

Thus, we have found the conditions for selective amination of dihalobenzenes with secondary cyclic amines and polyamines. The reactions studied do not cover all synthetic possibilities of the catalyzed amination in the series of polyhaloaromatic compounds. At present, the search for selective conditions of amination of these compounds with different amines is in progress.

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## Preparation of aqueous solutions of rare-earth element diphthalocyanines

P. N. Moskalev,\* A. I. Sibilev, and M. A. Sibileva

B. N. Konstantinov St. Petersburg Nuclear Physics Institute, Russian Academy of Sciences,  
188350 Gatchina, Leningrad Region, Russian Federation.

Fax: +7 (812) 713 6025. E-mail: moskalev@hep486.pnpi.spb.ru

Diphthalocyanines of rare-earth elements (REE)  $\text{PcMPc}^{\cdot-}$  (where Pc is the dianion of phthalocyanine  $(\text{C}_{32}\text{H}_{16}\text{N}_8)^{2-}$ ,  $\text{Pc}^{\cdot-}$  is the monoanion-radical of phthalocyanine  $(\text{C}_{32}\text{H}_{16}\text{N}_8)^{1-}$ , and M is the REE cation in the oxidation state 3+) is characterized by the "sandwich" molecular structure.<sup>1,2</sup> They exhibit various properties and hence can be used in different areas of science and technology.<sup>1,2</sup> However, these compounds are insoluble in water, which restrict their field of application, especially as biologically active substances.<sup>3</sup> We found that complexes of REE diphthalocyanines with polyvinylpyrrolidone (PVP) with a molar ratio of the monomer unit of polyvinylpyrrolidone ( $-\text{VP}-$ ) in PVP to REE diphthalocyanine  $>25:1$  are soluble in water without limit, the value of characteristic viscosity in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ , which is proportional to the specific volume of macromolecules in solutions, being 10% above this value for the initial PVP.

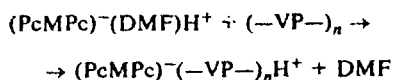
Complexes were synthesized as follows.  $\text{PcTmPc}^{\cdot-}$  powder (0.43 g) obtained according to a known procedure<sup>4</sup> was dissolved in 10 mL of DMF containing 1 vol.% of hydrazine hydrate at 100 °C for 30 min. A prepared solution of monoanion  $(\text{PcTmPc})^{\cdot-}$  was added to a solution of PVP (2.1 g, mol. weight 12400–2100) in

2 mL of DMF. The reaction mixture was concentrated in air at 70–80 °C to the consistency of a paste and heated *in vacuo* at 120–130 °C for 1 h. A dark blue friable substance (2.4 g) was obtained with the calculated molar ratio ( $-\text{VP}-$ ): thulium diphthalocyanine = 50:1. The electronic absorption spectrum of its aqueous solution in the range 400–800 nm exhibits a bifurcated Q band characteristic of the monoanion:  $\text{Q}'$  (632 nm) and  $\text{Q}''$  (710 nm), which is due to the resonance interaction of the equivalent chromophores of two Pc ligands in the diphthalocyanine anion.<sup>2,5</sup> Using this method, we prepared water-soluble complexes of lanthanide (from praseodymium to lutecium, except for promethium), scandium, and yttrium diphthalocyanines with PVP. Depending on the kind of REE in the diphthalocyanine or the solvent type, a weak indication of the state of the  $\text{PcMPc}^{\cdot-}$  radical, characterized by an unsplit Q band of the Pc ligand and poor absorption of the  $\text{Pc}^{\cdot-}$  radical in the range 400–500 nm, appear in the spectra of the complexes.<sup>2,5</sup> This can indicate the presence of the electron transfer state between the REE diphthalocyanine ion and PVP in the water-soluble complexes obtained. An increase in viscosity detected experimentally attests that the hydrodynamic sizes of polymeric molecules

increase as they form complexes with REE diphthalocyanines.

Based on data from the electronic absorption spectra of solutions, one can assume that the immobilization of REE diphthalocyanine on PVP occurs with the participation of the diphthalocyanine anion (PcMPc)<sup>-</sup>.

A proton exchange accompanied by proton localization at the nitrogen atom of polyvinylpyrrolidone



and the removal of DMF lead to a solid complex that is soluble in water owing to hydration of the hydrophilic polymeric support.

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