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Synthesis and spectral characteristics of cyclohexylmethoxy-substituted phthalocyanines of rare-earth elements

I. P. Kalashnikova,[a] S. E. Nefedov,[b] L. G. Tomilova,[a]★ and N. S. Zefirov[a]

[a]*Institute of Physiologically Active Compounds, Russian Academy of Sciences,*
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (496) 524 9508. E-mail: tom@org.chem.msu.su
[b]*N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,*
31 Leninsky prosp., 119991 Moscow, Russian Federation

New symmetrical metal complexes of the rare-earth element phthalocyanines were synthesized by the reaction of 4,5-bis(cyclohexylmethoxy)phthalonitrile, obtained for the first time, with the rare-earth element salts, as well as starting from the corresponding free phthalocyanine. A correlation between method of the synthesis and the reaction product compositions was studied. Structures of the complexes obtained were confirmed by mass spectrometry, X-ray crystallography, and electronic absorption spectroscopy. All the metal complexes are well soluble in organic solvents.

Key words: phthalocyanines, rare-earth elements, electronic absorption spectra, mass spectrometry, X-ray analysis.

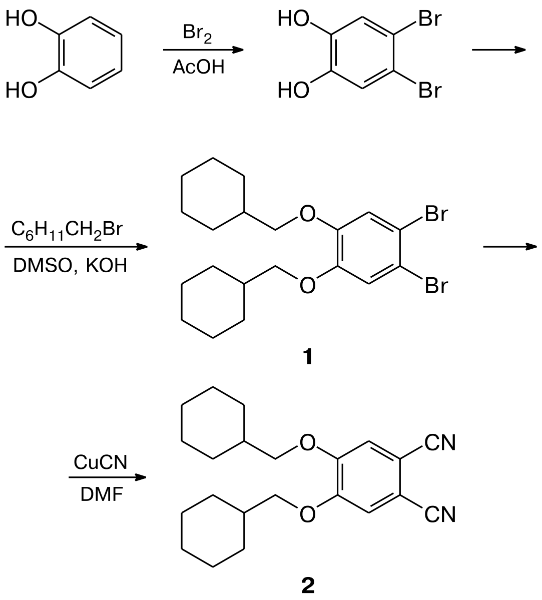
Phthalocyanine metal complexes, including phthalocyanines of the rare-earth elements (REE), belong to the unique class of macrocyclic compounds, which nowadays are widely applied as the pigments,[1,2] components of chemical sensors,[3—5] electrochromic devices,[6] photoconducting materials,[1,7] and semi-conductors.[8,9] Due to their properties and characteristics, phthalocyanines can be widely used in diverse fields such as catalysis,[10,11] nonlinear optics,[12] peptide synthesis,[13] and photodynamic therapy.[14,15]

Physical and chemical characteristics of phthalocyanines depend on the complex structures, including the number of macrocycles in the molecule, the nature of the central metal ion, and peripheral substituents.

Benzyloxy-substituted REE diphthalocyanines, studied by us earlier,[16,17] had electrochromic properties and showed high efficiency in limitation of powerful laser radiation. In order to study the influence of the peripheral substituents, we synthesized hydrogenated analogs of the benzyloxy-substituted phthalocyanines, *viz.*, symmetrical cyclohexylmethoxy-substituted phthalocyanine complexes of Lu, Dy, Er, Eu, and Sm.

The synthesis of the starting phthalogene is given in Scheme 1. The bromination of pyrocatechol was carried out according to the procedures described earlier.[18,19] The reaction of 4,5-dibromopyrocatechol with cyclohexylmethyl bromide in anhydrous DMSO in the presence of KOH gave 4,5-bis(cyclohexylmethoxy)-1,2-dibromobenzene (**1**) in 64% yield, the cyanation of which by the Rosenmund—Braun method[19—21] afforded dinitrile (**2**) in 61% yield.

Scheme 1



The use of such a phthalonitrile allowed us to obtain phthalocyanine complexes with peripheral substituents, which can exist in various conformational forms of the chair—boat type, at the same time, being well soluble in organic solvents.

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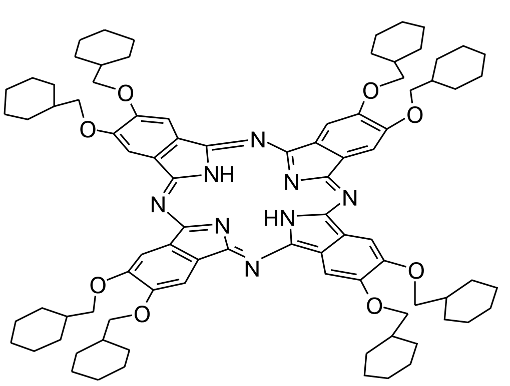

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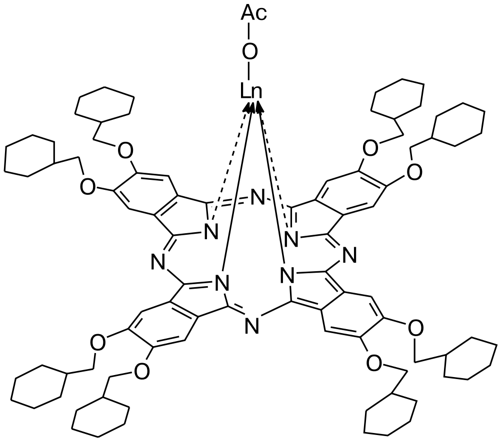

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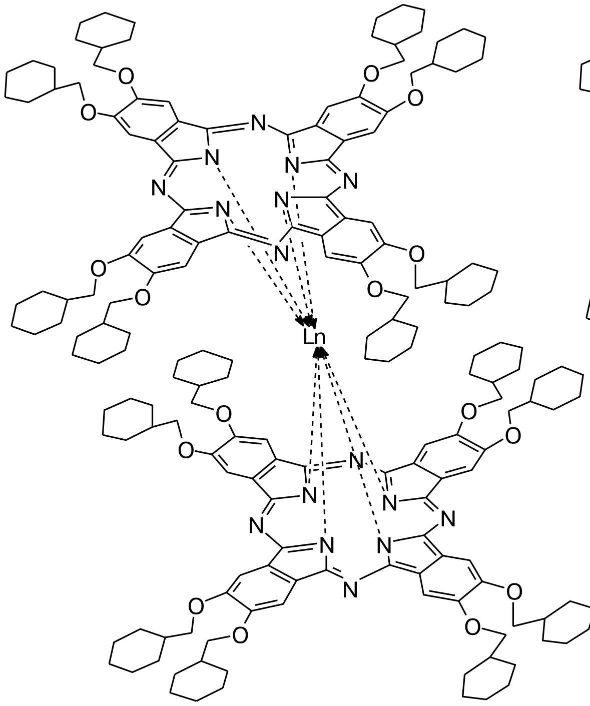
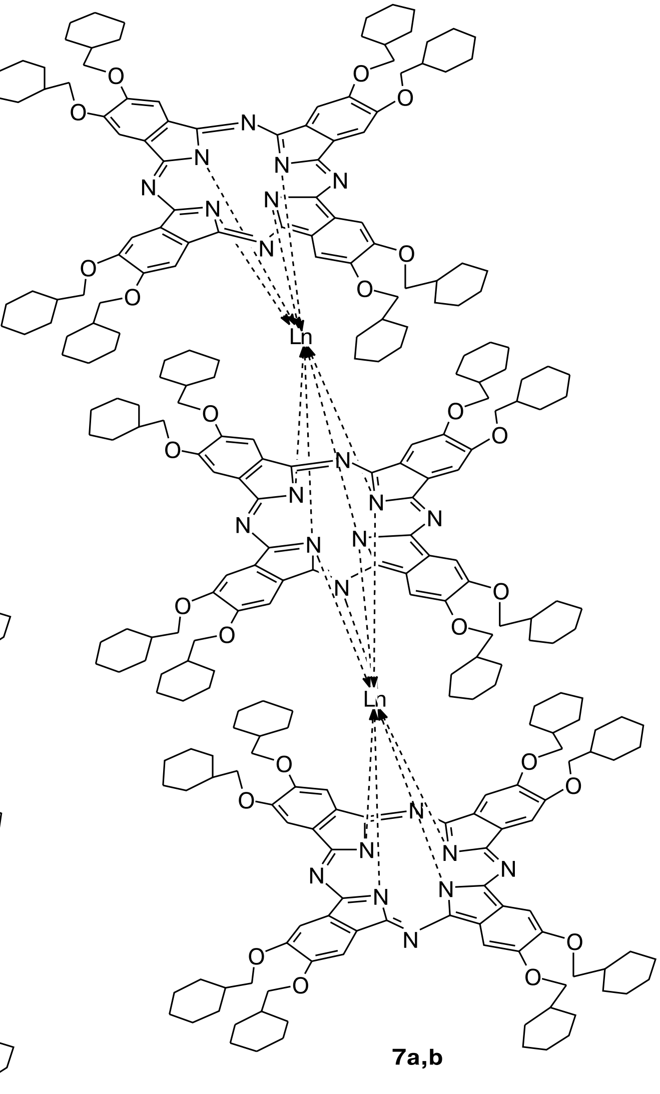
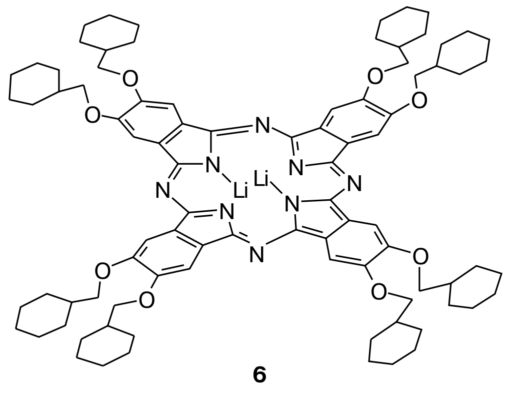


5a—e



7a,b



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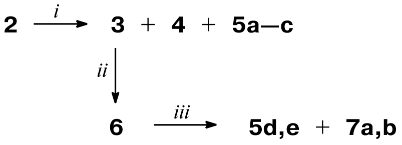
Phthalocyanine complexes of Lu, Dy, and Sm were obtained directly from phthalonitrile **2** and the corresponding REE salt in *n*-pentanol in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) under inert atmosphere for 7 h (Scheme 2, Table 1).

Scheme 2



Ln = Lu (**5a**), Dy (**4**, **5b**), Sm (**5c**), Er (**5d**, **7a**), Eu (**5e**, **7b**);
X = OAc, OCHO

Reagents: *i.* LnX_3, *n*-pentanol, DBU; *ii.* Li (metal), MeOH; *iii.* $Ln(acac)_3$, *n*-pentanol.

It was found that in addition to the target diphthalocyanine (compounds **5a—c**), there is free octacyclohexylmethoxyphthalocyanine (**3**) in the reaction mixture and in case of dysprosium, monophthalocyanine $Dy[Pc(OCH_2C_6H_{11})_8]OAc$ (**4**) is presented as well. Products **3**, **4**, and **5a—c** were isolated from the reaction mixtures by column chromatography and characterized by spectrophotometry and MALDI-TOF method. Phthalocyanine **3**, being a by-product, has low solubility in *n*-pentanol and crystallizes upon cooling of the reaction mixture, while the sandwich REE complexes remain in the solution. Due to this, the main portion of compound **3** can be separated by filtration of the reaction mixture. Chromatographic separation of Dy mono- and diphthalocyanines (**4** and **5b**) is based on the significant differences in their R_f values (0.28 and 0.90, respectively, silica gel, $CHCl_3$).

After purification with hot methanol in a Soxhlet extractor, phthalocyanine **3** was used for the synthesis of Er and Eu metal complexes (compounds **5d,e**). Here, we were challenged by the problem with the low solubility of phthalocyanine **3** in higher alcohols. On account of this, attempted synthesis according to the procedure described earlier[22] was no success. On the basis of the electronic absorption spectra (EAS) data, it was found that the poorly soluble phthalocyanine **3** does not form $[Pc(OCH_2C_6H_{11})_8]^{2-}$ dianion in the presence of such a strong base as DBU. That is why the metal complexes are not formed under these conditions even in the presence of a large excess of a REE salt. The use of the more basic REE acetylacetonates instead of acetates did not make any difference.

Table 1. Reaction conditions, reaction product composition, and yields of diphthalocyanines*

Starting reagent	REE salt	τ/h	Reaction products	Yield of diphthalocyanine (%)
1	$Lu(OCHO)_3 \cdot 2H_2O$	7	**3, 5a**	20
	$Dy(OAc)_3 \cdot 4H_2O$	7	**3, 4, 5b**	16
	$Sm(OAc)_3 \cdot 4H_2O$	7	**3, 5c**	28
3	$Er(OAc)_3 \cdot 4H_2O$	7	—	—
	$Er(acac)_3$	7	**5d**	Traces
6	$Er(acac)_3$	5	**5d, 7a**	34
	$Eu(acac)_3$	5	**5e, 7b**	37

* DBU was used as the base, in case of the starting compound **6**, a base was not used.

The REE metal complexes were successfully synthesized from free phthalocyanine **3** through the formation of the intermediate compound, *viz.*, dilithium derivative $Li_2[Pc(OCH_2C_6H_{11})_8]$ (**6**), which gives $[Pc(OCH_2C_6H_{11})_8]^{2-}$ dianion in the solution. Attempted preparation of the dilithium complex from free phthalocyanine in the solution of lithium methoxide similarly to the procedures for naphthalocyanines[23,24] gave no result in our case. Compound **3** is not dissolved in the freshly prepared MeOLi solution in methanol to form $Li_2[Pc(OCH_2C_6H_{11})_8]$ complex even under prolonged heating. The suspended phthalocyanine **3** was gradually dissolving in MeOH with the formation of compound **6** only when the finely dispersed crushed lithium metal was added to this suspension. During this, a characteristic double-band EAS of free phthalocyanine transforms into the single-band spectrum corresponding to its dianion. The EAS data for compounds **3** and **6** are given in Table 2.

Table 2. MALDI-TOF spectra and EAS of phthalocyanines

Compound	MALDI-TOF, *m/z*	*M* (calculated)	λ_{max}/nm ($CHCl_3$)
$C_{88}H_{114}N_8O_8$ (**3**)	1412	1411.90	354, 414, 663, 702
$C_{90}H_{115}DyN_8O_{11}$ (**4**)	1631	1631.42	352, 620, 686
$C_{176}H_{224}LuN_{16}O_{16}$ (**5a**)	2995	2994.73	368, 481, 603, 673
$C_{176}H_{224}DyN_{16}O_{16}$ (**5b**)	2982	2982.26	369, 489, 613, 679
$C_{176}H_{224}N_{16}O_{16}Sm$ (**5c**)	2974	2970.12	371, 495, 619, 685
$C_{176}H_{224}ErN_{16}O_{16}$ (**5d**)	2987	2987.02	369, 485, 609, 676
$C_{176}H_{224}EuN_{16}O_{16}$ (**5e**)	2972	2971.72	371, 495, 617, 683
$C_{88}H_{112}Li_2N_8O_8$ (**6**)	—	1423.76	360, 592, 635, 662*
$C_{264}H_{336}Er_2N_{24}O_{24}$ (**7a**)	4561	4564.16	345, 415, 635, 657
$C_{264}H_{336}Eu_2N_{24}O_{24}$ (**7b**)	4529	4533.57	346, 405, 579, 663

* EAS value in acetone.

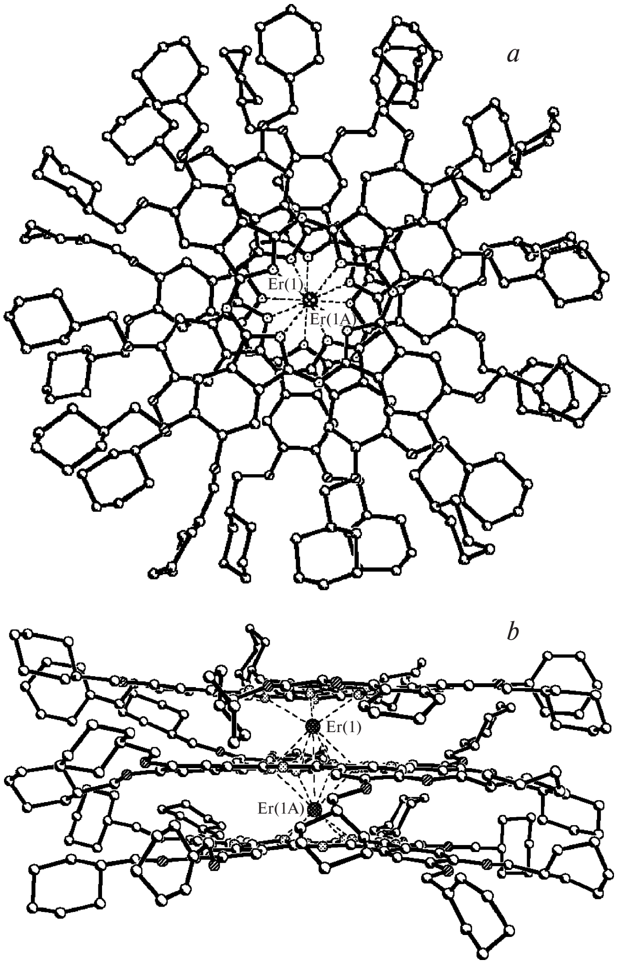


Fig. 1. Horizontal (*a*) and front (*b*) projections of molecule **7a**.

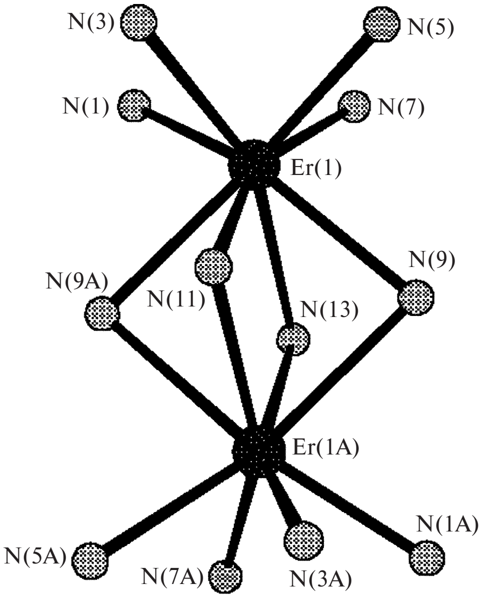


Fig. 2. Immediate coordinate environment of Er atoms in molecule **7a**.

Diphthalocyanine complexes of Er and Eu were obtained by the reaction of dilithium complex **6** with REE salts in *n*-pentanol. Acetylacetonates of Er and Eu were used as the source of the REE cations. It was found that the reaction takes place in the absence of DBU, giving a small amount of triple-decker REE phthalocyanines (**7a,b**) as the by-products. Products **7a,b** were isolated in pure form by column chromatography and characterized by spectrophotometry and MALDI-TOF method. In addition, erbium triple-decker complex **7a** was isolated in the crystalline form from the THF solution and characterized by X-ray method. According to the X-ray data, in the triple-decker sandwich complex **7a**, two $\mathrm{Er}^{\mathrm{III}}$ atoms, being on the non-bonding metal—metal distance of 3.4866(12) Å in length, are bound with four N atoms, belonging to the bridged phthalocyanine fragment (Er—N(9) is 2.607(9) Å, Er—N(11) is 2.580(9) Å, Er—N(13) is 2.593(9) Å). Molecular structure of **7a** is given in Figure 1, *a*, *b*. The coordinate environment of each metal atom, *viz.*, a distorted square antiprism, is supplemented with four N atoms of the peripheral phthalocyanine ligand (Er—N(1) is 2.322(9) Å, Er—N(3) is 2.329(9) Å, Er—N(5) is 2.336(9) Å, Er—N(7) is 2.329(9) Å) with turn the angle between the internal and external decker of 26.1° (Fig. 2). In the crystal unit, there are two solvate molecules of pentan-2-ol, a small amount of which is presented in *n*-pentanol used as the solvent in this synthesis, as well as six solvate molecules of water, the H atoms of four of them having the contacts with the O atoms of the oxocyclohexane substituents (O...H is 2.01 Å), while the other two, with the N atoms of the external deckers.

The complexes obtained are characterized by spectrophotometry. The EAS data attest that diphthalocyanines **5a—e** are the free-radical neutral forms $[\mathrm{Pc}^{\bullet -}\mathrm{Ln}^{3+}\mathrm{Pc}^{2-}]$: in the spectra of these compounds, there is a Q-band at 673—685 nm characteristic of phthalocyanines and a band at 481—495 nm on account of the presence of the $\mathrm{Pc}^{\bullet -}$ free-radical fragment in the molecule. The Soret-band has the maximum in the region 368—371 nm. Analysis of the EAS also demonstrates such features characteristic of this class of compounds as bathochromic shift of the Q-band and wiggle satellite from 673 and 603 nm for Lu diphthalocyanine to 685 and 619 nm for Sm diphthalocyanine, respectively, which is caused by an increase in ionic radius of a lanthanide. There is also a bathochromic shift of the band corresponding to the free-radical fragment, while there is only a slight change in position of the Soret-band. In the spectrum of Dy monophthalocyanine (**4**), there is no band at 489 nm characteristic only of diphthalocyanines, while a bathochromic shift of the Q-band and wiggle satellite by 7 nm for Dy monophthalocyanine relatively to the corresponding Dy diphthalocyanine could be seen. The Soret-band here has a hypso-

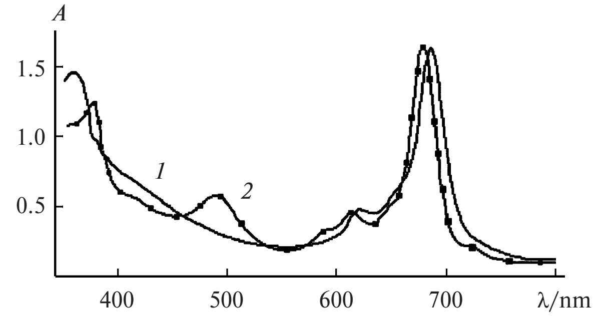


Fig. 3. Electronic absorption spectra of dysprosium mono- (**4**) and diphthalocyanine (**5b**) (*1* and *2*, respectively).

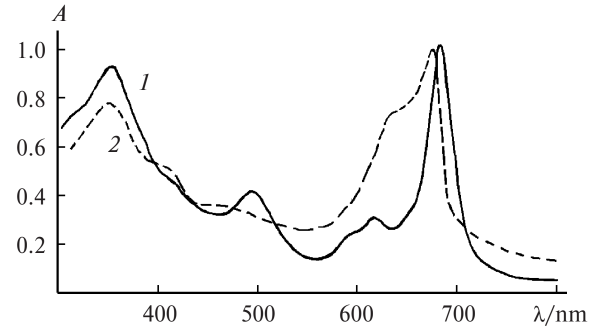


Fig. 4. Electronic absorption spectra of europium di- (**5e**) and triphthalocyanine (**7b**) (*1* and *2*, respectively).

chromic shift. The spectra of cyclohexylmethoxy-substituted Dy mono- and diphthalocyanines are given in Fig. 3; there is a distinction between the EAS of triple-decker phthalocyanines and diphthalocyanines. Positions of the Soret-band and Q-band maxima are close, while the Q-band of the triple-decker complex is considerably broadened and has a profound shoulder, which can be, apparently, explained by the sterical hindrance caused by bulky substituents.[22] The EAS of Eu di- and triple-decker phthalocyanines are given in Fig. 4.

From the data published by us earlier, it follows that position of the Q-band virtually does not change for acyclic hexadecaalkoxy-substituted diphthalocyanines with the alkoxy substituents of different length and it is at ~664—669 and 674—680 nm for Lu and Sm diphthalocyanines, respectively.[19,25] Close values were observed for diphthalocyanines with aromatic benzyloxy substituents.[16] From the data in Table 3 it follows that for alicyclic peripheral substituents, the Q-band bathochromically shifts by ~10 nm.

Table 3. Position of Q-band maximum of some hexadeca-substituted diphthalocyanines $Ln[Pc(OR)_8]_2$ (Ln = Lu, Sm)

Ln	R	λ_{max}/nm ($CHCl_3$)
Lu	Pr	660 [19]
	C_5H_{11}	669 [25]
	CH_2Ph	662 [16]
	$CH_2C_6H_{11}$	673*
Sm	Pr	680 [19]
	C_5H_{11}	675 [25]
	CH_2Ph	675 [16]
	$CH_2C_6H_{11}$	685*

* Determined in the present work.

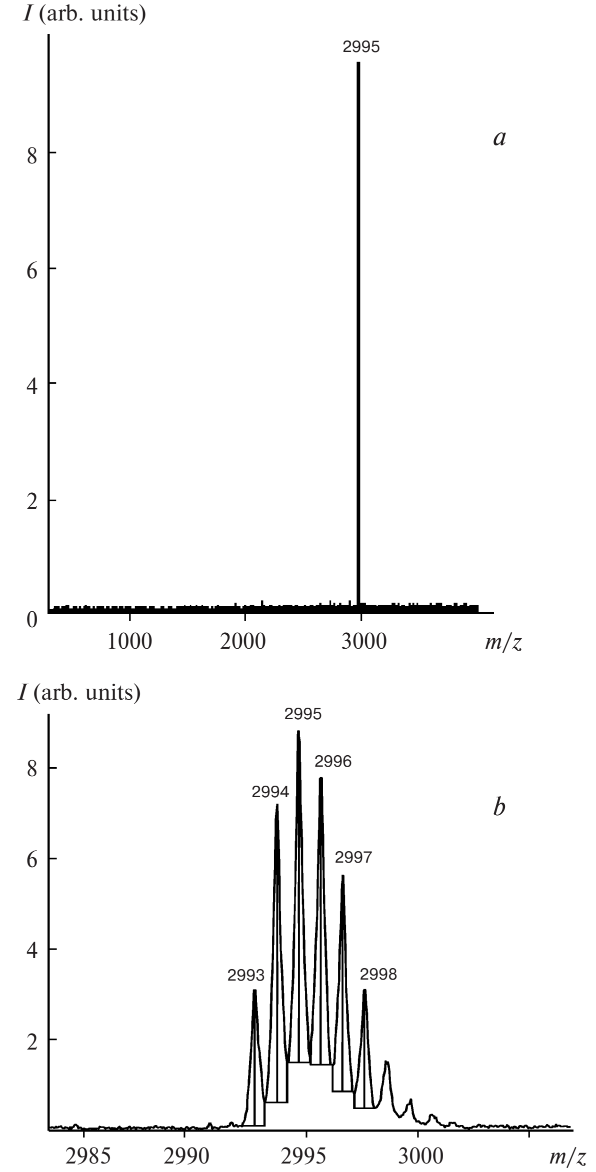


Fig. 5. MALDI-TOF spectrum of diphthalocyanine **5a** (*a*) and the molecular ion peak (*b*).

The MALDI-TOF method was used for the mass spectrometry study. In the mass spectra of the compounds, single-charged peaks with the weights corresponding to the molecular ions were observed. The spectrophotometric and mass spectrometric data are given in Table 2. The MALDI-TOF spectra and molecular ion peak of Lu diphthalocyanine are given in Fig. 5.

Experimental

n-Pentan-1-ol (pure grade) was used after distillation, DMF (pure for analysis grade) and DMSO (chemically pure) were distilled *in vacuo* and dried with barium oxide. For the synthesis of compound **1**, KOH (pure for analysis grade) was used. Cyclohexylmethyl bromide (Lancaster, 98%) was used without additional purification. For the synthesis of phthalocyanines, formates, acetates, and acetylacetonates of the corresponding lanthanides (pure for analysis grade) were used. NMR spectra were recorded on a Bruker DPX-200 spectrometer (200 MHz, relatively to Me_4Si). EAS spectra were recorded on a Specord UV—Vis spectrophotometer (Carl Zeiss), mass spectra were recorded on a VISION-2000 instrument (MALDI-TOF).

Column chromatography was performed on Lancaster Silica Gel 60 (0.060—0.200 mm) and on polymeric Bio-Beads S-X1 packing material.

X-ray analysis of compound **7a** • $6H_2O$ • • $Me(CH_2)_2CH(OH)Me$ was performed on a SMART APEX diffractometer, CCD detector (λ(Mo-Kα) = 0.71073 Å, graphite monochromator, ω-scanning technique, $2\theta_{max} = 46°$); $C_{274}H_{348}N_{24}O_{32}Er_2$, $M = 4824.28$, monoclinic syngonia, space group $C2/c$, $a = 46.883(9)$ Å, $b = 26.394(5)$ Å, $c = 22.847(4)$ Å, $\alpha = 114.117(2)°$, $V = 25804(8)$ Å^3 (120 K), $Z = 4$, $d_{calc} = 1.242$ g cm^{-3}, 17887 measured reflections, 8508 independent reflections with $F^2 > 2\sigma(I)$, $\mu = 0.717$ mm^{-1}, $R_1 = 0.0874$, $wR_2 = 0.1827$. The peripheral cyclohexylmethoxy fragments are disordered over few positions, the multiplicity of which was not precisely detected. Hydrogen atoms were geometrically generated and refined using a riding model. All the calculations were carried out with the use of SAINT[26] and SHELXTL-97 program packages.[27]

4,5-Bis(cyclohexylmethoxy)-1,2-dibromobenzene (1). Powdered KOH (10.77 g, 0.192 mol) was added to anhydrous DMSO (50 mL) with stirring at ~20 °C. After 5 min, dibromopyrocatechol (6.52 g, 0.024 mol) and cyclohexylmethyl bromide (17.24 g, 0.097 mol) were sequentially added to the mixture. The reaction mixture was initially stirred in an ice bath for 30 min and then, at ~20 °C for 4.5 h. After the reaction was over, the mixture was poured into ice water (200 mL), extracted with dichloromethane (4×30 mL), sequentially washed with diluted aqueous NaOH (2×30 mL) and water, and dried with $MgSO_4$. After the solvent and excess cyclohexylmethyl bromide were evaporated *in vacuo*, a mobile red oil was obtained, which was dissolved in benzene and subjected to column chromatography on alumina (eluent, benzene). After the solvent was evaporated, the product was recrystallized from ethyl acetate—hexane (1 : 1) to obtain colorless crystals (7.04 g, 64%), m.p. 73—74 °C. Found (%): C, 52.13; H, 6.09; Br, 34.76. $C_{20}H_{28}Br_2O_2$. Calculated (%): C, 52.19; H, 6.13; Br, 34.72. ^{1}H NMR ($CDCl_3$), δ: 0.90—1.40 (m, 10 H, C_6H_{11}); 1.60—1.90 (m, 12 H, C_6H_{11}); 3.70 (d, 4 H, OCH_2, J = 5.8 Hz); 7.00 (s, 2 H, C_6H_2).

4,5-Bis(cyclohexylmethoxy)phthalonitrile (2). A mixture of dibromide **1** (7.00 g, 0.015 mol) and CuCN (4.09 g, 0.046 mol) in anhydrous DMF (90 mL) was refluxed for 7 h. After cooling, almost all the solvent was evaporated, dichloromethane (50 mL) and concentrated aq. ammonia (500 mL) were added to the residue, and the mixture was stirred for 1 day. The precipitate formed was filtered off, washed with water, and dried. The filtrate was extracted with dichloromethane (3×15 mL), the combined organic extracts were washed with water and dried with $MgSO_4$. The solvent was evaporated at reduced pressure to obtain additional crop of the product (0.3 g). The combined product was recrystallized from ethanol and sublimated *in vacuo* to obtain white crystals (3.21 g, 61%), m.p. 131—133 °C. Found (%): C, 75.00; H, 8.07; N, 7.90. $C_{22}H_{28}N_2O_2$. Calculated (%): C, 74.96; H, 8.01; N, 7.95. ^{1}H NMR ($CDCl_3$), δ: 10.98—1.43 (m, 10 H, C_6H_{11}); 1.60—1.95 (m, 12 H, C_6H_{11}); 3.80 (d, 4 H, OCH_2, J = 5.8 Hz); 7.04 (s, 2 H, C_6H_2).

Lutetium(III) 2,2´,3,3´,9,9´,10,10´,16,16´,17,17´,23,23´,24,24´-hexadeca(cyclohexylmethoxy)diphthalocyanine (5a). A mixture of phthalonitrile **2** (400 mg, 1.13 mmol), $Lu(OCHO)_3$ • $2H_2O$ (49 mg, 0.14 mmol), and DBU (128 mg, 0.84 mmol) was refluxed for 7 h in *n*-pentanol (25 mL) under argon atmosphere. After cooling, the formed precipitate of phthalocyanine **3** was filtered off and washed with aq. methanol. The filtrate was concentrated, ethyl acetate (15 mL) was added to it, and the mixture was refluxed for 15 min and cooled. An additional amount of phthalocyanine **3**, undissolved in ethyl acetate, was filtered off. The solution of the diphthalocyanine **5a** in ethyl acetate was concentrated, the residue was dissolved in $CHCl_3$ and subjected to column chromatography on silica gel (eluent, benzene—MeOH, 10 : 1). After evaporation of the solvent, compound **5a** as a dark green powder was obtained (83 mg, 20%). Phthalocyanine **3** was placed in the Soxhlet apparatus, extracted with methanol from tars and admixture of the starting phthalonitrile **2**, and dried *in vacuo*.

Dysprosium(III) 2,3,9,10,16,17,23,24-octa(cyclohexylmethoxy)phthalocyanine monoacetate (4) and dysprosium(III) 2,2´,3,3´,9,9´,10,10´,16,16´,17,17´,23,23´,24,24´-hexadeca(cyclohexylmethoxy)diphthalocyanine (5b). The synthesis was carried out similarly to the procedure for compound **5a** from phthalonitrile **2** (400 mg, 1.13 mmol) and $Dy(OAc)_3$ • $4H_2O$ (58 mg, 0.14 mmol). A by-product, phthalocyanine **3**, was isolated as in the procedure for **5a**. A mixture of soluble products **4** and **5b** was separated by column chromatography (SiO_2, $CHCl_3$), with diphthalocyanine **5b** being the first to elute and monophthalocyanine **4** being the second. Compounds **4** (67 mg, 29%) and **5b** (80 g, 16%) were obtained.

Samarium(III) 2,2´,3,3´,9,9´,10,10´,16,16´,17,17´,23,23´,24,24´-hexadeca(cyclohexylmethoxy)diphthalocyanine (5c) was obtained similarly to compound **5a** from phthalonitrile **2** (400 mg, 1.13 mmol) and $Sm(OAc)_3$ • 4 H_2O (56 mg, 0.14 mmol) in the presence of DBU (128 mg, 0.84 mmol). The yield was 116 mg (28%).

Dilithium 2,3,9,10,16,17,23,24-octa(cyclohexylmethoxy)phthalocyanine (6). Finely dispersed lithium metal (4.5 mg, 0.63 mmol) was added to a suspension of phthalocyanine **3** (300 mg, 0.21 mmol) in methanol (40 mL) and the reaction mixture was refluxed for 4 h under inert atmosphere. After cooling, the solvent was evaporated, the residue was placed in the Soxhlet apparatus to extract the product **6** with anhydrous acetone, filtering off the insoluble in acetone LiOH and unreacted phthalocyanine **3**. The solvent was evaporated to obtain 250 mg of dilithium derivative **6** as the dark green solid substance, which was further used without additional purification. The EAS data of product **6** are given in Table 2.

Erbium(III) 2,2´,3,3´,9,9´,10,10´,16,16´,17,17´,23,23´,24,24´-hexadeca(cyclohexylmethoxy)diphthalocyanine (5d) and dierbium(III) tris[2,3,9,10,16,17,23,24-octa(cyclohexylmethoxy)phthalocyanine] (7a). A mixture of derivative **6** (100 mg, $7.02 \cdot 10^{-5}$ mol) and $Er(acac)_3$ (22 mg, $4.68 \cdot 10^{-5}$ mol) in *n*-pentanol (20 mL) was refluxed for 12 h under inert atmosphere. After cooling, the solvent was evaporated *in vacuo*, the residue was dissolved in $CHCl_3$. The tars and the small admixture of the metal-free phthalocyanine were separated off by column chromatography (SiO_2, $CHCl_3$), then, products **5d** and **7a** were separated by additional chromatography (Bio-Beads, THF). The solvent was evaporated to obtain compounds **5d** (35 mg, 34%) and **7a** (5 mg, 4.7%).

Europium(III) 2,2´,3,3´,9,9´,10,10´,16,16´,17,17´,23´,23,24,24´-hexadeca(cyclohexylmethoxy)diphthalocyanine (5e) and dieuropium(III) tris[2,3,9,10,16,17,23,24-octa(cyclohexylmethoxy)phthalocyanine] (7b) were obtained from derivative **6** (100 mg, $7.02 \cdot 10^{-5}$ mol) and $Eu(acac)_3$ (21 mg, $4.68 \cdot 10^{-5}$ mol) similarly to the synthesis of **5d**. Diphthalocyanine **5e** (38 mg, 37%) and triple-decker complex **7b** (3.5 mg, 3.2%) were isolated.

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