Synthesis and physicochemical properties of highly soluble tetra-*tert*-butyl-2,3-naphthalocyanine complexes of lanthanides

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Tetra-*tert*-butyl-2,3-naphthalocyanine complexes of lanthanides were obtained by the reaction of tetra-*tert*-butyl-2,3-naphthalocyanine with lanthanide salts. Oxidation and aggregation of these complexes were studied by electronic and ESR spectroscopies.

Key words: naphthalocyanines, lanthanide complexes; electronic spectroscopy.

Phthalocyanine compounds are unique objects for the study of electronic coordination effects and the nature and peculiarities of the macrocyclic effect and can serve as models for investigation of photosynthesis. The existence of the extended multi-contour conjugation system in molecules of these compounds determines their color and semiconducting and catalytic properties, while their ability to form complexes with the majority of metals and the ease of introduction of functional groups into ligands make it possible to change these properties over a wide range.[1] Unlike d-metals, f-elements form with phthalocyanine ligands complexes of two types with a metal : ligand ratio equal to 1 : 1 or 1 : 2.[2] Complexes of the latter, "sandwich" type, in which a metal ion is clamped between two phthalocyanine ligands, are more typical of lanthanides and actinides. Phthalocyanines of lanthanides have pronounced electro- and chemochromic properties, due to which they are very attractive objects for use in sensors.[3] The linear annelation of the phthalocyanide ligand results in the formation of 2,3-naphthalocyanine derivatives that possess several interesting properties, *e.g.*, optical.[4] Information about lanthanide 2,3-naphthalocyanine complexes in the literature is quite lacking. In this work, we have synthesized some lanthanide mononaphthalocyanine complexes and have studied some of their properties.

Results and Discussion

The introduction of bulky *tert*-butyl groups into molecules of phthalocyanine complexes and their analogs, in particular, naphthalocyanines, dramatically increases their solubility in organic solvents[5] and exerts almost no effect on the electronic structure of the complexes. Therefore, 6-*tert*-butyl-2,3-dicyanonaphthalene synthesized by the known procedure in the Diels—Alder reaction was chosen as the initial nitrile. The lanthanide complexes based on it are green crystalline substances (m.p. >250 °C). They are highly soluble in benzene, chloroform, and pyridine, somewhat more poorly soluble in aprotic dipolar solvents, and insoluble in water. In the presence of acid, the complexes decompose *via* the following scheme:

$$2,3\text{-NcLnX} + 2\ \text{HA} = 2,3\text{-NcH}_2 + \text{LnXA}_2,$$

where 2,3-Nc is 2,3-naphthalocyanine.

Electronic absorption spectra (EAS) of the compounds obtained were studied in the range of 300—900 nm (Table 1). They contain the *Q* band at 760—780 nm (π—π*-transition) that has vibrational satellites and the *B* band in the UV range, which is likely a

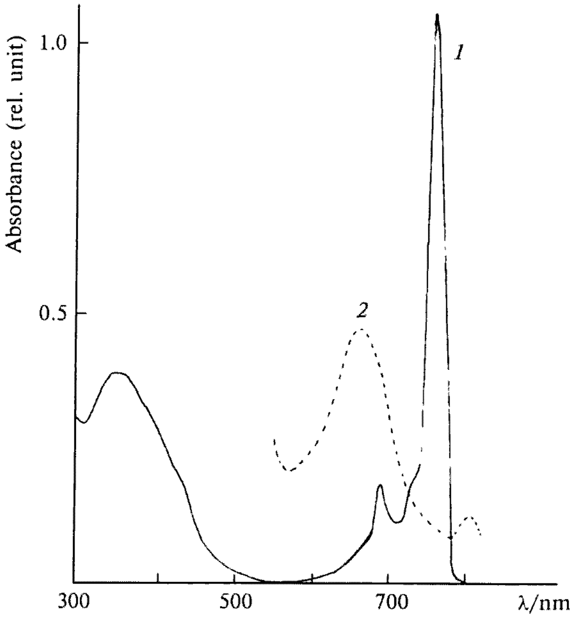

Fig. 1. Electronic absorption spectra of Bu^t_4-2,3-NcHoOAc complex (*1*) and its oxidized form (*2*) in toluene.

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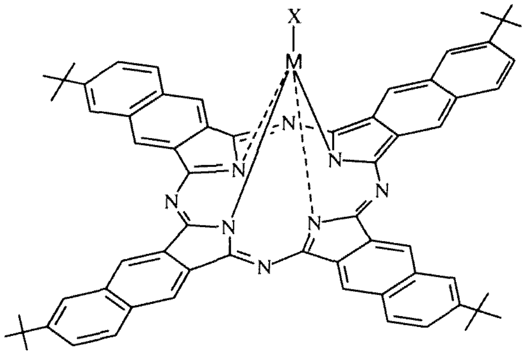
Table 1. Electronic absorption spectra of lanthanide tetra-*tert*-butyl-2,3-naphthalocyanine complexes, Bu^t_4-2,3-NcLnX, and their oxidized forms in benzene



Ln	X	λ/nm (log ε) Q	λ/nm (log ε) B	Ratio of intensities of bands
Lu	dpm	769 (5.13), 740 sh (4.46), 683 (4.42)	410 sh (4.3), 340 (4.47), 333 br (4.53)	5.03 : 1.08 : 1.0 : 0.8 : 2.28 : 2.4
Dimeric form		769, 683 sh, 649	400, 360, 333 br	1.0 : 0.34 : 2.1 : 0.82 : 0.95 : 2.8
Oxidized form		815, 687		1.0 : 4.12
Lu	acac	770, 740 sh, 684	414 sh, 349, 333 br	5.5 : 1.1 : 1.0 : 1.2 : 2.8 : 2.7
Lu	OAc	770, 740 sh, 683	410 sh, 333 br	5.06 : 1.3 : 1.0 : 0.9 : 2.86
Dimeric form		770, 683 sh, 645	430, 360, 333 br	1.0 : 0.4 : 2.6 : 0.8 : 2.4 : 2.8
Oxidized form		820, 693		1.0 : 4.5
Lu	Cl	767, 740 sh, 683	410 sh, 345, 333 br	5.8 : 1.3 : 1.0 : 0.78 : 2.1 : 2.12
Tm	OAc	769 (5.19), 739 sh (4.61), 685 (4.51)	409 sh (4.38), 345 (4.80), 333 br (4.79)	5.67 : 1.2 : 1.0 : 1.82 : 2.37
Dimeric form		769, 636	410 sh, 400 sh, 380, 333 br	1.0 : 1.9 : 0.67 : 0.8 : 0.91 : 3.0
Oxidized form		810, 683		1.0 : 2.92
Er	OAc	763, 740 sh, 6812	410 sh, 360 sh, 345, 333 br	5.6 : 1.2 : 1.0 : 1.8 : 2.6 : 2.4 : 2.2
Ho	OAc	763, 738 sh, 681	409 sh, 333 br	5.8 : 1.1 : 1.0 : 1.6 : 2.1
Tb	OAc	765, 740 sh, 683	411 sh, 345, 331 br	5.5 : 1.3 : 1.0 : 1.6 : 2.45 : 2.4
Gd	OAc	765, 739 sh, 681	410 sh, 345, 330 br	5.1 : 1.3 : 1.0 : 1.9 : 2.7 : 2.8
Eu	OAc	763, 740 sh, 682	410, 334 br	5.7 : 1.2 : 1.0 : 1.62 : 2.15
Eu	Cl	768, 740 sh, 682	410 sh, 345, 329 br	5.6 : 1.1 : 1.0 : 1.6 : 2.3 : 2.4
Dimeric form		768, 682 sh, 643	430, 400, 333 br	1.0 : 0.3 : 3.0 : 0.9 : 1.1 : 3.4
Sm	OAc	765, 740 sh, 681	400 sh, 349, 333 br	5.3 : 1.1 : 1.0 : 1.1 : 2.2 : 2.1
Nd	Cl	766, 739 sh, 680	410 sh, 340, 333 br	5.6 : 1.2 : 1.0 : 2.2 : 3.1 : 2.95
Pr	OAc	766 (5.12), 740 sh (4.41), 683 (4.41)	407 sh (4.39), 360 (4.65), 345 (4.76), 333 br (4.82)	5.1 : 0.98 : 1.0 : 0.95 : 1.5 : 1.96 : 2.39

superposition of several bands. The typical spectrum is presented in Fig. 1.

Bisphthalocyanine compounds are the main by-products in the synthesis of lanthanide monophthalocyanine complexes. The use of dimethylsulfoxide results in the stabilization of the monophthalocyanine complex due to the coordination with the solvent, which along with an excess of a lanthanide salt allows one to obtain monophthalocyanine complexes as main products.[6] The application of this strategy to naphthalocyanine derivatives also provides good results. However, the formation of bis-derivatives is more characteristic of the latter.

The linear annelation of the phthalocyanine ligand results in a strong change in its electronic structure.[7]

It is manifested in EAS as a considerable (100—150 nm) bathochromic shift of the *Q* band to the short-wave IR range: it is localized at 780 nm for pure 2,3-naphthalocyanine.[8] The complexation with the lanthanide ion results in the 3—18-nm hypsochromic shift of the *Q* band (see Table 1). For the same lanthanide ion, the axially coordinated ligand exerts almost no effect on the position of the long-wave band. At the same time, in the case of phthalocyanine complexes, the introduction of different axial ligands results in some shift of the *Q* band.[9] It has been shown previously[10] that the *Q* band corresponds to the intraligand transfer of an electron from the highest occupied molecular orbital of the ligand to its lowest unoccupied molecular orbital. Therefore, an increase in the covalent character of the metal—ligand bond should favor the stronger effect of the metal ion and the type of the axial ligand on the position of this absorption band. The virtual absence of the effect of the axially coordinated ligand on the position of the *Q* band in the complexes studied testifies, in

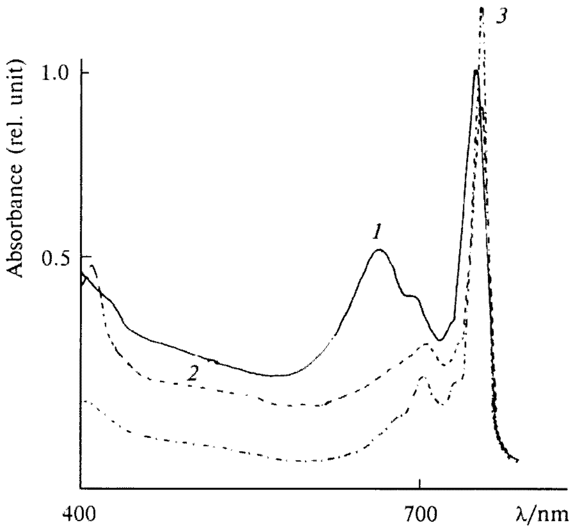


Fig. 2. Solvatochromic effects of 2,3-mononaphthalocyanine complexes using the example of Bu^t_4-2,3-NcLuOAc complex: *1*, acetonitrile, *Q* band at 760 nm; *2*, DMSO, *Q* band at 767 nm; *3*, pyridine, *Q* band at 767 nm.

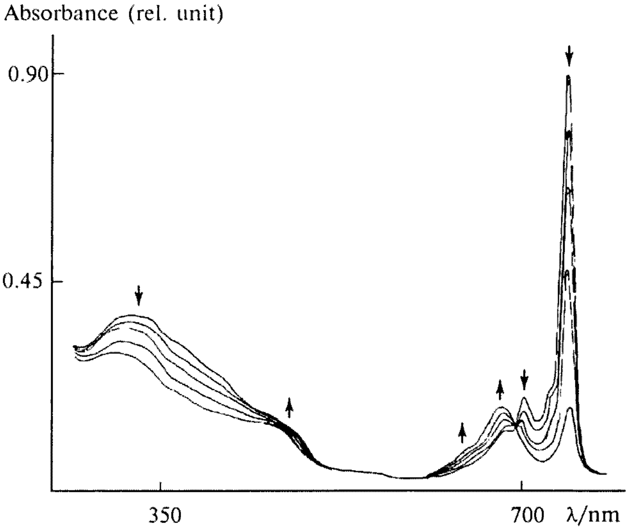


Fig. 3. Dynamics of dimerization of Bu^t_4-2,3-NcTmOAc complex in toluene.

our opinion, that the character of lanthanide 2,3-naphthalocyanine complexes is more ionic than that of their phthalocyanine analogs. Lanthanide 2,3-naphthalocyanine complexes demonstrate a pronounced solvatochromic effect, which can be illustrated by the example of the Bu^t_4-2,3-NcLuOAc complex (Fig. 2). As can be seen from these data, the shift of the *Q* band can reach 8 nm. The band at 420 nm is present along with the *Q* and *B* bands in EAS of the complexes in DMSO. A similar band is observed in the spectra of the ligand and of aluminum and vanadyl complexes in the same solvent[11]; hence, it cannot be the band of the metal—ligand or ligand—metal charge transfer. However, additional studies are required to elucidate the nature of this band.

Lanthanide tetra-*tert*-butyl-2,3-naphthalocyanines undergo dimerization in noncoordinating solvents. This results in a decrease in the intensity of the *Q* band, and a new band at 635—645 nm appears in the spectrum (Fig. 3, see Table 1). The same hypsochromic shift of the *Q* band is also observed upon dimerization of crown ether-containing complexes of phthalocyanines.[14] The color of the dimerized complex changes from green to blue. The dynamics of the transition of the green monomeric form in toluene into the blue dimeric form is characterized by the appearance of isobestic points (see Fig. 3). The addition of a strongly coordinating solvent, for example, alkylamine, decomposes the dimer and results in the formation of the initial monomeric form.

Unlike naphthalocyanine complexes of d-metals,[4] 2,3-naphthalocyanine complexes of lanthanides are more stable and do not decompose in solution at least for several weeks. Additional studies are undoubtedly necessary to reveal the mechanism of stabilization of 2,3-naphthalocyanine complexes by lanthanide ions. At the same time, the stabilization of oxidized forms of lanthanide diphthalocyanine complexes is well known. For example, one of the phthalocyanine ligands in the green form of these complexes is single-electron oxidized, while these compounds are very stable.

As shown previously, naphthalocyanine complexes of d-metals have lower oxidation potentials than their phthalocyanine analogs.[4] Air oxygen is enough for their oxidation in solution, which results in their decomposition. Lanthanide 2,3-naphthalocyanine complexes are also oxidized in solutions by bromine titration according to the scheme

$$\text{2,3-NcLnX} - \bar{e} \rightarrow [\text{2,3-NcLnX}]^{+\cdot}.$$

This results in considerable changes in EAS. Two bands at 690 and 820 nm appear instead of the *Q* band and its vibrational satellites. The color of the complex changes from green to red. In order to answer the question about the localization of an electron in the radical cation formed, we have studied the ESR spectra of the oxidized forms of lutetium naphthalocyanine complexes. The strong ESR signal with $g = 2.0025$ is recorded for these complexes.

The conclusion that a free electron is delocalized on the macrocyclic ligand can be drawn by analogy with the green form of lutetuim bisphthalocyanine[13] and the single-electron oxidized form of lutetium monophthalocyanine[12] complexes. 2,3-Naphthalocyanine complexes of lanthanides are promising materials for sensors due to their chemochromic properties.

Experimental

Electronic absorption spectra were recorded on a Specord M-40 spectrophotometer, using a concentration of

10^{-4}—10^{-6} mol L^{-1}. ESR spectra were recorded on an RE 1306 instrument with a working frequency of 3 cm. Commercial solvents purified by standard procedures[16] were used. Initial 6-*tert*-butyl-2,3-dicyanonaphthalene and tetra-*tert*-butyl-2,3-naphthalocyanine were synthesized by the procedure described previously.[15] Lanthanide salts (analytically pure or reagent grade) were used.

Lanthanide complexes were synthesized from tetra-*tert*-butyl-2,3-naphthalocyanine and corresponding salts (Lu, Tm, Er, Ho, Tb, Gd, Eu, Sm, and Pr acetates; Lu, Eu, and Nd chlorides) or tris-β-diketonates (lutetium dipivaloylmethanate (dpm) or acetylacetonate (acac)) according to the procedure presented below.

Synthesis of Bu^t_4-2,3-NcLuOAc (general procedure). Tetra-*tert*-butyl-2,3-naphthalocyanine (938 mg, $1 \cdot 10^{-3}$ mol) and anhydrous lutetium acetate (0.7 g, $2 \cdot 10^{-3}$ mol) were added to 100 mL of anhydrous DMSO. The mixture was heated to boiling with stirring and kept for 30—40 min. The reaction was controlled by EAS. The reaction mixture was cooled to -20 °C, filtered, and poured into a saturated aqueous solution of KCl (200 mL). The precipitate formed was filtered off, washed with water, and dried *in vacuo* at 70 °C. Yield 580 mg (49.5 %). Found (%): C, 67.46; H, 5.29; N, 9.90; Lu, 14.42. $C_{66}H_{53}N_8O_2Lu$. Calculated (%): C, 67.68; H, 5.08; N, 9.97; Lu, 14.94.

EAS of the complexes are presented in Table 1. Complexes of 2,3-naphthalocyanines with thulium acetate, holmium acetate, lutetium dipivaloylmethanate, and lutetium acetylacetonate were additionally purified by column chromatography on Al_2O_3 (benzene as an eluent).

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