is completed in 16 h.

Compounds **VIII–XI** were isolated after diluting the reaction mixture with water followed by extraction with chloroform. The organic phase in each case was washed with water, the solvent was distilled off, and the residue was washed with 80% ethanol and dried.

The sandwich complexes **I–IV** were synthesized in accordance with Scheme 2 by the reaction of dilithium phthalocyanine obtained by heating phthalonitrile in 1-hexanol in the presence of lithium metal, with the compounds **VIII–XI** in the same solvent at boiling the reaction mixture for 6 h.

In each case, at the end of the process the alcohol was distilled off at a reduced pressure, the reaction mixture was treated with 10% acetic acid, the precipitate formed was washed with hot 80% ethanol and dried. Compounds **I–IV** were purified by column chromatography. Their composition and structure was confirmed by elemental analysis, vibrational, ^{1}H NMR, and electron spectroscopy.

Vibrational spectra of compounds **I–IV**, as expected, are similar to each other. Each contains intense bands in the region of 2956–2854 cm^{-1} corresponding to the CH bond vibrations of the alkyl substituents, characteristic bands in the region 856–879 cm^{-1} corresponding to the N–M vibrations, the bands in the region 1361–1383 cm^{-1}, typical of the radical fragment of phthalocyanine ($\mathrm{Pc}^{\bullet}$), and the band at 1448–1462 cm^{-1} reflecting vibrations of the C–N bonds. Splitting of these bands points to the non-equivalence of chromophores [14, 15]. The position of the characteristic bands in the IR spectra of compounds **I– IV** depends on the ionic radius of the metal (R_M). Table 1 lists the vibration frequencies of the respective bonds.

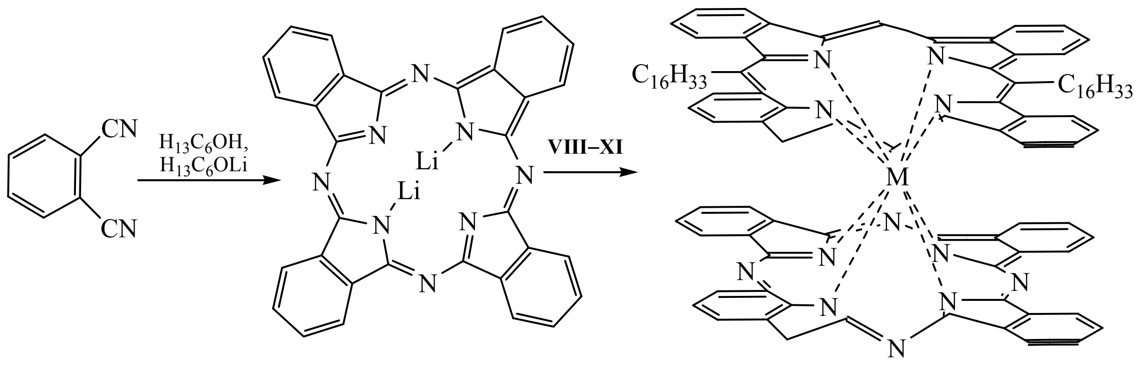
As follows from these data, the increase in the ionic radius of the metal (at the coordination number equal to eight) leads to a shift of the bands of the N–M vibrations and vibrations of the radical fragment of phthalocyanine to the low-frequency region (Figs. 1a, 1b).

As to the positions of the bands corresponding to the C–N vibrations in phthalocyanine and porphyrin chromophores, we did not find any relationship between their position and the ionic radius of the metal.

^{1}H NMR spectrum of compound **III** (Table 2) contains four groups of signals. In the weak field at 9.23 ppm there is a singlet corresponding to the resonance of the two *meso*-protons of the porphyrin fragment. Two singlets at 7.86 and 7.79 ppm correspond to the resonance of the 32 protons of benzene rings and isoindole fragments of phthalocyanine (Pc) and tetrabenzoporphyrin (TBP), respectively. In the strong field there is a multiplet at 2.19 ppm corresponding to the resonance of 60 protons of the methylene groups of alkyl substituents, and, finally, a singlet at 1.27 ppm corresponding to the resonance of 6 protons of terminal methyl groups. The ^{1}H NMR spectra of complexes **I, II, IV** are similar in nature to the spectrum of compound **III**. The signals positions are given in Table 2.

Due to the paramagnetic nature of the lanthanides, the proton signals are significantly shifted. Thus, the signals of protons in the meso-positions of the porphyrin macrocycle are shifted upfield by 0.55–2.77 ppm compared with their position (11.12 ppm) in the

Scheme 2.



I–IV

M = Y (**I, VIII**), Nd (**II, IX**), Gd (**III, X**), Dy (**IV, XI**).

Table 1. IR spectral parameters of complexes **I–IV**, ν, cm^{-1}

Comp. no.	M	r_M, nm	N–M	$Pc^{\bullet}$	C–N
I	Y	0.116	856	1364	1443, 1446
II	Nd	0.125	879	1383	1452, 1461
III	Gd	0.115	862	1361	1453, 1462
IV	Dy	0.127	883	1373	1448, 1465

Table 2. ^{1}H NMR spectral parameters of compounds **I–IV** in $CDCl_3$, δ, ppm

Comp. no.	M	*meso*-H	Pc-H	TBP-H	CH_2	CH_3
I	Y	9.19 s	7.84 s	7.76 s	1.26 m	0.88 s
II	Nd	8.35 s	7.87–7.82 m	7.76–7.68 m	1.29 m	0.89 s
III	Gd	9.23 s	7.86 s	7.79 s	2.19 m	1.27 s
IV	Dy	10.57 s	8.08–7.88 m	7.79–7.62 m	1.43 m	0.95 s

spectrum of the zinc complex **VII**. The signals of the protons of the benzene rings of the tetrabenzoporphyrin chromophores, as well as of alkyl substituents, are in the same areas as in the spectrum of compound **VII**, except for complex **III**: in the spectrum of the latter the proton signals of alkyl substituents are shifted downfield by 0.5–0.9 ppm.

Among the most important characteristics of the sandwich-type complexes the data of electron absorption spectroscopy should be mentioned. The electronic spectroscopy is the simplest and most informative method of identifying the “green” and “blue” forms of sandwich compounds.

The electron absorption spectrum of complex **I** solution in chloroform (Fig. 2, *1*) is characterized by a strong band with the maximum at 665 nm and a less intense band at 687 nm, evidencing the presence of the phthalocyanine radical fragment, and the ratio of their intensities is equal to 1.46: 1. Thus, complex **I** exists in chloroform mainly in the neutral-radical “green” form. Replacing chloroform by DMF with the addition of 1% hydrazine hydrate as reducing agent leads to certain changes (Fig. 2, curve *2*). The band with maximum at 687 nm disappears while a band at 617 nm appears, which is more intense than the band at 666 nm. The intensity ratio of the two latter becomes equal to 1:0.93. This fact indicates the transformation of **I** in the presence of reducing compound into the anionic “blue” form. In both cases, the bands at 434 and 420 nm correspond to the tetrabenzoporphyrin *B* bands, and at 349 and 345 nm, to the *B* bands of phthalocyanine.

The electron absorption spectra of the gadolinium complex **III** (Fig. 3) are similar by their characteristics to the spectrum of compound **I**. We noted only a 5–7 nm red shift of the bands in the *Q* region and a slightly smaller splitting of *Q* band in the chloroform solution (Fig. 3, curve *1*). In addition, the intensity of the *Q* bands increases with respect to *B* bands of tetrabenzoporphyrin chromophore located in the same area as in the spectrum of the complex **I**.

The electron absorption spectra of the complex **II** with neodymium (Fig. 4) differ markedly from the spectra of the compounds **I** and **III** by the character and position of the maxima of absorption bands. In the spectra of complex **II** the resonance splitting of the *Q* band is significantly reduced, while its relative intensity increases. The bands at 433 and 416 nm corresponding to the *B* bands of tetrabenzoporphyrin are

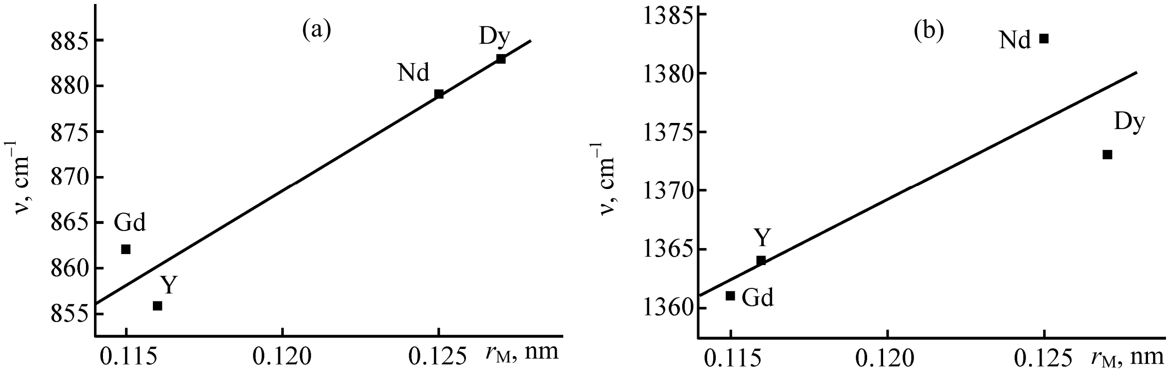


Fig. 1. Dependence of the position of the bands (a) N–M and (b) ($Pc^{\bullet}$) on the metal ionic radii.

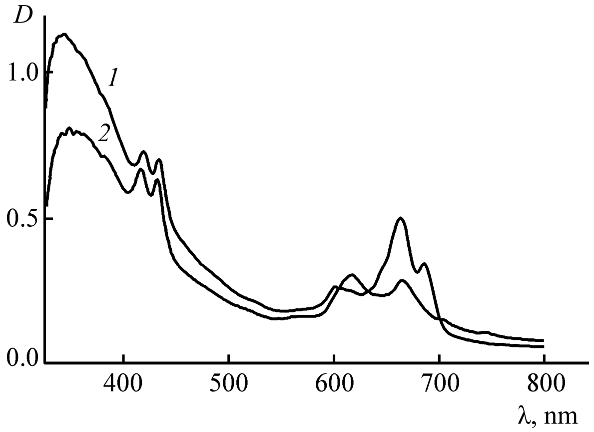


Fig. 2. Electron absorption spectra of compound **I:** (*1*) in $CHCl_3$, (*2*) in DMF +1% of $NH_2NH_2·H_2O$.

less resolved, while the band at 478 nm in the spectrum in chloroform (Fig. 4, curve *1*) corresponding to electronic transitions in the phthalocyanine radical fragment becomes more pronounced. These combined facts suggest a significantly stronger interaction between the porphyrin and phthalocyanine chromophores.

An even stronger interaction of these chromophores was observed in the dysprosium complex **IV**. The resonance splitting of *Q* band is significantly reduced in the spectrum of its solution in chloroform (Fig. 5, curve *1*), while in the spectrum in DMF with the addition of hydrazine hydrate (Fig. 5, curve *2*) it increases. The band at 455 nm in the spectrum in chloroform becomes even more pronounced that shows the radical nature of the phthalocyanine fragment. On the contrary, the *B* bands of porphyrin chromophore become even less intense.

Thus, the spectral properties of the synthesized complexes to a large extent depend on the nature of the metal present in their composition. It is interesting to note that judging from the electron absorption spectra the interaction between the phthalocyanine and tetrabenzoporphyrin chromophores is stronger in the case of complexes with neodymium **II** and dysprosium **IV**, although the ionic radii of these lanthanides are large, 0.125 and 0.127 nm respectively. On the contrary, the interaction of the phthalocyanine and porphyrin fragments is weaker in the complexes with gadolinium **III** and yttrium **I**, whose ionic radii are much smaller: 0.115 and 0.116 nm, respectively.

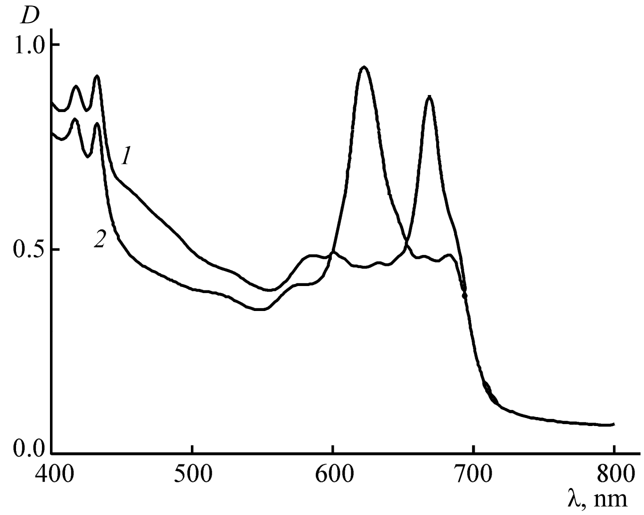


Fig. 3. Electron absorption spectra of compound **III**: (*1*) in $CHCl_3$, (*2*) in DMF +1% of $NH_2NH_2·H_2O$.

A consequence of increasing interaction between the chromophores is a decrease in the relative intensities of the bands corresponding to tetrabenzoporphyrin *B* bands. The plot of intensity ratio of *Q* and *B* bands vs the ionic radii of lanthanide complexes **I**–**IV** is shown in Fig. 6.

Perhaps, the unusual properties of the complexes **I**–**IV** should be attributed to the increase in the distortion of the planar structure of porphyrin fragments with the decreasing distance between them and the fragments of phthalocyanine caused by the smaller ionic radius of the metal, resulting in a weakening of the π–π interaction between the chromophores.

EXPERIMENTAL

The electron absorption spectra of the compounds were measured on a Hitachi UV-2001 spectrophotometer, the ^1H NMR spectra (internal reference TMS) on a Bruker Avance-500 instrument, the IR spectra on an Avatar 360 FT-IR spectrophotometer in the region of 400–4000 cm^{-1}, from the films on TlI glass, the mass

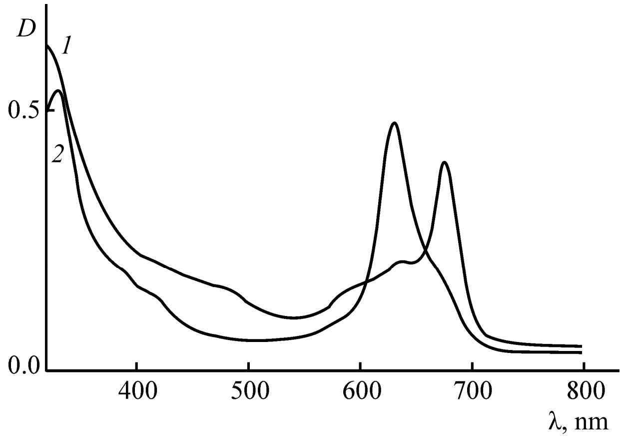


Fig. 4. Electron absorption spectra of compound **II**: (*1*) in $CHCl_3$, (*2*) in DMF +1% of $NH_2NH_2·H_2O$.

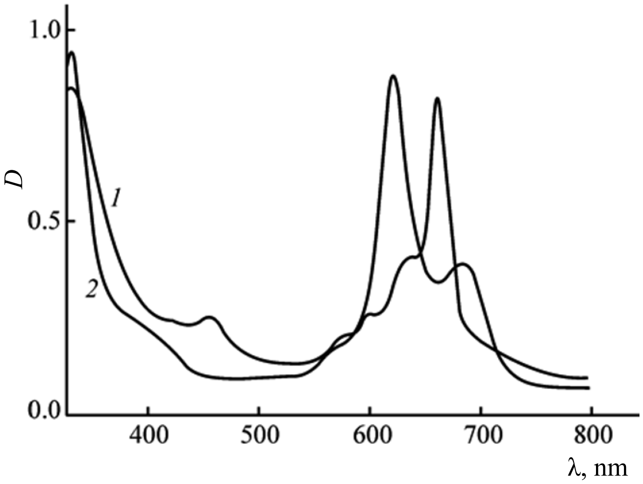


Fig. 5. Electron absorption spectra of compound **IV**: (*1*) in $CHCl_3$, (*2*) in DMF +1% of $NH_2NH_2·H_2O$.

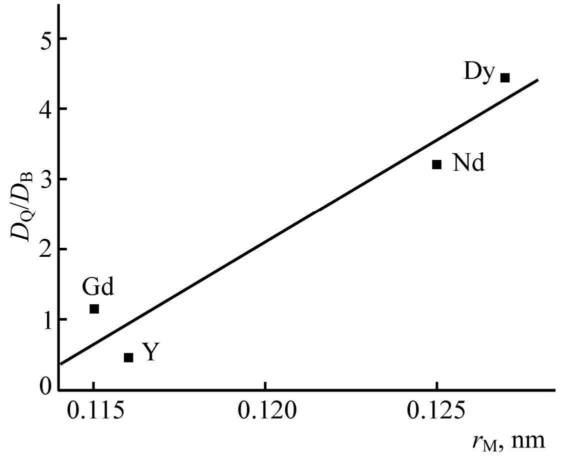


Fig. 6. Dependence of the intensity ratio of *Q* and *B* bands on the ionic radius of metal.

spectrum was recorded on a Bruker Reflex III spectrometer (MALDI–TOF, dithranol matrix). Elemental analysis was performed on a FlashEA 1112 CHNS–O Analyzer.

Zinc *meso-trans*-di(hexadecyl)tetrabenzoporphyrinate (VII). A mixture of 0.02 mol of compound **VI**, 0.04 mol of stearic acid, and 0.05 mol of zinc oxide was heated to 320°C and kept at this temperature for 1 h, then cooled and extracted with CCl_4 in a Soxhlet apparatus. The extract was chromatographed on a column filled with aluminum oxide of II degree of activity by Brockmann (eluent CCl_4–dioxane mixture, 2:1 by volume), collecting the main green area. Yield 3.3 g (32%). Dark-green substance, readily soluble in benzene, chloroform, CCl_4, hexane, poorly soluble in acetone. Electron absorption spectrum (CCl_4), λ_{max}, nm (log ε): 402 (4.59), 427 (5.02), 579 (4.03), 626 (4.50). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 11.12 s (2H), 7.77–7.41 m (16H), 2.26 m (4H), 1.33 s (56H), 0.85 m (6H). Mass spectrum, *m*/*z*: 1020 $[M]^+$. Found, %: C 80.22; H 8.76; N 5.12. $C_{68}H_{84}N_4Zn$. Calculated, %: C 79.85; H 8.28; N 5.48.

***meso-trans*-Di(hexadecyl)tetrabenzoporphyrin (V)**. 0.5 g of complex **VII** was dissolved in 50 ml of concn. sulfuric acid and maintained at 20°C for 2 h. The solution was then diluted with 150 ml of water, the precipitate formed was filtered off, washed on the filter sequentially with 150 ml of 20% solution of ammonia and 100 ml of water, and dried. The residue was dissolved in CCl_4 and chromatographed on a column filled with aluminum oxide of II degree of activity by Brockmann (eluent CCl_4–dioxane, 2:1 by volume), collecting the main green area. Yield 0.35 g (77%). Dark-green substance, readily soluble in benzene, chloroform, CCl_4, hexane, and poorly soluble in acetone. Electron absorption spectrum (CCl_4), λ_{max}, nm (log ε): 419 (4.86), 433 (4.90), 565 (4.15), 603 (4.35), 608 (4.37), 616 (4.35), 663 (4.28) . ^1H NMR spectrum ($CDCl_3$), δ, ppm: 5.11 s (2H), 7.78–7.43 m (16H), 2.22 m (4H), 1.30 s (56H), 0.86 m (6H), –2.35 s (2H). Found, %: C 85.20; H 10.12; N 5.42. $C_{68}H_{86}N_4$. Calculated, %: C 85.13; H 9.03; N 5.84.

Complexes VIII–IX. *General procedure*. 0.1 mmol of compound **V** was dissolved in 25 ml of DMF and 3 mmol of the corresponding metal chloride was added. The reaction mixture was heated for 16 h at reflux, cooled, diluted with 50 ml of water, and extracted with 50 ml of chloroform. The extract was washed with water, the solvent was distilled off, and the residue was washed with 50 ml of 80% aqueous ethanol and dried.

Chloroittrium *meso-trans*-di(hexadecyl)tetrabenzoporphyrinate (VIII). Yield 0.10 g (91%), dark-green powder, soluble in toluene, chloroform, acetone, DMF. The electron absorption spectrum (CCl_4), λ_{max}, nm (D/D_{max}): 629 (0.30), 430 (1.00). Found, %: C 76.22; H 8.11; N 4.99. $C_{68}H_{84}ClN_4Y$. Calculated, %: C 75.50; H 7.83; N 5.18.

Chloroneodimium *meso-trans*-di(hexadecyl)tetrabenzoporphyrinate (IX). Yield 0.10 g (83%), dark-green powder, soluble in toluene, chloroform, acetone, DMF. The electron absorption spectrum (CCl_4), λ_{max}, nm (D/D_{max}): 622 (0.27), 423 (1.00). Found, %: C 72.31; H 8.25; N 4.54. $C_{68}H_{84}ClN_4Nd$. Calculated, %: C 71.83; H 7.45; N 4.93.

Chlorogadolinium *meso-trans*-di(hexadecyl)tetrabenzoporphyrinate (X). Yield 0.11 g (92%), dark-green powder, soluble in toluene, chloroform, acetone, DMF. The electron absorption spectrum (CCl_4), λ_{max}, nm (D/D_{max}): 624 (0.29), 424 (1.00). Found, %: C 71.88; H 8.17; N 4.43. $C_{68}H_{84}ClGdN_4$. Calculated, %: C 71.01; H 7.36; N 4.87.

Chlorodysprosium *meso-trans*-di(hexadecyl)tetrabenzoporphyrinate (XI). Yield 0.10 g (92%), dark-green powder, soluble in toluene, chloroform, acetone, DMF. The electron absorption spectrum (CCl_4), λ_{max}, nm (D/D_{max}): 628 (0.28), 427 (1.00). Found, %: C 71.54; H 7.89; N 4.19. $C_{68}H_{84}ClDyN_4$. Calculated, %: C 70.69; H 7.33; N 4.85.

Sandwich complexes of type I–IV. *General procedure*. To a solution of dilithium phthalocyanine prepared by boiling 0.3 g of phthalonitrile in 20 ml of 1-hexanol in the presence of 0.05 g of lithium metal for 2 h, was added 0.10 g of metalloporphyrin **VIII–IX**. The reaction mixture was heated at reflux for 6 h, and then alcohol was distilled off in a vacuum, the reaction mixture was treated with 50 ml of 10% solution of acetic acid, washed with 30 ml of hot 80% ethanol, and dried. The residue was dissolved in chloroform and chromatographed on a column filled with aluminum oxide of II degree of activity by Brockmann (eluent chloroform), collecting the main green area.

***meso-trans*-Di(hexadecyl)tetrabenzoporphyrin-ittrium-phthalocyanine (I)**. Yield 55 mg (38%), dark-green powder, soluble in toluene, chloroform, acetone, DMF. The electron absorption spectrum, λ_{max}, nm (D/D_{max}): $CHCl_3$, 687 (0.30), 665 (0.44), 602 (0.23) and 434 (0.62), 420 (0.64), 345 (1.00). DMF + 1% of $N_2H_4{\cdot}H_2O$ – 666 (0.34), 617 (0.37), 432 (0.78), 417 (0.82), 349 (1.00). IR spectrum, ν, cm^{-1}: 2955, 2867, 1578, 1524, 1446, 1443, 1364, 1163, 1114, 856, 763, 639, 556. Found, %: C 78.01; H 6.17; N 10.12. $C_{100}H_{100}{\cdot}N_{12}Y$. Calculated, %: C 77.05; H 6.47; N 10.78.

***meso-trans*-Di(hexadecyl)tetrabenzoporphyrin–neodimium–phthalocyanine (II)**. Yield 57 mg (40%), dark-green powder, soluble in toluene, chloroform, acetone, DMF. Electron absorption spectrum, λ_{max}, nm (D/D_{max}): $CHCl_3$, 677 (0.65), 635 (0.34), 478 (0.26), 433 (0.32), 416 (0.34), 320 (1.00). DMF + 1% of $N_2H_4{\cdot}H_2O$, 670sh, 631 (0.88), 430 (0.21), 416 (0.28), 331 (1.00). IR spectrum, ν, cm^{-1}: 2944, 2854, 1722, 1661, 1532, 1461, 1452, 1383, 1279, 1134, 1082, 951, 879, 761, 720, 547. Found, %: C 74.88; H 7.15; N 9.76. $C_{100}H_{100}N_{12}Nd$. Calculated, %: C 74.41; H 6.24; N 10.41.

***meso-trans*-Di(hexadecyl)tetrabenzoporphyrin–gadolinium–phthalocyanine (III)**. Yield 58 mg (41%), dark-green powder, soluble in toluene, chloroform, acetone, DMF. Electron absorption spectrum, λ_{max}, nm (D/D_{max}): $CHCl_3$, 670 (0.94), 602 (0.53), 478sh, 434 (1.00), 419 (0.97). DMF + 1% of $N_2H_4{\cdot}H_2O$, 683 (0.51), 624 (1.00), 433 (0.86), 418 (0.87). IR spectrum, ν, cm^{-1}: 2956, 2867, 1572, 1520, 1462, 1453, 1361, 1297, 1227, 964, 862, 806, 767, 705. Found, %: C 74.55; H 5.13; N 9.88. $C_{100}H_{100}{\cdot}GdN_{12}$. Calculated, %: C 73.81; H 6.19; N 10.33.

***meso-trans*-Di(hexadecyl)tetrabenzoporphyrin–dysprosium–phthalocyanine (IV)**. Yield 60 mg (42%), dark-green powder, soluble in toluene, chloroform, acetone, DMF. Electron absorption spectrum, λ_{max}, nm (D/D_{max}): $CHCl_3$, 662 (0.97), 634 (0.48), 455 (0.300), 330 (1.00). DMF + 1% of $N_2H_4{\cdot}H_2O$, 684 (0.42), 621 (0.93), 413 sh, 331 (1.00). IR spectrum, ν, cm^{-1}: 2950, 2877, 1465, 1448, 1422, 1373, 1321, 1115, 1063, 883, 768, 731, 498. Found, %: C 74.87; H 6.22; N 9.74. $C_{100}H_{100}DyN_{12}$. Calculated, %: C 73.58; H 6.17; N 10.30.

REFERENCES

1. Simpson, T.R.E., Cook, M.J., Petty, M.C., Thorpe, S.C., and Russel, D.A., *Analyst.*, 1996, vol. 121, no. 10, p. 1501.
2. Krier, A., Parr, T., Davidson, K., and Collins, R.A., *Adv. Mater.*, 1996, vol. 6, no. 4, p. 203.
3. Ceyhan, T., Yağlioğlu, G., Ünver, H., Salih, B., Erbil, M.K., Elmali, A., and Bekaroğlue, Ö., *Makrogeterotsikly.*, 2008, vol. 1, no. 1, p. 44.
4. Lukyanets, E.A., Pukhtina, E.V., Ulanova, L.A., and Kovaleva, M.A., *Appl. Radiat. Isotop.*, 1996, vol. 47, nos. 11–12, p. 1541.
5. Balenko, V.G., et al., *Kvant. Elektron.*, 1989, vol. 16, no. 3, p. 615.
6. Jiang, J., Choi, M.T.M., Law, W.-F., Chen, J., and Ng, D.K.P., *Polyhedron.*, 1998, vol. 17, no. 22, p. 3903.
7. Bai, M., et al., *J. Mater. Chem.*, 2003, vol. 13, no. 6, p. 1333.
8. Lu, F., et al., *New J. Chem.*, 2004, vol. 28, no. 9, p. 1116.
9. Chabach, D., et al., *J. Am. Chem. Soc.*, 1995, vol. 117, no. 33, p. 8548.
10. Jiang, J., Mak, T.C.W., and Ng, D.K.P., *Chem. Ber.*, 1996, vol. 129, no. 8, p. 933.
11. Kudrik, E.V., Islyaikin, M.K., and Shaposhnikov, G.P., *Zh. Obshch. Khim.*, 2000, vol. 70, no. 5, p. 821.
12. Galanin, N.E., Yakubov, L.A., and Shaposhnikov, G.P., *Zh. Org. Khim.*, 2008, vol. 44, no. 6, p. 928.
13. Kudrik, E.V., Islyaikin, M.K., and Frantseva, S.V., *Zh. Obshch. Khim.*, 1997, vol. 67, no. 7, p. 1202.
14. Clarisse, C. and Riou, M.T., *Inorg. Chim. Acta.*, 1987, vol. 130, no. 1, p. 139.
15. Ostendorp, G. and Homborg, H.Z., *Z. Anorg. Allg. Chem.*, 1996, vol. 622, no. 7, p. 1222.