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КОМПЛЕКСЫ ЭРБИЯ И ЛЮТЕЦИЯ «СЭНДВИЧЕВОГО» ТИПА, СОДЕРЖАЩИЕ ФРАГМЕНТЫ ТЕТРААНТРАХИНОНОПОРФИРАЗИНА И ЗАМЕЩЕННЫХ ФТАЛОЦИАНИНОВ

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Настоящая работа касается синтеза и спектральных свойств металлокомплексов эрбия и лютеция «сэндвичевого» типа, содержащих тетраантрахинонопорфиразиновые, а также фталоцианиновые фрагменты. Взаимодействием тетраантрахинонопорфиразина эрбий(лютеций)ацетата с избытками фталонитрила, 4-хлор-, 4-бромфталонитрила и незамещенного фталонитрила получены комплексы «сэндвичевого» типа несимметричного строения. Соединения экстрагировали из реакционной смеси подходящим органическим растворителем (ДМФА или толуолом) и очищали длительной экстракцией примесей ацетоном в аппарате Соксклета. Окончательную очистку осуществляли методом колоночной хроматографии. Полученные комплексы – твердые вещества зеленого цвета, обладающие растворимостью в ДМСО, ДМФА и концентрированной серной кислоте. Состав и строение комплексов подтверждали данными элементного анализа, ИК и электронной спектроскопии. Найденные значения содержания элементов находятся в хорошем соответствии с вычисленными. Исследовано влияние химического строения новых соединений «сэндвичего» типа на их спектральные свойства и возможные области применения. В частности, при анализе электронных спектров поглощения обнаружено, что металл, природа заместителей в тетраантрахиноновом фрагменте и замена атомов водорода на атомы галогена во фталоцианиновом фрагменте незначительно влияют на характер и положение максимумов поглощения. В связи с тем, что традиционной областью использования соединений фталоцианинового ряда является их применение в качестве светопрочных красителей и пигментов, были проведены исследования колористических свойств, синтезированных органорастворимых металокомплексов эрбия и лютеция. Установлено, что соединения проявляют свойства пигментов и красителей для полимерных материалов, таких как полистирол и полиэтилен. Кроме этого, определены температурные параметры термоокислительной деструкции и установлено, что полученные фталоцианины «сэндвичего» типа обладают высокой устойчивостью к термоокислительной деструкции.

Ключевые слова: металлокомплексы эрбия и лютеция, фталоцианины, фрагменты тетраантрахинонопорфиразина, «сэндвичевого» типа комплексы, синтез, свойства

ERBIUM AND SANDWICH-TYPE LUTETIUM COMPLEXES CONTAINING FRAGMENTS OF TETRAANTHRACHINOPORPHIRAZINE AND SUBSTITUTED PHTHALOCYANINES

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The present work relates to the synthesis and spectral properties of erbium and sandwich type metal complexes containing tetraanthraquinoporphyrazine as well as phthalocyanine fragments. By reacting tetraanthrachinoporphirazine erbium (lutetium) acetate with excess phthalonitrile, 4-chloro, 4-bromophthalonitrile and unsubstituted phthalonitrile, sandwich-type complexes of an unsymmetrical structure were obtained. The compounds were extracted from the reaction mixture with a suitable organic solvent (DMF or toluene) and purified by prolonged extraction of impurities with acetone in a Soxlet apparatus. Final purification was carried out by column chromatography. The obtained complexes are green solids having solubility in DMSO, DMF, and concentrated sulfuric acid. The composition and structure of complexes were confirmed by elemental analysis, IR and electron spectroscopy. Influence of chemical structure of new "sandwich" compounds on their spectral properties and possible applications has been investigated. In particular, when analyzing the electron absorption spectra, it was found that the metal, the nature of the substituents in the tetraanthraquinone moiety and the replacement of hydrogen atoms with halogen atoms in the phthalocyanine moiety slightly affect the nature and position of the absorption maxima. Studies have been carried out on the coloristic properties of synthesized organosoluble metal complexes erbium and lutetium. The compounds have been found to exhibit the properties of pigments and dyes for polymeric materials such as polystyrene and polyethylene. The temperature parameters of thermal oxidative degradation were determined and it was found that the obtained "sandwich" type phthalocyanines have high resistance to thermal oxidative degradation.

Key words: erbium and lutetium metal complexes, phthalocyanines, tetraanthraquinoporphirazine fragments, "sandwich" type complexes, synthesis, properties

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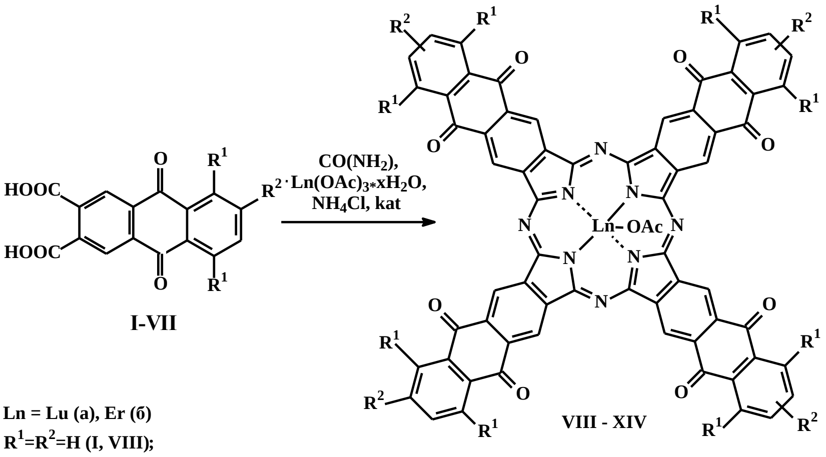
The chemistry of porphyrin series macrocycles has long been the subject of intensive research due to the enormous importance and ever-expanding practical application as pigments, dyes, organic semiconductor materials, catalysts for oxidation processes, thermo- and light-stabilizers, liquid crystals, gas sensors, pale carrots and analytical reagents [1-11].

The most important feature of phthalocyanines (Pc) is the possibility of their chemical modification. Phthalocyanines of various structures have unique spectral, electrochromic, magnetic and semiconductor properties due to a multi-circuit aromatic coupling system. These compounds are capable of forming complexes with many elements of the periodic system. Of particular interest are lanthanide phthalocyaninates. These metals, having large ion radii and high coordination numbers, are able to form sandwich compounds with phthalocyanines and their analogues. The latter are characterized by overlapping the π-orbitals of the ligands, depending on the value of the ionic radius of the lanthanide. The presence of such an effect opens up new possibilities for the use of sandwich compounds as materials for molecular electronics [12] and nonlinear optics [13], sensors [14-16], ionizing radiation sensors [17], as well as electrochromic materials [18]. Numerous methods are currently known for the synthesis of diphthalocyaninates of both symmetric and asymmetric structure [19-22]. A significant number of works also concern the synthesis and properties of «sandwich» type complexes containing phthalocyanine molecules. However, information about such complexes combining the molecules of tetraaantrachinoporphirazine and phthalocyanines in their composition is not about-external in the literature.

The present work relates to the synthesis and spectral properties of erbium and sandwich type metal complexes containing tetraanthraquinoporphyrazine as well as phthalocyanine fragments.

The starting compounds for the synthesis of "sandwich" complexes were tetraanthrachi-nonoporphyrazines **VIII-XIV**, prepared by urea method from dicarboxyanthrachinonic acids **I-VII** in the presence of urea, metal acetate (Er, Lu), ammonium chloride and ammonium molybdate as a catalyst (*Scheme 1*). The reaction mass was heated to 180 °C, then, after melting, the temperature was adjusted to 200 °C and held for 3 h.

It should be noted that due to the significant ionic radius of the metal, the reaction proceeds from relatively slowly, in contrast to complexation with divalent metals, curable under such conditions in 0.5 h [23]. The obtained complexes are blue-green solids. All compounds dissolve well in DMSO, DMF. Complexes **IX, XIII, XIV** dissolve well in toluene and chloroform.



I-VII

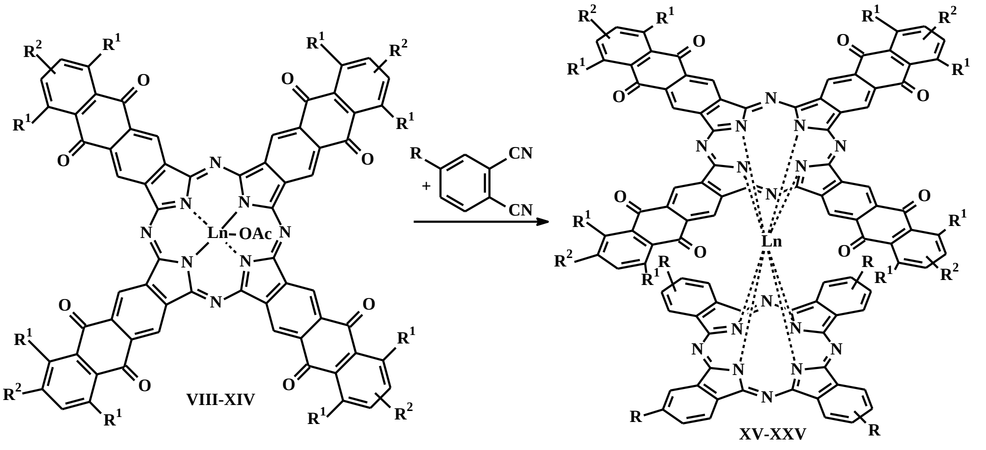
VIII - XIV

Ln = Lu (a), Er (б)
R^1=R^2=H (I, VIII);
R^1=H, R^2=CH_3 (II, IX), R^2=OCH_3 (III, X), R^2=COOH (IV, XI), R^2=$PhSO_3H$ (V, XII);
R^2=H, R^1=OCH_3 (VI, XIII), R^1=$OCO(CH_2)_{14}CH_3$ (VII, XIV).

Scheme 1
Схема 1

Attempts to chromatographically purify the synthesized metal complexes were unsuccessful, since as a result of column chromatography on both alumina and silica, the substance could not be desorbed from the column by any of the eluents. Therefore, further purification of compounds **VIII-XIV** was carried out by treating them with concentrated hydrochloric acid, water and acetone.

Heating a mixture of compounds (**VIII-XIV**) with excess phthalonitrile, 4-bromophthalonitrile and 4-chlorophthalonitrile at a temperature of 280 °C for 2 h leads to the formation of sandwich complexes of the composition of tetraanthrachinoporphyrazine - Ln - phtalocyanine (**XV-XXV**), according to



VIII-XIV

XV-XXV
Ln = Lu (a), Er (б)
R = H, Br, Cl
R^1=R^2=H, R=Br (XV);
R^1=H R^2=CH_3 R=H (XVI) R=Cl (XVII), R^2=OCH_3 R=Cl (XVIII) R=H (XIX),
R^2=COOH R=H (XX) R=Br (XXI), R^2=$PhSO_3H$ R=H (XXII);
R^2=H, R^1=OCH_3 R=Br (XXIII) R=Cl (XXIV), R^1=$OCO(CH_2)_{14}CH_3$ R=H (XXV).

Scheme 2
Схема 2

The compounds (**XV-XXV**) were extracted from the reaction mixture with a suitable organic solvent (DMF or toluene) and purified by prolonged extraction of acetone impurities in a Soxlet apparatus. Final purification was carried out by column chromatography.

The obtained complexes are green solids having solubility in DMSO, DMF, and concentrated sulfuric acid. The composition and structure of complexes **VIII-XXV** were confirmed by elemental analysis, IR and electron spectroscopy. The found values of the content of the elements are in good accordance with the calculated values.

The nature of the IR spectra of the initial lanthanide complexes of tetraanthrachine porphyrase **VIII-XIV** is similar to the spectra of phthalocyanine series compounds with bands in the intervals 3400, 1246-1300, 1170-1188, 1100-1150, 910-950, 850-880, 770-780, 734-736 cm^{-1}. At the same time, a number of bands characteristic of anthraquinone should be noted (in the regions 1650-1700 cm^{-1} and 2800-2900 cm^{-1}). In addition, the IR spectra of compounds (**Xa, b, XIIa, b, XIVa**) are characterized by the presence of a band responsible for the oscillation of the SAr-O-C bond (1115-1149 cm^{-1}).

In the IR spectra of the compounds of the "sandwich" structure (**XVa, b-XXVa, b**) there are inintensity bands at 1368-1388 cm^{-1} indicating the presence of a radical fragment of phthalocyanine [24]. A lower intensity band in the 1458-1495 cm^{-1} region characterizes the co-swan of C-N and C-C tetrapyrrole chromophores. In the spectra of complexes (**XVb, XVII b, XXIb, XXIIb**) there are bands at 888-901 cm^{-1} characteristic of vibration of N-Er bonds in octacoordinated complexes [25]. Also in the IR spectra (**XVIb, XVIII b, XIX a, XXIIb, XXIVb, XXVa**) of the compounds there are bands characteristic of valence vibrations of the Cap-Hal bond at 717-754 cm^{-1}.

The results of studies of electron absorption spectra (UV-spectra) of tetraanthraquinone-porphyrazines VIII-XIV and "sandwich" type **XV-XXV** complexes based on them are presented in Table 1 and in Fig. 1-4.

UV-spectra in DMF for tetraanthrachinoporphyrazines **VIII-XIV** are similar: in the long-wave part of the spectrum in the area of 688-690 nm, the Q-band is observed, at 650-660 nm – an oscillatory satellite. Judging by the intensity ratio of these bands, the synthesized compounds are present in this solvent in the associated form (Fig. 1). In addition, it can be seen that the nature of the substituents introduced into the tetraanthraquinoporphyrazine fragments does not affect the appearance of the spectral curve and the position of the long-wave absorption bands in the UV-spectra of these complexes (Table 1).

Table 1

Position of maxima of absorption bands in UV-spectra of erbium and lutetium complexes of "sandwich" type, XVI a, b – XXV a, b

Таблица 1. **Положение максимумов полос поглощения в ЭСП комплексов эрбия и лютеция «сэндвичевого» типа, XVIa,б – XXVa, б**

№	Complexes	Ln	UV-spectra, λ_{max}, nm
1	**XV**	Er	H_2SO_4: 435, 835 DMF: 626, 688, Toluene: 353, 627, 657, 693 Chloroform: 350, 626, 694
2	**XVI**	Lu	H_2SO_4: 437, 837 DMF: 620, 689 Toluene: 357, 628, 656, 693 Chloroform: 352, 628, 655, 693
3	**XVII**	Er	H_2SO_4: 433, 836 DMF: 621, 686 Toluene: 354, 627, 661, 693 Chloroform: 370, 626, 659, 691
4	**XVIII**	Lu	H_2SO_4: 406, 797, 833 DMF: 686 Toluene: 360, 626, 656, 692 Chloroform: 358, 626, 654, 692
5	**XIX**	Lu	H_2SO_4: 436, 835 DMSO: 622, 690
6	**XX**	Lu	H_2SO_4: 435, 833 DMF: 628, 657, 688 Toluene: 352, 628, 657, 695 Chloroform: 351, 626, 655, 692
7	**XXI**	Er	H_2SO_4: 434, 818 DMF: 623, 687 Toluene: 348, 629, 657, 694 Chloroform: 322, 627, 699
8	**XXII**	Er	H_2SO_4: 426, 832 DMF: 656, 688
9	**XXII**	Lu	H_2SO_4: 433, 835 DMF: 657, 689
10	**XXIII**	Er	H_2SO_4: 440, 830 DMF: 634, 692
11	**XXIV**	Lu	H_2SO_4: 431, 834 DMF: 622, 685
12	**XXV**	Lu	H_2SO_4: 441, 835 DMF: 623, 687

One of the most important characteristics of sandwich-type complexes is their electron-throne absorption spectra, which allows the simplest and most informative method to identify the "green" and "blue" forms of such compounds. UV-spectra of complexes

(**XVa, b-XVIII a, b, XXa, b-XXIa, b**) in chloroform, toluene (Fig. 2, curve 1) are characterized by an intense band with a maximum at 691-699 nm and a less intense band at 655-659 nm, evidencing the presence of a radical phthalocyanine fragment, wherein the ratio of their intensities is equal to 1:(0.48-0.58). Thus, in chloroform and toluene, complexes exist, generally, in a neutral radical green form.

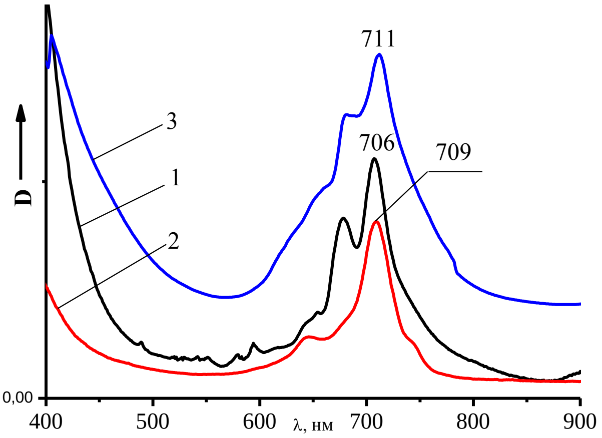


Fig. 1. UV-spectra in DMF 1 – **VIIIb**; 2 – **XIb**; 3 – **XIb**
Рис. 1. Электронные спектры поглощения в ДМФА 1 – **VIIIб**; 2 – **XIIб**; 3 – **XIб**

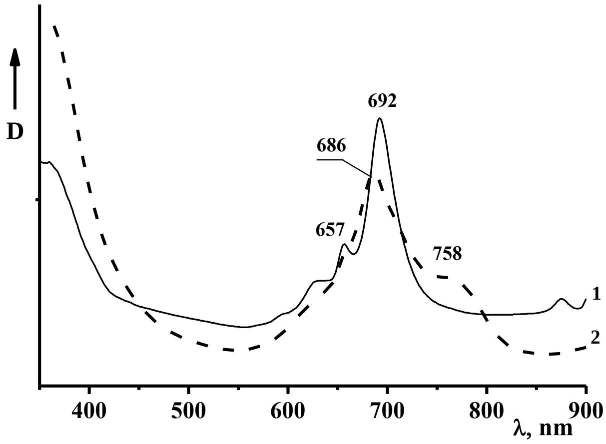


Fig. 2. UV-spectra of complex **XIX a**: **1** – toluene; **2** – DMF
Рис. 2. Электронный спектр поглощения комплекса **XIXa**: **1** – толуол; **2** – ДМФА

During the transition from chloroform and toluene to DMF, the ESP of the compounds (**XVa, b-XXVa, b**) (Fig. 2, curve 2) are changed. Band intensity at 655-659 nm decreases. It is observed at a maximum of 686-692 nm and a shoulder at 758 nm. This fact indicates the transition of the compounds (**XVIa, b-XXVa, b**) to the anionic "blue" form. As for Soré bands, the effect of the nature of the solvent on their position is insignificant, and it is observed in the region of 341-356 nm.

It has been found that the metal, the nature of the substituents in the tetraanthraquinonoporphyrazine moiety and the replacement of hydrogen atoms with halogen atoms in the phthalocyanine moiety have little effect on the nature and position of the absorption maxima.

The transition from organic solvents to concentrated sulfuric acid for all synthesized complexes is accompanied by a significant bathochromic shift of long-zero absorption bands. Moreover, the value of this shift significantly exceeds that for the corresponding metal complexes of tetraanthraquinoporphyrazines with d-metals [26].

The electron absorption spectra of the initial lanthanide-tetraanthrachinoporphyrazines, **VIIIa,b - XIVa,b** in concentrated sulfuric acid are characterized by the presence of several bands of different intensity in the regions: Soré bands 344-385 nm, characterized by pain-neck intensity, Q bands at 786-792 nm and an oscillating satellite at 667-670 and 703-708 nm (Fig. 3) Comparison of the spectra of the compounds (**VIIIa,b - XIVa,b**) with the spectra of the corresponding copper and cobalt complexes [23, 26, 27] shows that the replacement of the metal atom with erbium or lutetium leads to a bathochromic shift of the long-wave absorption band by 45-48 nm, without affecting oscillatory satellites.

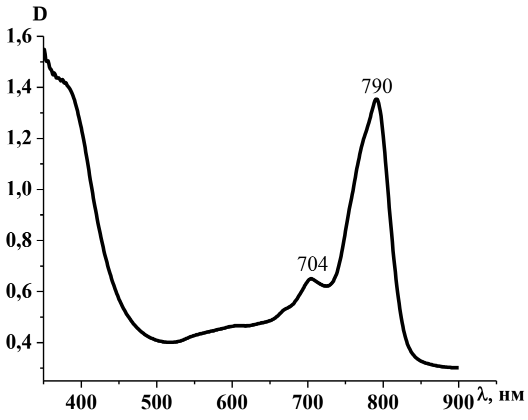


Fig. 3. UV-spectrum **VIIIa** in H_2SO_4
Рис. 3. ЭСП комплекса **VIIIa** в H_2SO_4

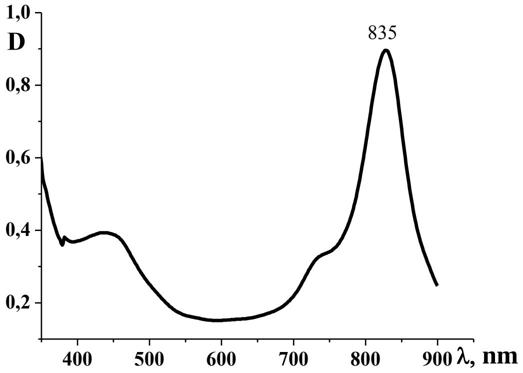


Fig. 4. UV-spectrum **XIVa** in H_2SO_4
Рис.4. ЭСП комплекса **XIVa** в H_2SO_4

UV-spectra of sandwich-type complexes in sulfuric acid are characterized by the presence of an in-intensity Q-band in the region of 820-840 nm (Table 1, Fig. 4). At the same time, its bathochromic shift is recorded in comparison with the ESP of the corresponding lanthanide complexes of tetraanthraquinoporphyrazines (for example, Fig. 3 and Fig. 4). The nature of the substituents has little effect on the position of the Q band (Table 1).

Considering the possibility of using synthesized phthalocyanines at high temperatures in the presence of air oxygen, it seems advisable to study their resistance to thermal oxidative degradation. In the present work, thermal oxide destruction of phthalocyanines of the "sandwich" structure of erbium and lutetium (**XVb, XVIII a, XXIIa, b-XXV, b**) is investigated. The results are shown in Table 2.

Table 2

Thermooxidizing destruction of compounds XVb, XVIIIa, XXIIa,b-XXVa,b

Таблица 2. **Термоокислительная деструкция соединений XVб, XVIIIa, XXIIa,б-XXVa,б**

№	Complex	Maximum start temperature weight loss, °C	Temperature maximum ekzoeffekt, °C
XVb	TAQPa(R'=H)$_4$ErPc(R=Br)$_4$	320	440
XVIIIa	TAQPa(R'=OCH$_3$)$_4$LuPc(R=Cl)$_4$	408	501
XXIIa	TAQPa(R'=PhSO$_3$H)$_4$LuPc(R=H)$_4$	320	387
XXIIb	TAQPa(R'=PhSO$_3$H)$_4$ErPc(R=H)$_4$	405	508
XXIIIb	TAQPa(R'=OCH$_3$)$_4$ErPc(R=Br)$_4$	220	420
XXIVa	TAQPa(R'=OCH$_3$)$_4$LuPc(R=Cl)$_4$	250	422
XXVa	TAQPa(R'=OCO(CH$_2$)$_{14}$LuPc(R=H)$_4$	300	408

When studying the resistance of the obtained complexes to thermo-oxidative destruction, the general problem in their behavior was noted. At the first stage, when heated from 25 °C to 200 °C, a slight decrease in the mass of the tested samples (15%) is fixed on the TG curves. An additional controll on the IR and electronic absorption spectra of the compounds **XVb, XVa, XXIIa, b-XXVa, b**, fixed before the start of the experiment, and after heating to 200 °C, showed their identity. This indicates that the changes recorded on derivatograms are not associated with degradation processes in the molecules of metal complexes **XVb, XVa, XXIIa, b-XXVa, b**.

With further heating to 380-501 °C, in our opinion, there are transformations involving peripheral groups with the formation of, inter alia, oligomeric structures. Finally, at higher temperatures (400-580 °C, Table 2), phthalocyanine and porphyrazine rings are destroyed to produce lutetium or erbium oxides.

When comparing compounds **XXIIa** and **XXIIb**, it was found that complexes with erbium have the greatest stability. Unfortunately, we could not find any pattern related to the influence of the peripheral environment.

Application of phthalocyanine compounds is their use as light-resistant dyes and pigments. In this regard, studies were carried out on the coloristic properties of synthesized organoluble metal complexes erbium and lutetium. Compounds **XVb, XVIa, XVIIb, XVIIIa, XXa, XXIb, XXIIa,b** have been found to exhibit pigments and dyes for polymeric materials such as polystyrene and polyethylene.

Thus, the template condensation of substituted o-dicarboxylic acids of anthraquinone with metal salts (lutetium or erbium) for the first time synthesized new metal complexes of tetraanthraquinoporphyrazines with rare earth elements. Methods of their cleaning are offered.

By reacting the obtained lanthanid-tetraanthraquinonoporphyrazines with different phthalonitriles, new metal complexes of the "sandwich" type combining tetraanthraquinonoporphyrazine and phthalocyanine fragments were synthesized.

Influence of chemical structure of new "sandwich" compounds on their spectral properties and possible applications has been investigated. In particular, in the analysis of UV-spectra, it was found that the metal, the nature of the substituents in the tetraanthraquinone moiety and the replacement of hydrogen atoms with halogen atoms in the phthalocyanine moiety slightly affect the nature and position of the absorption maxima. In addition, they have been found to exhibit the properties of pigments and dyes for polystyrene and polyethylene. Finally, temperature parameters of thermal oxidative degradation were determined and it was found that the obtained "sandwich-something" type phthalocyanines have high resistance to thermal oxidative destruction.

EXPERIMENTAL-METHODICAL PART

The research was performed using resources of the Center for Collective Use, Ivanovo State University of Chemical Technology "ISUCT".

Elemental analysis was performed on a Flash EA 1112 CHNS-O Analyzer.

Electron absorption spectra (UV-vis) were recorded in organic solvents (DMF, toluene, chloroform), aqueous alkaline solutions (1% sodium hydroxide solution) and concentrated sulfuric acid on a UV/VIS Perkin Elmer Spectrometer Lambda 200 spectrophotometer at room temperature in the wavelength range (250-1000) nm.

IR spectra were recorded on an Avatar 360 FT-IR ESP device in the 400-4000 cm^{-1} region in quartz glass films.

Thermal-oxidative destruction studies were carried out on a thermoanalytic device consisting of a derivatograph 1000D of the company IOM, Hungary, a software-hardware complex and a PC (IHR RAS Ivanovo) [28]. Samples of tetraanthraquinoporphyrazines metal complexes weighing 10-30 mg were placed in a platinum crucible and heated in an air atmosphere at a rate of 5 degrees × min^{-1} in an air atmosphere.

Dyeing and coloristic analysis were carried out according to procedures [29, 30].

Starting ortho-dicarboxylic acids **I-VIII** were prepared according to the procedure [31].

Synthesis of metal complexes of tetraanthraquinoporphyrazine **VIIa,b-XIV a,b**.

General methodology. In a quartz vial was placed a triturated mixture of 0.60 mmol of the corresponding 2,3-dicarboxyanthraquinones, 4.00 mmol (0.24 g) of urea, 0.18 mmol of metall acetate (Erbium or lutetium), 0.40 mmol (0.02 g) of ammonium chloride and 0.01 mmol (0.002 g) of ammonium molybdate. The mass was slowly heated to 180 °C for an hour and held for 3 hours. After cooling, the reaction mixture was ground, transferred to a Schott filter, washed with 5% hydrochloric acid and water until a solid residue was removed in the wash liquid, applied to the object stack and evaporated. Then, it was dried at 100 C, then washed in a Soxlet apparatus with acetone for 10 h.

***The synthesis of erbium tetraanthraquinonoporphirazine (*VIIIb**) was carried out according to the general procedure using 0.65 g of 2, 3-dicarboxyanthraquinone.

Synthesis of tetra- (6-methyl) anthraquinonoporphirazine metal complexes (**IXa, b**) was carried out according to the general procedure using 0.18 g of 2,3-dicarboxy-6-methylanthraquinone.

Synthesis of lutetium tetra- (6-methoxy) anthraquinonoporphyrazine (Xa) was carried out on a total meta-wild using 0.18 g of 2,3-dicarboxy-6-methoxyanthraquinone.

The synthesis of tetra- (6-carboxy) anthraquinoporphyrazine metal complexes **(XI a,b)** was carried out according to the general procedure using 0.20 g of 2,3,6-tricarboxyanthraquinone.

Synthesis of tetra- (6-sulfophenyl) anthrachinoporphirazine (*XII a,b*) metal complexes was carried out according to the general procedure using 0.27 g of 2,3-dicarboxy-6- (para-sulfophenyl) anthrachinone.

Synthesis of metal complexes of tetra- (5, 8-dimethoxes) anthraquinoporphirazine **(XIII a,b)** was carried out according to the general procedure using 0.20 g of 2, 3-dicarboxes-5,8-dimethoxyanthraquinone.

Synthesis of tetra- (5, 8-dicaprinoxa) anthraquinoporphirazine lutetium **(XIVa)** was carried out according to the general procedure using 0.20 g of 2, 3-dicarboxy-5,8dicaprinoxyanthraquinone.

The output and elemental analysis data for metal complexes **VIII-XIV** are shown in Table 3.

Synthesis of phthalocyanines of "sandwich" type XVa, b - XXVa, b.

General methodology. In a quartz vial was placed a triturated mixture of 0.017 mmol of the corresponding substituted tetraanthraquinoporphirazine (**VIII-XIV**) and 0.1 mmol of phthalonitrile or its 4-chloro (4-bromo) substituted. The reaction mass was

Table 3

Yield and elemental analysis of metallophthalocyanines VIII-XIV

Таблица 3. **Выход и данные элементного анализа металлофталоцианинов VIII – XIV**

№	Yield, g (%)	Gross - a formula	Elemental analysis data. Found/is calculated, %		
			C	H	N
VIIIб	0.36 (47)	$C_{64}H_{24}N_8O_8Er$	64.0/64.1	2.0/2.2	9.3/9.1
IXa	0.10 (72)	$C_{68}H_{32}N_8O_8Lu$	64.4/64.6	2.9/2.6	8.6/8.9
IXб	0.08 (70)	$C_{68}H_{32}N_8O_8Er$	65.2/65.0	2.8/2.6	9.0/8.9
Xa	0.16 (78)	$C_{68}H_{32}N_8O_{12}Lu$	61.9/61.5	2.9/2.4	8.7/8.4
XIa	0.12 (74)	$C_{68}H_{24}N_8O_{16}Lu$	59.3/59.0	2.0/1.8	8.0/8.1
XIб	0.10 (70)	$C_{68}H_{24}N_8O_{16}Er$	59.7/59.3	2.0/1.8	8.1/8.2
XIIa	0.09 (37)	$C_{88}H_{40}N_8S_4O_{20}Lu$	56.9/56.7	2.4/2.2	6.3/6.1
XIIб	0.09 (37)	$C_{88}H_{40}N_8S_4O_{20}Er$	57.6/57.9	2.5/2.2	6.4/6.1
XIIIa	0.07 (62)	$C_{72}H_{40}N_8O_{16}Lu$	59.3/59.7	2.6/2.8	7.3/7.7
XIIIб	0.09 (64)	$C_{72}H_{48}N_8O_{16}Er$	60.5/60.0	2.6/2.8	7.4/7.8
XIVa	0.06 (68)	$C_{192}H_{264}N_8O_2Lu$	71.4/71.2	7.9/8.1	3.4/3.5

slowly heated to 180 °C for an hour, after cooling it was ground, transferred to a Schott filter, washed with 5% aqueous hydrochloric acid, water and acetone, was then subjected to acetone extraction in a Soxhlet apparatus for 10 h. Dried at 100 °C.

Output and data of elemental analysis of metal complexes **XIVa, b-XXVa, b** are given in Table 4.

Table 4

Yield and data of elemental analysis of "sandwich" type metalophthalocyanines

Таблица 4. **Выход и данные элементного анализа металофталоцианинов «сэндвичегого» типа**

№	Yield, g (%)	Gross - a formula	Elemental analysis data. Found/is calculated, %		
			C	H	N
XVб	0.09 (47)	$C_{96}H_{36}N_{16}O_8Br_4Er$	56.8/56.1	1.6/1.8	11.0/11.1
XVIa	0.08 (42)	$C_{100}H_{48}N_{16}O_8Lu$	67.6/67.2	2.7/2.1	12.6/12.0
XVIIб	0.16 (63)	$C_{100}H_{44}N_{16}O_8Cl_4Er$	63.0/63.4	2.3/2.5	11.8/11.6
XVIIIa	0.16 (63)	$C_{100}H_{44}N_{16}O_{12}Cl_4Lu$	60.4/61.0	2.3/2.1	11.3/11.1
XIXa	0.06 (32)	$C_{100}H_{48}N_{16}O_{12}Lu$	65.4/65.2	2.7/2.5	12.1/12.0
XXa	0.06 (32)	$C_{100}H_{40}N_{16}O_{16}Lu$	63.5/63.0	2.2/2.4	11.7/12.0
XXIб	0.09 (47)	$C_{100}H_{36}N_{16}O_{16}Br_4Lu$	61.3/61.0	1.9/2.0	11.3/11.5
XXIIa	0.09 (47)	$C_{120}H_{56}N_{16}O_{20}S_4$ Lu	61.6/61.8	2.5/2.4	9.5/9.7
XXIIб	0.07 (37)	$C_{120}H_{56}N_{16}O_{20}S_4$ Er	61.8/62.0	2.5/2.6	9.5/9.6
XXIIIб	0.12 (58)	$C_{104}H_{52}N_{16}O_{16}Br_4Er$	55.2/55.6	2.4/2.6	9.8/10.4
XXIVa	0.07 (37)	$C_{104}H_{52}N_{16}O_{16}Cl_4Lu$	59.7/60.1	2.6/2.3	10.6/10.2
XXVa	0.06 (32)	$C_{224}H_{280}N_{16}O_{24}Lu$	71.7/71.6	7.5/7.8	5.9/6.2

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