Europium(III) phthalocyanine complexes with 8-oxyquinoline

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

[a]G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, 49 ul. Tropinina, 603950 Nizhnii Novgorod, Russian Federation. Fax: +7 (831) 462 7497. E-mail: kseniyamaksimova@bk.ru
[b]Institute of Organic and Macromolecular Chemistry, University of Bremen, Leobener Str. NW2, 28359 Bremen, Germany. Fax: +49 (421) 218 4935

Europium(III) phthalocyanine complexes containing 8-oxyquinoline fragments were synthesized. The complexes were identified and structurally characterized by IR and UV-Vis absorption spectroscopy and mass spectrometry.

Key words: phthalocyanine, lanthanides, 8-oxyquinoline.

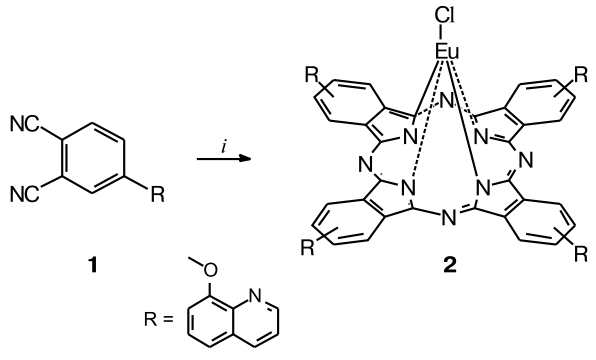
Phthalocyanines (Pc) and their metal complexes are conventionally used as dyes and pigments. In recent decades, these compounds have also found use as homogeneous and heterogeneous catalysts, photosensitizers for the photodynamic therapy of malignant tumors, active components of sensor devices, and chemo-, electro-, and solvatochromic materials. It is the chemo- and electrochromic properties discovered in lanthanide phthalocyanine complexes, which were synthesized in the 1960s, that stimulated the study of this type of complexes.[1—5] Lanthanides form several types of compounds with phthalocyanines, which differ in the lanthanide-to-macrocycle ratio (Ln : Pc). Monophthalocyanine (Ln : Pc = 1 : 1), sandwich or double-decker (Ln : Pc = 1 : 2), and triple-decker (Ln : Pc = 2 : 3) complexes are known. Due to the structural features, the properties of phthalocyanine complexes can be varied in a wide range by varying the nature of the substituents in the phthalocyanine ligand; in the case of monophthalocyanine complexes, by varying the extracoordinate ligands as well. Extracoordinate mixed-ligand lanthanide monophthalocyanine complexes are poorly known. Four types of complexes of this subgroup, *viz.*, (Pc)Ln(OAc), (Pc)Ln(acac), (Pc)Ln(acac)$_2$, and Li[(Pc)Ln(acac)],[6—10] were systematically studied. The design of new compounds having specific properties due to a combination of the macrocyclic ring, the lanthanide ion, and extracoordinate ligands extends the scope of their use. Methods for the synthesis and the spectroscopic and electrochemical properties of oxyquinoline-substituted divalent metal phthalocyanines were described in the literature.[11,12] It is known that the introduction of substituents increases the solubility of phthalocyanine complexes, which, in turn, makes it possible to prepare film composites with the use of different procedures. The aim of the present study was to synthesize europium(III) phthalocyanine complexes containing the bulky electron-donating substituent, *viz.*, the 8-oxyquinoline fragments.

Results and Discussion

We synthesized new europium(III) complexes with oxyquinoline-substituted phthalocyanine using 4-(quinolin-8-yloxy)phthalonitrile (**1**), which was prepared by the nucleophilic substitution of 8-hydroxyquinoline (8-HQ) for the nitro group of the 4-nitrophthalonitrile. The reaction was carried out in the presence of K_2CO_3 at room temperature in DMSO under an argon atmosphere.[11]

The mononuclear complex, *viz.*, europium tetra-(quinolin-8-yloxy)phthalocyanine chloride (**2**, Eu(Pc^1)Cl), was synthesized in 36% yield from phthalonitrile **1** and $EuCl_3$ in *n*-pentanol in the presence of 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) (Scheme 1). In addition, the europium(III) diphthalocyanine complex EuH(Pc^1)$_2$ (**3**) was isolated from the reaction mixture in low yield (4%).

Scheme 1

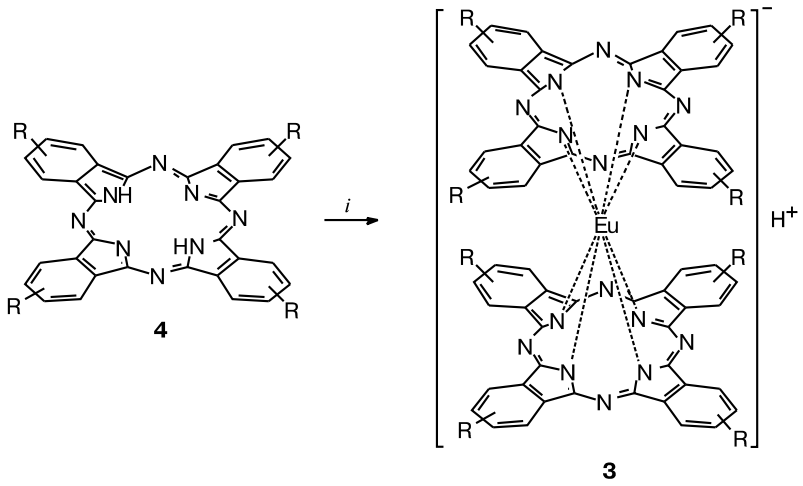


i. $EuCl_3$, DBU, *n*-$C_5H_{11}OH$, argon, 130 °C, 3 h

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 263—266, February, 2011.

1066-5285/11/6002-269 © 2011 Springer Science+Business Media, Inc.

Scheme 2



i. $EuCl_3$, DBU, *o*-DCB, argon, 180 °C, 24 h

Complex **3** was synthesized in higher yield (29%) by the reaction of free tetra(quinolin-8-yloxy)phthalocyanine (**4**, H_2Pc[1]) (see Ref. 11) with anhydrous europium(III) chloride in boiling *o*-dichlorobenzene (*o*-DCB) in the presence of DBU under an inert atmosphere during 24 h (Scheme 2). Under these conditions, no formation of monophthalocyanine complex **2** was observed.

Phthalocyanine compounds **2** and **3** are highly soluble in both polar and nonpolar organic solvents, in particular, in benzene, chloroform, carbon tetrachloride, and aliphatic hydrocarbons.

8-Hydroxyquinoline is a bidentate ligand, which is of interest for the formation of stable complexes with metal ions due to the steric proximity of the nitrogen atom and the hydroxy group.

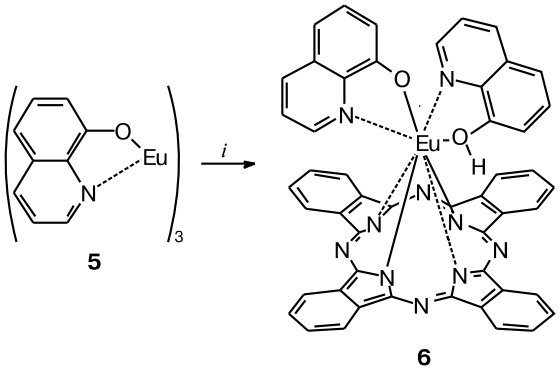
We examined the possibility of preparing extracoordinate mixed-ligand europium(III) complexes. It was shown that this type of complexes is formed by the reaction of phthalocyanine H_2Pc with europium 8-hydroxyquinoline complex (**5**, $Eu(Q)_3$) in *o*-DCB (Scheme 3). As a result, we isolated the europium monophthalocyanine complex Eu(Pc)(Q)(HQ) (**6**) in 14% yield. This complex is readily soluble in most of organic solvents (acetone, DMF, methanol, and chloroform).

The yield of monophthalocyanine complex **6** prepared directly from phthalonitrile and $Eu(Q)_3$ (**5**) in *n*-pentanol was only 2%, the complex being additionally coordinated by solvent molecules.

The resulting compounds were characterized by mass spectrometry, elemental analysis, and IR and UV-Vis absorption spectroscopy.

UV-Vis absorption spectroscopy is a valuable method for the investigation, identification, and quantitative determination of phthalocyanines and their analogs.[13,14] Almost in all cases, the synthesis of lanthanide phthalocyanine complexes resulted in the formation of mixtures of bis- and mono-derivatives. The composition of the reaction products can be determined by UV-Vis spectroscopy already in the first step of the analysis of the reaction mixtures. The absorption spectra of the europium(III) monophthalocyanine complexes show two intense absorption bands at 300—400 nm (the Soret band) and 660—700 nm (Q band). The absorption band of the reduced form of bisphthalocyanine is observed at 630 nm. The UV-Vis absorption spectrum of **6** is identical to those of usual unsubstituted metal phthalocyanines, whereas the absorption bands of substituted complexes **2** and **3** containing the 8-oxyquinoline fragment are bathochromically shifted due to the extension of the π-system (Table 1).

Scheme 3



i. H_2Pc, $EuCl_3$, *o*-DCB, argon, 180 °C, 24 h

IR spectroscopy allows one to determine the purity of the phthalocyanine complexes, to be more precise, the absence of the unconsumed starting compounds, *viz.*, free phthalocyanine, whose characteristic absorption band is

Table 1. UV-Vis absorption spectra of europium(III) phthalocyanine complexes **2**, **3**, and **6**

Complexes	Solvent	λ_{max}/nm (I/I_0)
2	DMF	683 (0.73), 335 (0.27)
	MeOH	680 (0.46), 335 (0.19)
3	DMF	685 (0.22), 634 (0.43), 342 (0.46)
	MeOH	684 (0.21), 636 (0.53), 339 (1.12)
6	DMF	673 (1.88), 607 (0.43), 330 (0.90)
	MeOH	673 (0.85), 608 (0.17), 332 (0.58)

observed at 1007 cm^{-1}, and phthalonitrile, whose characteristic absorption band of cyano groups appears at 2220 cm^{-1}. The IR spectra of all the resulting complexes have absorption bands of the phthalocyanine ligand (1605, 1565, 1314, 1082, and 791 cm^{-1}). In the IR spectra of substituted complexes **2** and **3**, the absorption bands at 1245 cm^{-1} are assigned to Ar—O—Ar stretching vibrations. The IR spectra of complex **6** show an intense absorption band at 1100 cm^{-1} due to chelation with the involvement of the nitrogen atom.

The mass spectra of complexes **2**, **3**, and **6** also confirm their structures. The mass spectrum of double-decker complex **3** contains the intense molecular ion peak $[Eu(Pc^1)_2]^-$ at m/z 2320; the mass spectrum of the monophthalocyanine complex contains the ion peak $[Eu(Pc^1)Cl + Cl]^-$ at m/z 1308. Mixed-ligand complex **6** is characterized by a peak at m/z 977 corresponding to $[M + Na]^+$, which confirms the formation of the complex Eu(Pc)(Q)(HQ).

To sum up, europium tetra(quinolin-8-yloxy)phthalocyanine chloride ($Eu(Pc^1)Cl$), europium octa(quinolin-8-yloxy)diphthalocyanine ($EuH(Pc^1)_2$), and europium bis-(8-hydroxyquinoline)phthalocyanine (Eu(Pc)(Q)(HQ)) were synthesized for the first time.

Experimental

All reagents (analytical grade) were from Fluka and Aldrich and were used without additional purification. The solvents were purified according to standard procedures immediately before use. All syntheses were carried out under an argon atmosphere. Silica gel 60 (40—63 μm, Merck) was used for column chromatography. 4-(Quinolin-8-yloxy)phthalonitrile (**1**) and tetra-(quinolin-8-yloxy)phthalocyanine (**4**) were synthesized according to known procedures.[11] Europium 8-hydroxyquinoline complex (**5**) was synthesized according to a method described earlier.[15] Anhydrous europium(III) chloride was prepared according to a procedure published earlier.[16]

The electrospray ionization mass spectra (ESI-MS) were obtained on a Bruker Esquire LC instrument. The UV-Vis absorption spectra were measured on a Perkin—Elmer Lambda 25 spectrophotometer in 0.5- and 1.0-cm quartz cells (DMF as the solvent). The IR spectra were recorded on a Perkin—Elmer Spectrum 1000 spectrometer in Nujol mulls.

Europium(III) tetra(quinolin-8-yloxy)phthalocyanine chloride, $Eu(Pc^1)Cl$ (2). A mixture of compound **1** (0.84 g, 3.1 mmol), $EuCl_3$ (0.10 g, 0.39 mmol), and DBU (0.41 g, 2.7 mmol) in *n*-pentanol (5 mL) was refluxed with stirring for 3 h. The reaction mixture was cooled, the products were precipitated with hexane, the precipitate was extracted with acetone in a Soxhlet apparatus, and the solvent was removed *in vacuo*. The product was isolated by column chromatography on silica gel eluting successively with acetone and DMF. Elution with acetone afforded the complex $Eu(HPc^1)(Pc^1)$ (**3**) in a yield of 38 mg (4%); elution with DMF gave the major product, *viz.*, the complex $Eu(Pc^1)Cl$ (**2**), in a yield of 0.18 g (36%) as the dark-blue solid. Found (%): C, 63.09; H, 2.91; N, 13.59. $C_{68}H_{36}N_{12}O_4EuCl$. Calculated (%): C, 64.20; H, 2.83; N, 13.21. IR, ν/cm^{-1}: 1245 (Ar—O—Ar), 1605, 1565, 1314, 1082, 791 (Pc^1). MS (ESI), m/z: 1308 $[M + Cl]^-$.

Europium(III) octa(quinolin-8-yloxy)diphthalocyanine, $Eu(HPc^1)(Pc^1)$ (3). A mixture of phthalocyanine **4** (0.42 g, 0.39 mmol), $EuCl_3$ (0.10 g, 0.39 mmol), and DBU (0.41 g, 2.7 mmol) in *o*-DCB (5 mL) was refluxed with stirring for 24 h. The reaction mixture was cooled, the products were precipitated with hexane, the precipitate was extracted with acetone in a Soxhlet apparatus, and the solvent was removed *in vacuo*. The product was isolated by column chromatography on silica gel (acetone as the eluent). The complex $Eu(HPc^1)(Pc^1)$ (**3**) was obtained in a yield of 0.26 g (29%). Found (%): C, 70.58; H, 3.11; N, 14.02. $C_{136}H_{73}N_{24}O_8Eu$. Calculated (%): C, 70.31; H, 3.14; N, 14.48. IR, ν/cm^{-1}: 1245 (Ar—O—Ar), 1605, 1565, 1314, 1082, 791 (Pc^1). MS (ESI), m/z: 2320 $[M]^-$.

Europium(III) bis(8-hydroxyquinoline)phthalocyanine, Eu(Pc)(Q)(HQ) (6). A mixture of phthalocyanine (H_2Pc) (0.26 g, 0.51 mmol), $Eu(Q)_3$ (**5**) (0.30 g, 0.51 mmol), and DBU (0.56 g, 3.6 mmol) in *o*-DCB (5 mL) was refluxed with stirring for 24 h under argon. The reaction mixture was cooled, the products were precipitated with hexane, the precipitate was extracted with acetone in a Soxhlet apparatus, and the solvent was removed *in vacuo*. Complex **6** was obtained in a yield of 0.07 g (14%). Found (%): C, 62.01; H, 3.26; N, 14.15. $C_{50}H_{29}N_{10}O_2Eu$. Calculated (%): C, 62.96; H, 3.04; N, 14.69. IR, ν/cm^{-1}: 1065 (Pc), 1596 (Ar), 1565 (Pc), 1496 (Ar), 1314 (Pc), 1100 (C—O), 1082 (Pc), 792 (Pc), 603 (Eu—O). MS (ESI), m/z: 977 $[M + Na]^+$.

This study was financially supported by the Russian Foundation for Basic Research (Project Nos 08-03-97054 and 09-03-97045), the Ministry of Education and Science of the Russian Federation (Federal Target Program "Scientific and Scientific-Pedagogical Personnel of the Innovative Russia", Federal Contract P337), and the German Academic Exchange Service (Deutscher Akademischer Austausch Dienst, DAAD, Germany) in the framework of the Eastern-European Collaboration of the University of Bremen.

References

1. P. N. Moskalev, A. I. Sibilev, V. P. Sedov, *Elektrokhimiya*, 1988, **24**, 1319 [*Sov. Electrochem.* (*Engl. Transl.*), 1988, **24**, No. 10].
2. P. N. Moskalev, I. S. Kirin, *Zh. Fiz. Khim.*, 1972, **46**, 1778 [*Russ. J. Phys. Chem. A* (*Engl. Transl.*), 1972, **46**, No. 7].

3. P. Turek, P. Petit, J. Simon, R. Even, B. Boudjema, G. Guillaud, M. Maitrot, *J. Am. Chem. Soc.*, 1987, **109**, 5119.
4. M. P. Moskalev, I. S. Kirin, *Zh. Obshch. Khim.*, 1966, **36**, 497 [*J. Gen. Chem. USSR* (*Engl. Transl.*), 1966, **36**].
5. J. S. Schirk, J. R. Lindle, F. J. Bartoli, M. E. Boyle, *J. Phys. Chem.*, 1992, 96, 5847.
6. V. Nemykin, V. Y. Chernii, S. V. Volkov, *J. Chem. Soc., Dalton Trans.*, 1998, 2995.
7. V. N. Nemykin, A. Yu. Tsivadze, N. B. Subbotin, N. A. Kostromina, S. V. Volkov, *Koord. Khim.,* 1996, **22**, 315 [*Russ. J. Coord. Chem.* (*Engl. Transl.*), 1996, **22**, 297].
8. V. E. Pushkarev, M. O. Breusova, E. V. Shulishov, Yu. V. Tomilov, *Izv. Akad. Nauk, Ser. Khim.*, 2005, 2024 [*Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 2087].
9. N. B. Subbotin, L. G. Tomilova, N. A. Kostromina, E. A. Lukryanets, *Zh. Obshch. Khim.*, 1986, **56**, 397 [*J. Gen. Chem. USSR* (*Engl. Transl.*), 1986, **56**, No. 2].
10. H. Sugimoto, T. Higashi, M. Mori, *Chem. Lett.*, 1982, 801.
11. M. Naksi, A. Cihan, *Transition Met. Chem.*, 2005, **30**, 89.
12. Y. Hai-ling, Y. Jin, F. Qiang, M. Ji-cheng, L. Wei-li, *Chem. Res. Chin. Univ.*, 2008, **24**, 123.
13. J. Simon, J.-J. André, *Molecular Semiconductors: Photoelectrical Properties and Solar Cells*, Springer Verlag, Berlin, 1985, 288 pp.
14. J. Mack, M. J. Stillman, *Coord. Chem. Rev.*, 2001, **319**, 993.
15. J. Stary, *The Solvent Extraction of Metal Chelates*, Pergamon, Oxford, 1964.
16. G. Brauer, *Handbuch der Präparativen Anorganischen Chemie*, Ferdinand Enke Verlag, Stuttgart, 1978.

Received November 26, 2009;
in revised form November 2, 2010