Synthesis and Spectral Properties of Sandwich *meso*-Tetramethyltetrabenzoporphyrin–Phthalocyanine Complexes with Lutetium, Erbium, Yttrium, and Lanthanum

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Abstract—The reaction of phthalimide with zinc(II) propanoate gave *meso*-tetramethyltetrabenzoporphyrinatozinc(II) whose demetalation afforded the corresponding free base. The latter was used to synthesize complexes with lutetium, erbium, yttrium, and lanthanum. Heating of these complexes with excess phthalonitrile led to the formation of sandwich *meso*-tetramethyltetrabenzoporphyrin–phthalocyanine complexes. Spectral properties of the resulting compounds were studied.

Unique structure of rare-earth metal diphthalocyaninates makes them promising for use as sensors [1–3], materials for ionizing radiation probes [4], dyes for passive synchronization of laser modes [5], and electrochromic materials [6]. Up no now, numerous methods for the synthesis of both symmetric and unsymmetric diphthalocyaninates have been reported [7–10]. However, data on sandwich-like complexes containing phthalocyanine and porphyrin molecules are very scanty. Mixed-ligand complexes of rare-earth metals with tetraphenylporphyrin and octaethylporphyrin were described [11]. It was shown that such complexes considerably differ from diphthalocyaninates in spectral and electrochemical properties. The reason is that the ligands possess different redox potentials; therefore, the unpaired electron in the corresponding one-electron oxidation product is localized on the phthalocyanine fragment. Rare-earth metal complexes like phthalocyanine–metal–tetrabenzoporphyrin were reported only in [12], where the synthesis and properties of lutetium and gadolinium complexes were described. We have found no published data on dimeric structures containing *meso*-alkyl-substituted tetrabenzoporphyrin and phthalocyanine fragments, though such compounds may attract interest from the practical viewpoint.

In the present article we report on the synthesis and spectral parameters of sandwich complexes **I–IV** with lutetium, erbium, yttrium, and lanthanum containing phthalocyanine and *meso*-tetramethyltetrabenzopor-

Scheme 1.

V

Scheme 2.

VII–X → **I–IV**

$C_6H_4(CN)_2$-*o*
$-Cl^-$, $-H^{\cdot}$
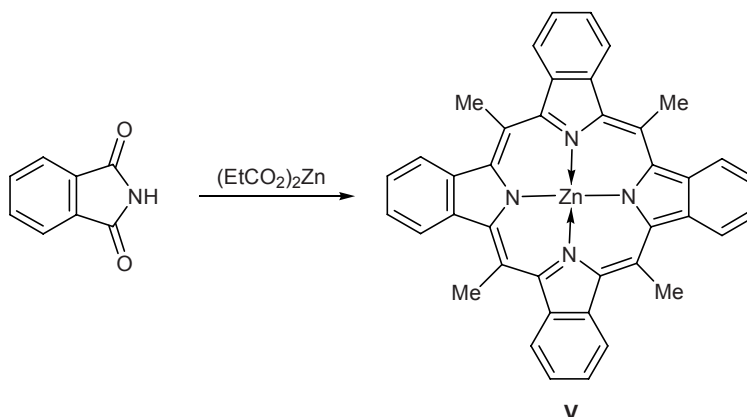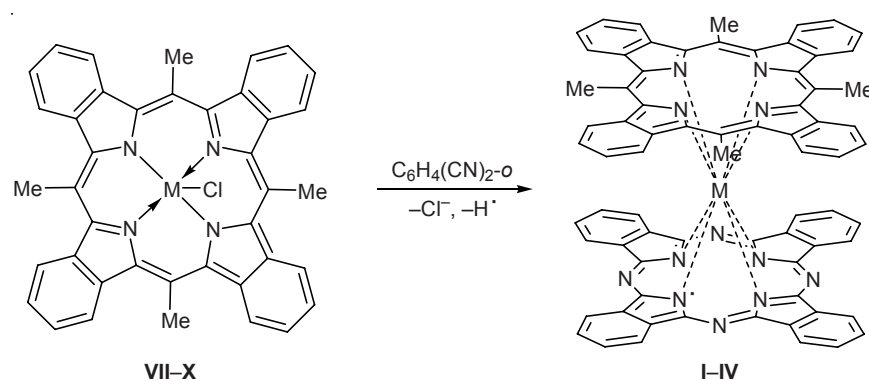
I, **VII**, M = Lu; **II**, **VIII**, M = Er; **III**, **IX**, M = Y; **IV**, **X**, M = La.

phyrin fragments. As starting compound for the synthesis of complexes **I–IV** we used *meso*-tetramethyltetrabenzoporphyrinatozinc(II) (**V**) which was obtained according to a one-pot procedure (unlike the procedure described in [13]), by reaction of phthalimide with zinc(II) propanoate at 310°C (reaction time 1.5 h; Scheme 1). Porphyrin complex **V** was isolated and purified by column chromatography. Treatment of **V** with concentrated sulfuric acid gave the corresponding free ligand, *meso*-tetramethyltetrabenzoporphyrin (**VI**), which was also purified by chromatography. Compounds **V** and **VI** are dark green crystalline powders which are readily soluble in DMF and pyridine and poorly soluble in chloroform and acetone. Their structure was confirmed by elemental analysis, electronic and vibrational spectroscopy, and mass spectrometry (compound **VI**).

The electronic absorption spectrum of complex **V** is very similar to the spectrum of tetrabenzoporphyrinatozinc(II) [14], indicating that the presence of methyl groups in the *meso* positions weakly affects the electronic and geometric structure of the porphyrin macroring. Ligand **VI** is characterized by insignificant red shift ($\Delta\lambda$ = 3–5 nm) of the principal absorption maxima relative to those in the spectrum of tetrabenzoporphyrin [14] and smaller splitting of the Q band, which is also typical of *meso*-tetraaryl-substituted tetrabenzoporphyrins [15, 16]. The band at 3312 cm^{-1} in the IR spectrum of **VI** corresponds to stretching vibrations of the N–H bonds, strong bands in the region 3000–2800 cm^{-1} characterize vibrations of C–H bonds in the methyl groups, bands at 1730 and 1501 cm^{-1} arise from vibrations of C=C bonds, and C–N bonds in the macroring give rise to absorption bands at 1501 and 1465 cm^{-1}. The electron-impact mass spectrum of **VI** contained the molecular ion peak

with *m/z* 566 and fragment ion peaks with *m/z* 551 $[M-CH_3]^+$, 521 $[M-3CH_3]^+$, and 506 $[M-4CH_3]^+$.

By reaction of **VI** with rare-earth metal chlorides in boiling dimethylformamide (reaction time 6 h) we obtained *meso*-tetramethyltetrabenzoporphyrin complexes **VII–X** with lutetium, erbium, yttrium, and lanthanum containing chloride ion as extra ligand. The progress of the reactions was monitored by spectrophotometry, following disappearance from the spectrum of the reaction mixture of bands typical of ligand **VI**. Complexes **VII–X** were isolated by diluting the reaction mixtures with water; the precipitate was filtered off, washed with water, and dried. Attempted purification of complexes **VII–X** by column chromatography resulted (according to the electronic absorption spectra) in their partial (**VII–IX**) or complete (**X**) demetalation. Therefore, compounds **VII–X** were used without additional purification to synthesize complexes **I–IV**. Sandwich-like complexes **I–IV** were prepared according to the procedure described in [12], by reaction of **VII–X** with excess phthalonitrile at 290°C over a period of 1 h. When the reaction was complete, excess phthalonitrile was distilled off under reduced pressure, and products **I–IV** were isolated and purified by column chromatography, taking into account their enhanced solubility in polar organic solvents.

Electronic absorption spectrum is among the most important characteristics of sandwich complexes. Electronic spectroscopy is the simplest and most informative method for the identification of different relatively stable forms of sandwich-like compounds, which are commonly referred to as *green* and *blue* [17].

The electronic absorption spectrum of lutetium complex **I** in chloroform (Fig. 1, *1*) contains a strong maximum at λ 660 nm and a less intense band with its maximum at λ 693 nm, their intensity ratio being

2.77:1. The band at λ 693 nm belongs to the blue from of **I**, for the porphyrin ligand is a stronger π-electron-donor, and electron transfer to the phthalocyanine fragment involves vacant 5d orbitals of the central metal ion [12]. The presence of a band with its maximum at λ 457 nm indicates that molecule **I** contains *meso*-tetramethyltetrabenzoporphyrin radical fragment. Thus complex **I** in chloroform exists mainly as neutral radical green form. The electronic absorption spectrum of complex **I** changes in going from chloroform to dimethylformamide containing 1% of hydrazine hydrate as reducing agent (Fig. 1, *2*). The maximum at λ 660 nm shifts to shorter wavelengths (λ 613 nm), the relative intensity of the band at λ 694 nm considerably increases, and the intensity ratio of these bands becomes 1:1.86. These findings together with the lack of absorption in the region λ 450–460 nm suggest that compound **I** in the presence of a reducing agent is converted into anionic blue form. In both cases, the diffuse band in the region λ 423–427 nm arises from electronic transitions in the conjugation system of the tetrabenzoporphyrin ligand (Soret band).

The electronic absorption spectrum of complex **I** in acetone containing 1% of hydrogen peroxide (Fig. 2) displayed the Q-band with its maximum at λ 658 nm, diffuse band at λ 475 nm, and a band in the near-IR region (λ 996 nm). The position and shape of the two latter bands indicate that complex **I** in the presence of oxidant undergoes one-electron oxidation to radical cation form which resembles the red form of di-phthalocyaninatolutetium [18].

The electronic absorption spectra of erbium complex **II** are fairly similar to those of compound **I**. We can note only insignificant ($\Delta\lambda$ = 1–3 nm) red shift of the principal absorption maxima in chloroform. In the spectrum recorded from a solution in DMF with addition of hydrazine hydrate, the Soret band belonging to the porphyrin macroring appears at a longer wavelength, λ_{max} 434 nm. This may be due to increased electron density in the tetrabenzoporphyrin ligand as a result of its remoteness from the phthalocyanine fragment since the ionic radius of erbium is larger than that of lutetium.

Yttrium complex **III** displayed considerably different pattern in the electronic absorption spectra. The spectrum in chloroform (Fig. 3, *1*) contained three maxima in the Q-band region, at λ 692, 662, and 606 nm. The band at λ 606 nm, corresponding to the tetrabenzoporphyrin ligand, suggests appreciably weaker interaction between the porphyrin and phthalo-
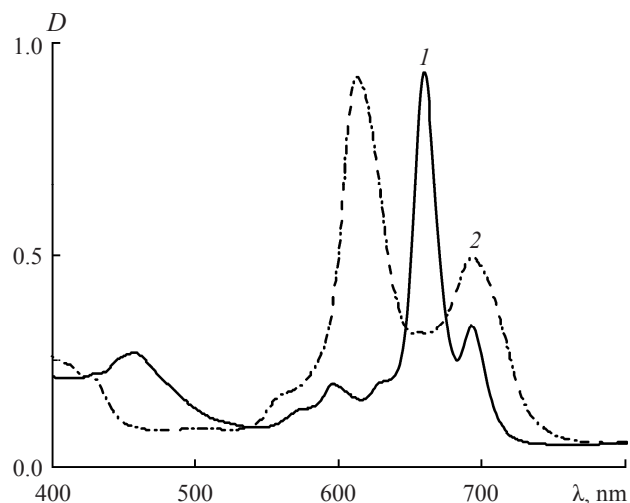

Fig. 1. Electronic absorption spectra of (phthalocyaninato)-(5,10,15,20-tetramethyltetrabenzoporphyrinato)lutetium(III) (**I**) in (*1*) chloroform and (*2*) dimethylformamide containing 1% of hydrazine hydrate.
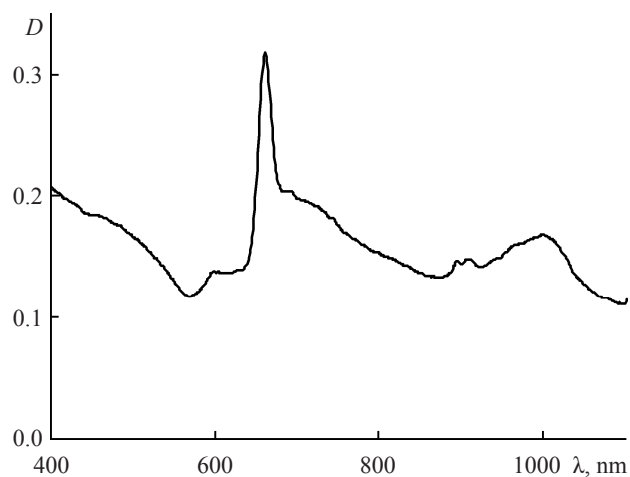

Fig. 2. Electronic absorption spectrum of (phthalocyaninato)-(5,10,15,20-tetramethyltetrabenzoporphyrinato)lutetium(III) (**I**) in acetone containing 1% of hydrogen peroxide.

cyanine chromophores, which is related to increase in ionic radius in going from Lu^{3+} and Er^{3+} to Y^{3+}. In the region λ 400–450 nm we also observed three absorption bands with their maxima at λ 444, 429, and 414 nm; the two latter may be identified as Soret band of the tetrabenzoporphyrin ligand. The band at λ 444 nm is related to that observed in the region λ 480–510 nm of the spectra of green rare-earth di-phthalocyaninates; it belongs to the radical phthalocyanine fragment. A weaker absorption band with its maximum at λ 507 nm characterizes electronic transitions in the radical porphyrin fragment. The above spectral parameters are typical of weaker interaction between the phthalocyanine and tetrabenzoporphyrin
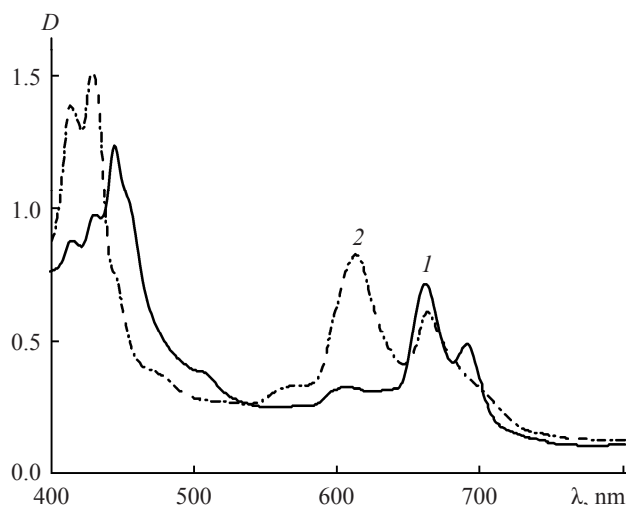
Fig. 3. Electronic absorption spectra of (phthalocyaninato)-(5,10,15,20-tetramethyltetrabenzoporphyrinato)yttrium(III) (**III**) in (*1*) chloroform and (*2*) dimethylformamide containing 1% of hydrazine hydrate.

Fig. 4. Electronic absorption spectra of (phthalocyaninato)-(5,10,15,20-tetramethyltetrabenzoporphyrinato)lanthanum(III) (**IV**) in (*1*) chloroform and (*2*) dimethylformamide containing 1% of hydrazine hydrate.

systems in complex **III** compared to **I** and **II**. The electronic absorption spectrum of the blue form of **III** (Fig. 3, *2*) contains two bands in the *Q*-band region (λ_{max} 633 and 613 nm); the bands at λ 428 and 413 nm are retained, and the lack of absorption at λ 444 and 507 nm indicates the absence of radical fragments.

In the visible region of the electronic spectrum of lanthanum complex **IV** in chloroform (Fig. 4, *1*) we observed maxima at λ 663, 609, 443, 428, and 409 nm. The lack of absorption in the region 500–600 nm indicates the absence of radical tetrabenzoporphyrin fragment, i.e., the unpaired electron is localized over the phthalocyanine ligand. In going from chloroform to DMF containing hydrazine hydrate (Fig. 4, *2*), the bands at λ 603, 443, 429, and 416 nm in the visible region are conserved, while the long-wave band
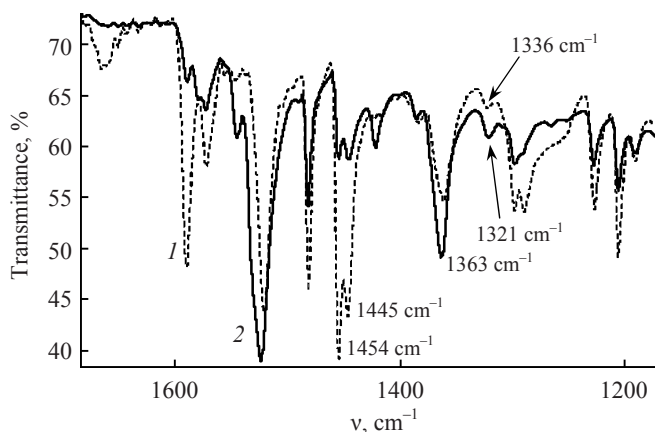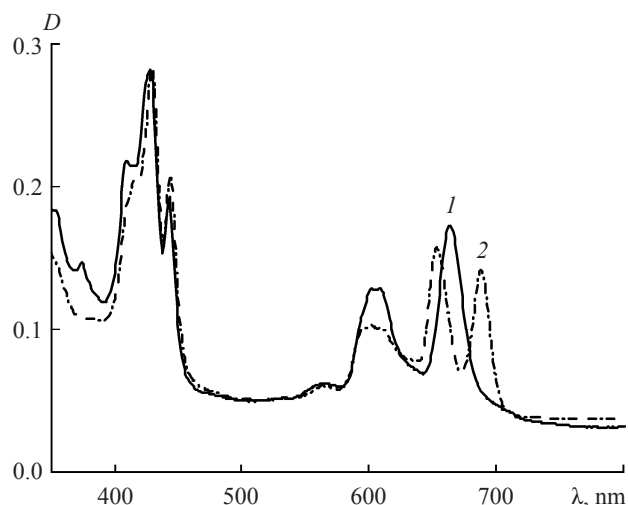
(λ_{max} 663 nm in CHCl$_3$) is converted into two maxima at λ 688 and 653 nm. This pattern indicates almost complete independence of the chromophores in complex **IV** due to large ionic radius of La^{3+}.

IR spectroscopy is widely used to identify various metal diphthalocyaninates. It was found [19] that all green rare-earth diphthalocyaninates are characterized by the presence of an absorption band in the region 1310–1330 cm^{-1} and that its position depends on the metal ionic radius: increase in the latter is accompanied by high-frequency shift of the absorption maximum. This band indicates the presence of an unpaired electron delocalized over both phthalocyanine fragments. In the IR spectra of complexes **I–IV**, recorded from TlI$_3$ glass-supported films, we also observed absorption bands in the region 1340–1320 cm^{-1}; this means that the examined complexes in crystal exist in the green from. As with diphthalocyaninates, the absorption maximum shifts toward higher frequencies as the ionic radius of the metal increases. For example, Lu^{3+} and La^{3+}complexes **I** and **IV** displayed absorption bands at 1336 and 1321 cm^{-1}, respectively (Fig. 5).

In addition, the IR spectra of complexes **I–IV** contained strong absorption bands in the regions 1455–1445 and 1365–1360 cm^{-1}. These bands are related to those observed in the IR spectra of rare earth diphthalocyaninates [20], and they belong to stretching vibrations of C–N and C–C bonds in the phthalocyanine macroring. However, the band at 1456 cm^{-1} in the IR spectrum of lutetium diphthalocyaninate is not split [20], whereas the corresponding band in the spec-

Fig. 5. IR spectra of complexes (*1*) **I** and (*2*) **IV**.

trum of complex **I** is split into two components with their maxima at 1454 and 1445 cm^{-1} (Fig. 5, *1*). The observed splitting reflects nonequivalence of the ligands and is also typical of complexes **II–IV**.

Thus we can conclude that increase in the ionic radius of rare-earth metal ion in sandwich-type *meso*-tetramethyltetrabenzoporphyrin–phthalocyanine complexes is accompanied by weakening of π–π interaction between the porphyrin and phthalocyanine fragments, which determines spectral parameters of the complexes.

EXPERIMENTAL

The electronic absorption spectra were measured on a Hitachi UV-2001 spectrophotometer. The IR spectra were recorded in the region 400–4000 cm^{-1} on an Avatar 360 FT-IR instrument from samples prepared as films applied onto TlI$_3$ glass. The mass spectrum was obtained on a Varian Saturn 2000R GC–MS system. The elemental compositions were determined using a Flash EA 1112 CHNS–O Analyzer.

5,10,15,20-Tetramethyltetrabenzoporphyrinato-zinc(II) (V). A mixture of 3.0 g (0.02 mol) of phthalimide and 4.0 g (0.02 mol) of zinc(II) propanoate was placed in a quartz test tube, and the tube was heated to 310°C and kept for 1.5 h at that temperature. The mixture was cooled, the melt was ground and dissolved in a minimal amount of pyridine, and the solution was applied to a column charged with aluminum oxide of activity grade II according to Brockmann. The column was eluted with toluene–pyridine (50:1, by volume), and the major green fraction was collected. Removal of the solvent gave 0.63 g (22%) of compound **V** as a dark green finely crystalline powder which is readily soluble in pyridine and DMF, sparingly soluble in chloroform and acetone, and insoluble in water. Electronic absorption spectrum (acetone), λ$_{max}$, nm (logε): 625 (4.58), 575 (4.28), 425 (5.01). IR spectrum, ν, cm^{-1}: 3061, 2923, 2866, 1730, 1501, 1465. Found, %: C 75.28; H 4.55; N 8.24. C$_{40}$H$_{28}$N$_4$Zn. Calculated, %: C 76.25; H 4.48; N 8.89.

5,10,15,20-Tetramethyltetrabenzoporphyrin (VI). Complex **V**, 0.60 g, was dissolved in 10 ml of concentrated sulfuric acid, and the solution was kept for 2 h at 20°C and poured into 50 ml of water. The precipitate was filtered off, washed with 20 ml of water and 20 ml of a 10% ammonia solution, dried, and dissolved in a minimal amount of pyridine. The solution was applied to a column charged with alumi-

num oxide of activity grade II according to Brockmann. The column was eluted with toluene–pyridine (50:1, by volume), and the major green fraction was collected. Removal of the solvent gave 0.42 g (78%) of compound **VI** as a dark green finely crystalline powder which is readily soluble in pyridine and DMF, sparingly soluble in chloroform and acetone, and insoluble in water. Electronic absorption spectrum (acetone), λ$_{max}$, nm (logε): 665 (4.08), 605 (4.12), 435 (4.97), 421 sh (4.79). IR spectrum, ν, cm^{-1}: 3312, 2922, 2871, 1730, 1501, 1465. Mass spectrum, *m/z* (I_{rel}, %): 566 [M]$^+$ (100), 551 [$M - CH_3$]$^+$ (78), 521 [$M - 3CH_3$]$^+$ (71), 506 [$M - 4CH_3$]$^+$ (60). Found, %: C 84.91; H 5.66; N 8.92. C$_{40}$H$_{30}$N$_4$. Calculated, %: C 84.78; H 5.34; N 9.88.

5,10,15,20-Tetramethyltetrabenzoporphyrin complexes VII–X with lutetium, erbium, yttrium, and lanthanum (*general procedure*). Porphyrin **VI**, 0.2 mmol, was dissolved in 10 ml of DMF, 3 mmol of the corresponding rare earth metal chloride was added, and the mixture was heated for 6 h at the boiling point. The mixture was diluted with 30 ml of water, and the precipitate was filtered off, washed with 30 ml of water, and dried.

Sandwich complexes I–IV (*general procedure*). A mixture of 0.05 g of complex **VII–X** and 0.5 g of phthalonitrile was heated for 1 h at 290°C. Excess phthalonitrile was distilled off under reduced pressure, the residue was dissolved in toluene, and the solution was applied to a column charged with aluminum oxide of activity grade II according to Brockmann. The column was eluted with toluene to collect the major green fraction.

(Phthalocyaninato)(5,10,15,20-tetramethyltetra-benzoporphyrinato)lutetium(III) (I). Yield 0.016 g (20%); complex **I** is readily soluble in toluene, chloroform, acetone, and DMF. Electronic absorption spectrum, λ$_{max}$, nm (D/D_{max}): in CHCl$_3$: 693 (0.36), 660 (1.00), 628 (0.21), 595 (0.21), 457 (0.29), 430 (0.24); in DMF containing 1% of hydrazine hydrate: 694 (0.54), 613 (1.00), 562 (0.19), 427 (0.24); in acetone containing 1% of hydrogen peroxide: 997 (0.53), 658 (1.00), 475 (0.56). IR spectrum, ν, cm^{-1}: 3067, 2922, 2871, 1736, 1660, 1590, 1574, 1520, 1479, 1454, 1445, 1360, 1336, 1280, 1268, 1230, 1212. Found, %: C 70.01; H 3.66; N 13.98. C$_{72}$H$_{44}$LuN$_{12}$. Calculated, %: C 69.06; H 3.54; N 13.42.

(Phthalocyaninato)(5,10,15,20-tetramethyltetra-benzoporphyrinato)erbium(III) (II). Yield 0.012 g

(15%); complex **II** is readily soluble in toluene, chloroform, acetone, and DMF. Electronic absorption spectrum, λ_{max}, nm (D/D_{max}): in CHCl$_3$: 694 (0.13), 663 (1.00), 634 (0.18), 599 (0.21), 457 (0.15), 432 (0.20); in DMF containing 1% of hydrazine hydrate: 688 (0.48), 619 (1.00), 561 (0.20), 434 (0.23). IR spectrum, ν, cm^{-1}: 3066, 2928, 2875, 1730, 1664, 1592, 1571, 1517, 1476, 1451, 1444, 1362, 1335, 1269, 1236. Found, %: C 70.42; H 3.48; N 13.86. $C_{72}H_{44}ErN_{12}$. Calculated, %: C 69.49; H 3.56; N 13.51.

(Phthalocyaninato)(5,10,15,20-tetramethyltetrabenzoporphyrinato)yttrium(III) (III). Yield 0.010 g (8%); complex **III** is readily soluble in toluene, chloroform, acetone, and DMF. Electronic absorption spectrum, λ_{max}, nm (D/D_{max}): in CHCl$_3$: 692 (0.39), 662 (0.58), 606 (0.26), 507 (0.31), 444 (1.00), 429 (0.79), 414 (0.71); in DMF containing 1% of hydrazine hydrate: 664 (0.40), 613 (0.54), 428 (1.00), 413 (0.91). IR spectrum, ν, cm^{-1}: 3062, 2921, 2880, 1728, 1654, 1586, 1578, 1515, 1472, 1459, 1446, 1360, 1329, 1277, 1221. Found, %: C 73.84; H 4.20; N 14.77. $C_{72}H_{44}N_{12}Y$. Calculated, %: C 74.16; H 3.80; N 14.41.

(Phthalocyaninato)(5,10,15,20-tetramethyltetrabenzoporphyrinato)lanthanum(III) (IV). Yield 0.006 g; complex **IV** is readily soluble in toluene, chloroform, acetone, and DMF. Electronic absorption spectrum, λ_{max}, nm (D/D_{max}): in CHCl$_3$: 663 (0.61), 609 (0.45), 443 (0.68), 428 (1.00), 409 (0.78); in DMF containing 1% of hydrazine hydrate: 688 (0.50), 653 (0.56), 603 (0.36), 444 (0.73), 429 (1.00), 416 (0.72). IR spectrum, ν, cm^{-1}: 3071, 2922, 2871, 1739, 1525, 1476, 1454, 1445, 1359, 1321, 1282, 1233, 1213. Found, %: C 71.98; H 3.79; N 14.55. $C_{72}H_{44}LaN_{12}$. Calculated, %: C 71.11; H 3.65; N 13.82.

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