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Lanthanide Complexes of Alkylsulfamoyl-Substituted Phthalocyanines

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Abstract—The extra-ligand complexes obtained in the reaction of tetra-4-[6',8'-di(*N*,*N*-diethylsulfamoyl)-2'-naphtyloxy]phthalocyanine with erbium or ytterbium acetylacetonates were characterized by elemental analysis, IR and electronic spectroscopy.

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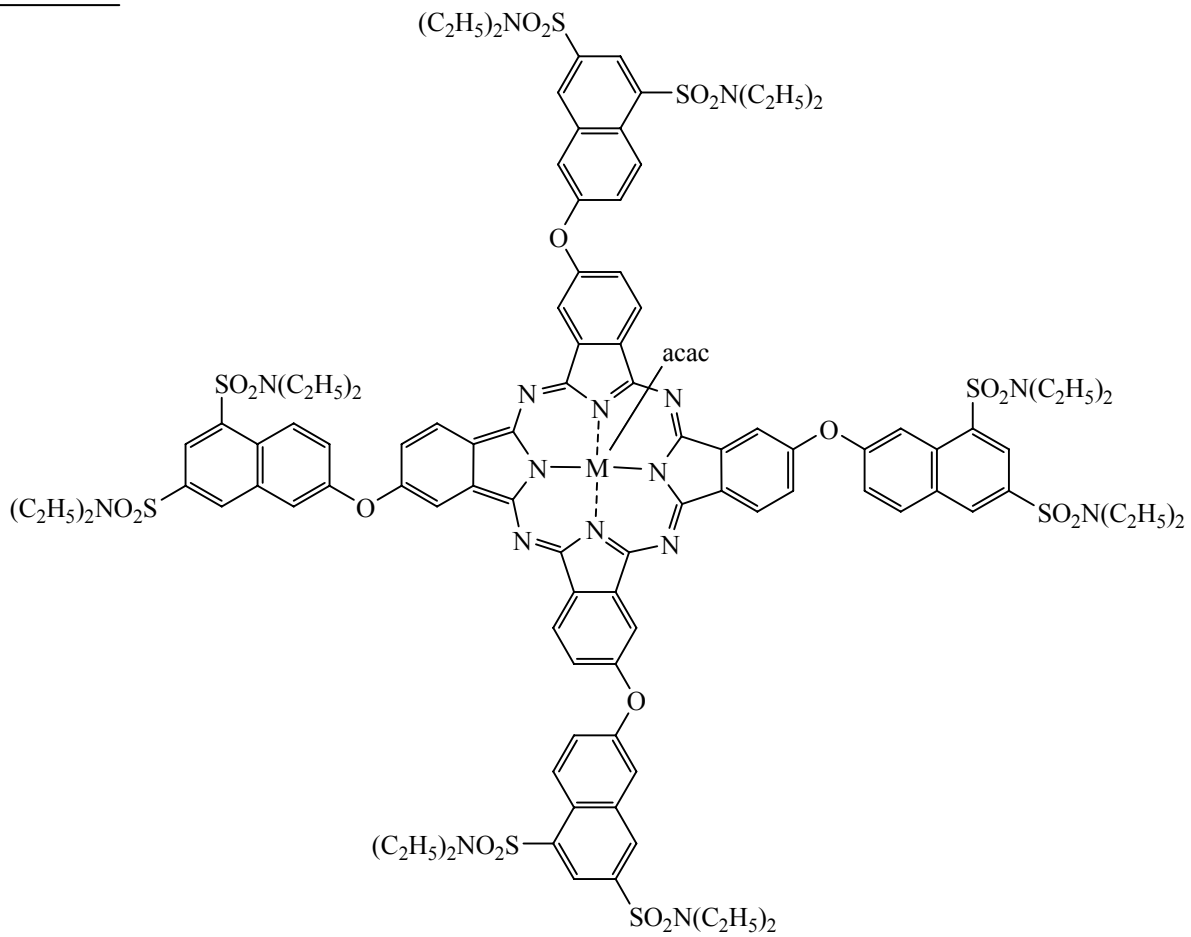
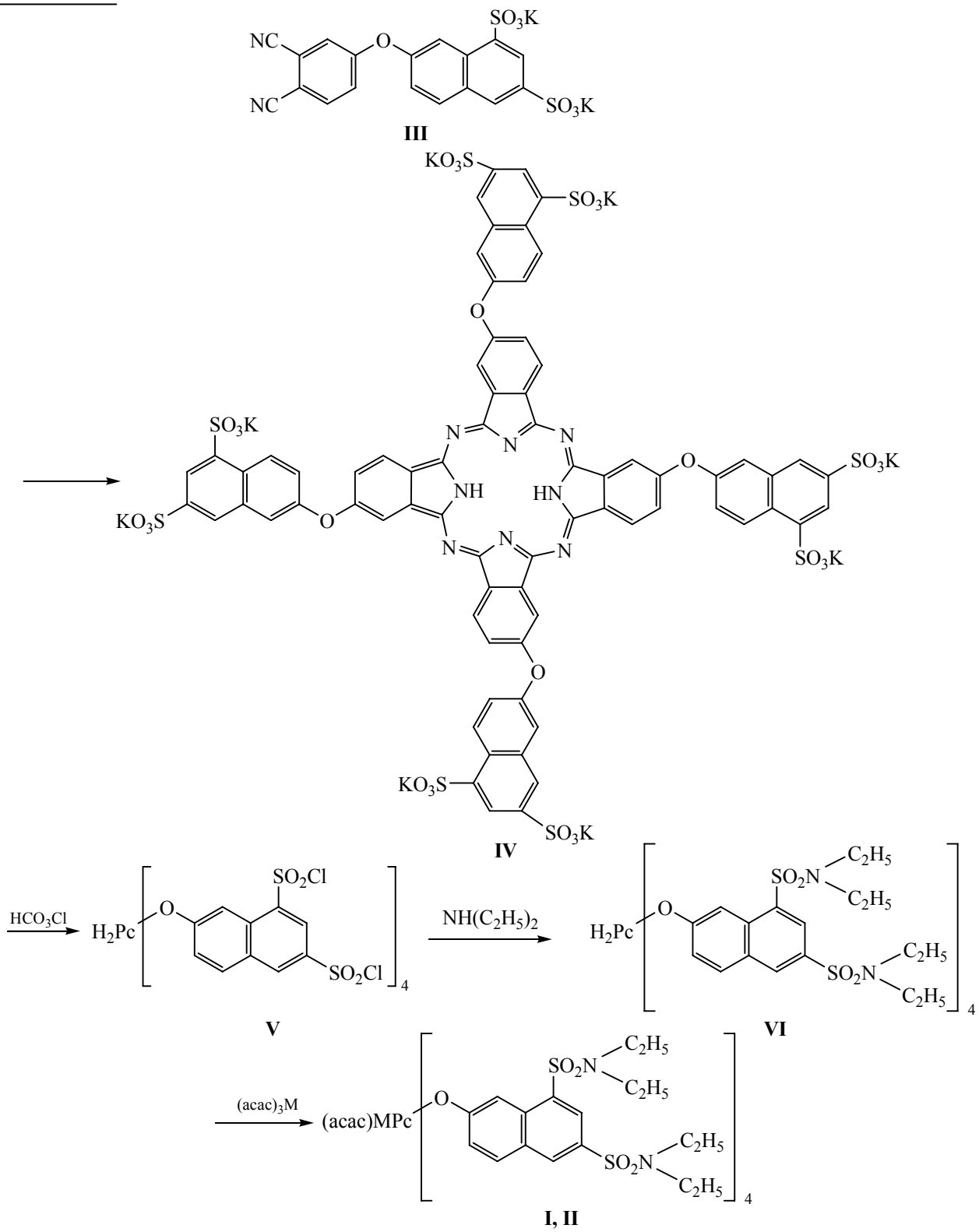
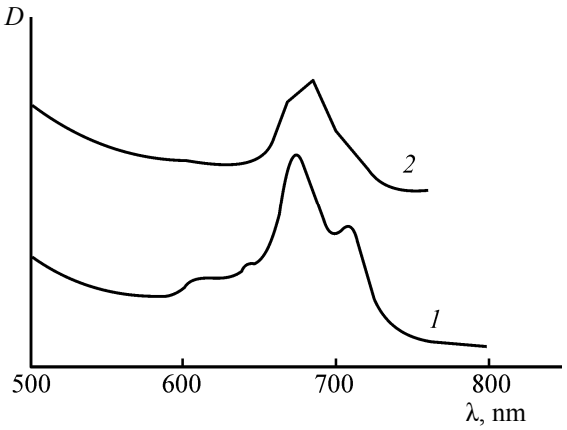
Metal complexes of phthalocyanines (MPs) are promising materials for practical applications [1, 2]. Their high thermal stability, kinetic stability and chromophore properties are due to the presence of a multi-circuit conjugated aromatic system. Among the porphyrin and phthalocyanine compounds their complexes with lanthanides and actinides are of particular interest [3–7]. Owing to their large ionic



M = Er (**I**), Yb (**II**).

radii and high coordination numbers, lanthanides form several types of compounds with phthalocyanines differing by composition and structure [8–14]. As known, one direction of the chemical modification of phthalocyanines is functional substitution in the benzene rings. The introduction of various substituents in the phthalocyanine molecule can widely change their physicochemical properties [15–19], in particular,





EAS in chloroform. (*1*) compound **VI**, (*2*) compound **I.**

the introduction of alkylsulfamoyl groups provides a high solubility in organic solvents, which greatly expands their possible practical applications.

In this paper we present the data on the synthesis and study of the spectral properties of lanthanide complexes with alkylsulfamoyl-substituted phthalocyanines containing acetylacetonate anion as an extraligand.

The starting compound for the synthesis of complexes **I** and **II** was 4-bromophthalonitrile from which, using the reaction of nucleophilic substitution of bromine 4-[(6',8'-disulfo-2'-naphthyl)oxy]phthalonitrile was synthesized [20].

The complexes of lanthanides with 6',8'-di(*N*,*N*-diethylsulfamoyl)-substituted tetra-4-[(-2'-naphthyl)oxy]-phthalocyanine containing acetylacetonate-anion as an extraligand were synthesized according to the scheme bellow.

By heating nitrile **III** with excess K_2CO_3 compound **IV** was synthesized. The sulfonyl chloride **V** was obtained by treating compound **IV** with excess chlorosulfonic acid and thionyl chloride. Compound **VI** was prepared by the reaction of sulfonyl chloride **V** with excess diethylamine in boiling acetone.

The synthesized compounds **IV–VI** are substances of dark green color. Compound **IV**is well soluble in water, DMSO, compound **V,** in acetone, and **VI,** in chloroform and DMF.

The composition and structure of the compounds **IV–VI** were confirmed by elemental analysis, IR and electronic spectroscopy.

In the IR spectra of metal-free compound **IV** the most important are the bands of symmetric and asymmetric stretching S=O vibrations at 1038 cm^{-1} and 1109 cm^{-1}, as well as a strong broad band in the region of 1210–1220 cm^{-1} corresponding to the Ar–O–Ar stretching vibrations. A strong band at 1000–1012 cm^{-1}, characteristic of unsubstituted metal-free phthalocyanine is slightly shifted to the high-frequency region [21]. The IR spectra of compound **VI** include the absorption bands corresponding to the C−S stretching vibrations (1150–1200 cm^{-1}) and the bands corresponding to symmetric (1155 cm^{-1}) and asymmetric (1332 and 1351 cm^{-1}) stretching vibrations of the sulfamide group. The absorption in the region 2851–2923 cm^{-1} belongs to the symmetric and asymmetric vibrations of CH bonds.

The EAS of tetra-4-[(6',8'-disulfo-2'-naphthyl)oxy] phthalocyanine **IV** in DMSO is characterized by the presence of two strong absorption bands in the region of 674–703 nm. The introduction of *N*,*N*-dialkylsulfamoyl groups increases the solubility of the

Position of bands in the EAS and IR spectra of synthesized compounds

Comp. no.	λ_{max} (D/D_{max}), nm (chloroform)	IR spectrum, ν, cm^{-1}
I	640 sh (0.21), 684 (1.00)	2928, 2862 (C–H), 1148 (C–S), 1329, 1344 [ν_s (S=O), SO_2NH], 1150 [ν_{as} (S=O), SO_2NH], 1210 (Ar–O–Ar)
II	641 sh (0.28), 683 (1.00)	2923, 2851 (C–H), 1150 (C–S), 1332, 1351 [ν_s (S=O), SO_2NH], 1155 [ν_{as} (S=O), SO_2NH], 1210 (Ar–O–Ar)
IV	645 sh (0.36), 612 sh (0.29), 701 (0.8), 674 (1)[a]	1010 (NH), 1038 [ν_s (S=O)], 1109 [ν_{as} (S=O)], 1210 (Ar–O–Ar)
V	674 (0.93), 703 (1.00)[a]	1010 (NH), 1380 [ν_s (S=O), SO_2Cl], 1185 [ν_{as} (S=O), SO_2Cl], 1211 (Ar–O–Ar)
VI	672 (1.00), 707 (0.72)	1012 (NH), 2928, 2852 (C–H), 1146 (C–S), 1333, 1342 [ν_s (S=O), SO_2NH], 1151 [ν_{as} (S=O), SO_2NH], 12110 (Ar–O–Ar)

[a] ESP in DMSO.

complexes in organic solvents, but practically does not affect the position of the bands in the electron absorption spectrum. Thus, the EAS of **VI** in chloroform is characterized by two absorption bands in the regions of the wavelength 672 and 707 nm and the Soret band at 372 nm in the UV part of the spectrum. The the spectrum pattern is similar to that of the source sulfonyl chloride **V** (674, 703 nm) (see figure).

The metallation of the obtained alkylsulfamoyl derivative **VI** was performed by refluxing with erbium or ytterbium acetylacetonate in acetone

It should be noted that the synthesis of metal complexes **I** and **II**) is possible without preliminary purification of intermediate products at all stages.

It is known that upon complexation with metals, as well as at the formation of ionic forms of the ligand ($H_2Pc \rightarrow Pc^{2-}$) high-symmetry species are formed (symmetry increases from D_{2h} to D_{4h}), resulting in reduced number of bands in the EAS [22]. In our work, these changes are also clearly visible. In particular, upon transformation of the metal-free *N*,*N*-dialkylsulfamoyl derivative **VI** into metal complexes **I**, **II** in the spectra of solutions in chloroform two strong long-wavelength bands disappear and one band (*Q*-band) appears at 683–684 nm (see the figure and the table). Note that the metal nature practically does not affect the position of the bands.

EXPERIMENTAL

Electron absorption spectra of the synthesized compounds were recorded on a spectrophotometer HITACHI U-2001 at room temperature in the range of 300–900 nm, solvents DMF, DMSO, chloroform. IR spectra were obtained on an AVATAR 360 FT-IR ESP spectrophotometer. Samples were prepared by ordinary pelletizing with KBr. Elemental analysis was performed on a FlashEA 1112 CHNS-O Analyzer (ISUCT).

Tetra-4-[(6',8'-disulfo-2'-naphthyl)oxy]phthalocyanine (IV). A mixture of 1.1 g (2 mmol) of dipotassium 4-[(6'8'-disulfo-2'-naphthyl)oxy]phthalonitrile with 0.64 g (5 mmol) of potassium carbonate was heated with stirring to 200–210°C and kept at this temperature for 30 min. The reaction mixture became blue-green. The resulting phthalocyanine was extracted with DMSO and then precipitated from the solution by the adding anhydrous ethanol. The precipitate was filtered off and washed with ethanol in a Soxhlet apparatus. The final purification was carried out by chromatography on silica gel M 60 (eluent DMF–water in a ratio of 1: 1). After distilling off the eluent in a vacuum, the residue was kept in a vacuum drying cabinet at 80ºC till the constant weight. Yield 0.50 g (58%). Found, %: C 50.70, H 2.20, N 6.30, S 14.80. $C_{72}H_{42}N_8O_{28}S_8$. Calculated, %: C 50.20; H 2.40; N 6.50; S 14.90.

Tetra-4-[(6',8'-dichorosulfono-2'-naphthyl)oxy]-phthalocyanine (V). To 0.5 g (0.3 mmol) of tetra-4-[(6',8'-disulfo-2'-naphthyl)oxy]phthalocyanine (**IV**) was added 60 mmol of chlorosulfonic acid and 60 mmol of thionyl chloride. The mixture was heated for 4 h at 60°C and then for 1 h at 75–80°C. After cooling, the reaction mixture was poured onto ice containing sodium chloride. The precipitate dropped was filtered on a porous frit filter and washed with cold brine until neutral washings. The reaction product was dried in a vacuum. Yield: 0.42 g (78%). Found, %: C 46.00; H 1.90. $C_{72}H_{34}C_{l8}N_8O_{20}S_8$. Calculated, %: C 46.20; H 1.80.

Tetra-4-[6',8'-di(*N*,*N*-diethylsulfamoyl)-2'-naphtyl-oxy]phthalocyanine (VI). Preliminary 8 mmol of diethylamine was dissolved in a small amount of acetone (~ 20 ml), the solution was added to 0.5 mmol of the sulfonyl chloride **V,** and the mixture was refluxed for 5 h. The solution was filtered through a paper filter, the filtrate was evaporated. Final purification was performed by chromatography on silica gel M60 (eluent chloroform). Yield 0.53 g (49%). Found, %: C 50.00; H 2.20; N 6.80; S 14.50. $C_{104}H_{114}N_{16}O_{20}S_8$. Calculated, %: C 50.20; H 2.40; N 6.50; S 14.90.

Acetylacetonatoerbium tetra-4-[6',8'-di(*N*,*N*-diethylsulfamoyl)-2'-naphtyloxy]phthalocyanine (I). A mixture of 0.1 mmol of compound **VI** and 0.15 mmol of erbium acetylacetonate were dissolved in acetone. The resulting solution was heated to boiling and kept at this temperature for 1 h. The solution was evaporated, the product is extracted with DMF and chromatographed for purification on silica gel M60 (eluent DMF). Yield 0.44 g (78%). Found, %: C 54.00; H 4.70; N 9.50; S 10.70. $C_{110}H_{119}$ Er $N_{16}O_{22}S_8$. Calculated, %: C 54.20; H 4.90; N 9.20; S 10.50.

Ytterbium acetylacetonate tetra-4-[6',8'-di(*N*,*N*-diethylsulfamyl)napht-2-yloxy]phthalocyanine (II) was synthesized along the above procedure from 0.1 mmol of compound **VI**. Yield: 0.46 g (79%). Found, %: C 54.30; H 4.60; N 9.70; S 10.90. $C_{110}H_{119}N_{16}$· $O_{22}S_8Yb$. Calculated, %: C 53.90; H 4.80; N 10.10; S 10.40.

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