

The first synthesis of methyl- and methoxy-substituted metal(III) diphthalocyanines

Maria A. Ovseevich, Larisa G. Tomilova,* Evgeniya G. Kogan and Nikolai S. Zefirov

Department of Chemistry, M. V. Lomonosov Moscow State University, 119899 Moscow, Russian Federation. Fax: +7 095 939 0290; e-mail: tom@org.chem.msu.su

Synthesis of previously unknown methyl- and methoxy-substituted Lu and Tb diphthalocyanines has been developed and their spectral characteristics have been compared.

Considerable attention is currently being paid to phthalocyanine and diphthalocyanine complexes of rare earth elements (REE) due to their unique optical and conductive properties.

It was supposed in 1971 that the introduction of bulky substituents (such as *tert*-butyl) prevents intermolecular interaction. This results in an increase in solubility and the emergence of a determinable melting point.¹ That is the reason for the interest demonstrated by a number of recent studies in compounds based on phthalocyanine with bulky substituents and polar groups in the benzene rings.^{2–9} Compounds with weakly-polar, non-bulky substituents (ethyl, methylethoxy, pentyl, heptyl) are rarely described.^{9,10} Moreover, all these substituted metal complexes are usually monophthalocyanines while only a few papers deal with diphthalocyanines (Pc₂M).^{8,10}

In this paper we describe the synthesis and spectral characteristics of the hitherto unknown diphthalocyanines MePc₂M and MeOPc₂M (M = Lu, Tb) based on octamethyl- and octamethoxy-phthalocyanines (4,5-Me₂)₄PcH₂ and (4,5-MeO₂)₄PcH₂. Due to the high coordination number of REE not only planar, but also sandwich-type REE complexes can be obtained. We have established that diphthalocyanines (Pc₂Ln) can be obtained *via* the corresponding monophthalocyanines (PcLnX), transformable into the neutral stable free radical form of diphthalocyanines [Pc²⁻Ln³⁺Pc⁻]⁰.

Sandwich-type diphthalocyanines were synthesized by fusion of a mixture of the corresponding REE salt and 4,5-dimethyl- or 4,5-dimethoxy-phthalonitrile (molar ratio 1:8). The temperature was gradually raised from 150 to 250 °C and held at 250 °C for 3.5 h for Lu and 2 h for Tb. The first stage of complexation is formation of monophthalocyanine with further transformation into diphthalocyanine. Neither the increase of reaction time to 9 h, nor the increase of temperature up to 350 °C involves formation of the so-called blue form that was observed in the case of non-substituted or *tert*-butyl-substituted diphthalocyanines.¹¹ Purification of the diphthalocyanines obtained was carried out by recrystallisation from H₂SO₄ and DMF and then by thin layer chromatography on Silufol.

Moreover, Pc₂Ln may be obtained by reaction of PcLnX with the corresponding free phthalocyanines. We have developed a method of synthesis for (4,5-Me₂)₄PcH₂ and (4,5-MeO₂)₄PcH₂ *via* the corresponding PcLi₂ in isoamyl alcohol and found that the template synthesis is not good enough for these compounds.

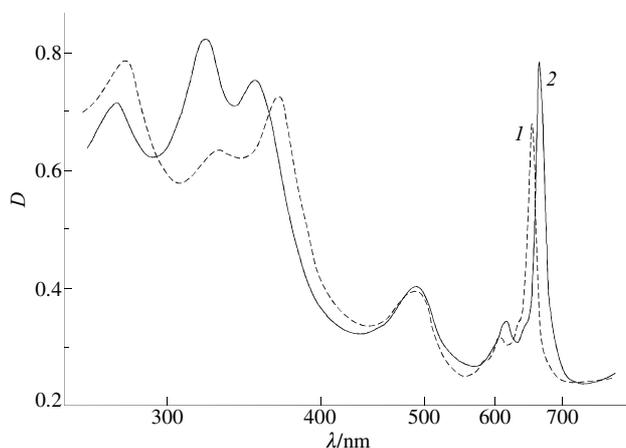
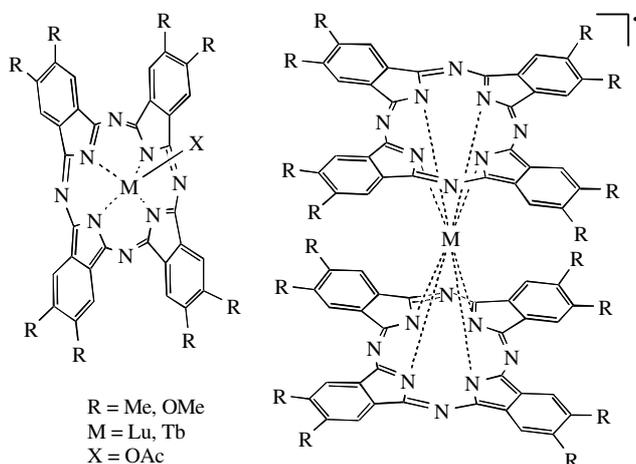


Figure 1 Absorption spectra of MeOPc₂Lu (1) and MePc₂Lu (2) in CHCl₃.

Compounds (4,5-Me₂)₄PcH₂ and (4,5-MeO₂)₄PcH₂ were purified by recrystallisation from H₂SO₄ and washing with hot DMF. The elemental analysis, UV/VIS and chromatographic data confirmed the purity of the substances. The spectrum of (4,5-Me₂)₄PcH₂ and (4,5-MeO₂)₄PcH₂ is characterized by a Q-band split (670 and 700 nm) attributed to D_{2h} symmetry in contrast to D_{4h} for metallic complexes.

While metal-free phthalocyanines (4,5-Me₂)₄PcH₂ and (4,5-MeO₂)₄PcH₂ are soluble only in *n*-chloronaphthalene, their diphthalocyanine complexes with REE are readily soluble even in CHCl₃. Therefore, diphthalocyanines can be purified by column chromatography on alumina.[†]

The electronic absorption spectra (EAS) demonstrate that the green diphthalocyanine forms [Pc⁻Ln³⁺Pc²⁻]⁰ may be obtained both by the first and the second methods of synthesis. The absorption spectra of MePc₂Lu and MeOPc₂Lu show a Q-band at about 670 nm corresponding to electron transfer between the and * orbitals of the phthalocyanine ring, and a band at about 480 nm attributed to the presence of an unpaired electron in the Pc⁻ fragment. The Soret band is in the region of 350 nm (Figure 1).

The results of the elemental analysis, spectral and chromatographic investigations of the compounds obtained indicate the formation of sandwich-type phthalocyanine complexes. The UV/VIS and near IR spectra of all the substances obtained were studied. We compared the spectra of the corresponding Tb and Lu complexes taking into account the influence of the REE ionic radii on the Q-band position: *e.g.* the Q-band of MePc₂Tb is observed at 680 nm whereas the MePc₂Lu band is observed at 674 nm. We have detected the influence of the phthalocyanine ring substituents on the position of the Q-band in the spectra of the REE complexes (*e.g.* the Q-band of Pc₂Lu is located at

† For MePc₂Lu. Found (%): C 67.12, 67.21; H 4.30, 4.22; N 15.85, 15.94. Calc. for C₈₀H₆₄N₁₆Lu (%): C 67.46; H 4.53; N 15.73.

For MeOPc₂Lu. Found (%): C 57.42, 57.53; H 4.02, 4.18; N 13.48, 13.22. Calc. for C₈₀H₆₄N₁₆O₁₆Lu (%): C 57.18; H 3.84; N 13.34.

For MePc₂Tb. Found (%): C 68.38, 68.42; H 4.65, 4.72; N 15.40, 15.48. Calc. for C₈₀H₆₄N₁₆Tb (%): C 68.22; H 4.58; N 15.91.

For (4,5-Me₂)₄PcH₂. Found (%): C 76.95, 76.84; H 5.58, 5.66; N 17.60, 17.64. Calc for C₄₀H₃₄N₈ (%): C 76.65; H 5.47; N 17.88.

654 nm while that of MeOPc_2Lu is observed at 664 nm, and that of MePc_2Lu at 674 nm).

We have demonstrated that these complexes can be successfully used in sensors, as they are capable of forming ordered Langmuir-Blodgett monolayers. The thermal stability of many diphthalocyanine complexes allows us to prepare evaporated thin solid films, which can also be used in sensors. Now we are studying the absorption of various gases on Langmuir-Blodgett and evaporated thin solid films.

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