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LETTERS TO THE EDITOR

Europium Monophthalocyanine Complex with Glycine

K. N. Maksimova[a], N. L. Bazyakina[a], O. N. Suvorova[a], and D. Wöhrle[b]

[a] *Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, ul. Tropinina 49, Nizhnii Novgorod, 603950 Russia*
e-mail: kseniyamaksimova@bk.ru

[b] *Institut für Organische und Makromolekulare Chemie, Universität Bremen, Leobener Straße NW 2, 2800 Bremen 33, Germany*

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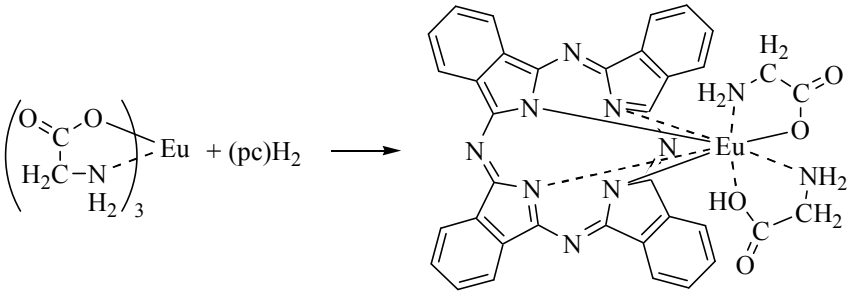
Phthalocyanines (pc) of rare-earth metals (REM) due to the ability of the lanthanide ions to form compounds with high coordination numbers afford three types of complexes with the ratio of metal to the macrocycle (M : pc): mono- (1:1) (**I**), sandwich or double-decker (1:2) (**II**) and triple-decker (2:3) (**III**) complexes [1, 2]. Design of new compounds of type **I** possessing specific properties by combination of the macrocycle, lanthanide ion, and extracoordinated ligands can expand the limits of application of phthalocyanines. Europium complexes are known to be successfully used as paramagnetic probes in biological tests to gain structural information on proteins, nucleotides, and amino acids [3, 4]. Structure and stability of α-amino acid complexes of REM are of independent interest since α-amino acids are present in the composition of living cells and any information on their interaction with other compounds is valuable. The goal of the present work was to synthesize the europium monophthalocyanine complex with glycine.

Monophthalocyanine mixed-ligand complexes of lanthanides **I** are prepared as a rule by reductive cyclotetramerization of *o*-phthalonitriles (PN) in the presence of salts of lanthanides, or by the reaction of metallation of the macrocyclic ligand (pcH_2) with lanthanide compounds. The syntheses are carried out in high-boiling solvents in the presence of an organic base, e.g., DBU (1,8-diazabicyclo[5.4.0]undec-7-ene). The reactions afford mixtures of the mono- (**I**) and bis-phthalocyanines (**II**). When using equimolar amounts of the reagents, hydrated europium complexes, and no catalyst the yield of monophthalocyanine decreases and the reaction results mainly in bis-phthalocyanine. The products were separated (after extraction with organic solvents) by column chromatography.

The maximum yield of the europium phthalocyanine(glycinate)(glycine) (pc)Eu(gly)(glyH) was reached by refluxing the metal-free phthalocyanine with europium glycine complex in *o*-dichloro-benzene (*o*-DCB) for 24 h. The amino acid europium complex was obtained by evaporation of concentrated solutions of stoichiometric amounts of the europium salt and the amino acid.



The compound was characterized by mass-spectrometry, elemental analysis, IR and electron spectroscopy.

In the electron absorption spectrum of the europium monophthalocyanine complex with glycine two intense bands are observed at 340 nm (Cope band) and 670 nm (*Q* band). Analysis of the IR spectra of the complex has shown that both the carboxy and the amino groups participate in the coordination of the molecules of amino acid in the mixed monophthalocyanine complex. Characteristic absorption bands of the COO^- group are observed at 1603 cm^{-1}. The absence in the IR spectra the bands belonging to NH_3^+ group (1585, 1492, and 516 cm^{-1}) allows to assume that the amino group participates in the coordination by forming strong chelate structure. According to the IR spectroscopy data, one molecule is coordinated while another one is covalently bonded to the europium ion, which is consistent with the coordination number and valence of the metal. In all mass spectra an intense peak of the molecular ion is observed. According to the MS analysis, the mixed-ligand europium phthalocyanine complex with glycine contains two molecules of the ligand, the peak with *m/z* 837 in the spectrum refers to $[M + Na]^+$, the peak with *m/z* 762, to $[M - gly + Na]^+$.

Therefore, the europium monophthalocyanine complex with extracoordinated ligand glycine, (pc)Eu(gly)(glyH), is prepared for the first time. The complex is found to have the composition $H(pc)EuL_2$ with one molecule of the ligand covalently bound to europium, and another one forming a coordination bond. The europium monophthalocyanine complex with glycine, unlike conventional metallophthalocyanines, is readily soluble in various organic solvents expanding the range of its practical application and allowing its introduction into film compositions.

Europium phthalocyanine(glycinate)(glycine). In a flask containing 5 ml of *o*-DCB was charged 0.41 g of $(pc)H_2$ (0.80 mmol), 0.30 g of $Eu(gly)_3$ (0.80 mmol), and 0.85 g of DBU (5.6 mmol) in the ratio of 1:1:7. The reaction mixture was refluxed with vigorous stirring for 24 h in an argon atmosphere, cooled, the products were precipitated with hexane, the precipitate was separated, washed with hexane, extracted with acetone in the Soxhlet apparatus, the solvent was removed in a vacuum. The mixture of products was separated by column chromatography on silica gel with acetone as an eluent. Yield of (pc)Eu(gly)(glyH) 0.17 g (28%). UV spectrum (methanol), λ_{max}, nm (rel. int.): 671 (1.68), 607 (0.36), 341 (0.73). UV spectrum (acetone), λ_{max}, nm (rel. int.): 669 (1.50), 638 (0.37). Found, %: C, 52.64; H, 3.01. $C_{36}H_{25}N_{10}O_4Eu$. Calculated, %: C, 53.00; H, 3.07. IR spectrum (mineral oil), ν, cm^{-1}: 1603c (COO^-). Mass spectrum (ESI, DMF), *m/z*: 837 $[M + Na]^+$.

ESI mass spectra were recorded on a Bruker Esquire LC instrument. Electron absorption spectra were obtained on a Perkin-Elmer Lambda 25 spectrophotometer. IR spectra were registered on a Perkin-Elmer Spectrum 1000 spectrometer.

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REFERENCES

1. Kasuga, K. and Tsutsui, M., *Coord. Chem. Rev*., 1980, vol. 32, no. 1, p. 67.
2. Moskalev, P.N., *Koord. Khim*., 1990, vol. 16, no. 2, p. 147.
3. Tsukube, H. and Shinoda, S., *Chem. Rev*., 2002, vol. 102, p. 2389.
4. Jaakkola, L., Peuralahti, J., Hakala, H., Kunttu, J., Tallqvist, P., Mukkala, V.-M., Ylikoski, A., and Hovinen, J., *Bioconjugate Chem*., 2005, vol. 16, p. 700.