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Erbium and Ytterbium Complexes of Various Composition with Tetraphenylporphyrazine

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Abstract—Complexes of the metal : ligand = 1 : 1 composition have been obtained via reactions of tetraphenylporphyrazine with erbium and ytterbium acetates. Based on them, heteroleptic complexes of the 1 : 2 composition containing phthalocyanine and tetraphenylporphyrazine ligands have been prepared.

Keywords: tetraphenylporphyrazine, heteroleptic complex, synthesis, spectral properties

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Chemical modification of lanthanide-porphyrazines (either via introduction of various substituents at the macrocycle or via formation of sandwich-type compounds) extends the range of physical and chemical properties of the complex compounds and brings new knowledge on their features of complex compounds structure and reactivity.

Lanthanide-porphyrazines with different metal-to-ligand ratios (1 : 1, 1 : 2, or 2 : 3) have drawn emerging attention of researchers in various areas of science and industry [1–4]. Properties of heteroleptic complexes in solutions are defined by complicated interaction of between the two macrocycles and of the both macrocycles with the central metal ion. Of such complexes, organosoluble compounds are of particular interest. It is well known that substitution with phenyl groups increase solubility of the complexes in organic solvents, making their purification easier and expanding their practical applications range [5].

In this work we report on the preparation of heteroleptic erbium and ytterbium complexes **VI** and **VII** containing phthalocyanine and tetraphenylporphyrazine ligands at the metal atom basing on the corresponding porphyrazine 1 : 1 complexes. The prepared products, synthesized for the first time, were similar to diphthalocyanines.

The free ligand **III** used further to prepare the metal complexes was synthesized according to the scheme below [6]. The complex formation was performed in boiling DMF (Scheme 1).

Formation of the magnesium complexes, their demetallization, and the subsequent complex formation with lanthanides were monitored by means of spectrophotometry [7].

The prepared compounds were characterized by elemental analysis, IR and electronic absorption spectroscopy.

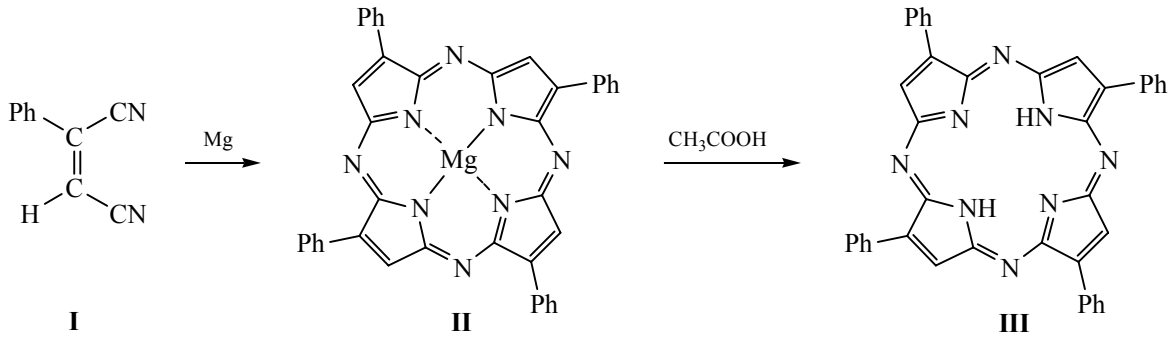
Complexes **VI** and **VII** were obtained via heating (305–310°C, 1 h) a mixture of tetraphenylporphyrazine complexes (**IV** and **V**, respectively) with a 20-fold excess of phthalonitrile. Phthalonitrile acted as both a reagent and the reaction medium (Scheme 2).

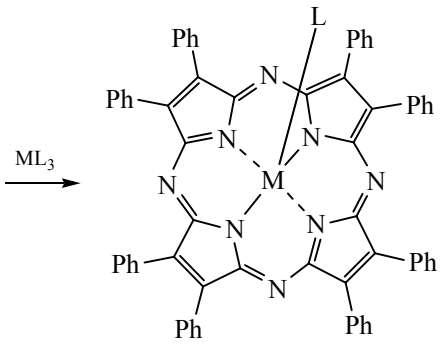
Completeness of the reaction was estimated via monitoring disappearance of the absorption band at 631–632 nm (characteristic of the initial metal complexes) in the electronic absorption spectra of the reaction mixture. Simultaneously, a strong band at 617–619 nm appeared in the spectrum along with a weaker band at 686 nm.

The produced metal complexes were purified via column chromatography on aluminum oxide (Brockman I degree) eluting with benzene.

Characteristic IR absorption bands at 1330–1310 cm^{-1}, present in the spectrum of compound **VII**, suggested that the solid complex existed in the "green" form. The

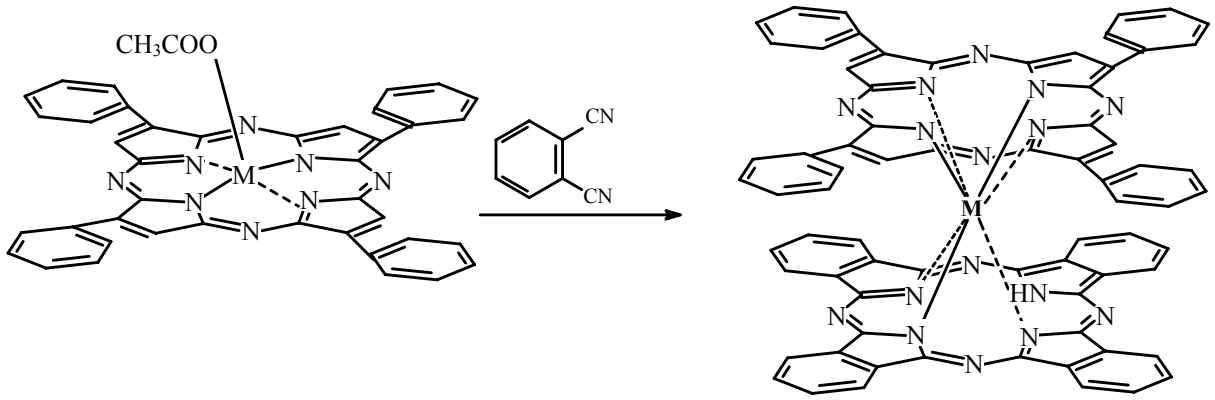
Scheme 1.





M = Er (**IV**), Yb (**V**), L = CH_3COO.

Scheme 2.



M = Er (**IV, VI**), Yb (**V, VII**).

bands characteristic of the metal-free phthalocyanine (1000–1010 cm^{-1}) were absent. Similarly to diphthalocyanines, absorption at 1455–1445 and 1365–1360 cm^{-1} was assigned to C–N and C–C bonds vibrations in the phthalocyanine ligand, respectively [8–10]. IR spectrum of complex **VII** was closer to the spectrum of (AcO)YbPc than to the spectrum of complex **V**; contrary to the expectation, the former spectrum was not an additive combination of the latter two. The presence of two structurally different ligands in complex **VII** induced neither splitting nor broadening of the IR absorption bands. The shape of the spectrum of complex **VII** suggested that electronic structures of its ligands were "leveled off" due to the interaction via the complex-forming metal, and hence became almost identical.

One of the easiest, however, informative methods of identification of the sandwich-type complexes is electronic absorption spectroscopy. As was stated

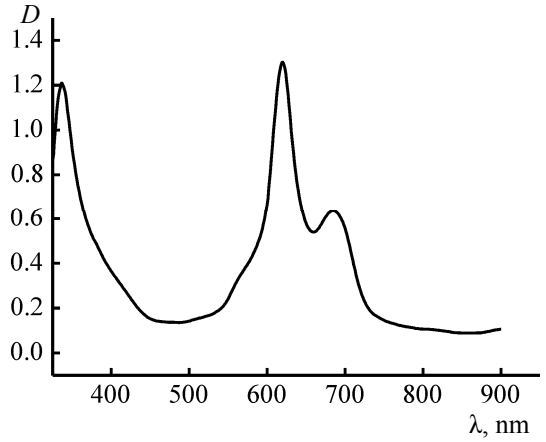


Fig. 1. Electronic absorption spectrum of complex **VII** in DMF.

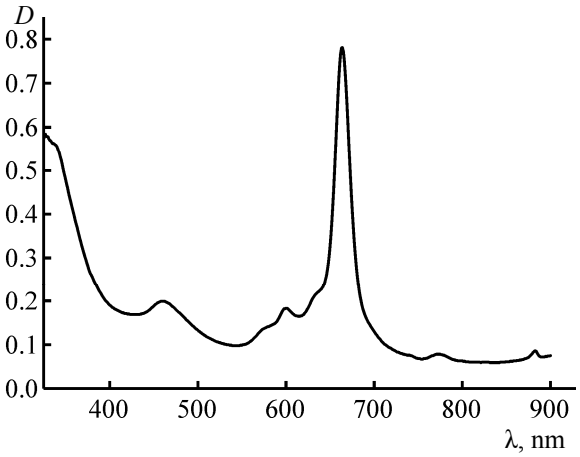


Fig. 2. Electronic absorption spectrum of complex **VII** in chloroform.

above, the spectra of sandwich complexes in aprotic solvents (for example, in DMF) contained two absorption bands in the long-wavelength region (Fig. 1).

The spectrum of the complexes solution in the solvents of lower nucleophilicity (for example, in chloroform or benzene) [10] was noticeably different. In that case, the *Q*-band was not split into two peaks, and a weak band appeared at 450–480 nm (Fig. 2). Such spectral changes were caused by the fact that the "blue" form (with the imine hydrogen atom transferred to the aprotic solvent molecule as proton) was converted into the "green" form (with hydrogen atom localized at the transannular nitrogen atom).

EXPERIMENTAL

Electronic absorption spectra were recorded with a HITACHI U-2001 spectrophotometer at 300-900 nm at room temperature. IR spectra were recorded with an AVATAR 360 FT-IR ESP spectrophotometer (KBr pellets). Elemental analysis was carried out using a CHNS-O Flash E A 1112 series analyzer.

Erbiumtetraphenylporphyrazine acetate (IV). A mixture of 0.1 mmol (61.8 mg) of tetraphenylporphyrazine **III** and 0.15 mmol (52.5 mg) of erbium acetate was dissolved in DMF. The resulting solution was refluxed during 30 min. The solvent was evaporated off, the product was extracted with chloroform and subject to chromatographic purification on a M 60 silica (eluent DMF). Yield 63.3 mg (75.2%). Electronic absorption spectrum (chloroform), λ_{max}, nm: 369, 631. Found, %: C 57.9; H 3.8; N 12.2; O 4.7. $C_{42}H_{27}N_8O_2Er$. Calculated, %: C 59.8; H 3.2; N 13.3; O 3.8.

Ytterbiumtetraphenylporphyrazine acetate was obtained similarly from 61.8 mg of **III** and 52.5 mg of ytterbium acetate. Yield 63.4 mg (74.8%). Electronic absorption spectrum (chloroform), λ_{max}, nm: 367, 632. Found, %: C 58.0; H 3.9; N 12.8; O 4.9. $C_{42}H_{27}N_8O_2Yb$. Calculated, %: C 59.4; H 3.2; N 13.2; O 3.8.

Phthalocyanineerbiumtetraphenyltetraazaporphin (VI). A mixture of 0.07 mmol (58.9 mg) of erbiumtetraphenyltetraazaporphin acetate **IV** and 5.84 mmol (747.5 mg) of phthalonitrile was heated up in a quartz ampoule at 305–310°C during 60 min. After cooling, excess of phthalodinitrile was removed in vacuum at 200°C. The product was subject to chromatographic purification and dried in vacuum (10^{-3} Pa) at 210–220°C. Yield 43.3 mg (47.8%). IR spectrum, ν, cm^{-1}: 1318. Electronic absorption spectrum (DMF), λ_{max}, nm: 332, 617, 686. Found, %: C 65.0; H 3.5; N 18.0. $C_{72}H_{41}N_{16}Er$. Calculated, %: C 66.6; H 3.2; N 17.3.

Phthalocyanineytterbiumtetraphenyltetraazaporphin (VII) was obtained similarly from 59.4 mg of ytterbiumtetraphenyltetraazaporphin acetate **V**. Yield 41.4 mg (45.4%). IR spectrum, ν, cm^{-1}: 1314. Electronic absorption spectrum (DMF), λ_{max}, nm: 334, 619, 686. Found, %: C 65.2; H 3.6; N 18.4. $C_{72}H_{41}N_{16}Yb$. Calculated, %: C 66.3; H 3.1; N 17.2.

REFERENCES

1. Moskalev, P. N. and Alimov, N.I., *Zh. Neorg. Khim*., 1975, vol. 20, no. 10, p. 26.
2. Lebedeva, T.A., Kulinich, V.P., Shaposhnikov,G.P., Efimova, S.V., Korzhenevskii, A.B., and Koifman, O.I., *Russ. J. Gen. Chem*., 2007, vol. 77, no. 11, p. 1893. DOI: 10.1134/S1070363207110175.
3. Pushkarev, V.E., Breusova, M.O., and Shulishov, E.V., *J. Porphyrins Phthalocyanines*, 2006, vol. 10, p. 827.
4. Shaposhnikov, G.P, Kulinich, V.P, and Maizlish, V.E., *Modifitsirovannye ftalotsianiny i ikh strukturnye analogi* (Modified Phthalocyanines and their Structural Analogues), Moscow: URSS, 2012.
5. Kopranenkov, V.N. and Luk'yanets, E.A., *Izv. Akad. Nauk, Ser. Khim*., 1995, no. 12, p. 2320.
6. Stuzhin, P.A, Migalova, I.S., and Berezin, B.D, *Koord. Khim.,* 1994, vol. 20, no. 6, p. 444.
7. Berezin, B.D., *Koordinatsionnye soedineniya porfirinov i ftalotsianina* (Coordination Compounds of Porphyrins and Phthalocyanine), Moscow: Nauka, 1978.
8. Clarisse, C. and Riou, M.T., *Inorg. Chim. Acta*, 1987, vol. 130, p. 139.
9. Ostendorp, G. and Homborg, H., *Z. Anorg. Allg. Chem*., 1996, vol. 622, no. 7, p. 1222.
10. Kulinich, V.P, Shaposhnikov, G. P, and Maizlish, V.E., *Koord. Khim*., 1994, vol. 20, no. 11, p. 866.