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Lanthanide Complexes with Alkylsulfamoyl-Substituted Octaphenyltetraazaporphyrins

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Abstract—The reaction of alkylsulfamoyl-substituted octaphenyltetraazaporphyrin with tris(acetylacetonato)-lutetium(III) tris(acetylacetonato)ytterbium(III) gave the corresponding coordination compounds which were characterized by elemental compositions and IR and electronic absorption spectra.

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Over past decades, a keen interest in lanthanide complexes with substituted porphyrins and porphyrazines has been related to some their specific properties, such as electrochromism, selective sensitivity to several gases, biological activity, etc. [1–3]. These compounds were proposed to use as luminescent labels in cancer diagnostics [4, 5]. The ability of lanthanide ions in macrocyclic complexes to coordinate extra ligands is also interesting, for such coordination essentially changes some their properties.

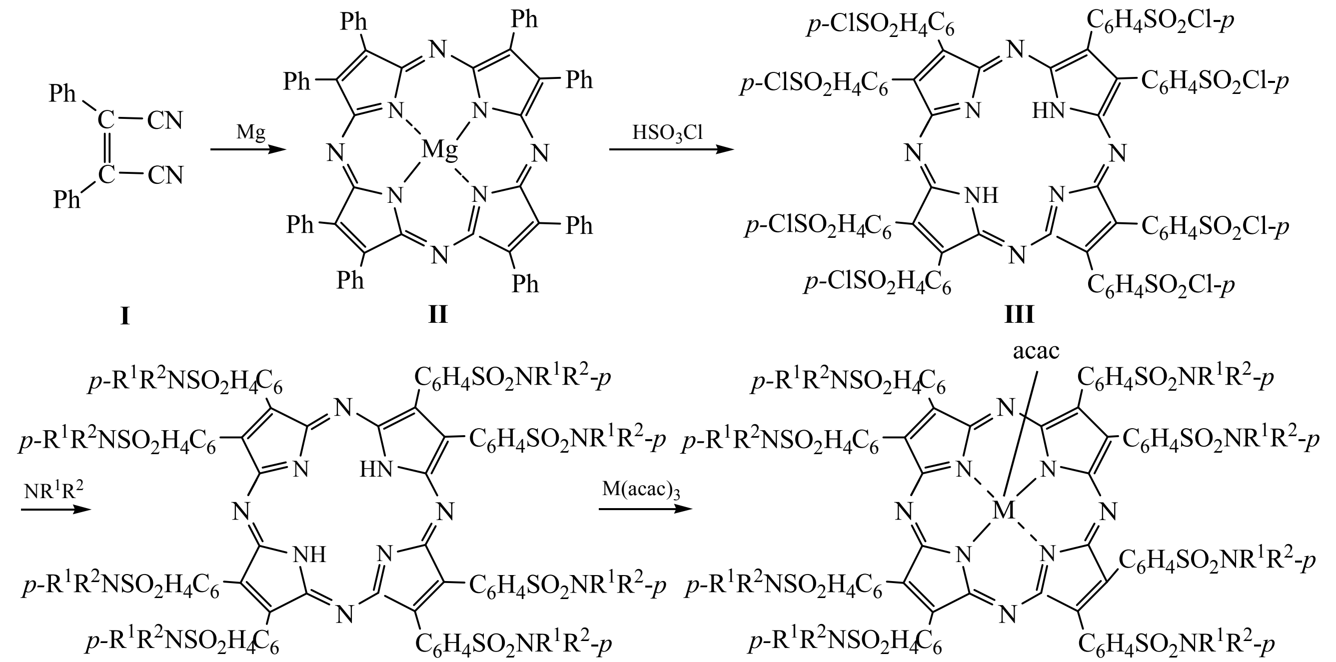
We previously showed that the ytterbium complex with octaphenyltetraazaporphyrin exhibits luminescent properties [6]. However, further studies and practical applications of porphyrazine complexes are strongly restricted because of their poor solubility. It is known [7] that introduction of hydrophobic groups into macroheterocycles considerably improves their solubility in organic solvents, which could extend the scopes of their study and practical use.

In the present article we report on the synthesis and spectral properties of lutetium and ytterbium complexes with alkylsulfamoyl-substituted octaphenyltetraazaporphyrins, having acetylacetonate anion as extra ligand. As starting compound we used diphenylmaleonitrile (**I**) which reacted with metallic magnesium to produce octaphenyltetraazaporphyrin magnesium complex **II**. Treatment of **II** with excess chlorosulfonic acid at room temperature [8, 9] gave octakis(sulfonyl chloride) **III**. The reaction was accompanied by demetalation. Compound **III** was isolated by extraction with acetone, excess primary (octadecylamine) or secondary amine (diethylamine) was added, and the mixture was heated for 18 h under reflux. Compounds **IV** and **V** were finally purified by column chromatography [8, 9].

Alkylsulfamoyl derivatives **IV** and **V** were subjected to metalation with tris(acetylacetonato)-lutetium(III) and tris(acetylacetonato)ytterbium(III) by heating in boiling DMF over a period of 40 min. The solvent was removed, and complexes **VI**–**IX** were extracted into chloroform and purified by column chromatography. Complexes **VI**–**IX** were isolated as dark green powders which were insoluble in water but readily soluble in weakly polar organic solvents. They were characterized by elemental analyses and IR and electronic absorption spectra.

The IR spectra of **VI**–**IX** contained absorption bands in the region 1350–1550 cm^{-1}, which are typical of tetraazaporphyrins [10]. The position of the other IR bands is indicated in table. It should be noted that the IR bands intrinsic to metal-free compounds **IV** and **V** were retained in the spectra of their complexes, but their position slightly changed.

Ingoing from ligands **IV** and **V** to metal complexes **VI**–**IX**, two strong long-wave absorption bands disappeared from the electronic spectra of solutions in chloroform and other neutral or proton-donor organic solvents, and one band appeared. It is known that coordination to metals leads to higher symmetry (from D_{2h} to D_{4h}); as a result, the number of absorption bands decreases [10]. The electronic spectra of metal-free



R^1 = H, R^2 = $C_{18}H_{37}$ (**IV**), R^1 = R^2 = C_2H_5 (**V**), R^1 = H, R^2 = $C_{18}H_{37}$, M = Yb (**VI**), Lu (**VII**), R^1 = R^2 = C_2H_5, M = Yb (**VIII**), Lu (**IX**).

compounds **IV** and **V** in aprotic solvents (DMF) almost coincide with those of their complexes **VI–IX** (see figure). On the whole, the spectral pattern of all complexes **VI–IX** in organic solvents is typical of most metal porphyrazines [10]. The position of the absorption band almost does not depend on the metal nature and alkyl chain length.

The solubilities (equilibrium concentrations at room temperature) of the ytterbium complexes with octaphenylporphyrazine and octakis(*p*-diethylsulfamoylphenyl)porphyrazine in DMF were estimated by the isothermal saturation method. As might be expected, introduction of phenyl and alkylsulfamoylphenyl substituents into porphyrazine macroring considerably improves the solubility. In going from (acac)YbTAP to (acac)YbTAP(Ph)$_8$ and (acac)YbTAP[$C_6H_4SO_2NEt_2$-*p*]$_8$ the solubility increases from 0.11 to 3.01 and 3.20 mM, i.e., by a factor of more than 30.

EXPERIMENTAL

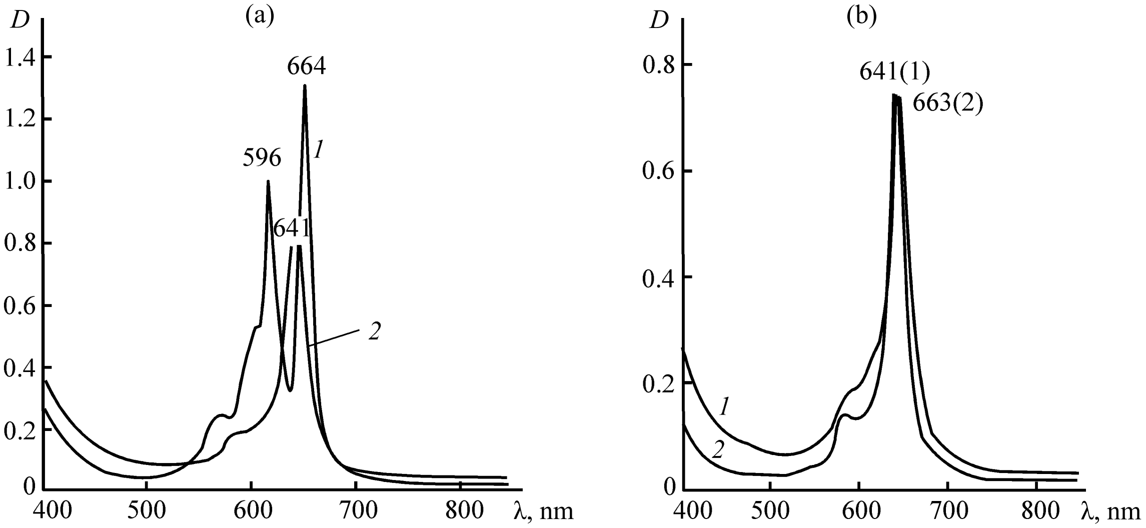
The electronic absorption spectra were measured in the λ range from 300 to 900 nm at room temperature on a Hitachi U-2001 spectrophotometer using chloroform and DMF as solvents. The IR spectra were obtained on a Thermo-Nicolet Avatar 360 FT-IR ESP instrument from samples pelleted with KBr. The elemental compositions were determined on a Flash EA 1112 Series CHNS-O analyzer. The solubilities were determined by isothermal saturation at room temperature [11].

Compounds **IV** and **V** were synthesized as described in [9].

(Acetylacetonato)[octakis(4-octadecylsulfamoylphenyl)porphyrazinato]ytterbium(III) (VI). A mixture of 357.0 mg (0.1 mmol) of octakis(4-octadecyl-

Absorption bands in the electronic ($CHCl_3$) and IR spectra of compounds **IV**–**IX**

Comp. no.	λ_{max}, nm	IR spectrum (KBr), ν, cm^{-1}
IV	372, 596, 664	3365 (NH, RNH); 2918, 2861 (CH); 1163 (SO, SO_2NH)
V	372, 597, 665	3371 (NH, RNH); 2921, 2855 (CH); 1165 (SO, SO_2NH)
VI	371, 641	3366 (NH, RNH); 2920, 2864 (CH); 1161 (SO, SO_2NH)
VII	370, 642	3365 (NH, RNH); 2923, 2852 (CH); 1158 (SO, SO_2NH)
VIII	370, 641	3369 (NH, RNH); 2919, 2856 (CH); 1160 (SO, SO_2NH)
IX	370, 642	3365 (NH, RNH); 2916, 2850 (CH); 1162 (SO, SO_2NH)



Electronic absorption spectra of compounds (*1*) **IV** and (*2*) **VI** in (a) chloroform and (b) DMF.

sulfamoylphenyl)porphyrazine (**IV**) and 70.5 mg (0.15 mmol) of tris(acetylacetonato)ytterbium(III) was dissolved in DMF, and the solution was heated to the boiling point and kept for 40 min at that temperature. The mixture was evaporated, the residue was extracted with chloroform, and the product was purified by chromatography on silica gel M 60 using chloroform as eluent. Yield 146.3 mg (38.1%). Found, %: C 66.0; H 9.1; N 5.2; O 8.0. $C_{213}H_{343}N_{16}O_{18}S_8Yb$. Calculated, %: C 66.5; H 8.9; N 5.8; O 7.5.

(Acetylacetonato)[octakis(4-octadecylsulfamoylphenyl)porphyrazinato]lutetium(III) (VII) was synthesized in a similar way from 357.0 mg of **IV** and 70.8 mg of tris(acetylacetonato)lutetium(III). Yield 144.4 mg (37.6%). Found, %: C 65.5; H 9.2; N 5.2; O 8.0. $C_{213}H_{335}N_{16}O_{18}S_8Lu$. Calculated, %: C 66.5; H 8.9; N 5.8; O 7.4.

(Acetylacetonato)[octakis(4-diethylsulfamoylphenyl)porphyrazinato]ytterbium(III) (VIII) was synthesized from 200.2 mg of octakis(4-diethylsulfamoylphenyl)porphyrazine (**V**) and 70.5 mg of tris(acetylacetonato)ytterbium(III). Yield 86.1 mg (37.9%). Found, %: C 54.9; H 6.0; N 9.8; O 14.2. $C_{101}H_{119}N_{16}O_{18}S_8Yb$. Calculated, %: C 53.3; H 5.2; N 9.8; O 12.6.

(Acetylacetonato)[octakis(4-diethylsulfamoylphenyl)porphyrazinato]lutetium(III) (IX) was synthesized from 200.2 mg of **V** and 70.8 mg of tris(acetylacetonato)lutetium(III). Yield 90.1 mg (39.6%). Found, %: C 52.4; H 5.9; N 9.3; O 13.5. $C_{101}H_{119}N_{16}O_{18}S_8Lu$. Calculated, %: C 53.2; H 5.2; N 9.8; O 12.6.

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