# Preparation and reactivity of metal-containing monomers
## 44.* Synthesis and structure of vinylporphyrins and their metal complexes

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Vinylporphyrins containing one vinyl group at the pyrrole or benzene ring and their complexes with $Cu^{2+}$ and $Zn^{2+}$ have been obtained by the Wittig reaction. Compounds obtained were characterized by physicochemical methods. X-ray diffraction analysis of 5-(4-vinylphenyl)-10,15,20-triphenylporphyrin has been carried out. It is likely that the inclusion of the vinyl group is accompanied by weak electron effects on the macrocycle. No nonequivalence of N—H bonds is observed in initial macrocycles.

**Key words:** vinylporphyrins, metal complexes; magnetic properties; crystal and molecular structure.

Polymeric metalloporphyrins are widely used as catalysts of many reactions[1] and as polymeric additives, which modify the properties of various compositions. There are two main ways for introducing porphyrin units into the polymer chain. The first of them is polymer-analogous transformations involving reactive peripheral groups (most often amino, carboxy, and sulfo groups) of substituted porphyrins and appropriate centers of polymers. In addition, this method is also realized in the case of nonsubstituted metalloporphyrins due to the additional coordination (extracoordination) with donating centers of polymeric ligands.[2,3] The second way includes reactions of condensation or polymerization of the corresponding monomers. Condensation processes are rather widely used for preparing macroporphyrins, while considerably less attention is given to polymerization and copolymerization of vinylporphyrins and their metal-containing derivatives. In our opinion, this is related to the lack of convenient methods for synthesizing initial monomers.

This work is devoted to synthesis and determination of structures of porphyrins and metalloporphyrins containing one vinyl group at the pyrrole or benzene cycle.

The method for assembling a substituted porphyrin directly at the stage of the cycle formation was developed for synthesis of vinylporphyrins and their metal complexes. Vinylporphyrins were obtained by the Wittig reaction, the reaction between the corresponding aldehydes and trimethylenephosphorane (phosphorus ylide). The abstraction of an α-proton from the corresponding phosphonium salt under the action of an appropriate base is the most general method for synthesizing phosphorus ylides. In this reaction, the strength of a base necessary for deprotonation depends on the acidity of the α-H atom in the phosphonium salt used.[4] If substituents are able to stabilize the negative charge due to induction or mesomeric effects, relatively weak bases can be used: ammonia or sodium carbonate. When there are no stabilizing factors, stronger bases are needed, for example, butyllithium; and the ligand exchange at the P atom often occurs when alkyllithium compounds are used. Therefore, we have chosen phenyllithium.

Triphenylmethylenephosphorane is the unstable ylide, which easily deprotonates water to form rapidly hydrolyzed phosphonium hydroxides. In this connection, it was prepared in an aprotic medium. In addition, such ylides are very reactive and react not only with carbonyl compounds, but also with water, oxygen, carbon dioxide, and alcohols. Transformations of these ylides were carried out under conditions that exclude the presence of the compounds mentioned.

The Wittig reaction can be performed by the generation of ylides under the action of potassium carbonate and butoxide in the presence of the phase transfer catalyst,[5] 18-crown-6-ether (18-C-6). Benzene or dichloromethane are usually chosen as organic solvents.

Porphyrinaldehydes can be prepared by different methods. In particular, *para*-formylphenyltriphenylporphyrin was synthesized by subsequent transformations (Scheme 1) under conditions similar to those described in one of the previous works.[6]

The initial monocyanoporphyrin was obtained by the so-called "mixed-aldehyde synthesis": condensation of pyrrole and a mixture of aldehydes in boiling xylene in

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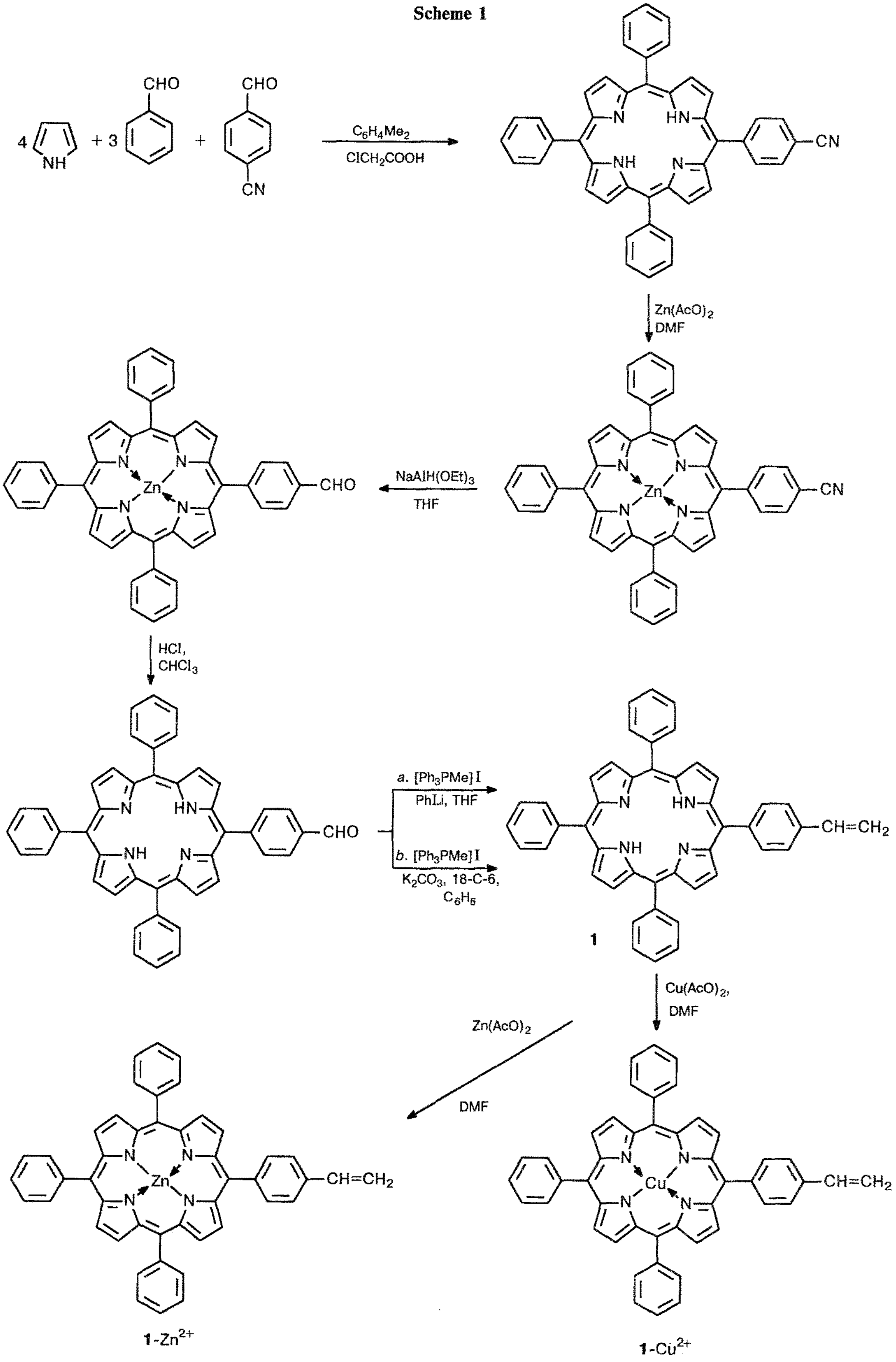
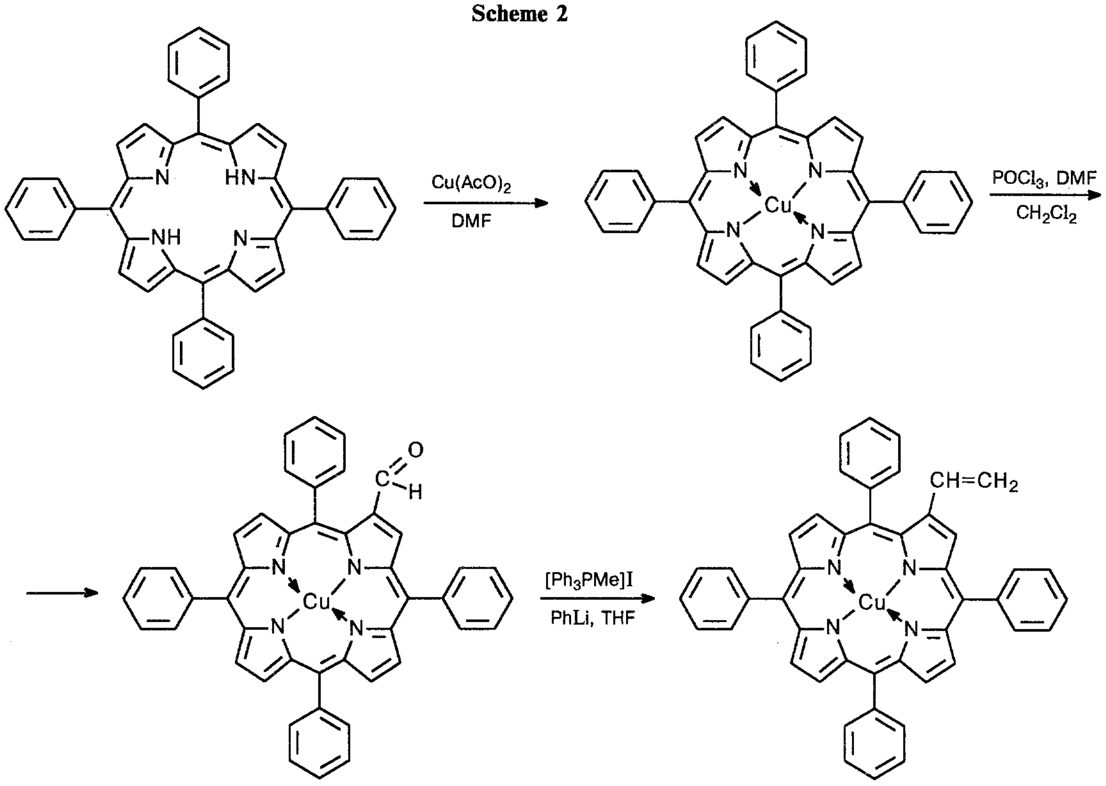
**Scheme 1**


4
+ 3
+
CHO
CHO
NH
CN
C6H4Me2
ClCH2COOH
N
HN
NH
N
CN
Zn(AcO)2
DMF
NaAlH(OEt)3
THF
Zn
CHO
HCl,
CHCl3
a. [Ph3PMe]I
PhLi, THF
b. [Ph3PMe]I
K2CO3, 18-C-6,
C6H6
CH=CH2
1
Cu(AcO)2,
DMF
Zn(AcO)2
DMF
Cu
1-Zn2+
1-Cu2+

**Scheme 2**



**2**-Cu$^{2+}$

the presence of monochloroacetic acid. The cyano group was reduced to the aldehyde group by sodium triethoxyaluminohydride in THF at 20 °C. Since only zinc complexes can be reduced in high yields, a Zn complex of monocyanoporphyrin was preliminarily synthesized (by reaction between the ligand and zinc acetate in boiling DMF). The copper complex was prepared by a similar procedure.

2-Formylphenylporphyrin and 2-vinyl-5,10,15,20-tetraphenylporphyrin complexes were prepared by the formylation according to Vilsmeier in boiling dichloroethane (Scheme 2) under conditions similar to those used in the synthesis of Ni complexes of vinylporphyrin.[7]

At each stage substances were separated by column chromatography and purified by recrystallization.

Parameters of synthesized 5-(4-vinylphenyl)-10,15,20-triphenylporphyrin (**1**), 2-vinyl-5,10,15,20-tetraphenylporphyrin (**2**), and their complexes with Zn$^{2+}$ and Cu$^{2+}$ (**1**-Zn$^{2+}$, **1**-Cu$^{2+}$, and **2**-Zn$^{2+}$, **2**-Cu$^{2+}$, respectively) are presented in Tables 1 and 2. In addition, we succeeded in growing crystals of **1**, which are dark brown, without pronounced faces, and are formed as twins.

A chip with a cross section of ~0.05 mm was chosen for X-ray diffraction analysis.

The compound belongs to the monoclinic system, space group $P2_1/a$. The molecule is placed in the inversion center in this centrosymmetric space group with the number of molecules in the unit cell equal to two. It follows that the structure should contain two vinyl fragments. However, the refinement of such a structure gave no satisfactory result. In addition, the coefficients of thermal vibrations of C atoms of the vinyl group were anomalously high, which could be due to statistical disordering of this fragment over two positions with a weight of 1/2. Further refinement by the least-squares method confirmed this assumption and gave the final value of the *R*-factor: $R$ = 0.078 in the full-matrix anisotropic approximation. Attempts to refine the structure in noncentrosymmetric space groups $P2_1$ and $Pa$ result in a drastic increase in the *R*-factor. Hydrogen atoms are not localized.

**Table 1**. Data of elemental analysis of compounds synthesized

| Compound | $\frac{\text{Found}}{\text{Calculated}}$ (%) | | | | Empirical formula |
|---|---|---|---|---|---|
| | C | H | N | M$^+$ | |
| **1** | 78.7<br>78.5 | 4.9<br>4.3 | 8.0<br>8.1 | 640<br>640.79 | $C_{46}H_{32}N_4$ |
| **1**-Cu$^{2+}$ | 78.5<br>78.7 | 4.2<br>4.3 | 7.4<br>7.6 | 702<br>702.32 | $C_{46}H_{30}N_4Cu$ |
| **1**-Zn$^{2+}$ | 76.2<br>76.4 | 4.0<br>4.1 | 7.0<br>7.1 | 704<br>704.15 | $C_{46}H_{30}N_4Zn$ |
| **2**-Cu$^{2+}$ | 78.5<br>78.7 | 4.3<br>4.3 | 7.6<br>7.7 | 702<br>702.32 | $C_{46}H_{30}N_4Cu$ |
| **2**-Zn$^{2+}$ | 76.6<br>76.4 | 4.4<br>4.1 | 7.2<br>7.1 | 704<br>704.15 | $C_{46}H_{30}N_4Zn$ |

**Table 2**. Parameters of $^1$H NMR and electronic absorption spectra

| Compound | $^1$H NMR (CDCl$_3$), δ | EAS, $\lambda_{max}$/nm (log ε) |
|---|---|---|
| **1** | −2.75 (s, 2 H, NH); 7.62—7.74 (m, 11 H, *m*-, *p*-H arom.); 8.12—8.22 (m, 8 H, *o*-, *o*′-H arom.); 8.76—8.88 (m, 8 H, β-pyrrole); 5.41—5.45 (d, 1 $H_A$, vinyl); 5.95—6.02 (d, 1 $H_B$, vinyl); 6.92—7.04 (dd, 1 $H_X$, vinyl) | 421 (5.66) |
| **1**-$Cu^{2+}$ | — | 418 (5.49) |
| **1**-$Zn^{2+}$ | 7.63—7.81 (m, 11 H, *m*-, *p*-H arom.); 8.1—8.27 (m, 8 H, *o*-, *o*′-H arom.); 8.85—9.02 (m, 8 H, β-pyrrole); 5.41—5.45 (d, 1 $H_A$, vinyl); 5.97—6.07 (d, 1 $H_B$, vinyl); 6.95—7.06 (dd, 1 $H_X$, vinyl) | 422 (5.64) |
| **2** | 5.63 (d, 1 $H_B$, vinyl); 6.15 (d, 1 $H_A$, vinyl); 6.86 (1 $H_X$, vinyl); 7.86 (9 H, *m*-, *p*-phenyl); 7.36 (d, 10 H, *o*-phenyl); 9.01 (d, 8 H, β-pyrrole) | 426 (5.75) |
| **2**-$Cu^{2+}$ | — | 421 (5.61) |
| **2**-$Zn^{2+}$ | — | 422 (5.64) |

**Table 3.** Bond lengths (*d*) in the molecule of **1**

| Bond | *d*/Å | Bond | *d*/Å |
|---|---|---|---|
| N(1)—C(3) | 1.40 | C(12)—C(19) | 1.52 |
| N(1)—C(6) | 1.38 | C(13)—C(14) | 1.34 |
| N(2)—C(8) | 1.33 | C(14)—C(15) | 1.39 |
| N(2)—C(11) | 1.39 | C(15)—C(16) | 1.39 |
| C(3)—C(4) | 1.37 | C(16)—C(17) | 1.31 |
| C(3)—C(12) | 1.47 | C(17)—C(18) | 1.41 |
| C(4)—C(5) | 1.36 | C(13)—C(18) | 1.43 |
| C(5)—C(6) | 1.43 | C(19)—C(20) | 1.36 |
| C(6)—C(7) | 1.43 | C(20)—C(21) | 1.42 |
| C(7)—C(8) | 1.42 | C(21)—C(22) | 1.41 |
| C(7)—C(13) | 1.49 | C(22)—C(23) | 1.33 |
| C(8)—C(9) | 1.46 | C(23)—C(24) | 1.39 |
| C(9)—C(10) | 1.31 | C(19)—C(24) | 1.38 |
| C(10)—C(11) | 1.48 | C(22)—C(25) | 1.48 |
| C(11)—C(12) | 1.33 | C(25)—C(26) | 1.36 |

*Note:* σ = 0.009—0.013 Å.

Thus, the X-ray diffraction study of compound **1** directly proved that this compound is 5-(4-vinylphenyl)-10,15,20-triphenylporphyrin (Fig. 1). The values of bond lengths and bond angles (Tables 3 and 4, respectively) are in the intervals of values typical of porphyrins. At the same time, the observed scatter in lengths of equivalent bonds is probably explained by the statistical disordering (see above).

The coordinates of atoms of structure **1** are presented in Table 5.

**Table 4**. Bond angles (ω) in the molecule of **1**

| Angle | ω/deg | Angle | ω/deg |
|---|---|---|---|
| C(3)—N(1)—C(6) | 104.1 | N(2)—C(8)—C(7) | 127.3 |
| C(8)—N(2)—C(11) | 108.5 | N(2)—C(8)—C(9) | 110.7 |
| N(1)—C(3)—C(4) | 110.9 | C(7)—C(8)—C(9) | 122.0 |
| N(1)—C(3)—C(12) | 121.6 | C(8)—C(9)—C(10) | 105.7 |
| C(3)—C(4)—C(5) | 108.6 | C(9)—C(10)—C(11) | 109.7 |
| C(4)—C(5)—C(6) | 106.0 | N(2)—C(11)—C(10) | 105.4 |
| N(1)—C(6)—C(5) | 110.3 | N(2)—C(11)—C(12) | 128.8 |
| N(1)—C(6)—C(7) | 124.1 | C(10)—C(11)—C(12) | 125.7 |
| C(5)—C(6)—C(7) | 125.5 | C(11)—C(12)—C(19) | 120.7 |
| C(6)—C(7)—C(8) | 123.8 | C(11)—C(12)—C(3)′ | 126.8 |
| C(6)—C(7)—C(13) | 115.7 | C(19)—C(12)—C(3)′ | 112.4 |
| C(8)—C(7)—C(13) | 120.5 | C(22)—C(25)—C(26) | 122.4 |

*Note:* σ = 0.9—1.5°.

**Table 5**. Coordinates of atoms and their isotropic temperature factors in the structure of **1**

| Atom | *x* | *y* | *z* | $B_{iso}$/Å$^2$ |
|---|---|---|---|---|
| N(1) | 0.0415(3) | 0.9470(7) | 0.2002(10) | 5.2(2) |
| N(2) | −0.0882(3) | 0.8606(6) | 0.0633(10) | 5.4(2) |
| C(3) | 0.1067(4) | 1.0000(9) | 0.2527(13) | 5.2(2) |
| C(4) | 0.1165(4) | 0.9380(11) | 0.3921(14) | 6.4(2) |
| C(5) | 0.0583(4) | 0.8475(10) | 0.4382(14) | 6.4(2) |
| C(6) | 0.0116(4) | 0.8534(8) | 0.3176(13) | 5.2(2) |
| C(7) | −0.0560(4) | 0.7715(8) | 0.3135(12) | 4.9(2) |
| C(8) | −0.1008(4) | 0.7808(8) | 0.1919(13) | 5.1(2) |
| C(9) | −0.1704(4) | 0.7013(10) | 0.1981(15) | 6.3(2) |
| C(10) | −0.1971(4) | 0.7372(10) | 0.0713(15) | 5.8(2) |
| C(11) | −0.1459(4) | 0.8381(9) | −0.0236(12) | 5.3(2) |
| C(12) | −0.1561(4) | 0.8983(8) | −0.1579(11) | 5.0(2) |
| C(13) | −0.0773(4) | 0.6704(8) | 0.4455(13) | 5.5(2) |
| C(14) | −0.0803(5) | 0.6975(10) | 0.6030(15) | 7.2(2) |
| C(15) | −0.1006(6) | 0.6002(14) | 0.7231(15) | 9.4(4) |
| C(16) | −0.1191(6) | 0.4657(13) | 0.6785(18) | 8.9(3) |
| C(17) | −0.1159(5) | 0.4356(11) | 0.5252(19) | 7.9(3) |
| C(18) | −0.0946(5) | 0.5325(10) | 0.4012(14) | 7.1(3) |
| C(19) | −0.2239(4) | 0.8584(9) | −0.2360(12) | 5.8(2) |
| C(20) | −0.2476(4) | 0.7390(11) | −0.3155(15) | 7.2(3) |
| C(21) | −0.3099(5) | 0.7035(12) | −0.3919(16) | 8.6(3) |
| C(22) | −0.3475(4) | 0.7897(13) | −0.3736(15) | 7.7(3) |
| C(23) | −0.3237(4) | 0.9052(10) | −0.2943(13) | 7.7(3) |
| C(24) | −0.2620(4) | 0.9408(9) | −0.2217(13) | 6.3(2) |
| C(25) | −0.4159(6) | 0.7543(14) | −0.4315(17) | 13.9(5) |
| C(26) | −0.4493(7) | 0.6310(16) | −0.4915(18) | 16.6(9) |

The orientation of phenyl rings relative to the plane of the porphyrin is characterized by the following torsion angles: C(6)—C(7)—C(13)—C(14), 66.3°; C(11)—C(12)—C(19)—C(20), −72.6°. The vinyl fragment is nearly coplanar to the plane of the phenyl ring: the C(21)—C(22)—C(25)—C(26) torsion angle is equal to 6.8°.

Additional information about structures and some properties of compounds **1**, **2**, and their metal complexes was obtained from data of other physicochemical methods. For example, in the IR spectra the extraplanar γC—H vibrations in pyrrole rings of porphyrins appear at 783, 785, and 783 cm$^{-1}$ for **1**, **1**-$Cu^{2+}$, and **2**-$Cu^{2+}$, respectively, which is somewhat lower than those for

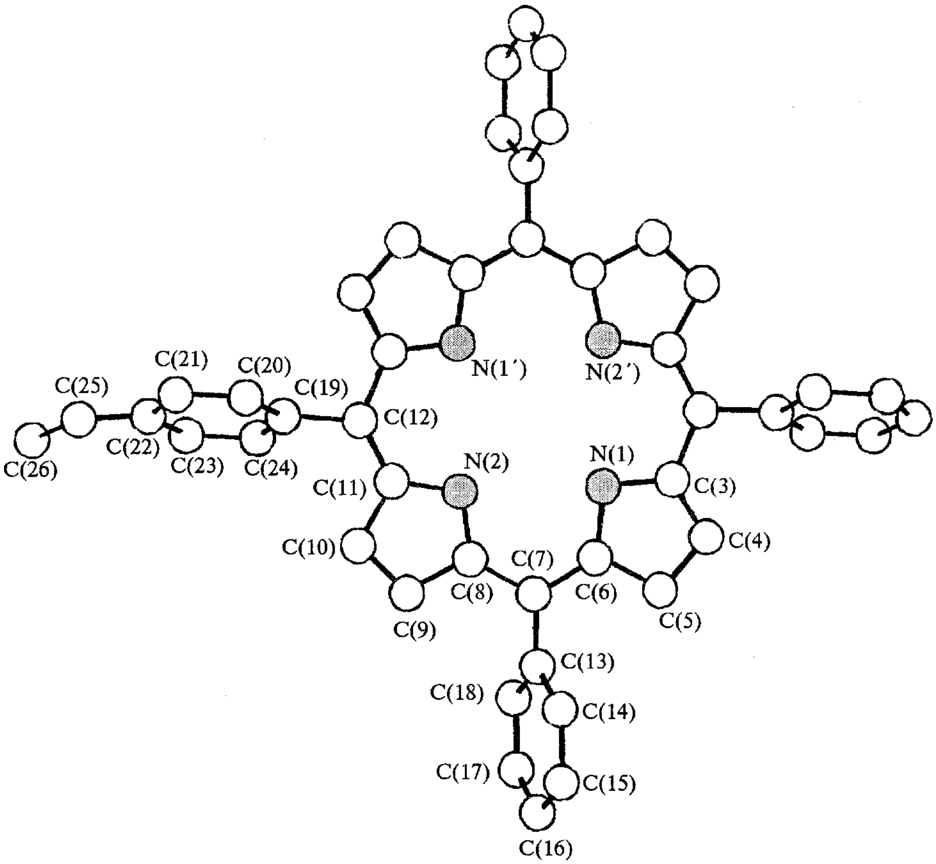


**Fig. 1.** Crystal structure of 5-(4-vinylphenyl)-10,15,20-triphenylporphyrin (**1**).

Mg-, Cu-, and Zn-tetraphenylporphyrins[8] (for the initial tetraphenylporphyrin, γC—H vibrations appear at 799 $cm^{-1}$). Thus, the complex formation exerts a weak effect on the positions of these absorption bands. The following frequencies correspond to vibrations of pyrrole rings: 1550, 1456, and 1459 $cm^{-1}$. It is difficult to draw a conclusion about the state of the exocyclic C=C bond, because the bands of its vibrations are overlapped with the absorption bands of the macrocycle. In principle, both the coordinational cavity and the π-system of the 16-membered macrocycle should not be substantially distorted when the vinyl group is introduced into the benzene or pyrrole ring, although the C=C bond is involved in the conjugation with the ring. No unambiguous information was obtained from electronic absorption spectra. The intense band in the nearest UV region (the Soret band) remains almost unchanged when $M^{2+}$ is introduced into the coordinational cavity, although its intensity decreases considerably in the case of compound **1** (see Table 2). The other bands in the visible range are even less sensitive to the change in the structures of vinylporphyrins and their complexes, although it is known[9] that the introduction of substituents in pyrrole rings results in a bathochromic shift of some bands in electronic spectra.

It follows from the data on $^1$H NMR spectroscopy (see Table 2) that the exocyclic vinyl group exerts a weak effect on the macrocycle. Despite an increase in the nonuniformity in the macrocyclic conjugation circuit, no nonequivalence of N—H bonds is observed in the molecule of **1**. It can only be mentioned that the introduction of a diamagnetic metal into the cycle results in a relatively weak (~0.1 ppm) chemical shift of signals of methine protons of the pyrrole ring to the region of a strong field. It is important that signals of protons of the vinyl group remain almost unchanged in this process.

Magnetochemical studies of paramagnetic complexes of $Cu^{2+}$ confirm their planar-square coordination ($\mu_{293\ K}$ = 1.89 $\mu_B$ and $\mu_{80\ K}$ = 1.85 $\mu_B$ for **1**-$Cu^{2+}$; $\mu_{293\ K}$ = 1.87 $\mu_B$ and $\mu_{80\ K}$ = 1.88 $\mu_B$ for **2**-$Cu^{2+}$), and the fact that $\mu_{eff}$ is temperature-independent indicates that the complexes are isolated. The temperature dependence of the magnetic susceptibility obeys the Curie law, which testifies that there are no exchange interactions between paramagnetic ions. This is also confirmed by the data of ESR spectroscopy. The products are isolated mononuclear complexes, whose spectra consist of the quartet of lines split on four equivalent nitrogen nuclei. The following parameters of the ESR spectra of isolated mononuclear complexes of $Cu^{2+}$ were obtained: $a_N$ = 19.9 G, $a_{Cu}$ = 100 G, $g_\parallel$ = 2.12, $g_\perp$ = 2.01.

Thus, vinylporphyrins and their metallocomplexes can serve as potential (co)monomers for preparing polymers containing the corresponding macrocycles at side chains. We intend to devote the next publication of this series to the synthesis of such polymers.

## Experimental

Electronic absorption spectra were obtained on a Specord UV-VIS spectrophotometer. $^1$H NMR spectra were recorded on a Bruker spectrometer with an operating frequency of 250 MHz for saturated solutions in $CDCl_3$ at 55 °C, and $SiMe_4$ was used as the internal standard. Elemental analysis was performed according to standard procedures. Thin-layer chromatography was carried out on Silufol UV-254 planes. $Al_2O_3$ (Brockmann I and III, standard grade) and IM-5/40 silica gel were used for column chromatography.

Magnetic susceptibilities of complexes **1**-$Cu^{2+}$ and **2**-$Cu^{2+}$ were measured on the Faraday balance at ~20 °C and at the temperature of liquid nitrogen in the field with the strength of 1 to 10 kG. The magnetic moment was calculated by the equation $\mu_{\text{eff}} = 2.84\sqrt{\chi_{\text{Cu}} T}$, where $\chi_{\text{Cu}}$ is the paramagnetic susceptibility referred to 1 g-at of copper. Diamagnetic corrections were determined experimentally.

Solvents were purified and dehydrated according to common procedures.[10] The Wittig salt, triphenylmethylphosphonium iodide,[11] phenyllithium,[12] *para*-cyanoaldehyde,[13] and sodium triethoxyaluminohydride[14] were obtained according to the literature data. Metal complexes of vinylporphyrins were synthesized under the conditions described in the previous work.[6]

**5-(4-Vinylphenyl)-10,15,20-triphenylporphyrin (1).** Anhydrous benzene (150 mL) and 5-(4-formylphenyl)-10,15,20-triphenylporphyrin (1 g, 0.14 mol) were placed in a 200-mL four-necked flask with a stirrer, a nitrogen inlet, and a reflux condenser with a calcium chloride tube. Purified nitrogen was passed through the flask, and 4.33 g (11.0 mmol) of finely powdered triphenylmethylphosphonium iodide, 1.93 g (1.4 mmol) of potassium carbonate, and 10 mg of 18-crown-6-ether were added. The mixture was boiled for 10 h with vigorous stirring. A residue was filtered off, the solvent was distilled off, and the dry residue was dissolved in toluene and chromatographed on a column with $Al_2O_3$ (Brockmann III standard grade). Vinylporphyrin was eluted with toluene and recrystallized from a chloroform—methanol (1 : 3) mixture. Yield 0.82 g (80 %).

**Synthesis of complex 1-$Zn^{2+}$.** Anhydrous THF (90 mL) and finely powdered triphenylphosphonium iodide (2.8 g, 7 mmol) were placed in a 200-mL four-necked flask with a stirrer, a nitrogen inlet, and a reflux condenser with a calcium chloride tube. A weak flow of purified nitrogen was passed through the flask. After 20 min 3.75 mL (4.5 mmol) of a 1.2 *N* ether solution of phenyllithium was added dropwise, and the solution was stirred for 10 min more at ~20 °C. Then 0.5 g (0.7 mmol) of a zinc complex of 5-(4-formylphenyl)-10,15,20-triphenylporphyrin was added; the mixture was washed with water (3×200 mL) and dried over $Na_2SO_4$. The solvent was distilled off, and the dry residue was dissolved in toluene and chromatographed on a column filled with $Al_2O_3$ (Brockmann III standard grade), using toluene as the eluent. The complex was recrystallized from a chloroform—methanol (1 : 3) mixture. Yield 0.33 g (66 %).

**Synthesis of complex 2-$Cu^{2+}$.** Anhydrous benzene (250 mL) and a copper complex of 2-formyl-5,10,15,20-tetraphenylporphyrin (1.8 g, 2.56 mol) were placed in a 500-mL four-necked flask with a stirrer, a nitrogen inlet, and a reflux condenser with a calcium chloride tube. Purified nitrogen was passed through the flask, and 7.74 g (19.2 mmol) of finely powdered triphenylmethylphosphonium iodide, 3.533 g (25.6 mmol) of potassium carbonate, and 18 mg of 18-crown-6-ether were added. The mixture was boiled at 10 h with vigorous stirring. A residue was filtered off, the solvent was distilled off to dryness, and the dry residue was dissolved in toluene and chromatographed on a column with $Al_2O_3$ (Brockmann III standard grade), using toluene as the eluent. The complex was recrystallized from a chloroform—methanol (1 : 3) mixture. Yield 1.64 g (88 %).

**Synthesis of zinc and copper complexes of porphyrin 1.** Acetate of the corresponding metal (2.29 mmol) was added with stirring to a boiling solution of 1.88 mmol of compound **1** in 120 mL of DMF. The mixture was boiled for 15 min. The zinc complex was precipitated with water from a hot solution; the precipitate was filtered off, washed with water, and dried at 120 °C. Yield 96 %. The copper complex was isolated by cooling the reaction mixture to 15 °C; the precipitate was filtered off, washed with water, and dried at 120 °C. Yield 95 %.

**X-ray diffraction analysis** of compound **1** was performed on a DAR-UM automated diffractometer with monochromatized Cu-Kα-radiation. The main crystallographic parameters: $C_{46}H_{32}N_4$, $a$ = 21.502(7) Å, $b$ = 10.534(5) Å, $c$ = 8.247(5) Å, $\gamma$ = 108.8°, $V$ = 1768.3 Å$^3$, $d_{\text{calc}}$ = 1.25 g cm$^{-3}$, space group $P2_1/a$. 1358 independent nonzero reflections were registered. No corrections for absorption were introduced ($\mu$ = 0.8 cm$^{-1}$). The structure of **1** was resolved by the direct statistical method. All calculations were performed on an IBM AT-286 personal computer by the AREN complex of programs.[15]

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