Octachloro- and Hexadecafluoro-Substituted Lanthanide(III) Phthalocyaninates: Synthesis and Spectral Properties

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Dedicated to Academician Aslan Yu. Tsivadze on the occasion of his Anniversary

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Octachloro- and hexadecafluoro-substituted lanthanide(III) monophthalocyaninates, which have not been described earlier, were obtained based on the corresponding nitriles using the template method. The possibility of both thermal and microwave activation of cyclization process was demonstrated. All target compounds were identified by MALDI TOF mass spectrometry, FTIR and 1H NMR spectroscopy. Strong downfield lanthanide-induced shifts of signals of aromatic protons were observed in the nuclear magnetic resonance spectra of europium and erbium complexes comparing with diamagnetic lutetium one. Bathochromic shift of the Q band (about 20 nm) was observed for hexadecachloro-substituted compounds comparing to octachloro-substituted analogs.

Keywords: Phthalocyanine, lanthanide, halogen, template synthesis, spectroscopy.

Octахлор- и гексадекафтор-замещенные фталоцианинаты лантанидов(III): синтез и спектральные свойства

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Неописанные ранее октахлор- и гексадекафтор-замещенные фталоцианинаты лантанидов(III) получены темплатным методом на основе соответствующих нитрилов. Показана возможность активации процесса циклизации как термически, так и с помощью микроволнового излучения. Все целевые соединения охарактеризованы методом масс-спектрометрии MALDI TOF, ИК и 1Н ЯМР спектроскопии. В 1Н ЯМР спектрах комплексов парамагнитных европия и эрбия наблюдается сильное смещение сигналов ароматических протонов в слабое поле по сравнению с комплексами диамагнитного лютеция. Батохромный сдвиг Q полосы (около 20 нм) наблюдается для гексадекачлор-замещенных комплексов по сравнению с октахлор-замещенными аналогами.

Ключевые слова: Фталоцианин, лантанид, галоген, темплатный синтез, спектроскопия.
**Introduction**

Phthalocyanines and relative compounds attract an interest of investigators in virtue of their chemical and photochemical stability and many possibilities of structural modifications.[1-3] For monophthalocyanine complexes there are three ways for structural transformations: introduction of peripheral and nonperipheral substituents in the macrocycle and the changing of central ions or counterion (in the case of metals with valence ≥3).[4,5] The presence of electron-withdrawing functional groups in phthalocyanine leads to shift of the first oxidation potential to the anodic region and corresponding increase of stability, and appearance of n-type conductivity.[6-8] Halogen-substituted phthalocyanines are one of the most widely used in practice group of macroheterocycles.[9] One of the most important application areas is organic transistors.[6,7,10-12] The main drawback of these compounds is their low solubility. It can be overcome employing the synthesis of phthalocyanine complexes with the lanthanide(III) ions. The presence of extra ligands and high coordination ability of lanthanides improves solubility of the complexes. Additional advantage of lanthanide phthalocyaninates is the possibility of axial ligand exchange reactions. Using this approach, in our recent publication,[13] the hybrid gold nanoparticles, covered by hexadecafluorosubstituted lanthanide phthalocyaninates, were prepared. Increase in reverse saturable absorption effect was observed in hybrid nanoparticles due to their plasmonic properties. Thus, an effective synthesis of novel halogen-substituted lanthanide phthalocyaninates is an important task, as well as a study of their properties. The present paper deals with the synthesis and spectral properties investigation of hexadecafluoro- and octachloro-substituted lanthanide phthalocyaninates. Thanks to their tendency to form the most stable single-decker complexes,[5,14,15] the elements of hexadecafluoro- and octachloro-substituted lanthanide phthalocyaninates. Noteworthy, that the synthetic approaches to hexadecafluoro- and octachloro-substituted lanthanide(III) phthalocyaninates were not described earlier in literature.

**Experimental**

All reactions were monitored by thin-layer chromatography (TLC) and UV-Vis until complete disappearance of the starting reagents unless otherwise specified. TLC was performed using Merck Aluminium Oxide F254 neutral flexible plates. Electronic absorption (UV-Vis) spectra were recorded on a Thermospectronic Helios-α spectrophotometer using quartz cells (1×1 cm). Matrix-assisted laser desorption/ionization time-of-flight (MALDI TOF) spectra were measured on an Applied Biosystems 4800 MALDI-TOF mass spectrometer, using cyano-4-hydroxycinnamic acid (CHCA) as the matrix. Elemental analysis (C, H, N), IR (KBr) νmax cm–1, 1H NMR (83.0 mg, 0.80 mmol), Er(OAc)3, 4H2O (83.0 mg, 0.20 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (119 µL, 0.80 mmol) were stirred in 3 mL of boiling isomyl alcohol for 4 h (TLC-control: AlO2, F254, toluene; UV-Vis control: THF). The reaction mixture was cooled to room temperature and a MeOH:H2O (4:1 V/V) mixture and dried at 70 °C to give compound 2a (186.0 mg, 93 %). UV-Vis (THF) λmax (I/Imax) nm: 346 (1.00), 639 (0.58), 677 (0.98). m/z (MALDI TOF) (%) 941 (100) [(M-OAc)+] IR (KBr) νmax cm–1: 1061–1080 (st–C–O) s, 1520–1551 (γ pyrrole) m, 1321–1485 (C–O) s, 1551–1643 (C=O) m.

**Preparation of 2,3,9,10,16,17,23,24-octachlorophthalocyaninatoeuropium acetate, 2b.**

**Approach A.** Dichlorophthalonitrile 1 (158.0 mg, 0.80 mmol), Er(OAc)3·4H2O (83.0 mg, 0.20 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (119 µL, 0.80 mmol) were stirred in 3 mL of boiling isomyl alcohol for 4 h (TLC-control: AlO2, F254, toluene; UV-Vis control: THF). The reaction mixture was cooled to room temperature and a MeOH:H2O (4:1 V/V) mixture and dried at 70 °C to give compound 2b (173.0 mg, 85 %). UV-Vis (THF) λmax (I/Imax) nm: 349 (0.56), 612 (0.26), 676 (1.00). m/z (MALDI TOF) (%) 1145 (100) [(M-OAc+CHCA]+] IR (KBr) νmax cm–1: 1063–1080 (st–C–O) s, 1520–1599 (γ pyrrole) m, 1321–1456 (C–O) s, 1520–1599 (C=O) s.

**Preparation of 2,3,9,10,16,17,23,24-octachlorophthalocyaninatoerbium acetate, 2c.**

Preparation of dichlorophthalonitrile 1 (158.0 mg, 0.80 mmol), Er(OAc)3·4H2O (83.0 mg, 0.20 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (119 µL, 0.80 mmol) were stirred in 3 mL of boiling isomyl alcohol for 4 h (TLC-control: AlO2, F254, toluene; UV-Vis control: THF). The reaction mixture was cooled to room temperature and a MeOH:H2O (4:1 V/V) mixture and dried at 70 °C to give compound 2c (200.0 mg, 98 %). UV-Vis (THF) λmax (I/Imax) nm: 349 (0.60), 612 (0.30), 676 (1.00). m/z (MALDI TOF) (%) 1153 (100) [(M-OAc+CHCA]+] IR (KBr) νmax cm–1: 1063–1080 (st–C–O) s, 1518–1556 (γ pyrrole) m, 1322–1454 (C–O) s, 1556–1641 (C=O) s. 1H NMR ([D8]THF, 293 K) δH ppm: 38.21 (s, H3).

**Preparation of 2,3,9,10,16,17,23,24-octachlorophthalocyaninatolutetium acetate, 2d.**

The mixture of dichlorophthalonitrile 1 (158.0 mg, 0.80 mmol), Lu(OAc)3·3H2O, F254, toluene; UV-Vis control: THF. The reaction mixture was cooled to room temperature and a MeOH:H2O (4:1 V/V) mixture and dried at 70 °C to give compound 2d (169.0 mg, 83 %). The characteristics were identical with those obtained by method (A).

**Preparation of 2,3,9,10,16,17,23,24-octachlorophthalocyaninatoindium acetate, 2e.**

Preparation of dichlorophthalonitrile 1 (158.0 mg, 0.80 mmol), Er(OAc)3·4H2O (83.0 mg, 0.20 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (119 µL, 0.80 mmol) were stirred in 3 mL of boiling isomyl alcohol for 4 h (TLC-control: AlO2, F254, toluene; UV-Vis control: THF). The reaction mixture was cooled to room temperature and a MeOH:H2O (4:1 V/V) mixture and dried at 70 °C to give compound 2e (200.0 mg, 98 %). UV-Vis (THF) λmax (I/Imax) nm: 349 (0.60), 612 (0.30), 676 (1.00). m/z (MALDI TOF) (%) 1153 (100) [(M-OAc+CHCA]+] IR (KBr) νmax cm–1: 1063–1080 (st–C–O) s, 1518–1556 (γ pyrrole) m, 1322–1454 (C–O) s, 1556–1641 (C=O) s. 1H NMR ([D8]THF, 293 K) δH ppm: 9.54 (s, H3).

**Preparation of 2,3,9,10,16,17,23,24-octachlorophthalocyaninatopalladionium acetate, 2f.**

The mixture of tetrachlorophthalonitrile 1 (200.0 mg, 1.00 mmol), Eu(OAc)3·3H2O (95.5 mg, 0.25 mmol) and hydroquinone (55 mg, 0.50 mmol) was transferred into a flask and heated at 180 °C for 30 min (TLC-control: SiO2, F254, toluene; UV-Vis control: THF). The reaction mixture was cooled to room temperature and a MeOH:H2O (4:1 V/V, Vtotal=100 mL) mixture was added. The precipitate was filtered and washed with a MeOH:H2O (4:1 V/V) mixture and dried at 70 °C to give compound 2f (65.5 mg, 26 %). UV-Vis (THF) λmax (I/Imax) nm: 400 (0.60), 612 (0.30), 680 (1.00). m/z (MALDI TOF) (%) 1066 (100) [(M-OAc+4F+CHCA]+] IR (KBr) νmax cm–1: 1184–1321 (st–C–F) m, 1578 (γ pyrrole) m, 1321–1458 (C–O) s, 1578 (C=O) s.
of tetrafluorophthalonitrile 3 (200.0 mg, 1.00 mmol), Er(OAc)₃, 3H₂O (104.0 mg, 0.25 mmol) and hydroquinone (55.0 mg, 0.50 mmol) was transferred into a flask and heated at 180 °C for 20 min (TLC-control: Al₂O₃, F₂54, toluene; UV-Vis control: THF). The reaction mixture was cooled to room temperature and a MeOH:H₂O (4:1 V/V, Vtotal = 100 mL) mixture was added. The precipitate was filtered and washed with a MeOH:H₂O (4:1 V/V) mixture and dried at 70 °C to give compound 4b (49.0 mg, 19 %). UV-Vis (THF) λmax (μm, nm): 400 (1.00), 682 (0.50). m/z (MALDI TOF) (%) 877 (100) [(M-OAc-3F]+CHCA), 893 (50) [(M-OAc-4F]+CHCA), 1082 (70) [(M-OAc-4F]+CHCA)]. IR (KBr) νmax cm⁻¹: 1182–1315 (st C-F) m, 1497–1593 (γ pyrrole) m, 1315–1446 (C-O) s, 1593–1612 (C=O) s.

Preparation of 1,2,3,4,9,10,11,15,16,17,18,22,23,24,25-hexadecafluorophthalocyaninatoaluminum(III) acetate, 4c. The mixture of tetrafluorophthalonitrile 3 (200.0 mg, 1.00 mmol), Lu(OAc)₃, 3H₂O (106.0 mg, 0.25 mmol) and hydroquinone (55.0 mg, 0.50 mmol) was transferred into a flask and heated at 180 °C for 20 min (TLC-control: Al₂O₃, F₂54, toluene; UV-Vis control: THF). The reaction mixture was cooled to room temperature and a MeOH:H₂O (4:1 V/V, Vtotal = 100 mL) mixture was added. The precipitate was filtered and washed with a MeOH:H₂O (4:1 V/V) mixture and dried at 70 °C to give compound 4c (31.0 mg, 12 %). UV-Vis (THF) λmax (μm, nm): 407 (1.00), 680 (0.60). m/z (MALDI TOF) (%) 981 (50) [(M-3F]+), 1115 (100) [(M-OAc+DHB-OH)]. IR (KBr) νmax cm⁻¹: 1182–1269 (st C-F) m, 1562 (γ pyrrole) s, 1410–1458 (C-O) s, 1562–1614 (C=O) s.

Results and Discussion

Octachloro-substituted lanthanide(III) phthalocyaninates were obtained starting from 4,5-dichlorophthalonitrile 1 by the template synthesis (Scheme 1). Selectivity of the monophthalocyanine formation was provided by 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), coordination of which to the lanthanide central ion results in steric hindrance and prevents undesirable formation of the sandwich-type complexes.[30] Moreover, the use of DBU as a base is preferred rather than employment of alkoxide ions because of the possibility of nucleophilic substitution for the electron-deficient systems.[31,32] Absence of sandwich-type by-products was proven by TLC, UV-Vis and MALDI TOF methods. The products of oligomerization of starting nitrile were removed by washing with MeOH. For erbium complex 2b the cyclization process was activated thermally or using microwave irradiation. In comparison with thermally activated process, microwave activation allows to decrease the time of synthesis from 4 h to 8 min. It is the first example of microwave-assisted synthesis of lanthanide monophthalocyanine. In literature, the microwave-assisted synthesis was described only for double-decker lanthanide phthalo- and naphthalocyaninates.[19-22]

Attempts to obtain hexadecafluoro-substituted complexes from nitrile 3 in boiling isomyl alcohol were unsuccessful. Probably, it can be explained by tendency of fluorine groups to nucleophilic substitution (for e.g. by i-AmO⁻). This process prevents the further cyclization due to the steric effect of four isomylxylo groups. Procedures for preparation hexadecafluoro-substituted complexes, which were described in literature (central metals – Zn, Cu, Ru),[23,24] presuppose the synthesis in the melt of initial nitrile 3. In a present case, this approach does not give target compounds 4.

Since the formation of phthalocyanine includes the reduction stage, we decided to use hydroquinone as a reducing agent and at the same time the reaction media (Scheme 2). The hydroquinone was earlier utilized in the synthesis metal-free phthalocyanines.[25]

The yields of target complexes 4a-c are comparable with those presented in literature for zinc and transition metal complexes.[23,24] It is noteworthy that solubility of hexadecafluoro-substituted complexes 4a-c in common organic solvents is lower, than solubility of octachloro- and hexadecafluoro-substituted analogues.

All the compounds obtained were characterized by the MALDI TOF mass spectrometry. The peaks of molecular ions were not observed. Instead of this, the cleavage of axial acetate and its substitution to the molecule of matrix under laser ionization was observed. It can be explained by high mobility of axial ions in lanthanide monophthalocyaninates. As an example, the mass spectrum of complex 2b is shown in Figure 1. This phenomenon is typical for lanthanide(III) phthalocyaninates and their analogs.[14,26-28]

The fragmentation of axial ligand shows the possibility of the ligand exchange during the formation of hybrid materials or sandwich-type complexes.[13,29]

In order to prove the presence of axial acetates and other important structural moieties in target complexes 2 and 4, the FTIR spectra were measured. Stretching vibrations of C=Cl bonds for compounds 2 were observed in the region of 1061–1080 cm⁻¹. Corresponding bands of C-F bonds for compounds 4 were observed in the region of 1182–1321 cm⁻¹. Skeletal vibrations of pyrrole fragments occupy the region from 1497 to 1599 cm⁻¹. The bands at 1315–1485 cm⁻¹ and at

Scheme 1. Synthesis of octachloro-substituted lanthanide phthalocyaninates 2a-c.
1520–1643 cm\(^{-1}\) were assigned to C-O and C=O vibrations of the acetate groups, respectively (Figure 2).

Notably, the same values were observed for acetates in literature\(^{[30]}\) and for perchlorinated phthalocyaninates of lanthanides, which were reported by us earlier.\(^{[13]}\)

In order to reach a better signal resolution in the \(^1\)H NMR spectra of phthalocyanines 2a-c, a polar coordinating solvent, namely, [D8]THF was used. The employment of \([D5]{\text{Py}}\) is undesirable because of the presumable overlapping of aromatic signals with the solvent ones. In the case of diamagnetic lutetium complex 2c, aromatic protons H\(_{Pc}\) are shifted downfield, comparing to phthalocyanine complexes without peripheral substituents (PcLuCl) or bearing electron-donating groups (\(\text{EtPcLuOAc}\) and \(\text{BuPcLuOAc}\)) (Table 1). This tendency remains for complexes with paramagnetic central ions.

\[\text{Scheme 2. Synthesis of hexadecafluoro-substituted lanthanide phthalocyaninates 4a-c.}\]
Table 1. 1H NMR data of lanthanide(III) phthalocyaninates.

<table>
<thead>
<tr>
<th>Compound</th>
<th>δ_H, ppm</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>11.19</td>
<td>[D8]THF</td>
</tr>
<tr>
<td>2b</td>
<td>38.21</td>
<td>[D8]THF</td>
</tr>
<tr>
<td>2c</td>
<td>9.54</td>
<td>[D8]THF</td>
</tr>
<tr>
<td>EtPcErOAc[31]</td>
<td>23.07</td>
<td>CDCl3: [D6]DMSO (3:1, V:V)</td>
</tr>
<tr>
<td>PcErCl[32]</td>
<td>18.81</td>
<td>[D6]DMSO</td>
</tr>
</tbody>
</table>

The presence of a paramagnetic central ion in complexes 2a and 2b results in a downfield shift of the aromatic proton signals comparing to lutetium analog 2c. The most downfield shifted signal of H_Pc protons of erbium complex 2c lies at 38.21 ppm. Noteworthy, the best resolved 1H NMR spectrum of 2b was measured at 60 °C. However, the signal of H_Pc protons is shifted upfield to 31.89 ppm comparing to the spectrum, which was measured at 20 °C.

In the UV-Vis spectra of lanthanide complexes 2 and 4 two absorption bands are observed: B band (at 350–400 nm) and Q band (at 670–680 nm). As it was shown earlier for other lanthanide monophthalocyaninates,[13,14] the lanthanide ion nature does not influence the Q band position (Table 2).

In comparison with hexadecachloro-substituted complexes (Cl16PcLnOAc), which were described by us earlier,[13] hexadecafluoro-substituted analogs 4a-c possess hypsochromic shift of Q band (Table 2). It can be explained by strong negative inductive effect (I−) of fluorine groups.

The presence of chlorine atoms in α- and β-positions results in bathochromic shift of the Q band (about 20 nm) for hexadecafluoro-substituted analogs 2 (Figure 3).

Table 2. UV-Vis data in THF.

<table>
<thead>
<tr>
<th>Compound</th>
<th>B band, nm</th>
<th>Q band, nm</th>
</tr>
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<tbody>
<tr>
<td>2a</td>
<td>346</td>
<td>677</td>
</tr>
<tr>
<td>2b</td>
<td>349</td>
<td>676</td>
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<tr>
<td>2c</td>
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<tr>
<td>4a</td>
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<td>4b</td>
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<td>4c</td>
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<td>680</td>
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<tr>
<td>Cl16PcEuOAc[13]</td>
<td>378</td>
<td>696</td>
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<td>Cl16PcErOAc[13]</td>
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<td>696</td>
</tr>
<tr>
<td>Cl16PcLuOAc[13]</td>
<td>363</td>
<td>699</td>
</tr>
</tbody>
</table>

Figure 2. FTIR spectra of erbium phthalocyaninates 2b (A) and 4b (B) in KBr.

Figure 3. UV-Vis spectra of complex 2c (solid line) and hexadecafluoro-substituted lutetium phthalocyaninates[13] (dashed line) in THF.

Conclusions

Novel octachloro- and hexadecafluoro-substituted lanthanide(III) phthalocyaninates were obtained using
the template method on the basis of corresponding phthalocyanines. In comparison with thermally activated synthesis of octachloro-substituted erbium phthalocyaninate, the employment of microwave assisted approach allows to decrease the time of synthesis from 4 h to 8 min. For the first time the accessibility of perfluorinated lanthanide(III) phthalocyaninates was reached by the use of hydroquinone as a reducing agent and reaction medium. Target compounds were identified by MALDI TOF mass spectrometry, FTIR spectroscopy. In the case of octachloro-substituted complexes, the 'H NMR spectra were measured revealing strong downfield lanthanide-induced shifts of signals of aromatic protons in europium and erbium complexes comparing with the diamagnetic lutetium one. The most downfield shifted signal of aromatic protons of erbium complex lies at 38.21 ppm. The influence of the nature of halogens and type of substitution on the position of the UV-Vis absorption maxima was shown. The \(Q\) bands are bathochromically shifted in a row: octachloro- < hexadecafluoro- < hexadecachloro-substituted complexes.

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References


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