ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 10, pp. 1910–1918. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © I.P. Kalashnikova, V.E. Baulin, A.Yu. Tsivadze, 2013, published in Zhurnal Obshchei Khimii, 2013, Vol. 83, No. 10, pp. 1704–1712.

Synthesis and Spectral Characteristics of Water-Soluble Pyridine-Containing Phthalocyanines of Cation Type

I. P. Kalashnikova[a,b], V. E. Baulin[a,b], and A. Yu. Tsivadze[b]

[a] *Institute of Physiologically Active Substances, Russian Academy of Sciences, Severnyi proezd, Chernogolovka, Moskow oblast, 142432 Russia*
e-mail: ikalashn@ipac.ac.ru

[b] *Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Moscow, Russia*

Received October 4, 2012

Abstract—Soluble in aqueous acids phthalocyanine ligands and metallophthalocyanines, containing the peripheral pyridine fragments were synthesized from the corresponding phthalodinitriles. The quaternization of the pyridine-containing phthalocyanines using 2-chloroethanol afforded water-soluble phthalocyanine ligands and metal complexes. The new compounds were characterized by NMR, EAS, and MALDI–TOF mass spectrometry.

DOI: 10.1134/S1070363213100198

Unique physical and chemical properties of phthalocyanine macrocycles and their metal complexes make them the objects of numerous fundamental and applied researches. Varying the nature of the peripheral substituents is a very effective approach to getting phthalocyanines with desired physical and chemical properties [1], among which the soluble phthalocyanines finding application as sensitizers in photodynamic therapy of cancer [2] and as the components of electroactive functional materials [3, 4] are of particular interest.

To provide the water solubility peripheral anionic or cationic substituents are introduced into the molecule of phthalocyanie [5]. Among such compounds the pyridine-containing phthalocyanines are very promising capable of quaternization at the pyridine nitrogen atom, which increases the solubility in water of the phthalocyanine ligands and their complexes.

Phthalocyanines containing 2-, 3- and 4-hydroxypyridine [6–10] and 2-mercaptopyridine substituents [11, 12] have been described. As quaternizing agents alkyl halides, dimethyl sulfate, and monochloroacetic acid were used typically [13, 14].

The present work deals with the synthesis of phthalocyanines containing 3- and 4-pyridylmethoxy fragments and their water-soluble derivatives, salts of [*N*-(2-hydroxyethyl)pyridinium-3-yl]methoxy- and [*N*-(2-hydroxyethyl)pyridinium-4-yl]-methoxyderivatives. The isomeric pyridine-containing phthalodinitriles **I** and **II** were synthesized from 4-nitrophthalodinitrile and, respectively, 4- and 3-pyridylmetanols. The synthesis was carried out in a single stage in an inert atmosphere in anhydrous DMSO. The freshly calcined finely powdered K_2CO_3 was used as base. was The preparation of 4-(pyridin-4-ylmethoxy)phthalonitrile was described previously giving 59% yield at 30°C in DMF within 60 h [13]. We found that an increase in the reaction temperature to 60°C was sufficient to complete the condensation in 24 h, the yield of compound **I** increased therewith to 69%. Under the same conditions, 4-(pyridine-3-ylmethoxy)phthalonitrile **II** was synthesized with a yield of 84%. The structure of the phthalodinitriles **I, II** was confirmed by ^1H, ^{13}C NMR spectroscopy. The initial phthtalogenes were used for the synthesis of free phthalocyanine ligands and phthalocyanine complexes with Mg^{II}, Co^{II}, and Zn^{II}. Phthalocyanine ligands synthesized from phthalodinitriles **I** and **II** in a mixture of methanol and *n*-pentanol in an inert atmosphere through the corresponding intermediates, the pryridine-containing dilithium phthalocyaninates that after separation were demetallated by treating with acetic acid. Magnesium phthalocyaninate was obtained from compound **II** and magnesium metal in anhydrous

n-butanol, phthalocyanine complexes of Co^{II} and Zn^{II} were synthesized from phthalodinitriles **I** and **II** and the metal acetates in *n*-pentanol in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).

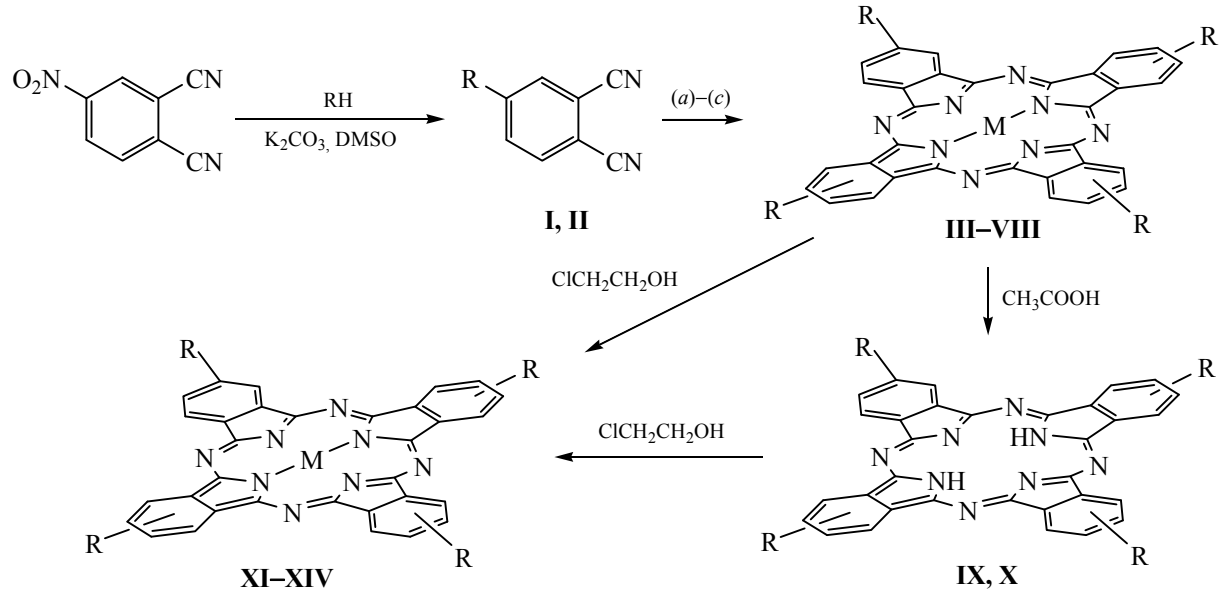
The majority of the pyridine phthalocyanine complexes are virtually insoluble in common organic solvents like chloroform, acetone and alcohol and soluble in pyridine. They are insoluble in water, but soluble in aqueous solutions of hydrochloric and hydrobromic acids to form respectively pyridinium hydrochloride or hydrobromide. The Co^{II} phthalocyaninates **IV** and **VI** are less soluble in organic solvents, including high-boiling polar solvents like DMSO and DMF. Free ligands **IX** and **X** are partially soluble in DMSO and DMF at room temperature, heating increases their solubility, but, despite this, the concentration of the solution is not sufficient to obtain high-quality NMR spectra. Complexes of Zn (**VII**) and Mg (**VIII**) are better soluble in DMSO, even at room temperature. Lithium phthalocyanine complexes **III** and **V** have the highest solubility, in particular, they are sufficiently soluble in hot acetone in contrast to other pyridine metallophthalocyanines. Compounds **III** and **V** are unstable, and readily lose the metal to form the corresponding free phthalocyanine **IX** and **X**, respectively, in the presence of trace moisture and acids, while magnesium phthalocyaninate **VIII** is quite stable at room temperature in dilute solutions of HCl. We have found that magnesium complex **XIII** transforms in the free ligand in solution of concentrated HCl at 50°C within 6 h. The cobalt complexes **IV** and **VI** are even more stable in acid solutions and practically do not undergo demetallation.

The synthesized phthalocyaninates were purified by sequential processing with different boiling organic solvents using a Soxhlet apparatus. Analytical samples of compounds for NMR spectroscopy were further purified by the chromatography on a short column packed with aluminum oxide using a mixture of pyridine–methanol, 30:1, as eluent. The quaternization of the pyridine-containing phthalocyaninates was performed in 2-chloroethanol, which was used both as the quaternizing agent and the solvent. Because the initial phthalocyanine complexes are only partially soluble in 2-chloroethanol in the cold, the quaternization was carried out at the boiling temperature to dissolve the source phthalocyaninate.

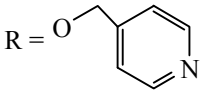
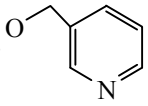
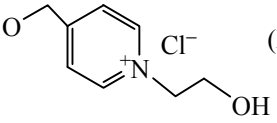
The cobalt complexes **IV** and **VI**, as well as free ligand **IX** dissolve much slower than zinc phthalocyaninate **VII**, therefore, the reaction time necessary to obtain compound **XIV** is three times shorter than that for obtaining similarly quaternized phthalocyanines **XI–XIII**. All complexes containing quaternary pyridine fragments are insoluble in acetone, chloroform, soluble in water and DMSO. We found, however, that aqueous solutions of these systems undergo association leading to a gradual precipitation, perhaps, due to the formation of numerous hydrogen bonds. The central metal ion has a significant effect on the rate of formation of associates: zinc phthalocyaninate **VII** forms associates slower than cobalt phthalocyaninates **IV** and **VI**. Processing with ultra sound can result in dissolving again the phthalocyaninate **VII** precipitated from water, which is not the case with Co complexes.

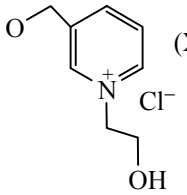
We found that quatertenized pyridine-containing phthalocyanine derivatives lose solubility in water at the storage in the solid state in a sealed vessel due to aggregation, which should be considered in future research.

Electron absorption spectra. The synthesized complexes were characterized by spectrophotometry. The EAS of phthalocyaninates of Co (**IV, VI, XI, XIII**), Zn (**VII, XIV**), and Mg (**VIII**) were recorded using pyridine as solvent, the spectra of Li phthalocyaninates (**III**, **V**) were taken in acetone. All EAS of the metallophthalocyanines are typical for this class of compounds. The *Q*-band in the spectra of the most soluble cobalt phthalocyaninates **IV** and **VI** are slightly broadened compared to the same peaks in the spectra of phthalocyaninates of Zn (**VII**), Mg (**VIII**), and Li (**III**, **V**). The EAS peaks in isomeric cobalt phthalocyaninates **IV** and **VI** are similar, the maxima positions differ only by 1–2 nm. The same is observed for the EAS of lithium phthalocyanines **III** and **V**. The *Q*-band and vibrational satellite in the spectra of phthalocyanines Zn (**VII**) and Mg (**VIII**) suffer a red shift (~20 nm) compared to similar peaks in the sptctra of compounds **IV** and **VI**. The absorption maxima of the Co (**XIII**) and Zn (**XIV**) complexes containing quaternized pyridine fragments, are close. The EAS of Co (**IV**, **VI**), Zn (**VII**), and Mg (**VIII**) phthalo-cyaninates in a dilute aqueous solution of HCl contain significantly broadened peaks, which indicates the presence in water of intermolecular associates of the macrocycles containing fragments of pyridine hydrochloride. Their *Q*-bands are characterized by a blue shift with respect to the absorption peak corresponding to phthalocyaninates with unprotonated pyridine substituents. The comparison of EAS of Mg (**VIII**) phthalocyaninate in pyridine and in HCl aqueous solution is shown in Fig. 1.



(*a*) Li, CH_3OH, *n*-$C_5H_{11}OH$; (*b*) $M(OAc)_2 \cdot nH_2O$, *n*-$C_5H_{11}OH$, DBU; (*c*) Mg, *n*-C_4H_9OH.

R =  (**I, III, IV, IX**);  (**II, V, VI, VII, VIII, X**);  (**XI, XII**);

 (**XIII, XIV**); M = 2H (**IX, X, XII**), 2Li (**III, V**), Co (**IV, VI, XI, XIII**), Zn (**VII, XIV**), Mg (**VIII**).

EAS of compounds **IX** and **X** in pyridine are characterized by a split *Q*-band, which is typical of free phthalocyanine ligands, so despite the fact that pyridine is a sufficiently strong base, no formation of the dianion in the pyridine solution has been detected. When a trace of CH_3ONa is added to a pyridine solution of the complex **IX** or **X** in methanol the typical two-band EAS turns into a narrow single peak due to the formation of the dianion $[Pc(OCH_2C_6H_5N)_4]^{2-}$. In aqueous solution of HCl compounds **IX** and **X** are in the form of the hydrochlorides, the nature of their EAS indicates the formation of intermolecular associates. The position of the main absorption bands in the EAS of compounds **IX** and **X** is almost the same. The EAS of the phthalocyanine ligand **IX** in various media is shown in Fig. 2.

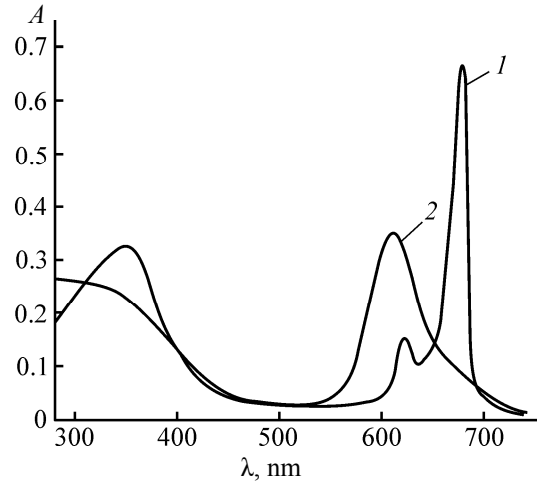


Fig. 1. ESP of magnesium 2,(3),9(10),16(17),23(24)-tetra-(3-pyridinemethoxy)phthalocyaninate (**VIII**) in (*1*) pyridine and (*2*) of its hydrochloride in aqueous HCl.

EAS of the solutions in pyridine of the compounds containing *N*-(2-hydroxyethyl)pyridinyl substituents are typical for this class of compounds: the spectra of metal complexes contain a *Q*-band with a vibrational satellite and a Soret band. In the spectrum of the free ligand **XII** the *Q*-band is split. The appearance of EAS of the aqueous solutions of compounds **XI-XIV** varies significantly. Numerous intermolecular interactions, in particular, the intermolecular hydrogen bonds, con-

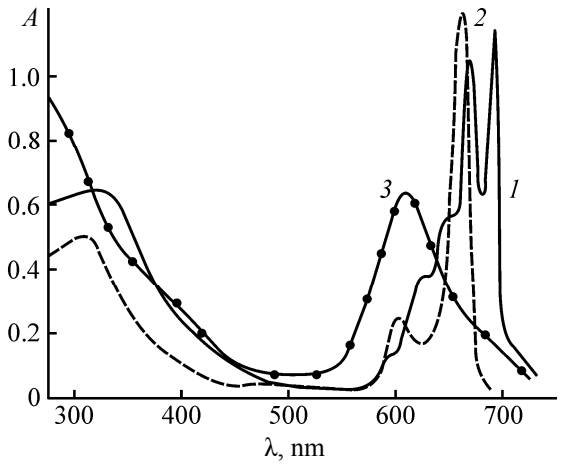


Fig. 2. ESP of 2,(3),9(10),16(17),23(24)-tetra-(4-pyridinemethoxy)phthalocyanine (**IX**) (*1*) in pyridine, (*2*) in solution of CH_3ONa in methanol, and (*3*) in 10% aqueous HCl.

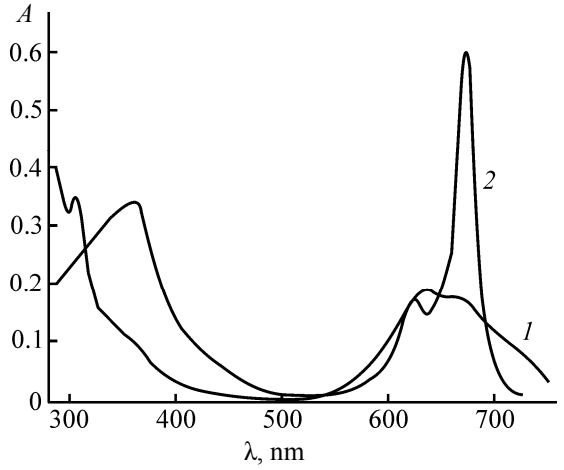


Fig. 3. ESP of zinc 2,(3),9(10),16(17),23(24)-tetra-[3-(*N*-2-oxyethyl)pyridinemethoxy]phthalocyaninate (**XIV**) (*1*) in water and (*2*) in pyridine.

tribute to the broadening of the peaks. Figure 3 shows the EAS of compound **XIV** registered in various conditions. The maxima of EAS for the synthesized compounds are listed in the table.

MALDI–TOF mass spectrometry and NMR spectroscopy. The MALDI–TOF mass spectra of compounds contain the peaks of molecular ions and the peaks corresponding to the fragments of the molecule. The spectra show that fragmentation occurs as the splitting of the peripheral substituents, starting with one pyridinyl group C_5H_4N, then splits off the pyridinemethylene fragment $CH_2C_5H_4N$, analogously splits off the second and following peripheral substituents. In the MALDI–TOF mass spectra of compounds **XI**–**XIV** containing fragments of quaternary pyridinium salts the peaks of the molecular ions are not found, but the signals are detected corresponding to the fragments of molecules containing residual $CH_2C_5H_4N^+CH_2$ fragment. Further splitting repeats completely the decay of non-quaternized pyridine complexes. The MALDI–TOF spectra of some of the compounds are shown in Figs. 4 and 5.

The structure of Zn (**VII**) and Mg (**VIII**) phthalocyaninates and related complexes **XII** and **XIV** well soluble in DMSO was confirmed by ^{1}H NMR spectroscopy. Satisfactory NMR spectra for the free ligands **IX-X** could not be obtained because of the low solubility in DMSO-d_6 and other solvents. For the same reason, and also because of the presence of paramagnetic metal, we could not get good NMR spectra of Co phthalocyaninates **IV**, **VI**, **XI**, and **XIII**. Free phthalocyanines **IX** and **X** are soluble in pyridine-d_5, but the presence of residual protons in the solvent complicates the analysis of the NMR spectrum, so we do not present these data in this report. The spectra of Zn (**VII**, **XIV**) and Mg (**VIII**) phthalocyaninates and free ligand (**XII**) contain a singlet of methylene protons at 5.6–5.7 ppm and signals of aromatic protons as multiplets in the weak field 7.7–9.0 ppm. Proton

ESP of phthalocyanine complexes and pyridine ligands

Comp. no.	Formula	Solvent	λ, nm
III	$C_{56}H_{36}Li_2N_{12}O_4$	Acetone	357, 603, 667
IV	$C_{56}H_{36}CoN_{12}O_4$	Pyridine	338, 603, 662
V	$C_{56}H_{36}Li_2N_{12}O_4$	Acetone	355, 604, 668
VI	$C_{56}H_{36}CoN_{12}O_4$	Pyridine	338, 605, 663
VII	$C_{56}H_{36}N_{12}O_4Zn$	″	360, 615, 686
VIII	$C_{56}H_{36}MgN_{12}O_4$	″	359, 619, 686
IX	$C_{56}H_{38}N_{12}O_4$	″	379, 620, 643, 673, 707
X	$C_{56}H_{38}N_{12}O_4$	″	380, 621, 643, 675, 710
XI	$C_{64}H_{56}Cl_4CoN_{12}O_8$	Pyridine	366, 619, 684
		H_2O	237, 630
XII	$C_{64}H_{56}Cl_4CoN_{12}O_8$	Pyridine	349, 619, 651, 676, 715
		H_2O	241, 607
XIII	$C_{64}H_{58}Cl_4N_{12}O_8$	Pyridine	366, 616, 681
		H_2O	236, 631
XIV	$C_{64}H_{56}Cl_4N_{12}O_8Zn$	Pyridine	351, 645, 678
		H_2O	373, 611

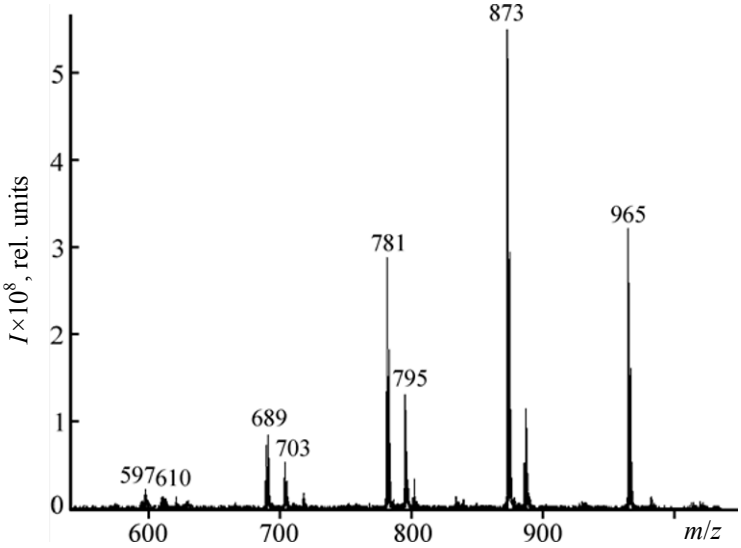


Fig. 4. MALDI–TOF spectrum of magnesium 2,(3),9(10),16(17),23(24)-tetra-(3-pyridinemethoxy)phthalocyaninate (**VIII**).

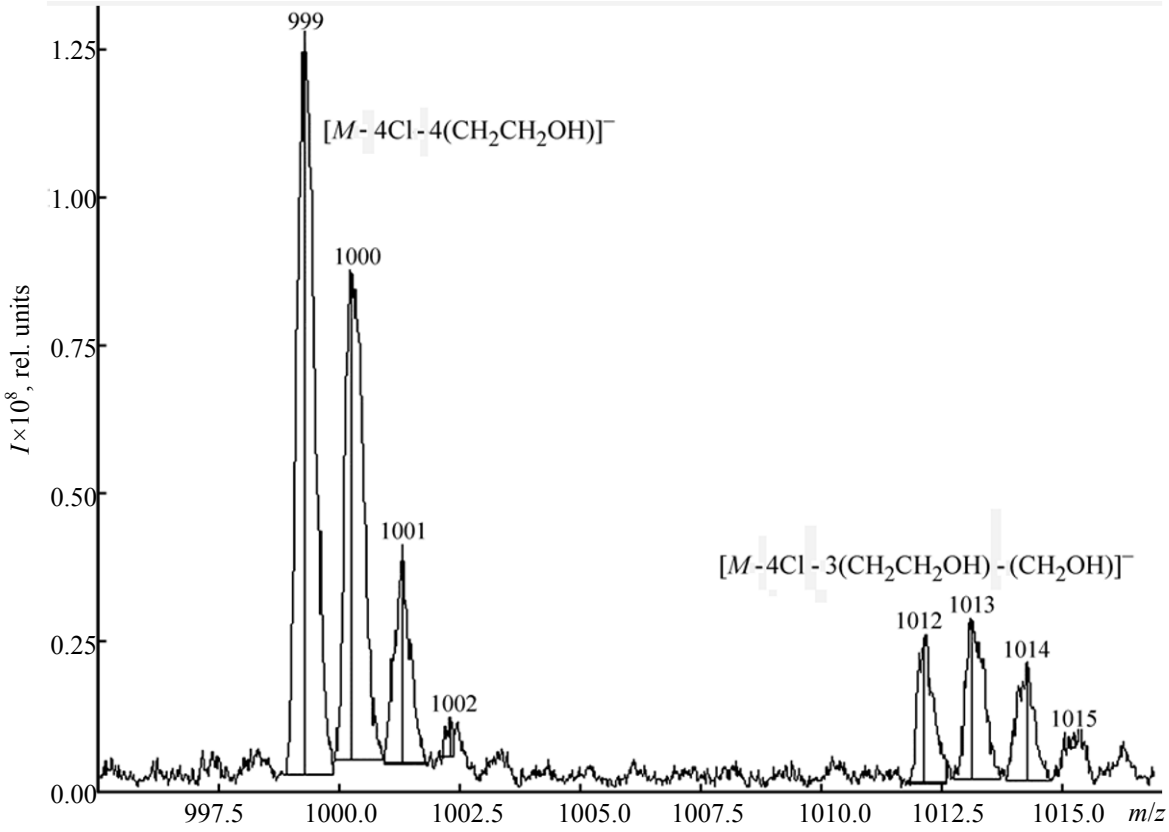


Fig. 5. Fragment of MALDI–TOF spectrum of cobalt 2,(3),9(10),16(17),23(24)-tetra-[3-(*N*-2-oxyethyl)pyridinemethoxy)-phthalocyaninate chloride (**XIII**).

signals of symmetrical pyridine ring of compound **XII** are two doublets in the region of 7.95 and 8.85 ppm, the signals of CH_2 protons of hydroxyethyl substituents are shifted downfield and appear as a broad singlet. Due to the deshielding effect of the ring current the proton signals of phthalocyanine complexes are shifted downfield by 0.3–0.4 ppm relative to the position of similar peaks in the initial phthalodinitriles

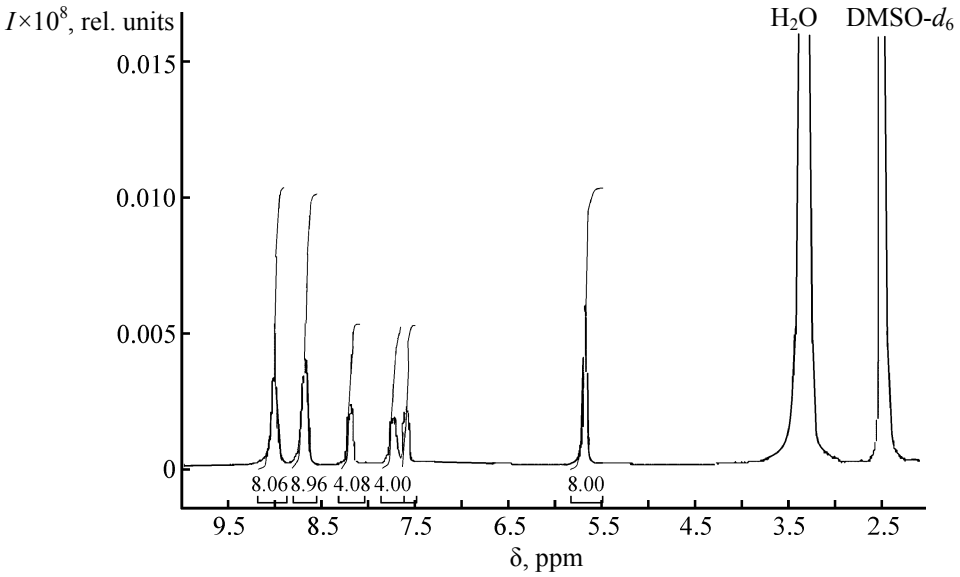


Fig. 6. ^{1}H NMR spectrum of zinc 2,(3),9(10),16(17),23(24)-tetra-(3-pyridinemethoxy)phthalocyaninate (**VII**) in DMSO-d_6.

I and **II**. Proton signals of OH groups of compounds **XII** and **XIV** and NH-protons of the ligand **XII** in DMSO-d_6 are not recorded. Since the tetrasubstituted phthalocyanines are mixtures of isomeric complexes, in the spectrum some broadening is observed of the signals compared to the corresponding signals of compounds **I** and **II**. In the spectra of quaternized derivatives **XII** and **XIV** compared with pyridine-substituted phthalocyanines the signals of aromatic and aliphatic protons are noticeable broadened, and at increase in the concentration of the complex in the sample the broadening of the signal increases indicating the associated state of the complex in DMSO.

EXPERIMENTAL

4-Nitrophthalonitrile (Acros organics, 99%) was used without further purification. K_2CO_3 of "chemically pure" grade was freshly calcined and powdered before use. Pentanol-1, butanol-1 of "pure" grade were dried by refluxing with sodium metal followed by distillation, DMSO of "pure" grade was distilled under a reduced pressure and dried with calcium hydride. In the synthesis of phthalocyaninates magnesium shavings (Aldrich, 98%) lithium metal (Aldrich, 98%) Co and Zn acetates of "pure for analysis" grade were utilized. Column chromatography was performed on Aluminum-oxide Brockmann II, neutral. NMR spectra were recorded on a spectrometer Bruker-DPX-200 (250.13 MHz), internal reference tetramethylsilane.

MALDI–TOF mass spectra were obtained on a mass spectrometer "Ultraflex" of Bruker Daltonics in the positive ion mode using reflektomode with the voltage applied to the target of 20 mV. The electron absorption spectra (EAS) in the visible and UV region were recorded on a spectrophotometer Cary-Varian 100 in rectangular quartz cells 10 mm thick.

4-(Pyridin-4-ylmethoxy)phthalonitrile (I). 1.73 g (0.01 mol) of 4-nitrophthalonitrila and 1.09 g of 4-piridinometanol (0.01 mol) were dissolved with stirring in 20 mL of anhydrous DMSO. Freshly calcined K_2CO_3 was added by portions at 60°C, and the reaction mixture was stirred at this temperature for 24 h. After cooling the mixture was poured into 100 mL of water, the resulting precipitate was filtered off and washed thoroughly several times with hot water. The product was dried in a vacuum. Yield 1.62 g (69.5%). mp 137–138°C. ^{1}H NMR (DMSO-d_6), δ, ppm: 5.32 s (2H, CH_2); 7.39 d (2H, arom., *J* 5.0 Hz), 7.48 m d.d (1H, arom.) *J* 9.0 Hz, *J* 2.3 Hz), 7.77 m (1H, arom.), 7.95 d (1H, arom., *J* 8.5 Hz), 8.54 d (2H, arom., *J* 5.1 Hz). ^{13}C NMR (DMSO-d_6), δ, ppm: 68.41, 107.22, 114.73, 115.13, 116.78, 119.40, 119.57, 121.04, 134.95, 143.64, 149.43, 160.68.

4-(Pyridine-3-ylmethoxy)phthalonitrile (II) was obtained from 1.73 g (0.01 mol) of 4-nitrophthalonitrile and 1.09 g of 3-piridinometanol (0.01 mol) in a procedure similar to the synthesis of compound **I**. Yield 1.97 g (84.5%). mp 139–140°C. ^{1}H NMR, ($CDCl_3$), δ, ppm: 5.29 s (2H, CH_2); 7.33 d.d (1H, arom., *J* 8.8 Hz, *J* 2.7 Hz), 7.43 d (1H, arom., *J* 2.7 Hz), 7.57 m (1H, arom.), 7.78 d (1H, arom., *J* 8.8 Hz), 7.99 d

(1H, arom., *J* 8.1 Hz), 8.71 d (1H, arom., *J* 4.7 Hz), with 8.88 (1H, arom). ^{13}C NMR ($CDCl_3$), δ, ppm: 68.34, 107.68, 115.16, 115.56, 117.30, 119.75, 119.91, 123.98, 130.71, 135.35, 136.05, 148.38, 149.42, 161.24.

Lithium 2,(3),9(10),16(17),23(24)-tetra-(4-pyridinemethoxy)phthalocyaninate (III). To a solution of 16 mL of anhydrous *n*-pentanol and 3 mL of anhydrous methanol was added 47 mg (6.77 mmol) of lithium and the mixture was stirred under dry argon to dissolve metal. To this solution was added 400 mg (1.70 mmol) of 4-(pyridin-4-ylmethoxy)phthalonitrile **I**, the mixture was heated to boiling and boiled for 18 h. After cooling the mixture was filtered, the white precipitate on the filter was washed with dry acetone. The filtrate was evaporated and the residue was placed in a Soxhlet apparatus and organic impurities were removed with hot hexane. Yield 312 mg (78%).

Cobalt 2,(3),9(10),16(17),23(24)-tetra-(4-pyridinemethoxy)phthalocyaninate (IV). A mixture of 280 mg (1.2 mmol) of phthalonitrile **I**, 70 mg (0.3 mmol) of $Co(OAc)_2{\cdot}4H_2O$, 0.2 mL of DBU was heated in 25 mL of *n*-hexanol for 16 h. After cooling the dark-blue precipitate was filtered off, washed with alcohol, placed in a Soxhlet apparatus, and extracted successively with boiling hexane, methanol, acetone. Yield 250 mg (83.3%). Mass spectrum (MALDI–TOF), *m/z*: 1000 $[M]^+$, 921 $[M - C_5H_4N]^+$, 908 $[M - CH_2C_5H_4N)]^+$, 830 $[M - CH_2C_5H_4N - C_5H_4N]^+$, 816 $[M - 2CH_2C_5H_4N]^+$, 737 $[M - 2CH_2C_5H_4N - C_5H_4N]^+$, 723 $[M - 3CH_2C_5H_4N]^+$, 645 $[M - 3CH_2C_5H_4N - C_5H_4N]^+$, 631 $[M - 4CH_2C_5H_4N]^+$.

Lithium 2,(3),9(10),16(17),23(24)-tetra-(3-pyridinemethoxy)phthalocyaninates (V) was obtained from 400 mg (1.70 mmol) of 4-(pyridine-3-ylmethoxy) phthalonitrile **II** and 47 mg (6.77 mmol) of lithium by a procedure similar to the synthesis of compound **III**. Yield 325 mg (81%).

Cobalt 2,(3),9(10),16(17),23(24)-tetra-(3-pyridinemethoxy)phthalocyaninates (VI) was obtained from 280 mg (1.2 mmol) of compound **II**, 70 mg (0.3 mmol) of $Co(OAc)_2{\cdot}4H_2O$ by a procedure similar to the sybthesis of compound **IV**. Yield 265 mg (88.3%). Mass spectrum (MALDI–TOF), *m/z*: 1000 $[M]^+$, 921 $[M - C_5H_4N]^+$, 908 $[M - CH_2C_5H_4N]^+$, 830 $[M - CH_2C_5H_4N - C_5H_4N]^+$, 816 $[M - 2CH_2C_5H_4N]^+$, 737 $[M - 2CH_2C_5H_4N - C_5H_4N]^+$, 723 $[M - 3CH_2C_5H_4N]^+$, 645 $[M - 3CH_2C_5H_4N - C_5H_4N]^+$, 631 $[M - 4CH_2C_5H_4N]^+$.

Zinc 2,(3),9(10),16(17),23(24)-tetra-(3-pyridinemethoxy)phthalocyaninate (VII). A mixture of 500 mg (2.1 mmol) of compound **II**, 120 mg (0.53 mmol) of $Zn(OAc)_2{\cdot}2H_2O$, 0.2 mL of DBU was heated in 25 mL of *n*-hexanol for 8 h. After cooling, the dark-blue precipitate was filtered off, washed with hexane and with alcohol, placed in a Soxhlet apparatus and extracted with boiling acetone. An analytical sample was dissolved in pyridine and purified by column chromatography (Al_2O_3), a mixture of pyridine–methanol, 30:1, was used as eluent. Yield 360 mg (68%). ^{1}H NMR (DMSO-d_6), δ, ppm: 5.69 s (8H, CH_2); 7.60 m (4H, arom., *J* 6.00 Hz), 7.72–7.77 m (4H, arom); 8.19–8.22 m (4H, arom), 8.67–8.69 m (8H, aromatic), 9.1 br.s (8H, arom.) MALDI–TOF *m/z*: 1006 $[M]^+$, 928 $[M - C_5H_4N]^+$, 914 $[M - CH_2C_5H_4N]^+$, 836 $[M - CH_2C_5H_4N - C_5H_4N]^+$, 822 $[M - 2CH_2C_5H_4N]^+$, 744 $[M - 2CH_2C_5H_4N - C_5H_4N]^+$, 730 $[M - 3CH_2C_5H_4N]^+$, 652 $[M - 3CH_2C_5H_4N - C_5H_4N]^+$, 638 $[M - 4CH_2C_5H_4N]^+$.

Magnesium 2,(3),9(10),16(17),23(24)-tetra-(3-pyridinemethoxy)phthalocyaninate (VIII). A mixture of 0.5 g (2.13 mmol) of compound **II** and 52 mg (2.13 mmol) of magnesium was heated in 10 mL of anhydrous *n*-butanol for 72 h. After cooling the solvent was evaporated in a vacuum. The residue was heated in a saturated aqueous solution of ammonium sulfate, the dark-green product was filtered off, placed in a Soxhlet apparatus, and the organic impurities were removed with hot acetone. Yield 420 mg (80%). An analytical sample was dissolved in pyridine and purified by column chromatography (Al_2O_3), using a mixture of pyridine–methanol, 30:1, as eluent. ^{1}H NMR (DMSO-d_6), δ, ppm: 5.66 s (8H, CH_2); 7.49–7.64 m (4H, arom), 7.65–7.83 m (4H, arom), 8.03–8.31 m (4H, arom), 8.54–8.87 m (8H, aromatic), 8.88–9.21 m (8H, arom.) MALDI–TOF *m/z*: 965 $[M]^+$, 887 $[M - C_5H_4N]^+$, 873 $[M - CH_2C_5H_4N]^+$, 795 $[M - CH_2C_5H_4N - C_5H_4N]^+$, 781 $[M - 2CH_2C_5H_4N]^+$, 703 $[M - 2CH_2C_5H_4N - C_5H_4N]^+$, 689 $[M - 3CH_2C_5H_4N]^+$, 610 $[M - 3CH_2C_5H_4N - C_5H_4N]^+$, 597 $[M - 4CH_2C_5H_4N]^+$.

2,(3),9(10),16(17),23(24)-Tetra-(4-pyridinemethoxy)phthalocyanine (IX). 312 mg (0.33 mmol) of lithium phthalocyaninate **III** was dissolved in dry acetone, 0.5 mL of acetic acid was added, and the mixture was kept for 1 h. The resulting precipitate was filtered off, dried, and purified in a Soxhlet apparatus, successively removing impurities with boiling methanol and acetone. Yield 217 mg (69%). MALDI–

TOF *m/z*: 943 $[M + H]^+$, 865 $[M - C_5H_4N]^+$, 851 $[M - CH_2C_5H_4N]^+$, 773 $[M - CH_2C_5H_4N - C_5H_4N]^+$, 759 $[M - 2CH_2C_5H_4N]^+$, 681 $[M - 2CH_2C_5H_4N - C_5H_4N]^+$, 667 $[M - 3CH_2C_5H_4N]^+$, 588 $[M - 3CH_2C_5H_4N - C_5H_4N]^+$, 575 $[M - 4CH_2C_5H_4N]^+$.

2,(3),9(10),16(17),23(24)-Tetra-(3-pyridinemethoxy)phthalocyanine (X) was obtained from 325 mg (0.34 mmol) of lithium phthalocyaninate **V** according to the method similar to the synthesis of **IX**. Yield 190 mg (58%). MALDI–TOF *m/z*: 943 $[M + H]^+$, 864 $[M - C_5H_4N]^+$, 850 $[M - CH_2C_5H_4N]^+$, 772 $[M - CH_2C_5H_4N - C_5H_4N]^+$, 759 $[M - 2CH_2C_5H_4N]^+$, 681 $[M - 2CH_2C_5H_4N - C_5H_4N]^+$, 667 $[M - 3CH_2C_5H_4N]^+$, 588 $[M - 3CH_2C_5H_4N - C_5H_4N]^+$, 575 $[M - 4CH_2C_5H_4N]^+$.

Cobalt 2(3),9(10),16(17),23(24)-tetra-[4-(*N*-2-oxyethyl)pyridinemethoxy]phthalocyaninate chloride (XI). To 120 mg (0.12 mmol) of cobalt phthalocyaninate **IV** was added 15 mL of 2-chloroethanol, the mixture was heated to boiling and boiled for 7 h. Thr precipitate gradually dissolved. The reaction mixture was filtered and the solvent was evaporated. The residue was purified successively in a Soxhlet apparatus by acetone, methanol. The product was dried in a vacuum. Yield 57 mg (36%). MALDI–TOF, *m/z*: 1013 $[M - 4Cl - 3CH_2CH_2ON - (CH_2OH)]^+$, 1000 $[M - 4Cl - 4CH_2CH_2ON]^+$, 921 $[M - 4Cl - 4CH_2CH_2ON - C_5H_4N]^+$, 908 $[M - 4Cl - 4CH_2CH_2ON - CH_2C_5H_4N]^+$, 830 $[M - 4Cl - 4CH_2CH_2ON - CH_2C_5H_4N - C_5H_4N]^+$, 816 $[M - 4Cl - 4CH_2CH_2ON) - 2\ CH_2C_5H_4N]^+$, 737 $[M - 4Cl - 4CH_2CH_2ON - 2CH_2C_5H_4N - C_5H_4N]^+$, 723 $[M - 4Cl - 4CH_2CH_2ON - 3CH_2C_5H_4N]^+$, 645 $[M - 4Cl - 4CH_2CH_2ON - 3CH_2C_5H_4N - C_5H_4N]^+$, 631 $[M - 4Cl - 4CH_2CH_2ON - 4CH_2C_5H_4N]^+$.

2(3),9(10),16(17),23(24)-Tetra-[4-(*N*-2-oxyethyl)-pyridinemethoxy]phthalocyanine chloride (XII) was obtained by the procedure analogous to the synthesis of **XI** from 120 mg (0.13 mmol) of phthalocyanine **IX**. The reaction time 5 h. Yield 82 mg (51%). ^{1}H NMR (DMSO-d_6), δ, ppm: 5.60 s (8H, CH_2); 6.97 br.s (8H, CH_2); 7.23 br.s (8H, CH_2); 7.45–7.48 m (12H, arom.), 7.95–7.97 g (8H, 4-Py, *J* 5.28 Hz), 8.85–8.87 g (8H, 4-Py, *J* 5.28 Hz). MALDI–TOF *m/z*: 943 $[M - 4Cl - 4CH_2CH_2ON]^+$, 864 $[M - 4Cl - 4CH_2CH_2ON - C_5H_4N]^+$, 850 $[M - 4Cl - 4CH_2CH_2ON - CH_2C_5H_4N]^+$, 772 $[M - 4Cl - 4CH_2CH_2ON - CH_2C_5H_4N - C_5H_4N]^+$, 759 $[M - 4Cl - 4CH_2CH_2ON - 2CH_2C_5H_4N\ ]^+$, 681 $[M - 4Cl - 4CH_2CH_2ON - 2CH_2C_5H_4N - C_5H_4N]^+$, 667 $[M - 4Cl - 4CH_2CH_2ON - 3CH_2C_5H_4N]^+$, 588 $[M - 4Cl - 4CH_2CH_2ON - 3CH_2C_5H_4N - C_5H_4N]^+$, 575 $[M - 4Cl - 4CH_2CH_2ON - 4CH_2C_5H_4N]^+$.

Cobalt 2,(3),9(10),16(17),23(24)-tetra-[3-(*N*-2-oxyethyl)pyridinemethoxy]phthalocyaninate chloride (XIII) was obtained from 120 mg (0.12 mmol) of cobalt phthalocyaninate **VI** by a procedure similar to the synthesis of compound **XI**. Yield 87 mg (55%). MALDI–TOF, *m/z*: 1013 $[M - 4Cl - 3CH_2CH_2ON - CH_2OH]^+$, 1000 $[M - 4Cl - 4CH_2CH_2ON]^+$, 921 $[M - 4Cl - 4CH_2CH_2ON - C_5H_4N]^+$, 908 $[M - 4Cl - 4CH_2CH_2ON - CH_2C_5H_4N]^+$, 830 $[M - 4Cl - 4CH_2CH_2ON - CH_2C_5H_4N - C_5H_4N]^+$, 816 $[M - 4Cl - 4CH_2CH_2ON - 2CH_2C_5H_4N]^+$, 737 $[M - 4Cl - 4CH_2CH_2ON - 2CH_2C_5H_4N - C_5H_4N]^+$, 723 $[M - 4Cl - 4CH_2CH_2ON - 3CH_2C_5H_4N]^+$, 645 $[M - 4Cl - 4CH_2CH_2ON - 3CH_2C_5H_4N - C_5H_4N]^+$, 631 $[M - 4Cl - 4CH_2CH_2ON - 4CH_2C_5H_4N]^+$.

Zinc 2,(3),9(10),16(17),23(24)-tetra-[3-(*N*-2-oxyethyl)pyridinemethoxy]phthalocyaninate chloride (XIV) was obtained by the procedure analogous to the synthesis of compound **XI** from 120 mg (0.12 mmol) of zinc phthalocyaninates **VII**. The reaction time was 2 h. Yield 102 mg (64%). ^{1}H NMR (DMSO-d_6), δ, ppm: 5.12 br.s (8H, CH_2); 5.72 s (8H, CH_2); 7.05 br.s (8H, CH_2); 7.74–7.80 m (8H, arom.) 8.21–8.25 br.s (4H, arom), 8.61–8.91 m (16H, arom.) MALDI–TOF *m/z*: 1006 $[M - 4Cl - 4CH_2CH_2ON]^+$, 928 $[M - 4Cl - 4CH_2CH_2ON - C_5H_4N]^+$, 914 $[M - 4Cl - 4CH_2CH_2ON - CH_2C_5H_4N]^+$, 836 $[M - 4Cl - 4CH_2CH_2ON - CH_2C_5H_4N - C_5H_4N]^+$, 822 $[M - 4Cl - 4CH_2CH_2ON - 2CH_2C_5H_4N]^+$, 744 $[M - 4Cl - 4CH_2CH_2ON - 2CH_2C_5H_4N - C_5H_4N]^+$, 730 $[M - 4Cl - 4CH_2CH_2ON - 3CH_2C_5H_4N]^+$, 652 $[M - 4Cl - 4CH_2CH_2ON - 3CH_2C_5H_4N - C_5H_4N]^+$, 638 $[M - 4Cl - 4\ CH_2CH_2ON - 4CH_2C_5H_4N]^+$.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (grant no. 12-03-00931_a).

REFERENCES

1. Tsivadze, A.Yu., *Russ. Chem. Rev*., 2004, vol. 73, no. 1, p. 5.
2. Ochner, M., *J. Photochem. Photobiol. B: Biol*., 1997, vol. 39, no. 1, p. 1.
3. Locklin, J., Shinbo, K., Onishi, K., Kaneko, F., Bao, Z., and Advincula, R.C., *Chem. Mater*., 2003, vol. 15, p. 1404.
4. He, C., Wu, Y., Shi, G., Duan, W., Song, W., and Song, Y., *Org. Electronics*, 2007, vol. 8, p. 198.
5. Dumoulin, F., Durmus, M., Ahsen, V., Nyokong, T., *Coord. Chem. Rev*., 2010, vol. 254, nos. 23–24, p. 2792.
6. Masilela, N. and Nyokong, T., *Dyes Pigments*, 2010, vol. 84, no. 3, p. 242.

7. Durmus, M. and Nyokong, T., *Inorg. Chem. Commun*., 2007, vol. 10, no. 3, p. 332.
8. Japok, J., Schnurpfeil, G., Gerdes, R., Gorun, S.M., Suvorova, O., Kudryavtseva, G.S., and Wohrle, D., *J. Porphyr. Phthalocyanines*, 2009, vol. 13, p. 346.
9. Banfi, S., Caruso, E., Buccafurni, L., Ravizza, R., Gariboldi, M., Monti, E., *J. Organomet. Chem*., 2007, vol. 692, p. 1269.
10. Spesia, M.B., Caminos, D.A., Pons, P., and Durantini, E.N., *Photodiagn. Photodyn. Ther*., 2009, vol. 6, p. 52.
11. Durmus, M. and Ahsen, V., *J. Inorg. Biochem*., 2010, vol. 104, p. 297.
12. Saydan, N., Durmus, M., Dizge, M.G., Yaman, H., Gurek, A.G., Antunes, E., Nyokong, T., and Ahsen, V., *J. Porphyr. Phthalocyanines*, 2009, vol. 13, p. 681.
13. Karaoğlu, H.R.P., Gül, A., and Koçak M.B., *Dyes Pigments*, 2008, vol. 76, p. 231.
14. Sakamoto, K., Kato, T., Okumura, E.O., Watanabe, M., and Cook, M.J., *Dyes Pigments*, 2005, vol. 64, p. 63.