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## Synthesis and Spectral Properties of Octacyanopyrazinoporphyrazine and Its Metallocomplexes

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**Abstract**—Octacyanopyrazinoporphyrazine was for first time synthesized by template tetramerization of tetracyanopyrazine, and its complexes with bivalent metals were prepared. The compounds obtained were characterized by MALDI–TOF mass spectral data, elemental analysis, IR, and electronic spectroscopy.

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The heteroisologs of phthalocyanine since recently attract attention of researchers as models for the different photophysical processes, as materials for electrochromic displays, media for optical recording of information, components of supramolecular systems, and as a basic substance of diagnostic, phototherapeutic and other drugs [1]. The published data show that octacyanophthalocyanines are highly active in the electrochemical and electrocatalytic processes, have a high inherent conductivity [2-4], and the azasubstitution on the phthalocyanine periphery not only allows to change the nature of the macrocyclic ligand, but also leads to interesting new properties. However, there are no reports on the synthesis and hence on the physical and chemical properties of octacyanopyrazinoporphyrazine and its metallocomplexes. This work concerns the synthesis and study of spectral properties

of octacyanopyrazinoporphyrazine  $Pzc(CN)_8H_2$  (II) and its complexes with bivalent metals,  $Pzc(CN)_8M$  (III–V).

As a starting compound we used tetracyanopyrazine (I), prepared by the condensation of diiminosuccinonitrile with diaminomalenitrile in the trifluoroacetic acid [5].



The octacyanopyrazinoporphyrazine metallocomplexes were prepared by melting and cyclotrimerization in solution.



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At the fusion of tetracyanopyrazine I with the corresponding metal acetates in the presence of a catalytic amount of ammonium molybdate a mixture formed of monomeric Pzc(CN)8M and oligomeric  $(PzsM)_n(CN)_m$  metallocomplexes of cyano-substituted tetrapyrazinoporphyrazines. From the reaction mixture three fractions were isolated by selective extraction. The compounds soluble in acetone were purified by column chromatography. According to elemental analysis, electronic and IR spectra they were identified as octacyanopyrazinoporphyrazine metallocomplexes [Pzc(CN)<sub>8</sub>M] (III–V). Yield of monomeric compounds at the preparation by this method did not exceed 45%. The fractions soluble in DMF or in DMF and/or H<sub>2</sub>SO<sub>4</sub> apparently are oligomers of different structure and degree of polymerization. As the presumed oligomeric structures include connected porphyrazine macrocycles, they can be characterized by the electron absorption spectra. In the electronic spectra of solutions of the oligomeric fractions in DMF there is an absorption band in the visible region and sharply increasing absorption near the UV region (Fig. 1). The similarity of visible spectra of oligomeric and monomeric metallocomplexes (Fig. 2) confirms the presence of the porphyrazine fragments. At the same time the spectral curves being generally analogous have also noticeable distinctions. In the electronic spectra of oligomeric compounds as compared with the low molecular analogs a decrease is observed in the intensity of the first absorption band with a simultaneous increase in its half-width. This evolution of the electronic spectra can be interpreted as an indication of the polymeric nature of the porphyrazine-containing substance.

In order to increase the yield of the target monomeric octacyanopyrazinoporphrazine metallocomplexes and simplify the process of isolation of the target products we have developed a method consisting in essence in the heating the tetracyanopyrazine **I** solution in sulfolane in the presence of an appropriate metal salt and a few drops of 1,8-diazabicyclo[5,4,0]undecene-7 (DBU) as a catalyst.



The yield of the target product increased more than 1.5-fold and became equal to 82, 78 and 72% for the respective compounds III–V, and the formation of

high-molecular products did not occur. Octacyanopyrazinoporphyrazine **II** was obtained directly by fusion of tetracyanopyrazine **I** at 200–210°C, yield 82%.

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**Fig. 1.** Electron absorption spectra of oligomeric fractions in DMF: (1) copper complex (2) zinc complex.

The obtained compounds **II–V** were purified by repeated washing with hot water, and then by reprecipitation from solution with concentrated sulfuric acid. The synthesized compounds are dark green powders, insoluble in water, dilute acids, and most organic solvents, except DMSO and DMF. It should be noted that the introduction of eight cyano groups at the periphery of the tetrapyrazinoporphyrazine complexes contributes to their solubility in acetone, which allowed to perform an additional purification of compounds by column chromatography on silica gel.

All the octacyanopyrazinoporphyrazines are obtained in hydrated form. The existence of stable hydrates of unsubstituted compounds was noted in several publications [6-8]. This is, apparently, a common feature of heterocyclic analogs of phthalocyanines. The phenomenon of formation of hydrated forms may be due to the strong interaction of water molecules with the heteroaromatic nuclei, or with a specific lattice structure of macrocyclic compounds including water molecule [7]. The presence in the IR spectra of absorption bands in the region of 3400 cm<sup>-1</sup> characteristic of crystallohydrate water molecules confirms qualitatively that the synthesized compounds are isolated in the hydrate form. The content of crystallohydrate water was determined gravimetrically. It should be noted that carrying out elemental analysis of octacyanopyrazinoporphyrazines met certain difficulties, as the phthalocyanine aza-analogs are difficultly decomposed under the conditions of combustion. As noted earlier [9], even heating in a vacuum in the presence of dehydrating agents do not always lead to complete removal of crystallization



Fig. 2. Electron absorption spectra of octacyanoporphyrazines in acetone.

water, therefore the difference between found and calculated values of the contents of elements can reach 3%. The compounds **II** and **IV** were identified by means of MALDI–TOF mass spectrometry. The MALDI–TOF mass spectra of  $Pzc(CN)_8H_2$  and  $Pzc(CN)_8Zn$  are similar, they contain the peaks corresponding to molecular ions of each compound as well as the peaks of the products of fragmentation.

The IR spectra of all synthesized compounds II-V (Fig. 3) are very similar suggesting the absence of a strong distortion of the ligand at the coordination with a metal. The IR spectra of octacyanopyrazinoporphyrazines are similar to the spectra of unsubstituted compounds [7], but the appearance of a band at 2230  $\text{cm}^{-1}$  should be noted corresponding to the vibrations of peripheral cyano groups. The band position and intensity are almost independent of the nature of the central metal atom. In the IR spectra of the phthalocyanine series the band in the region of 1000 cm<sup>-1</sup> is commonly attributed to the phthalocyanine ligand [10]. The IR spectrum of Pzc(CN)<sub>8</sub>H<sub>2</sub> we synthesized contains a band at 1048 cm<sup>-1</sup> and the decrease in the intensity of this band and the appearance of bands at 1096, 1092, and 1112  $\text{cm}^{-1}$  is observed at the formation of copper, zinc, and cobalt complexes, respectively, which is due to increased symmetry of the molecule framework from  $D_{2h}$  to  $D_{4h}$ at the coordination with the double charged metal atoms. Upon transition from compound II to III-V some bands, namely, at 431, 869, 1048, 1430, and 1628 cm<sup>-1</sup>, regularly shift to higher frequencies. The shift of the bands has been mentioned earlier for unsubstituted pyrazinoporphyrazines [7] and for



Fig. 3. IR spectra of octacyanoporphyrazines: (a) compound II, (b) compounds III, (c) compound IV, and (d) compound V.

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Compound	$\lambda_{\max}, nm$		
	Acetone	DMF	$H_2SO_4$
PzcH <sub>2</sub>	_	635 [6]	654 [7]
Pzc(tBu) <sub>4</sub> H <sub>2</sub>	_	636 [12]	665 [12]
$Pzc(CN)_8H_2(II)$	685	687	690
Pc(CN) <sub>8</sub> H <sub>2</sub>	712	696 [2]	747 [2]
PzcCu	_	629 [7]	647 [7]
Pzc(tBu) <sub>4</sub> Cu	_	629 [12]	667 [12]
$Pzc(CN)_8Cu(III)$	662	667	682
Pc(CN) <sub>8</sub> Cu	-	686 [2]	742 [2]
PzcZn	_	634 [7]	666 [7]
Pzc(tBu) <sub>4</sub> Zn	-	636 [12]	671 [12]
$Pzc(CN)_8Zn(IV)$	672	662	688
Pc(CN) <sub>8</sub> Zn	-	687 [2]	-
PzcCo	-	615 [6]	643 [7]
Pzc(tBu) <sub>4</sub> Co	-	617 [12]	645 [12]
$Pzc(CN)_8Co(V)$	651	651	675
Pc(CN) <sub>8</sub> Co	_	686 [2]	-

Position of *Q*-band in electron absorption spectra of tetraarenoporphyrazines

phthalocyanines [10]. The magnitude of the shift is not unambiguously determined by the degree of covalency and the strength of a metal–ligand bond. A strong background absorption in the region of 3000–4000 cm<sup>-1</sup> in the spectra of all the obtained compounds can be regarded as indirect confirmation of the presence of crystallohydrate water in these compounds.

Electron absorption spectra of the obtained compounds in organic solvents are presented in the table and in Fig. 2. The spectra are typical of tetrapyrazinoporphyrazine, its metal complexes, and their substituted derivatives [6, 11, 12] and include a strong Q-band in the long wavelength region (651–687 nm), and a Soret *B*-band in the UV region at 354–403 nm. Unfortunately, among the commonly used aprotic solvents, DMSO and DMF only are common for tetra*tert*-butyl-substituted and octacyano-substituted pyrazinoporphyrazines. Therefore, the influence of the cyano groups located on the periphery of the macrocycle on the electronic spectra could be estimated only for the solutions of these compounds in DMF.

It was shown previously [11, 12] that the introduction of tert-butyl groups at the periphery practically does not affect the Q-band: the shift of the band is no more than 4 nm. However, the modification of the ligand periphery by the introduction of cyano groups leads to a dramatic red shift of the first absorption band for Pzc(CN)<sub>8</sub>H<sub>2</sub>, and for its metallocomplexes: 55 nm for the compound free of metal and 38, 28, and 39 nm for copper, zinc, and cobalt complexes, respectively, which is undoubtedly due to the influence of the electron-acceptor CN groups on the macrocycle. It should be emphasized that the introduction of cyano groups does not alter the anomaly in the spectrum of the metal-free compound, appearing as the lack of the typical splitting of phthalocyanine Q-band in DMF and DMSO. The electronic spectra of Pzc(CN)<sub>8</sub>H<sub>2</sub> and its metallocomplexes in acetone are typical of phthalocyanine. Just as for tert-butyl-substituted pyrazinoporphyrazines in organic solvents, in the spectra of cyano-substituted compounds appear well identifiable Soret band at ~400 nm.

The effect of structural modification of the phthalocyanine molecule (azasubstitution) is revealed in a considerable increase in the dependence of spectral characteristics on the complex-forming metal. Thus, for octacyanophthalocyanine the complexation leads to a blue shift of the first absorption band by 10 nm for all the metals [2]. At the transformation of the metalfree octacyanopyrazinoporphyrazine into its metallocomplexes appears a blue shift equal to 20, 25, and 36 nm for copper, zinc, and cobalt complexes, respecttively, that is explained by the introduction of electronacceptor nitrogen atoms to the structure of phthalocyanine.

The combined effect of the two considered types of structural modification of the phthalocyanine molecule (aza-substitution and introduction of cyano groups) manifests as an increased dependence of the spectral characteristics on the used solvent. The solvato-chromism (change in the position of *Q*-band) is maximal in the case of the zinc complex, where 10 nm red shift occurs when actone is used as a solvent instead of DMF.

The electronic spectra of octacyanopyrazinoporphyrazines in concentrated  $H_2SO_4$  (Fig. 4) showed that the peripheral substitution has practically no effect on the character of protonation of these compounds. Just as in the case of PzcH<sub>2</sub> and its metallocomplexes, the first band in the spectra of solutions of compounds II-V in sulfuric acid suffers a red shift compared to its value in organic solvents. The shift magnitude depends on the complex-forming metal, that is well consistent with the current understanding of the polarization of chromophore framework at protonation. The coordination of Pzc(CN)<sub>8</sub>H<sub>2</sub> with the considered metals in sulfuric acid solutions leads to a shift of 15, 26 and 24 nm for copper, zinc, and cobalt complexes, respectively (compared with the position in organic solvents). This pattern is typical for the tetraareneporphyrazines aza-substituted at the periphery [13–16], since the introduction of electron-acceptor nitrogen atoms reducing the electron density in the main chromophore leads to greater involvement of the lone electron pairs of the nitrogen meso-atoms of the macrocycle into conjugation, and thereby significantly reduces their basicity.

## **EXPERIMENTAL**

The IR spectra were recorded on an Avatar 360 ESP FT-IR spectrophotometer in KBr tablets, the electron absorption spectra, on a Perkin Elmer Lambda 20 spectrophotometer in rectangular guartz cells of 0.1 to 1 cm thickness, the concentration of solutions  $10^{-4}$ to 10<sup>-6</sup> mol l<sup>-1</sup>. Elemental analysis was performed on the analyzer CHNS-O Flash EA. The MALDI-TOF mass spectra were obtained on a Ultraflex Bruker Daltonics mass spectrometer. For preparation of solutions were used organic solvents of chemically pure grade and sulfuric acid of high purity grade. Purity of the compounds obtained was checked by TLC on the Merck Silica Gel 60 plates. The column chromatography was performed on the Merck silica gel 0.040-0.063 mm. The metal acetates prior to application to the syntheses were dried in a vacuum for 10 h at 110°C. All solvents used in the work were purified by standard techniques just before their application.

2,3-Diiminosuccinonitrile was obtained by oxidation of diaminomalenitrile with dichlorodicyanobenzoquinone [17]. Yield 92%, mp 165–166°C. Found, %: C 45.55, 45.69, H 1.90, 1.88; N 52.55, 52.43. C<sub>4</sub>H<sub>2</sub>N<sub>4</sub>. Calculated, %: C 45.28, H 1.88; N 52.83. <sup>1</sup>H NMR spec-trum (DMSO- $d_6$ ),  $\delta$ , ppm to HMDS: 14.41 s (2H, NH).

**Tetracyanopyrazine (I)** was prepared by the condensation of diiminosuccinononitrile with diaminomalenitrile in trifluoroacetic acid [5]. Yield 69%, mp 274–276°C. Found, %: C 53.21, 53.18; N 46.80, 46.75.



Fig. 4. Electron absorption spectra of octacyanoporphyrazines,  $17.5 \text{ M H}_2\text{SO}_2$ .

 $C_8N_6$ . Calculated, %: C 53.33; N 46.67. IR spectrum (KBr tablet), cm<sup>-1</sup>: 2252 (C = N).

Octacyanopyrazinoporphyrazine  $Pzc(CN)_8H_2$ · 4H<sub>2</sub>O (II). 1 g of tetracyanopyrazine (I) was heated to 200–210°C, and the resulting melt was kept at this temperature for 5–10 min. The meet was cooled, washed with distilled water, and the precipitate was filtered off. The precipitate was chromatographed on silica gel, compound II was eluted with acetone, the eluate was evaporated to dryness. Yield of compound II 82%. Found, %: C 47.39, 47.52; H 1.26, 1.29; N 41.47, 41.45; O 7.92, 7.95. C<sub>32</sub>H<sub>10</sub>N<sub>24</sub>O<sub>4</sub>. Calculated, %: C 48.36; H 1.26; N 42.32; O 8.06. MS (Maldi– TOF), *m/z* 721 (calculated 722).

Octacyanopyrazinoporphyrazine metallocomplexes  $Pzc(CN)_8M\cdot nH_2O$  (III–V). A mixture of 0.18 g of octacyanopyrazine I with 0.25 mmol of copper, cobalt or zinc acetate, and a few drops of 1,8-diazabicyclo-[5,4,0]undecene-7 (DBU) was added to 15 ml of sulfolane, and the resulting solution was kept at 135°C for 2 h. The reaction mixture was cooled and poured into water, the precipitate was filtered off. The obtained metallocomplexes III–IV were chromatographed on silica gel using acetone as eluent.

Octacyanopyrazines are dark-green fine-crystalline compounds with a metallic luster, not melting up to 400°C, soluble in acetone.

**Complex** [ $C_{32}N_{24}Cu\cdot 3H_2O$ ] (III). Yield 82%. Found, %: C 44.87, 44.92; H 0.75, 0.76; N 39.25, 39.31; O 7.40, 7.46.  $C_{32}H_6N_{24}O_3Cu$ . Calculated, %: C 45.85; H 0.71; N 40.12; O 7.58.

**Complex** [C<sub>32</sub>N<sub>24</sub>Zn·2H<sub>2</sub>O] (IV). Yield 78%. Found, %: C 45.97, 45.82; H 0.51, 0.55; N 40.10, 40.12; O 7.79, 7.77. C<sub>32</sub>H<sub>4</sub>N<sub>24</sub>O<sub>2</sub>Zn. Calculated, %: C 46.75; H 0.48; N 40.92; O 7.95. MS (Maldi–TOF): *m/z* 784 (calc. 785).

**Complex** [ $C_{32}N_{24}Co\cdot 4H_2O$ ] (V). Yield 72%. Found, %: C 44.62, 44.21; H 0.93, 0.95; N 37.78, 37.85; O 7.48, 7.41.  $C_{32}H_8N_{24}O_4Co$ . Calculated, %: C 45.12; H 0.94; N 39.48; O 7.52.

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