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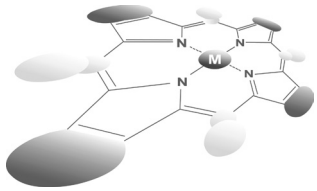

Ni(II) complex of octasubstituted tetraphenylporphine as a stationary phase for gas chromatography

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ABSTRACT: The Ni(II) complex of 5,10,15,20-tetrakis[3′,5′-di(2′′-methylbutyloxy)phenyl]porphine was synthesized and characterized by ^{1}H NMR, UV-vis spectroscopy and MALDI-TOF mass-spectrometry. The stationary phase on the base of synthesized Ni(II) complex was used for chromatographic separation of isomeric methyl- and dimethylpyridines. The high structural selectivity of this sorbent was explained by giving the results of DFT calculation of pyridine derivatives axial complexes with porphyrin Ni(II) complexes.

KEYWORDS: porphyrins; complexes; stationary phase; gas chromatography; selectivity.

INTRODUCTION

At present time the creation of high effective functional materials is the priority-driven task of research activities. Among the numerous classes of organic compounds the macroheterocycles are very perspective for these goal achievement [1, 2]. Thus substituted porphyrins, phthalocyanines and their metal complexes are used as the catalysts, semi-conductors, materials for optical storage devices or nonlinear optics [3]. These compounds reveal high chemical and thermal stability. The specific optical and emissive properties allow to apply them for high technological goals [4]. Development of new synthetic methods and structural modification of macroheterocycles resulted in detection of new practically valuable properties, for example, liquid-crystalline [5, 6]. Moreover, macroheterocyclic compounds are the perspective objects of supramolecular chemistry [7, 8].

Among the modern analytical methods chromatography is one of the most universal, widely used, accessible and productive. Chromatographic separation is based on the redistribution differences of sorbates between stationary and mobile phases. The nature of interaction which causes the coefficients of interphase redistribution can be different — dispersive, polar, electrostatic, H-bonds, *etc*. The method of ligand-exchange chromatography is based on the labile co-ordination linkage between a ligand and metal cation with formation of co-ordination compound or complex [9].

In view of high chemical selectivity metal complexes are perspective for chromatographic separation [10]. This opportunity can be illustrated by the Cu(II) and Ni(II) bis(4-decyloxyphenyloxycarbonyl)salicylal-*N*-dodecylamin]ates [11] which were effective for separation of dimethylpyridine isomers and heterocyclic nitrogen-containing mono- and polynuclear compounds. In this connection, an application of porphyrins and their metal complexes as stationary phases for chromatography is of great interest.

Another mechanism of separation can be connected with host–guest interaction where sorbate plays the guest role. It seems perspective the combination of these mechanisms for creation of stationary phase with high selectivity. The most interesting objects for this aim are macroheterocyclic compounds such as porphyrins and

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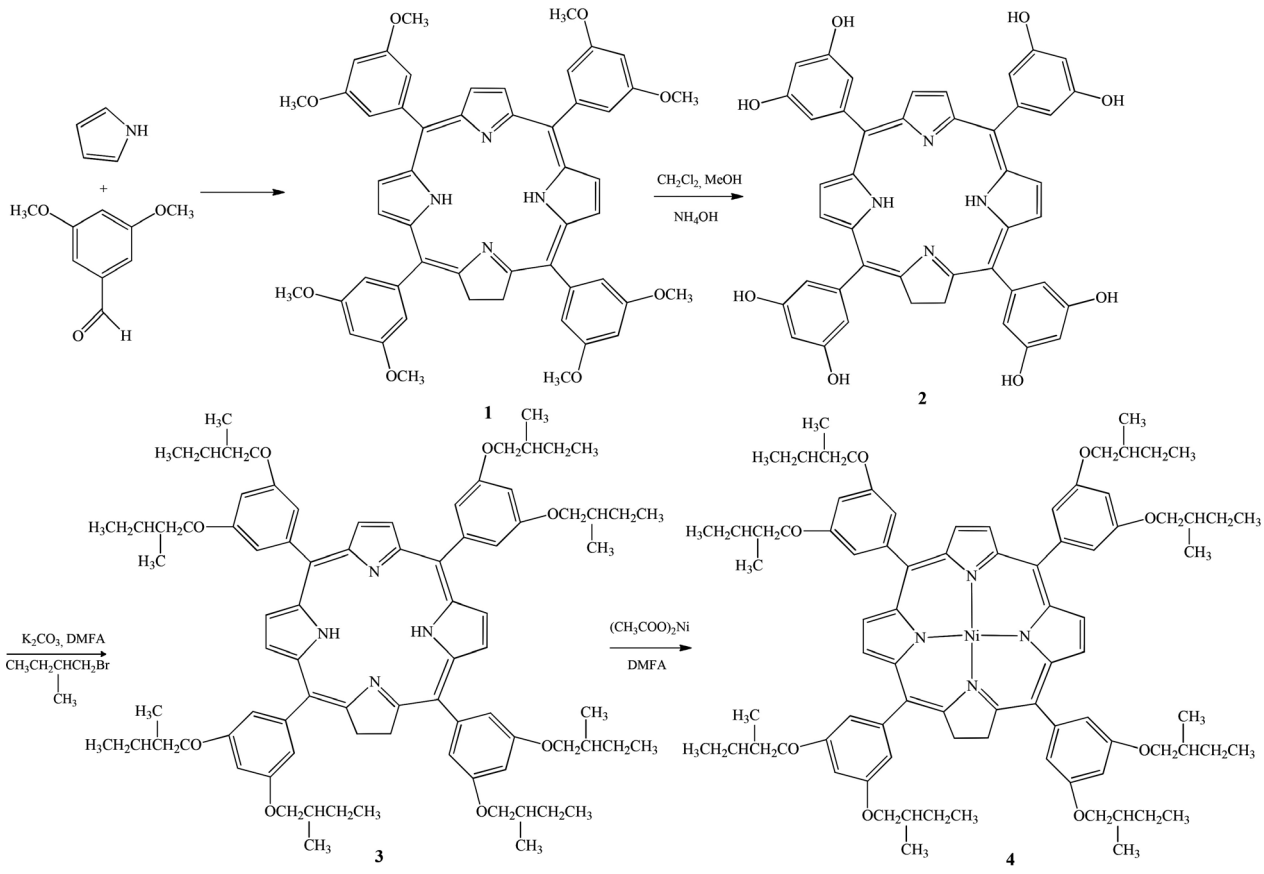
phthalocyanines. Metal complexes of phthalocyanines were studied as stationary phases deposited on solid carriers [12, 13]. These sorbents did not demonstrate high chromatographic properties. In addition an application of phthalocyanine complexes is limited to their high melting points and low solubility in organic solvents and it complicates the sorbents preparation. Considerable progress in modern macroheterocyclic chemistry allows to change their physical-chemical properties due to chemical modification. One of this means is the making of bulky hydrocarbon envelopes "over" and "under" macrocycle plane of tetraphenylsubstituted porphyrins. It allows to create favorable conditions for host–guest substances formation where the guests are the separating sorbates.

Thus this paper is devoted to synthesis, characterization and chromatographic application of Ni(II) complex of 5,10,15,20-tetrakis[3′,5′-di(2″-methylbutyloxy)phenyl] porphine.

RESULTS AND DISCUSSION

Taking into account the phenyl cores turning out from macrocycle plane the most efficient manner of hydrocarbon envelope creation with limited screening of reaction center is the introduction of branched alkyl substituents in 3,5-positions. Therefore the synthesis of necessary Ni(II) complex of 5,10,15,20-tetrakis[3′,5′-di(2″-methylbutyloxy)-phenyl]porphine (NiTPP-R_8) was carried out according to next Scheme 1.

Two approaches were used for NiTPP-R_8 synthesis. According to the first one (a) the condensation of pyrrol and 3,5-dimethoxybenzaldehide was carried out in boiling *p*-xylene in presence of trifluoroacetic acid. The product was chromatographed at first on Al_2O_3 then on silica gel. The final stage of purification was recrystallization in methanol. According to method (b) reaction of pyrrol and 3,5-dimethoxybenzaldehide was carried out in dichloromethane in presence of BF_3 under argon with subsequent addition of *p*-chloranil. This approach allowed to increase the yield of porphyrin (**1**) to 28% (18% on method a) and to obtain the product with high purity. Alkylation of 5,10,15,20-tetrakis(3,5,-dihydroxyphenyl)porphine (**2**) was carried out with 16-fold excess of bromo-2-methylbutane in DMFA in the presence of K_2CO_3 for 48 h without heating. Product (**3**) was chromatographed on Al_2O_3 and precipitated with methanol. For complex (**4**) obtaining the porphyrin (**3**) was refluxed with 10-fold excess Ni(II)acetylacetonate in DMFA for 3 h, then chromatographed on Al_2O_3 and precipitated with methanol.



Scheme 1.

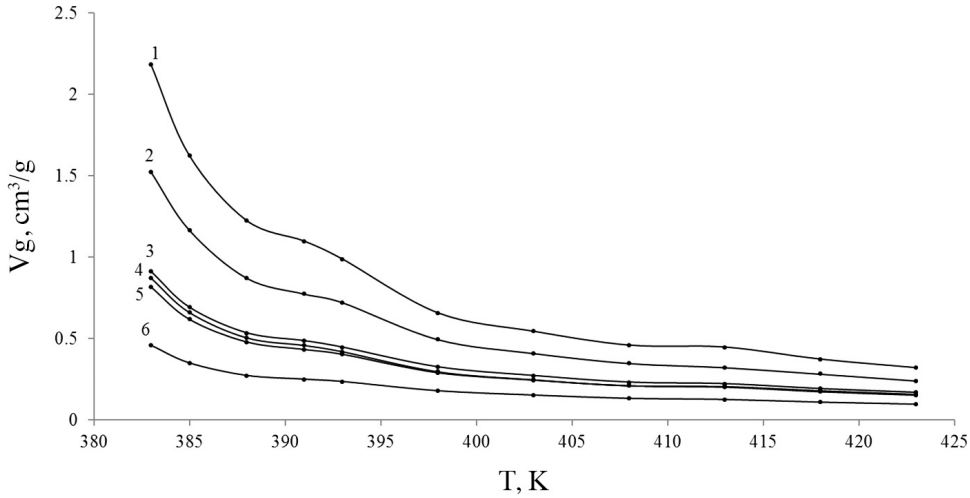


Fig. 1. Specific retention volume of lutidine isomers *vs*. temperature on a column with the stationary Ni-TPP-R_8 phase: (1) 3,4-; (2) 3,5-; (3) 2,3-; (4) 2,4-; (5) 2,5-; (6) 2,6-lutidine

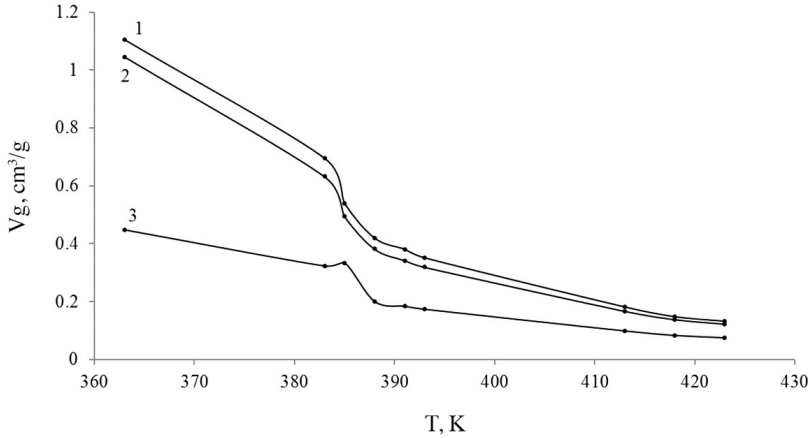


Fig. 2. Specific retention volume of picoline isomers *vs*. temperature on a column with the stationary Ni-TPP-R_8 phase: (1) 4-picoline; (2) 3-picoline; (3) 2- picoline

For synthesized Ni(II) complex test as the stationary phase the sorbent was obtained by the method presented in Experimental section. The isomers of methylpyridine (picolines) and dimethylpyridine (lutidines) able to co-ordination with central ion Ni(II) [14] were used as the test sorbates. *p*- and *m*-Xylenes were studied as the sorbates which are used to estimate the structural selectivity of stationary phases for gas chromatography [15].

For gas chromatography the retention time and the specific retention volume Vg are the main characteristics of sorbate behavior in chromatographic column [16]. The temperature dependence of specific retention volume for picoline and lutidine isomers on the sorbent with synthesized NI(II) complex (Ni-TPP-R_8) was presented in Figs 1 and 2.

The gradual diminution of Vg are observed with column temperature rise. The values Vg analysis shows the increase in sorptive capacity of Ni-TPP-R_8 at boiling temperature rise of sorbates studied. But for all that Ni(II) complex of porphyrin is sensible to spatial structure of pyridine derivatives.

For estimation of Ni-TPP-R_8 structural selectivity the ratio of specific retention times for spatial isomers $\alpha = \tau_1/\tau_2$ was calculated and listed in Table 1.

The values of α for separation of 3,4/3,5-lutidines and 4/3-picolines is of greatest interest owing to closeness of those isomer pairs boiling points. Earlier the attempts of these isomer pairs separation were made using liquid crystalline stationary phases. Thus sorbent on the base of liquid crystalline 4-butyloxy-4′-formylazobenzene has shown the selectivity coefficient of 3,4- and 3,5-lutidines separation 1.27 [17]. Supramolecular 4-cyanophenyl ester of 4[4′-(2-hydroxyethyloxy)phenylazo]cynnamic acid exhibits higher structural selectivity α = 1.30 for 3,4-/3,5-lutidines [18]. Structural selectivity of high temperature liquid crystalline tricyclic 4(4-cyanophenyl)-4′-(4-hydroxyhexyloxy)-benzylideneaniline with respect to 3,4- and 3,5-lutidines is equal 1.40 [19]. Liquid crystalline

Table 1. Maximum coefficients of structural selectivity

Sorbates	α (*t*, °C)	Sorbates	α (*t*, °C)
p/m-xylenes	1.005 (110)		
2,3/2,4-lutidines	1.10 (130)	3,4/2,6-lutidines	4.77 (110)
2,3/2,5-lutidines	1.12 (118)	3,4/3,5-lutidines	1.43 (110)
2,3/2,6-lutidines	1.99 (110)	3,5/2,3-lutidines	1.69 (112)
2,4/2,5-lutidines	1.07 (112)	3,5/2,4-lutidines	1.77 (112)
2,4/2,6-lutidines	1.90 (110)	3,5/2,5-lutidines	1.89 (112)
2,5/2,6-lutidines	1.78 (110)	3,5/2,6-lutidines	3.34 (112)
3,4/2,3-lutidines	2.40 (110)	4/3-picolines	1.11 (118)
3,4/2,4-lutidines	2.51 (110)	4/2- picolines	2.47 (90)
3,4/2,5-lutidines	2.68 (110)	3/2- picolines	2.34 (90)

Ni(II) and Cu(II) complexes also reveal selectivity with respect to 3,4- and 3,5-lutidines but the value of α did not exceed 1.30 [11]. Structural selectivity of 3- and 4-picolines separation on the sorbents with liquid crystalline stationary phases: low polar 4,4′-dimethoxyazoxybenzene and supramolecular 4-(2-hydroxyethyloxy)-4′-azoxybenzene is equal 1.11 and 1.17 correspondingly [20].

The data of Table 1 confirm the high structural selectivity of 5,10,15,20-tetrakis[3′,5′-di(2″-methylbutyloxy)-phenyl]porphine Ni(II) complex (NiTPP-R_8) with respect to 3,4- and 3,5-lutidines (α = 1.43) and 4- and 3-picolines (α = 1.11) and allow to select other spatial isomers of substituted pyridines and to use NiTPP-R8 as the stationary phase for quantitative chromatographic analysis of organic compounds in their mixtures. At the same time the selectivity of *m*- and *p*-Xylenes separation is very low (α = 1.005, Table 1). It is necessary to mention that xylenes are not able to form the stable complexes with metal ions in contrast to pyridine derivatives. Moreover the role of NiTPP-R_8 hydrocarbon envelopes in lutidines (picolines) chromatographic separation is not evident.

In this connection the DFT calculations of structures and physical-chemical properties of NiTPP (Ni(II) complex of 5,10,15,20-tetraphenylporphine), NiTPP-R_8 and their axial complexes with picolines and lutidines were carried out. These calculations were limited to the complexes with composition 1:1 taking into account the infinite dilution of sorbates at chromatographic experiment.

The data plotted in Fig. 3 exhibit the essential deviation of phenyl cores from the macrocyclic plane. This effect is connected with steric repulsion and allows to create the hydrocarbon shells near to Ni(II) ion. According to Fig. 3 and Table 2 pyridine derivatives form the stable axial complexes both with NiTPP and NiTPP-R_8.

The strength of co-ordination linkage can be evaluated by the bond length $r_{Ni–N}$. These data (Table 2) exhibit that introduction of 2-methylbutyloxy groups in 3,5-positions of NiTPP results in some weakening of co-ordination bond Ni-picoline and does not influence on the bond Ni-lutidine. This fact can be attributed to weak electronic effects of substituents in 3,5-positions of phenyl cycles. At the same time the total stability of axial complex should be defined by the complex formation energy (ΔE). For picoline axial complexes the six-fold strengthening in the case of NiTPP-R8 (Table 2) is accompanied by the weakening of co-ordination bonding and therefore is connected with interaction of sorbate with envelope aliphatic chains. This behavior confirms the significance of spatial environment at multipoint interaction of substrate with active center of receptor [21]. As the result of sorbate inclusion into "host" space aliphatic chains have been drawn together (the distance between opposite substituents was decreased from 16.54 to 16.4 Å, Table 2). This effect should be accompanied by strengthening the interaction of solute with porphyrins Ni(II) complex.

It is interesting to note that in the case of 3- and 4-picolines the total interaction energy remains practically equal (18.5 and 18.2 respectively), whereas for 3,4- and 3,5-lutidines the differentiation of interaction is exhibited at substituents introduction (ratio $\Delta E_{3,4}/\Delta E_{3,5}$ = 2.4 for NiTPP and $\Delta E_{3,4}/\Delta E_{3,5}$ = 3.4 for NiTPP-R_8, Table 2). The accordance of $\Delta E_{3,4}/\Delta E_{3,5}$ ($\Delta E_{4}/\Delta E_{3}$) and α (Table 1) confirms that ratio $\Delta E_1/\Delta E_2$ for isomers can be considered as the measure of structural selectivity.

EXPERIMENTAL

General

The ^{1}H NMR spectra were recorded on the spectrometer "500 MHz Bruker-Avance III" in $CDCL_3$. Chemical shifts were measured relatively tetramethylsilane in ppm (δ-scale TMS) with accuracy ±0.01 ppm. UV-vis spectra were recorded on the spectrophotometer "Perkin Elmer Lambda 20" in quartz cuvettes 1 cm. The solutions (2×10^{-6} M) in chloroform were studied. For mass-spectra registration the spectrometer "Axima Confidence (Shimadzu Biotech") was used. 2,4-dihydroxybenzoic acid with ratio 5000 mol/1 mol of compound studied was used as a matrix.

For gas-chromatographic experiment the steel column filled with a sorbent was prepared as follows. After measurement of internal volume of the column and weighing of solid carrier "Chromaton N-AW with specific surface 1 $m^2.g^{-1}$ and particles size 0.4–0.6 mm the carrier impregnation degree was calculated. The weighed amount of Ni(II) complex of 5,10,15,20-tetrakis[3′,5′-di(2″-methylbutyloxy)phenyl]porphine (NiTPP-R8) was dissolved in $CHCl_3$, added to known amount of solid carrier and heated with water bath at stirring to full solvent evaporation. The obtained sorbent was dried 24 h at 40 °C and residual pressure 2 Torr. The column preliminary washed with acetone was filled with obtained

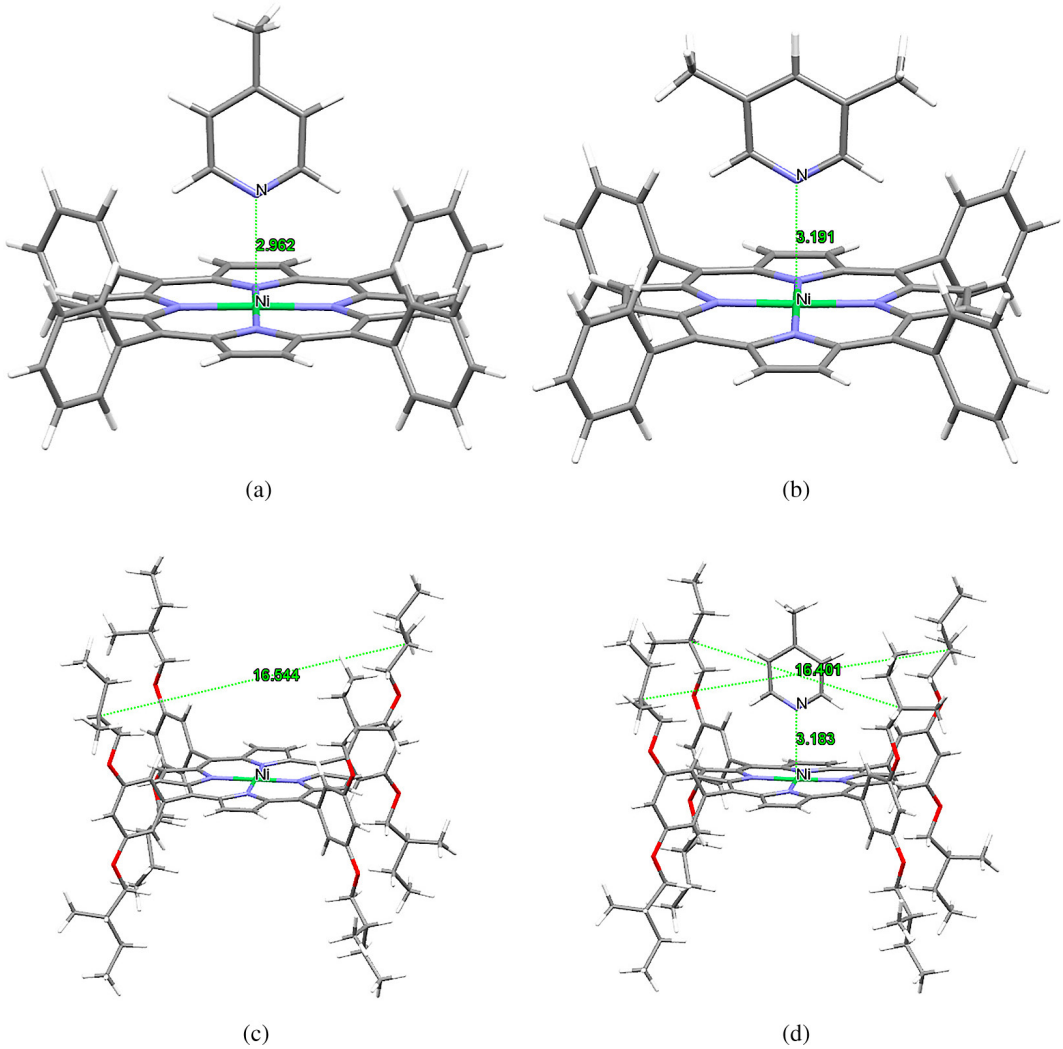


Fig. 3. Molecular structures of NiTPP-R_8 (c) and axial complexes (a) NiTPP + 4-picoline; (b) NiTPP + 3,5-lutidine; (d) NiTPP-R_8 + 4-picoline

Table 2. Formation energy of axial complexes (ΔE), co-ordination bond length ($r_{Ni–N}$) and distance between tertiary carbon atoms of opposite alkyl chains ($r_{c–c}$)

Structure	Δ*E*, kJ/mol	$r_{Ni–N}$, Å	Structure	$r_{c–c}$, Å	Δ*E*, kJ/mol	$r_{Ni–N}$, Å
NiTPP	—	—	NiTPP-R_8	16.54	—	—
NiTPP+Pyc3	-3.2	2.97	NiTPP-R_8+Pyc3	16.40	-18.5	3.03
NiTPP+Pyc4	-3.2	2.96	NiTPP-R_8+Pyc4	16.40	-18.2	3.18
NiTPP+Lu34	-8.2	3.18	NiTPP-R_8+Lu34	16.42	-6.8	3.18
NiTPP+Lu35	-3.4	3.19	NiTPP-R_8+Lu35	16.41	-2.0	3.19

sorbent and was conditioned 4 h at 180 °C in helium flow. Degree of impregnation was 10%.

Nine substituted pyridines were chosen as sorbates: dimethylpyridines (lutidines) (2,3-lutidine bp 161.2 °C, 2,4-lutidine bp 158.4 °C, 2,5-lutidine bp 157.0 °C, 2,6-lutidine bp 144.0 °C, 3,4-lutidine bp 179.1 °C, 3,5-lutidine bp 172.2 °C) and methylpyridines (picolines) (4-picoline bp 145.0 °C, 3-picoline bp 144.0 °C, 2-picoline bp 129.4 °C) (all from "Aldrich").

Retention times of sorbates were measured on gas chromatograph "Shimadzu GC-2014" with flame-ionization detector. Chromatograph was equipped with software tools "GC solution Chromatography Data System Version 2.4" which provide the maintenance of column, evaporator and detector temperature with accuracy ±0.1 °C, gas-carrier (helium) flow (60 mL.min^{-1}) and pressure at the inlet and outlet of the column. Small amounts of the sorbates at most 0.1 μL were introduced

in column to provide the infinitely diluted solutions and the rectilinear part of dissolution isotherm.

The autosampler "Shimadzu AOC-20i" with syringe 10 μL was used. Dead retention time was determined using propane. Deference between retention times of replicate observations did not exceed 0.5 s.

Specific retention volumes of test sorbates were calculated according to equation:

$$V_g = \frac{\tau_R - \tau_o}{m} \cdot F \cdot j \quad (1)$$

where τ_R — retention time of sorbate, s; τ_0 — retention time of propane, s; F — helium flow, mL.min^{-1}; m — mass of stationary phase, g; j — factor of gas compressibility which depends on pressure at the inlet to column (P_{in}) and P_{atm}:

$$j = \frac{3}{2} \cdot \frac{(P_{in}/P_{atm})^2 - 1}{(P_{in}/P_{atm})^3 - 1} \quad (2)$$

Synthesis

5,10,15,20-Tetrakis(3,5,-dimethoxyphenyl) porphine. Method a. Solution of 5 mL (0.072 mol) pyrrole and 12.0 g (0.072 mol) 3,5-dimethoxybenzaldehyde in 50 mL *p*-xylene was smoothly added to a boiling solution of 5.0 mL trifluoroacetic acid in 300 mL *p*-xylene. The mixture was refluxed for 1 h, the solvent was distilled off with water vapor, the residue was filtered off, washed with water and dried. The mixture was dissolved in benzene and chromatographed on Al_2O_3 (II Brockman degree). The porphyrin fraction was collected, evaporated, dissolved in benzene and repeatedly chromatographed on silica by benzene, then precipitated by the mixture with methanol. Yield 2.78 g (18.1%). **Method b.** 0.4 mL (3.2 mmol) BF_3 etherate was added to solution of 1.7 g (10 mmol) 3,5-dimethoxybenzaldehyde and 0.7 mL (10 mmol) pyrrole in 1000 mL dichloromethane (containing 0.4% ethanol) under argon. The mixture was stirred for 2 h, 1.7 g (7.32 mmol) *p*-chloranil was added, then the mixture was stirred 2.5 h and 1.0 mL (10.4 mmol) diethanolamine was added. Dichloromethane was distilled off, residue was washed with solution of KOH, filtered off, washed with water and dried at 70 °C. Yield 0.6 g (28.1%). ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 8.97s (8H, β-*H*); 7.43d (8H, *J* = 2.3 Hz, 2′,6′-*H*); 6.93t (4H, *J* = 2,3 Hz, 4′-*H*); 3.99s (24H, OCH_3); -2.79bs (2H, N*H*). UV-vis ($CHCl_3$): λ_{max}, nm (log ε) 644 (3.6), 589 (3.9), 550 (3.9), 515 (4.4), 421 (5.7). Rf: 0.83 (benzene–methanol 30:1); 0.93 ($CHCl_3$); 0.24 (benzene) (silufol). MS: *m/z* 855.61 (calcd. for $[M + H]^+$ 854.97).

5,10,15,20-Tetrakis(3,5,-dihydroxyphenyl) porphine. 5,10,15,20-tetrakis(3,5,-dimethoxyphenyl) porphine (1.0 g, 1.17 mmol) was dissolved in 30 mL dried dichloromethane, then under stirring and cooling (0 °C) the solution of 1.5 mL (15.9 mmol) BBr_3 in 15 mL dichloromethane added and stirred for a night without heating. Then under cooling methanol (5 mL) was added, solution was stirred for 1 h, then the mixture of conc. ammonia solution (5 mL) in water (50 mL) was added. The mixture was stirred for 30 min acetic acid was added to slight acidic reaction, organic solvents were distilled off. The residue was isolated, washed with water and dried at 70 °C. Yield 0.85 g (98%). MS: *m/z* 743.51 (calcd. for $[M + H]^+$ 742.74).

5,10,15,20-Tetrakis[3′,5′-di(2″-methylbutyloxy) phenyl]porphine. The grinded K_2CO_3 (2.0 g) was added to solution of 0.4 g (0.545 mmol) 5,10,15,20-tetrakis(3,5,-dihydroxyphenyl)porphine and 1.0 mL (8.3 mmol) 1-bromo-2-methylbutane in 20 mL DMFA. The mixture was stirred without heating for 48 h (control with thin-layer chromatography), then poured in 100 mL water, refluxed, cooled. The residue was filtered off, washed with water, dried, dissolved in dichloromethane and chromatographed on Al_2O_3 (II Brockman degree) with dichloromethane. The first fraction of porphyrin was collected. The eluate was evaporated and product was precipitated by methanol. Yield 0.58 g (83.0 %), mp 83–97 °C. Rf: 0.77 (benzene-hexane; 2:1) (silufol). UV-vis ($CHCl_3$): λ_{max}, nm (log ε) 646 (3.79), 590 (3.95), 555 (3.95), 516 (4.38), 422 (5.73). ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 9.01s (8H, β-*H*); 7.42s (8H, 2′,6′-*H*); 6.94t (4H, *J* = 2.1 Hz, 4′-*H*); 4.02m (8H, OC*H*); 3.95m (8H, OC*H*′); 1.99m (8H, C*H*); 1.66m (8H, CH_2); 1.34m (8H CH_2′); 1.10d (24H, J_2 = 6.8 Hz, CH_3); 1.00t (24H, J_2 = 6.8 Hz, CH_3); -2.78bs (2H, N*H*). MS: *m/z* 1304.67 (calcd. for $[M + H]^+$ 1303.82).

Ni(II) complex of 5,10,15,20-tetrakis[3′,5′-di(2″-methylbutyloxy)-phenyl]porphine. The solution of 0.5 g (0.38 mmol) 5,10,15,20-tetrakis[3′,5′-di(2″-methylbutyloxy)-phenyl]porphine and 1.0 g (3.9 mmol) Ni(II) acetylacetonate in 30 mL DMFA was refluxed for 3.0 h, then poured in water. The residue was filtered off, washed with water and dried at 70 °C. The precipitate obtained was dissolved in dichloromethane and chromatographed on Al_2O_3 (II Brockman degree). The porphyrins zone was evaporated and precipitated with methanol. Yield 0.47 g (91%), mp 73–80 °C. Rf: 0.80 (benzene-hexane; 1:1) (silufol). UV-vis ($CHCl_3$): λ_{max}, nm (log ε) 529 (4.35); 418 (5.48). ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 8.88s (8H, β-*H*); 7.20d (8H, *J* = 2.0 Hz 2′,6′-*H*); 6.84t (4H, *J* = 2.0 Hz, 4′-*H*); 3.95m (8H, OC*H*); 3.86m (8H, OC*H*′); 1.94m (8H, C*H*); 1.59m (8H, CH_2); 1.28m (8H, CH_2′); 1.06d (24H, J_2 = 6.8 Hz, CH_3); 0.97t (24H, J_2 = 6.8 Hz, Et-CH_3). MS: *m/z* 1361.44 (calcd. for $[M + H]^+$ 1360.498).

COMPUTATIONAL

The Ni(II) complexes of 5,10,15,20-tetrakis[3′,5′-di(2″-methylbutyloxy)-phenyl]porphine, 5,10,15,20-Tetraphenylporphine and their axial complexes with picoline and lutidine isomers were studied by density functional theory (DFT) computations utilizing the B3LYP hybrid

method [22] and 631d, p basic set [23]. All calculations described above were performed using the PC GAMESS 7.1 version12 of the GAMESS software package [24]. The preparation of the data for calculation and treatment of calculation results were carried out using software ChemCraft [25] and Mercury 3.8 [26].

Calculation of interaction energy Ni(II) complex-sorbate was carried out according to additive scheme:

$$\Delta E = E_{(\mathrm{NiTPP + Ad})} - (E_{\mathrm{NiTPP}} + E_{\mathrm{ad}}) \quad (3)$$

CONCLUSION

For the purpose of creation of new stationary phase for gas chromatography the Ni(II) complex of 5,10,15,20-tetrakis[3′,5′-di(2″-methylbutyloxy)phenyl]-porphine (NiTPP-R_8) was synthesized. It was characterized by ^{1}H NMR, UV-vis spectroscopy and mass-spectrometry. Structural selectivity of synthesized metal complex was studied by gas chromatography. The suggested stationary phase demonstrated high selectivity at chromatographic separation of methyl- and dimethylpyridine stereoisomers.

For the establishment of preferred mechanism of sorbates separation the DFT calculation of Ni(II) complex of 5,10,15,20-tetraphenylporphine (NiTPP), NiTPP-R_8 and their axial complexes with picolines and lutidines were carried out. It was shown that both co-ordination bonding and interaction sorbate-hydrocarbon envelope are the cause of chromatographic retention and structural selectivity of octasubstituted porphyrin Ni(II) complex.

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