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Tetraanthraquinonoporphyrazines: IV.[1] Synthesis and Study of Physicochemical Properties of Lanthanide-Porphyrazines Based on 1,4-Dichloroanthraquinone-2,3-dicarboxylic Acids

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Abstract—1,4-Dichloroanthraquinone-2,3-dicarboxylic acids have been prepared and further converted into the tetraanthraquinonoporphyrazine complexes with lanthanides (Nd, Tm, Er, Lu, and Gd). The influence of the introduced substituents and the nature of the metal ion on spectral properties of the compounds and their stability against thermooxidative decomposition has been discussed.

Keywords: 1,4-dichloroanthraquinone-2,3-dicarboxylic acid, tetraanthraquinonoporphyrazine, lanthanide

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Earlier studies have demonstrated the stability of tetraanthraquinonoporphyrazines against thermooxidative decomposition [2, 3], their high catalytic activity towards oxidation of sulfur-containing compounds [1, 4, 5], and mesomorphism [6]. Moreover, in the case of their substitution with carboxylic or sulfonate groups, these compounds have exhibited a high affinity towards cellulose fibers and can be applicable as direct dyes [1] with the properties approaching these of the industrial phthalocyanine dye, Direct Blue.

The earlier published reports have considered complexes of *d*-elements with tetra-(3,6-dichloroantraquinone)porphyrazines [7] containing no other peripheral substituents; however, the analogous complexes with *f*-elements (lanthanides) has remained unknown. At the same time, lanthanide complexes with porphyrazines have been known for the luminescent properties [8]. The introduction of a lanthanide at the coordination site of tetraanthraquinonoporphyrazine can extend the range of its practical applications. On top of that, lanthanide complexes of tetra-(3,6-dichloroanthraquinono)porphyrazines can serve as precursors in the synthesis of sandwich-type metal porphyrazines [8].

This work was aimed to prepare lanthanides complexes based on 1,4-dichloroanthraquinone-2,3-dicarboxylic acids and to elucidate the effect of their structure on spectral properties and stability against thermooxidative decomposition.

First, we prepared the previously unknown compounds: 1,4-dichloroanthraquinone- and 1,4-dichloro-6-(4'-sulfophenyl)anthraquinone-2,3-dicarboxylic acid (**4** and **5**, respectively). The synthesis was performed following the procedure described elsewhere [1] including acylation of benzene or biphenyl with 1,4-dichloropyromellitic dianhydride **1** followed by intramolecular cyclization of the formed substituted benzoyltrimellitic acids **2** and **3**. The intramolecular cyclization of compound **3** was accompanied by sulfation at the *para*-position of the phenyl substituent. The product yield with respect to the anhydride **1** was 27% (compound **4**) and 45% (compound **5**).

The products were identified using the data of IR [9] and ^{1}H NMR spectroscopy as well as elemental analysis.

IR spectra of compounds **4** and **5** contained a poorly resolved bands group with a maximum at 1701–1705 cm^{-1} (the C=O stretching vibrations) and a band at 750–760 cm^{-1} (the C–Cl stretching vibrations). Besides, the spectrum of compound **5** contained the bands assigned to symmetric O=S=O (1070 cm^{-1}) and asymmetric O=S=O (1113 cm^{-1}) stretching vibrations of the sulfo group.

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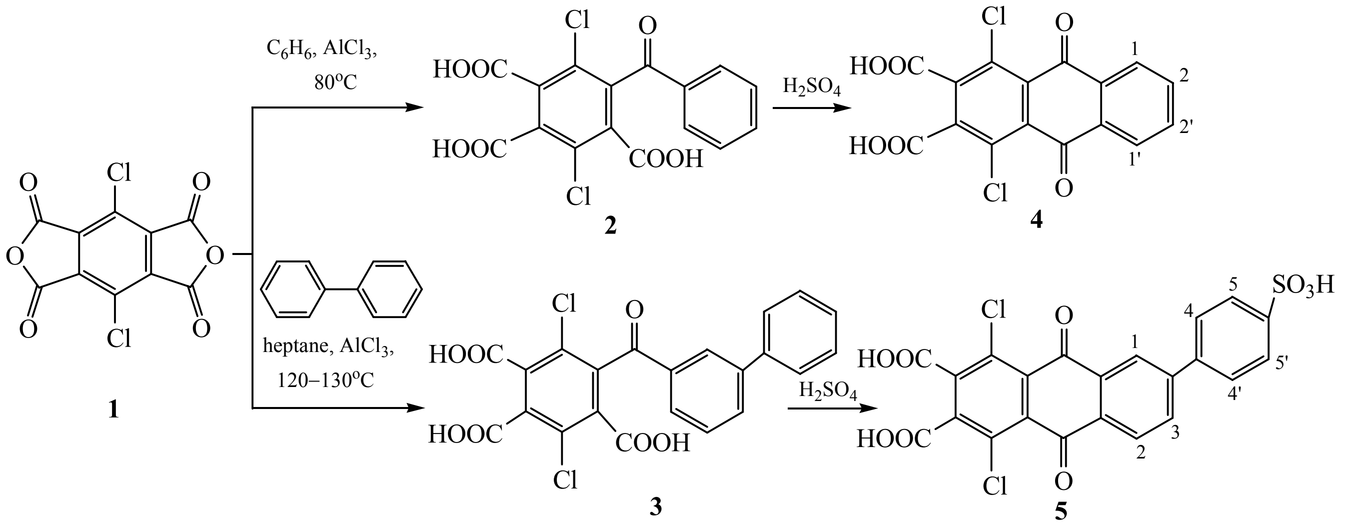
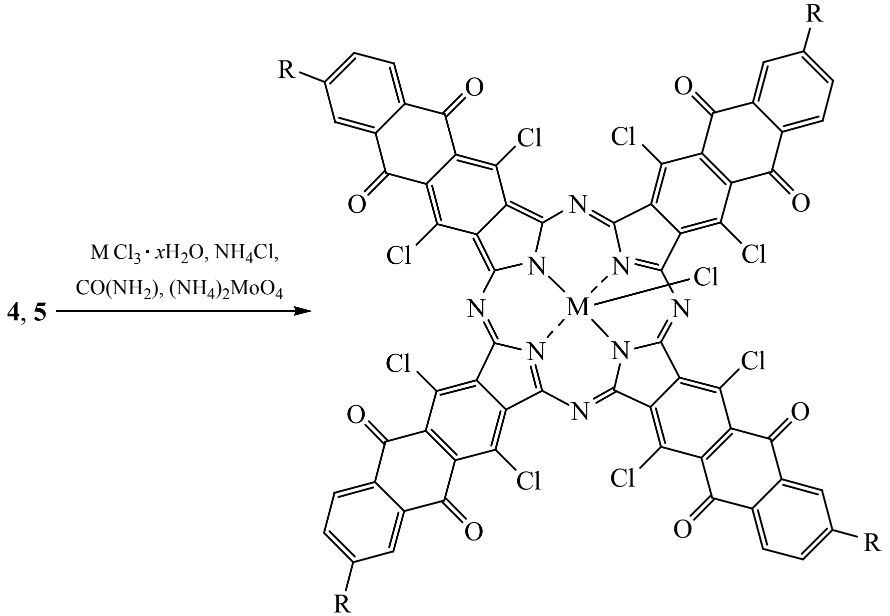
[1] For communication III, see [1].

Scheme 1.



Scheme 2.



6, **7**

M = Er (**a**), Lu (**b**), Tm (**c**), Nd (**d**), Gd (**e**); R = H (**6**), $C_6H_4SO_3H$ (**7**).

^1H NMR data for compounds **4** and **5** are given in the Experimental section.

Melting points of the 1,4-dichloro-substituted compounds **4** and **5** (232–234 and 280–282°C, respectively) were higher than those of the corresponding anthraquinone-2,3-dicarboxylic acids [10].

Complexes **6a–6e** and **7a–7e** of tetraanthraquinonoporphyrazines with a series of lanthanides were obtained via the reaction of compounds **4** and **5**, respectively, with chlorides of neodymium(III), thulium(III), erbium(III), lutetium(III), and gadolinium(III) at 180–200°C in the presence of urea, ammonium chloride, and ammonium molybdate (matrix synthesis). In order to prevent the formation of the sandwich-type complexes, the metal salt was taken in 110% ratio with respect to the reaction stoichiometry.

The so prepared complexes were blue-green powders; in contrast to the copper, cobalt, and nickel

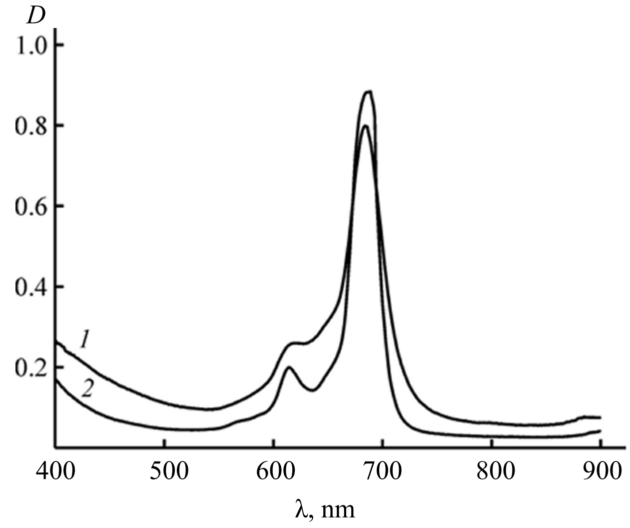


Fig. 1. Electronic absorption spectra of complexes (*1*) **6c** (6.3×10^{-6} mol/L) and (*2*) **7c** (5.8×10^{-6} mol/L) in DMF.

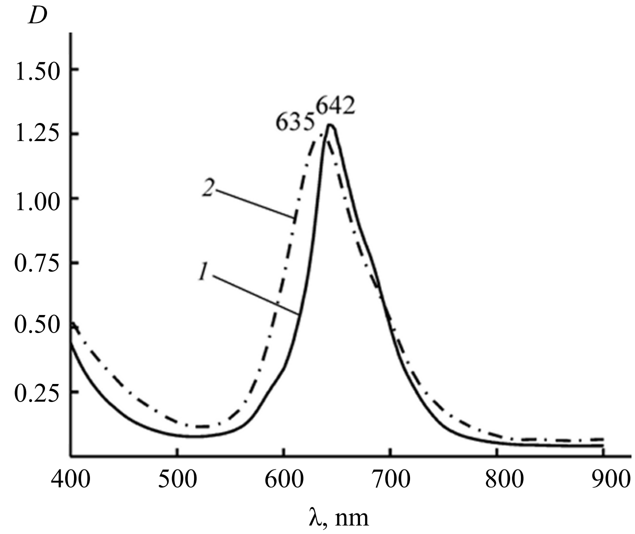


Fig. 2. Electronic absorption spectra of complexes (*1*) **7b** and (*2*) **7c** in aqueous ammonia (5 wt %). The complexes concentration 1.25×10^{-5} mol/L.

complexes of tetraanthraquinonoporphyrazines [1, 2], compounds **6a–6e** were soluble in DMF and DMSO due to the pyramidal structure of the MN_4 coordination core, weakening the intermolecular interactions.

Due to the presence of four sulfo groups in the molecules of compounds **7a–7e**, they were soluble in organic solvents as well as in alkali aqueous media. The complexes decomposed in concentrated sulfuric acid.

Compounds **6a–6e** and **7a–7e** were identified using the data of IR and electron absorption spectroscopy as well as elemental analysis. IR spectra of the prepared complexes contained the absorption bands assigned to the stretching vibrations of the functional groups present in compounds **4** and **5**.

Parameters of electronic absorption spectra and data of simultaneous thermal analysis[a] of compounds **6a**–**6e** and **7a**–**7e**

Comp. no.	λ_{max}, nm		ΔT, °C	T_{exo}, °C
	DMF	aq. NH_3		
6a	690	Insoluble	446–532	462
6b	691	Insoluble	442–540	468
6c	686	Insoluble	439–510	487
6d	689	Insoluble	440–580	502
6e	688	Insoluble	468–570	505
7a	694	640	430–500	461
7b	694	642	450–505	470
7c	689	635	–	–
7d	692	640	–	–
7e	691	637	–	–

[a] ΔT, temperature range of the fastest mass loss; T_{exo}, temperature of the highest exothermic effect, "–" not studied.

Electron absorption spectra of compounds **6a–6e** and **7a–7e** in DMF contained a strong *Q* band at 686–694 nm (see table). The position of that band was determined by the nature of the complex forming metal ion. In particular, the *Q* band of the lutetium(III) complex **6b** was observed at 691 nm. The replacement of the metal ion by erbium(III) (**6a**), neodymium(III) (**6d**), gadolinium(III) (**6e**), and thulium(III) (**6c**) resulted in the blue shift of the long-wavelength absorption maximums of the complex. However, the ionic radii of the lanthanides were fairly close; therefore, the observed shifts were quite small. The presence of the *para*-sulfophenyl substituents in the molecules of complexes **7a–7e** resulted in a slight red shift of the *Q* band (Fig. 1).

The diffuse absorption band in the spectra of aqueous ammonia solutions of complexes **7a**–**7e** at 635–645 nm (Fig. 2) evidenced the compounds association [11]. Even upon dilution to the complexes concentration of 10^{-7} mol/L the ratio of intensities of the absorption bands at 689–694 nm (the *Q* band of the monomeric complex) and at 640–650 nm (absorption of the associated form) remained practically the same. Hence, the associates were not completely broken down upon dilution.

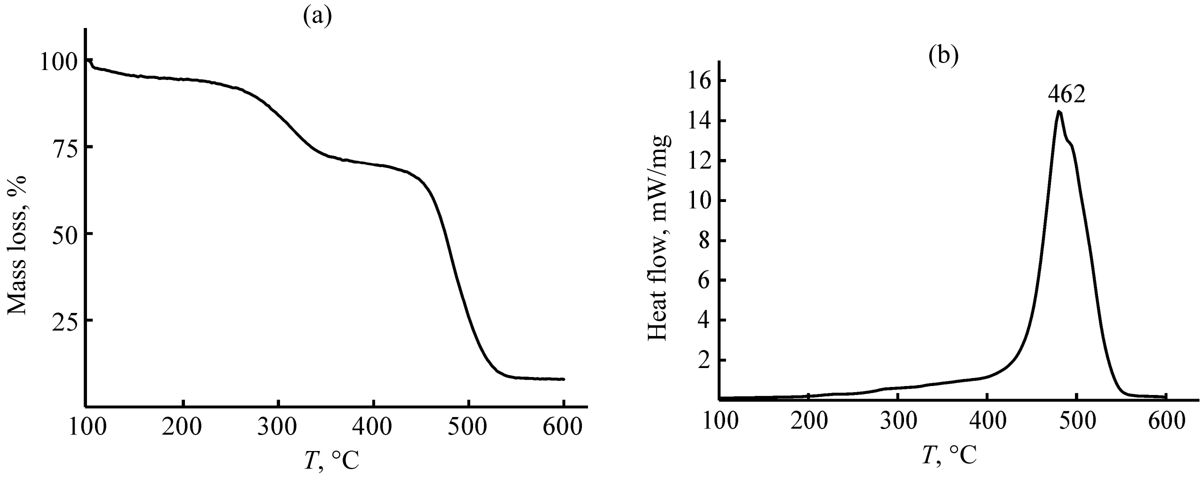


Fig. 3. Simultaneous thermal analysis of compound **6a**. (a) TG and (b) DSC.

Thermal analysis of the prepared complexes showed that the mass loss of 2–4% was observed upon heating at 80–120°C, evidently corresponding to elimination of the crystal hydrate and/or absorbed water.

In the case of the lanthanide complexes of tetra-(3,6-dichloroanthraquinono)porphyrazines **6a**–**6e**, the temperature corresponding to the strongest exothermic effect of the decomposition decreased in the **6e** > **6d** > **6c** > **6b** > **6a** series (see table).

According to the simultaneous thermal analysis data, the compounds **6a**–**6e** decomposition was a two-stage process. In the case of compound **6a**, the mass loss of 18.9% was observed at 259–342°C, assigned to elimination of eight chlorine atoms from each of the complex molecule (Fig. 2); the corresponding theoretical mass loss was 16.6%. The major mass loss (about 60%) observed at 450–550°C was assigned to deep decomposition of the organic part of the molecule, as confirmed by the prominent exothermic effect of the process. Thermal behavior of other complexes **6** was similar.

Introduction of the peripheral sulfophenyl groups in the complex structure further complicated the thermal decomposition process [cf. data for complexes **6a** (Fig. 3) and **7a** (Fig. 4)]. Decomposition of the erbium complex **7a** started with desulfonation, as confirmed by the data of mass spectral study of the volatile products evolved at that stage. Evolution of SO_2 (m/z = 64) and H_2O (m/z = 18) was observed at 180–300°C, the corresponding mass loss being 18.5% (Fig. 4a). Noteworthily, the complete desulfonation should have been accompanied by the mass loss of 17.6%. The DCS curve (Fig. 4b) contained an endothermic peak at 178–240°C. As was pointed above, evolution of SO_2 continued up to 300°C. That was likely due to the gradual heating of the specimen at the external temperature increase, leading to the stepwise evolution of sulfur dioxide. Further decomposition of compound **7a** involved the phenyl substituents, as confirmed by evolution of CO (m/z = 28) and H_2O (m/z = 18) at 300–357°C, the corresponding mass loss being 10.5%. The heating at 357–384°C was accompanied by elimination of chlorine atoms, and then the residual organic part of the molecule completely degraded. Noteworthily, the exothermic peak corresponding to the macrocycle thermal decomposition was observed at practically the same temperature for the complexes **6** and **7** of the same lanthanides (cf. data for complexes **6a**, **7a** and **6b**, **7b** in the table).

To summarize, the spectral features and the thermal behavior of the lanthanide complexes based on 1,4-dichloroanthraquinone- and 1,4-dichloro-6-(4'-sulfophenyl)anthraquinone-2,3-dicarboxylic acids prepared for the first time in this work were largely dependent on the ionic radius of the complex forming metal ion, that in turn was evidently crucial for determination of the complexes structure.

EXPERIMENTAL

Electron absorption spectra of the solutions in DMF and aqueous ammonia were recorded using a HITACHI U-2001 spectrophotometer at room temperature (300–900 nm). IR spectra of the pellets with KBr were recorded using an AVATAR 360FT-IR

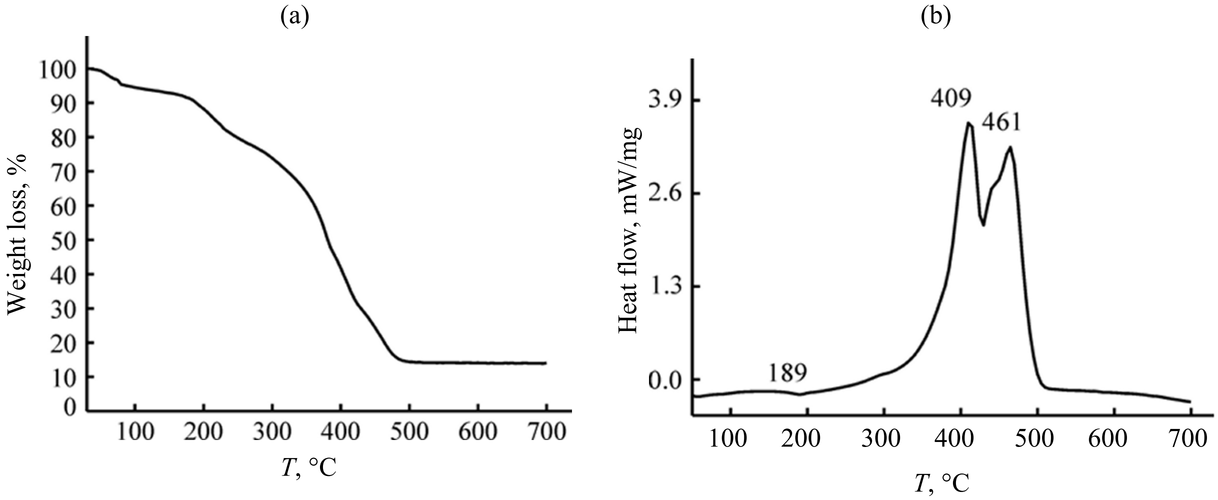


Fig. 4. Simultaneous thermal analysis of compound **7a**. (a) TG and (b) DSC.

spectrophotometer (400–4000 cm^{-1}). ^{1}H NMR spectra (DMSO-d_6) were registered using a Bruker DRX-500 spectrometer with TMS as internal reference. Elemental analysis was performed using a FlashEA$^{\text{TM}}$ 1112 elemental analyzer. Thermooxidative decomposition was studied using an STA 449 F3 Jupiter simultaneous thermal analyzer (Netzsch) (oxygen-argon atmosphere, heating rate 5 deg/min, platinum crucible). The specimens were annealed at 110°C during 2 h prior to the experiment.

All the above-listed experiments were carried out using the equipment installed at the Center for Joint Usage, Ivanovo State University of Chemistry and Technology.

1,4-Dichloroanthraquinone-2,3-dicarboxylic acid (4). *a.* 8.10 g (0.06 mol) of anhydrous $AlCl_3$ was added at stirring to a mixture of 5 g (0.023 mol) of dianhydride of 1,4-dichloropyromellitic acid and 15 mL of benzene, and the resulting mixture was maintained during 2 h at room temperature and 10 h at 80°C. The reaction mixture was then cooled and diluted with 50 mL of ice water. The obtained suspension was treated with hot solution of Na_2CO_3 and filtered. HCl was added to the filtrate till pH 3–4; the precipitate was filtered off, washed with water, and dried at 60–80°C.

b. Intramolecular cyclization. 20 mL of sulfuric acid monohydrate was introduced in a flask and heated to 130°C. 1.8 g of 1,4-dichlorobenzoyltrimellitic acid was introduced into the flask over 15 min at vigorous stirring, and the mixture was heated at 150°C during 5 h. The mixture was cooled, dissolved at heating in 100 mL of concentrated solution of Na_2CO_3, and filtered. The filtrate was acidified with HCl till precipitate formation; the precipitate was filtered off, washed with water till negative reaction for sulfate anions, and dried at 70–80°C. Yield 1.55 g (27%), mp 280–282°C. IR spectrum, ν, cm^{-1}: 3495 (OH), 1701 (C=O), 756 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 7.95 s (2H, H$^{1,1',2,2'}$), 8.23 s (2H, H^3), 12.01 s (3H, COOH). Found, %: C 50.30; H 1.23. $C_{16}H_6Cl_2O_6$. Calculated, %: C 52.63; H 1.63.

1,4-Dichloro-6-(4'-sulfophenyl)anthraquinone-2,3-dicarboxylic acid (5). *a.* 8.10 g (0.06 mol) of anhydrous $AlCl_3$ was added at stirring to a mixture of 7 g (0.023 mol) of dianhydride of 1,4-dichloropyromellitic acid, 6 g (0.038 mol) of biphenyl, and 15 mL of heptane. The mixture was maintained during 2 h at room temperature, refluxed during 3 h and heated at 120–130°C during 6 h after heptane distilling off. The reaction mass was cooled to ambient, and 50 mL of ice water was added. The obtained suspension was treated with hot solution of Na_2CO_3 and filtered. The filtrate was acidified with HCl to pH 3–4; the precipitate was filtered off, washed with water, and dried at 60–80°C.

b. Intramolecular cyclization. 20 mL of sulfuric acid monohydrate was introduced in a flask and heated to 130°C. 3.7 g 1,4-dichloro-(4'-phenyl)benzoyltrimellitic acid was introduced into the flask over 15 min at vigorous stirring, and the mixture was heated at 150°C during 5 h. The mixture was cooled, dissolved at heating in 100 mL of concentrated solution of Na_2CO_3, and filtered. The filtrate was acidified with HCl till precipitate formation; the precipitate was filtered off, washed with water till negative reaction for sulfate anions, and dried at 70–80°C. Yield 3.67 g (45%), mp 280–282°C. IR spectrum, ν, cm^{-1}: 3490 (OH), 1705 (C=O), 1113 (O=S=O$_{as}$), 1070 (O=S=O$_s$), 752 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 7.83 s (1H, H$^{3'}$), 8.10 s (4H, H$^{4,4'}$), 8.28 s (1H, H^2), 9.78 s (1H, H^1), 11.53 s (3H, SO$_3$H, COOH). Found, %: C 50.45; H 2.00; S 6.36. $C_{22}H_{10}Cl_2O_9S$. Calculated, %: C 50.69; H 1.93; S 6.15.

Complexes 6a–6e and 7a–7e *(general procedure).* The interaction of compound **4** (200 mg, 0.54 mmol) or **5** (200 mg, 0.41 mmol) with chloride of Nd(III), Tm(III), Er(III), Lu(III), or Gd(III) was carried out at 180–200°C in the presence of 0.24 g (4 mmol) of urea, 0.02 g (0.4 mmol) of ammonium chloride, and 0.02 g (0.01 mmol) of ammonium molybdate during 2 h. The obtained product was thoroughly ground, washed with dilute solution of hydrochloric acid and with water, and then extracted with acetone in the Soxhlet apparatus till the absence of solid residue in the extract.

Erbium tetra-(3,6-dichloroanthraquinone)porphyrazine (6a) was prepared from compound **4** and 57.5 mg (0.15 mmol) of $ErCl_3·6H_2O$. Yield 38 mg (16%). Found, %: C 51.3; N 7.3. $C_{64}H_{16}Cl_9N_8O_{20}Er$. Calculated, %: C 50.9; N 7.4.

Lutetium tetra-(3,6-dichloroanthraquinone)porphyrazine (6b) was prepared from compound **4** and 59.1 mg (0.15 mmol) of $LuCl_3·6H_2O$. Yield 43 mg (18%). Found, %: C 50.9; N 7.1. $C_{64}H_{16}Cl_9N_8O_{20}Lu$. Calculated, %: C 50.6; N 7.4.

Thulium tetra-(3,6-dichloroanthraquinone)porphyrazine (6c) was prepared from compound **4** and 57.2 mg (0.15 mmol) of $TmCl_3·6H_2O$. Yield 40 mg (17%). Found, %: C 50.6; N 7.4. $C_{64}H_{16}Cl_9N_8O_{20}Tm$. Calculated, %: C 50.8; N 7.4.

Neodymium tetra-(3,6-dichloroanthraquinone)porphyrazine (6d) was prepared from compound **4** and 54.1 mg (0.15 mmol) of $NdCl_3·6H_2O$. Yield 36 mg (15%). Found, %: C 50.8; N 7.4. $C_{64}H_{16}Cl_9N_8O_{20}Nd$. Calculated, %: C 51.6; N 7.5.

Gadolinium tetra-(3,6-dichloroanthraquinone)porphyrazine (6e) was prepared from compound **4** and 56.0 mg (0.15 mmol) of $GdCl_3·6H_2O$. Yield 41 mg (17%). Found, %: C 52.0; N 7.5. $C_{64}H_{16}Cl_9N_8O_{20}Gd$. Calculated, %: C 51.5; N 7.5.

Erbium tetra-[3,6-dichloro-8-(4'-sulfophenyl)anthraquinone]porphyrazine (7a) was prepared from compound **5** and 43.47 mg (0.15 mmol) of $ErCl_3·6H_2O$. Yield 35 mg (14%). Found, %: C 49.3; N 5.2; S 5.9. $C_{88}H_{32}Cl_9O_{20}N_8S_4Er$. Calculated, %: C 49.5; N 5.3; S 6.0.

Lutetium tetra-[3,6-dichloro-8-(4'-sulfophenyl)-anthraquinone]porphyrazine (7b) was prepared from compound **5** and 41.58 mg (0.15 mmol) of $LuCl_3·6H_2O$. Yield 44 mg (18%). Found, %: C 50.3; N 5.1; S 5.7. $C_{88}H_{32}Cl_9O_{20}N_8S_4Lu$. Calculated, %: C 49.3; N 5.2; S 6.0.

Thulium tetra-[3,6-dichloro-8-(4'-sulfophenyl) anthraquinone]porphyrazine (7c) was prepared from compound **5** and 43.06 mg (0.15 mmol) of $TmCl_3·6H_2O$. Yield 45 mg (18%). Found, %: C 48.3; N 5.1; S 6.1. $C_{88}H_{32}Cl_9O_{20}N_8S_4Tm$. Calculated, %: C 49.5; N 5.2; S 6.0.

Neodymium tetra-[3,6-dichloro-8-(4'-sulfophenyl)-anthraquinone]porphyrazine (7d) was prepared from compound **5** and 50.45 mg (0.15 mmol) of $NdCl_3·6H_2O$. Yield 30 mg (12%). Found, %: C 50.3; N 5.2; S 6.0. $C_{88}H_{32}Cl_9O_{20}N_8S_4Nd$. Calculated, %: C 50.5; N 5.3; S 6.1.

Gadolinium tetra-[3,6-dichloro-8-(4'-sulfophenyl)-anthraquinone]porphyrazine (7e) was prepared from compound **5** and 46.25 mg (0.15 mmol) of $GdCl_3·6H_2O$. Yield 38 mg (15%). Found, %: C 50.3; N 5.1; S 5.7. $C_{88}H_{32}Cl_9O_{20}N_8S_4Gd$. Calculated, %: C 49.7; N 5.2; S 6.0.

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