Synthesis and Spectroscopic Studies of Bismuth(III) Iodide Porphyrins

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Dedicated to Academician of the Russian Academy of Sciences Prof. I. P. Beletskaya on the occasion of her Birthday

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Synthesis of bismuth complexes of etioporphyrin II, protoporphyrin IX dimethyl ester and three tetraphenylporphyrin derivatives in which iodine atom is an extraligand, was carried out. Obtained compounds were characterized by mass spectrometry, UV-vis, 1 H NMR spectroscopy, and HPLC. The study of X-ray spectra showed that bismuth valence is +3. Bismuth atom coordinates four nitrogen atoms and one iodine atom. All four nitrogen atoms have equivalent binding energies. IR absorption spectra of free porphyrins bases and their bismuth complexes were studied. The comparison of IR absorption spectra of neat porphyrins shows no significant differences in vibrations of nitrogen-carbon cycles. As for bismuth complexes, vibrations bands of bismuth-iodine bonds ν(Bi-I) appear at 90–130 cm⁻¹ in the long-wavelength spectra regions, as well as deformation vibrations involving bismuth, iodine and nitrogen atoms δ(NBI) with frequencies 150–165 cm⁻¹, deformation vibrations of δ[Ni4] pyramid at ~300 cm⁻¹ and stretching vibrations bands of this complex fragment involving deformations of nitrogen-carbon ring, in the region of 335–375 cm⁻¹. Quantum-chemical calculations were conducted including calculations of the vibrational spectra, dipole moments, and charge distribution on atoms (according to Mulliken). It was found that complex of bismuth iodide with etioporphyrin II is the most polar among the studied series compounds.

Keywords: Bismuth, porphyrin, metallocomplexes, IR-spectroscopy, XPS, quantum chemical calculations.

Синтез и спектроскопические исследования порфиринатов висмута(III) иодида

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Осуществлен синтез висмутовых комплексов этиопорфирин II, ДМЭ протопорфирин IX и трех производных тетрафенилпорфирин, в которых атом иода является экстралигандом, был выделен. Полученные соединения были характеризованы методами масс-спектрометрии, электронной и 1 H ЯМР спектроскопии, ВЭЖХ. Изучение РФЭ-спектров комплексов показало, что висмут имеет валентность +3. Атом висмута координирует четыре атома азота и один атом йода, при этом в комплексах все энергии связей атомов азота выровнены. Изучены ИК спектры поглощения свободных оснований порфиринов и их висмутовых комплексов. Сравнение
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The compounds were characterized by UV-vis, 1H NMR spectroscopy, mass spectrometry and elemental analysis.

Along with hydrophobic bismuth complexes, kinetically labile complexes with tetrastilaphenyumphorphyrin in an anion form and 5,10,15,20-tetrakis(1-methyl-4-pyridyl)porphyrin in a cation form were synthesized. It is well-known that in its complexes bismuth has oxidation states +3 and +5, and its coordination number can vary from 3 to 10. Due to the large ionic radius of bismuth(III) 1.03 Å, it can not fit in porphyrin macrocycle plane, so bismuth is located above it. This fact leads to lability of bismuth-porphyrin complexes.

The objective of the study reported here was to search for planar complexes with a strongly polarized ‘apex’ metal-ligand bond - promising elements for a new electronic materials design. From this point of view bismuth(III) compounds with its spatially localized 6s2 orbital are the perspective targets. The problem solution involves the synthesis of various BiIII-polyporphyrins and their study by IR and X-ray spectroscopy methods, as well as analysis of porphyrin molecule spatial configuration influence on a possibility of complexation with bismuth iodide. Etioporphyrin II, whose bismuth(III) iodide complex thermal stability was studied previously, protoporphyrin IX dimethyl ester (PP IX DME) (1) and three tetrastilaphenyumphorphyrin derivatives (2-4) differ by substituents on phenyl rings and on macrocycle periphery, were selected as research objects (Figure 1).

Experimental

Electronic absorption spectra were recorded using UV-vis spectrophotometer Helios Alpha Local Control System (‘TermoSpectronic’, USA). Mass spectra were measured using Ultraflex TOF/TOF device (Bruker Daltonics, Germany), a matrix was 2,5-dihydroxybenzoic acid. The 1H NMR spectra in a δ(ppm) scale were obtained with a Bruker DPX-300 (300 MHz) (Germany) in deuterochloroform. HPLC was performed using Waters «Breeze» chromatograph on a Nova-Pack column with 18.4 μm, 4.6×150 mm. A substance was eluted with a mixture of water-acetontitrile (6:4), was detected at 400 nm. Silica gel Kieselgel 60 (Merck, Germany) was used for a column chromatography. X-Ray photoelectron spectroscopy (XPS) studies were performed using Kratos AXIS Ultra DLD electronic spectrometer (Kratos Analytical, UK) with a monochromatized X-ray source Al Kα (hv=1486.6 eV). FT-IR spectra were recorded using EQUINOX 55 spectrometer (Bruker, Germany). For study in the mid-IR-
1. a: \(M = 2H\)
b: \(M = \text{BiI}\)
2. a: \(R = (4\text{-CO}_2\text{MePh}); M = 2H\)
b: \(R = (4\text{-CO}_2\text{MePh}); M = \text{BiI}\)
3. a: \(R = \text{mesytyl}; M = 2H\)
b: \(R = \text{mesytyl}; M = \text{BiI}\)
4. a: \(R = \text{CF}_2\text{Ph}; M = 2H\)
b: \(R = \text{CF}_2\text{Ph}; M = \text{BiI}\)

**Figure 1.** Structural formulas of reviewed porphyrins and their bismuth complexes.

The binding energies of the core electrons of bismuth triiodide molecules, porphyrins and their iodide complexes with bismuth (eV).

Table 1. The binding energies of the core electrons of bismuth triiodide complexes with bismuth (eV).

| Compound          | Elements (photoelectron line) | N1s | C1s  | Bi4f | I3d  |
|-------------------|-------------------------------|-----|------|------|------|
| BiI               |                               | 164.5 | 159.2 | 630.8 | 619.6 |
| PP IX DME         |                               | 399.5 | 397.4 | 284.7 |      |
| BiI-PP IX DME     |                               | 398.5 |      | 284.7 | 164.4 | 159.2 | 630.3 | 618.8 |
| EP II             |                               | 399.4 | 397.4 | 287.5 | 284.7 |      |      |      |
| BiI-EP II         |                               | 398.4 |      | 284.7 | 164.4 | 159.2 | 630.3 | 618.7 |
| TPP(4-COO MePh)   |                               | 400.1 |      | 287.5 |      |      |      |      |
| BiI-TPP(4-COO MePh) |                             | 398.6 |      | 284.8 |      |      |      |      |
| TPPF20            |                               | 400.02 |      | 284.6 | 285.8 | 288  |      |      |
| BiI-TPPF20        |                               | 398.8 |      | 284.7 | 284.4 | 288  | 164.7 | 159.5 | 630.3 | 618.7 |
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The XPS data for the metal-containing and metal-free porphyrin compounds and the binding energies of the core electrons of nitrogen, carbon, bismuth and iodine atoms of the synthesized porphyrins samples and their iodide complexes with bismuth are summarized in Table 1 while the spectra are shown in Figure 2.

One can note the existence of two nitrogen atoms types (aza- and pyrro-) in the structure of all porphyrins molecules. Moreover, the binding energies of N1s electrons of nitrogen atoms in tetraphenylporphyrins are higher than the binding energies of proto- and etioporphyrins nitrogen atoms. As for the metallocomplexes spectra, degeneracy of the corresponding states is observed. Nevertheless, the binding energy of 1s-electrons of nitrogen atoms in the complexes, assuming the average value, remains higher for compounds with tetraphenylporphyrins. Doublets with the energy values close to the binding energies in bismuth triiodide were registered for 4f-electrons of bismuth, while the doublets for tetraphenylporphyrin complexes have slightly higher values. XPS spectra of BiI-PP IX DME and PP IX DME are shown in Figure 2.

Therefore, we conclude that the bismuth atom in the prepared complexes is coordinated with four nitrogen atoms with equal electron binding energies and one iodine atom. Taking into account the stereo-active unshared pair of 6s² electrons, the characteristic for Bi coordination number 6 is realized.

The comparison of IR absorption spectra of neat porphyrins considered in this paper, shows no significant differences in vibrations of nitrogen-carbon cycle. Frequencies of the deformational vibrations are summarized in Table 2. General increase in the number of observed adsorption bands parallels the increase in molecules complexity and the increase in the number of different CCC fragments, including aromatic rings.

One can note a slight increase in the cycle deformation vibrations frequencies δ(CNC) upon transition to the spectrum of tetraphenylporphyrin (2a). The picture naturally changes during the transition to bismuth complexes (Figure 3). The vibration bands of ν(Bi-I) bonds with frequencies 90–130 cm⁻¹ are observed in the long-wave spectra regions; motions of these heavy atoms perturb additional deformational vibrations of the nitrogen-carbon ring. The bands of deformational vibrations with the participation of bismuth, iodine and nitrogen atoms δ(NBiI) with frequencies 150–165 cm⁻¹ lie somewhat higher. The deformation vibration frequencies of the pyramid [BiN₄] lie even higher. And finally, the frequencies of stretching vibrations of this complex fragment involving deformations of the nitrogen-carbon ring, are in the region 335–375 cm⁻¹.

The quantum-chemical calculations were performed (Table 3), namely, the geometries of free bases and complexes with bismuth iodide were optimized; vibrational spectra, dipole moments and charge distributions on atoms (according to Mulliken) were calculated.

Calculated atomic charges indicate that the complex formation leads to the polarization of the porphyrin cycle. A positive charge increases one and a half times on carbon atoms associated with nitrogen. A negative charge on nitrogen atoms increases by almost one and a half times. At the same time, if the values of charges on nitrogen are equal for porphyrins molecules, then the transition to complexes leads to the differentiation of charges. The difference reaches 10 %. A significant positive charge is established for bismuth atoms in iodide complexes – 1.53, and even higher charge in hydroxy-complex – 1.58. The latter is compensated by a large negative charge on oxygen. But the hydroxylgroup charge as a whole is close to the negative charge on iodine atoms in iodide complexes.

The calculation of dipole moments gives the following values: 6.47 D for BiI-EP II and 3.87 D for BiI-TPPF.

It follows from the analysis of the populations of orbitals that 6s-electrons are localized to a large extent. The population of molecular orbitals for bismuth atoms is 1.80–1.86 e. At the same time, bismuth plays a role of an electron density translator from porphyrin cycle atoms to iodine atom.

**Figure 2.** XPS spectra of Bi-PP IX DME (black) and PP IX DME (blue).
Table 2. The vibrational frequencies of bismuth porphyrins complexes in the region of porphyrin cycle oscillations (cm⁻¹).

|                | BiI-PP IX DME | BiI-TMP    | BiI-TPPF₄ₓ | BiI-TPP(4-COOMePh) | BiI-EP II[14] |
|----------------|--------------|------------|------------|-------------------|--------------|
| v(ν, cm⁻¹)     | 110          | 117        | 91         | 103               | 80           |
| Assignment     | v(BiI)       | v(BiI)     | νas(BiN)   | v(BiI)            | v(BiI)       |
|                | 132          | 134        | 122        | 120               | 125          |
|                | 165          | 161        | 153        | –                 | 156          |
|                | 226          | 217        | 202        | 204               | 228          |
|                | 248          | 236        | 212        | 242               | δ(BiNC)      |
|                | 300          | 290        | 280        | 280               | δ(BiNC)      |
|                | 348          | 336        | 340        | 346               | δ(BiNC)      |
|                | 362          | 375        | 368        | 372               | δ(NBiN)      |
|                | 427          | 419        | 397        | 396               | δ(CNC)       |
|                | 500          | 470        | 471        | 467               | δ(CNC)       |
|                | 568          | 569        | 566        | 572               | δ(CNC)       |
|                | 643          | 640        | 646        | 637               | δ(CNC)       |
|                | 687          | 690        | 682        | 684               | δ(ring)      |

* Vibrational frequencies assignments were done on a basis of quantum-chemical calculations results.

Figure 3. The FT-IR spectra of TMP (3a) (red) and BiI-TMP complex (3b) (blue) in the frequency range of porphyrin cycle oscillations.
It should be noted that BiI-TPP(4-COOMePh) and BiI-EP II complexes have the greatest Bi-I bond polarity, that agrees with the maximum charge difference and the lower bond residual covalence.

The dipole moment vector of the molecule (Figure 4) deviates from the Bi-I bond direction under the influence of 6s-electrons.

Thus, the obtained results indicate that the complex of bismuth iodide with etioporphyrin II is the most polar of the studied compounds.

Conclusions

The comparative study of bismuth porphyrin complexes demonstrated that peripheral environment in a porphyrin macrocycle has a significant effect on a metallocomplexes yield. It was shown that the distortion of a spatial configuration in the case of pentafluorophenylporphyrin leads to a significant decrease in the complex yield. The low complex yield can be caused not only by its distorted structure, but also by the presence of electron-acceptor substituents weakening the Bi-N bound. In IR-spectra the vibrational bands with a participation of bismuth-iodine and bismuth-nitrogen bonds appear in the long-wave regions of the spectra due to coordination of bismuth ion with porphyrin macrocycles. The electronic structure features of Bi4f, N1s, C1s and I3d core levels were studied and the electronic structure change was revealed due to the insertion of central bismuth atom, which coordinates four nitrogen atoms (with equal electron binding energies) and one iodine atom. On the basis of quantum-chemical calculations, it was shown that the complex formation leads to the porphyrin cycle polarization. Dipole moments for all bismuth complexes have been determined, and the bismuth complex of etioporphyrin II appears to be the most polar.

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References

1. Yang Y., Ouyang R., Xu L., Li W., Feng K., Ouyang L., Yang Z., Zhou S., Miao Y. J. Coord Chem. 2015, 68, 379–397.
2. Yukhin Yu.M., Mikhailov Yu.I. *Chemistry of Bismuth Compounds and Materials*. Novosibirsk, SO RAN. 2001. 359 p. (in Russ.) [Юхин Ю.М., Михайлов Ю.И. Химия висмутовых соединений и материалов. Новосибирск, СО РАН, 2001. 359 c.]

3. Mashkovsky M.D. *Medications*. Moscow: Meditsina. 1993. Vol. 1. 390 (in Russ.) [Машковский М.Д. Лекарственные средства, Т. 1. М.: Изд-во Медицина, 1993. 390 c.]

4. Lipengolts A.A., Cherepanov A.A., Grigor’eva E.Yu., Kulakov V.N. *Rossijsky Bioterapevticheskij Zh.* 2016, 15(1), 58 (in Russ.).

5. Treibs A. *Lieb. Ann. Chem.* 1969, B, 728, 115–143.

6. Buchler J.W., Lay K.L. *Inorg. Nucl. Chem. Lett.* 1974, 10, 297–300.

7. Dehghani H., Ansari S., Ali R. *Bull. Chem. Soc. Japan*. 2007, 80, 518–522.

8. Michaudet L., Fasseur D., Guilard R., Ou Z., Kadish K.M., Dahaoui S., Lecomte C. *J. Porphyrins Phthalocyanines* 2000, 4, 261–270.

9. Lemon C.M., Brothers P.J., Boitrel B. *Dalton Trans.* 2011, 40, 6591–6609.

10. Le Gac S., Najjari B., Motreff N., Remaud-Le Saec P., Faiivre-Chauvet A., Dimanche-Boitrel M., Morgenstern A., Bruchertseifer F., Lachkar M., Boitrel B. *Chem. Commun.* 2011, 47, 8554–8556.

11. Yang N., Tanner J.A., Wang Z., Huang J.-D., Zhong B.-J., Zhu N., *Sun H. Chem. Commun.* 2007, 4413–4415.

12. Gomes M.L., De-Freitas-Silva G., Reis P.G., Melo M.N., Frezard F., Demicheli C., Idemori Y.M. *J. Biol. Inorg. Chem.* 2015, 20, 771–779.

13. Valicsek Z., Horvath O., Patoney K. *J. Photochem. Photobiol. A: Chemistry* 2011, 226, 23–35.

14. Golubev D.V., Rumyantseva V.D., Fomichev V.V. *Tonkii Khim. Tekhnol.* 2017, 12, 26–30 (in Russ.).

15. Laikov D.N. *Chem. Phys.* Lett. 1997, 281, 151–156.

16. Laikov D.N. *Chem. Phys. Lett.* 1997, 281, 151–156.

17. Smith K.M. *Porphyins and Metalloporphyins*. Elsevier. Amsterdam-Oxford-New York. 1975, p. 800.

18. Koifman O.I., Semeikin A.S., Berezin B.D. In: *Porphyins: Structure, Properties, Synthesis* (Enikolopyan N.S., Ed.). Moscow: Nauka, 1985. 205–212 (in Russ.) [Койфман О.И., Семейкин А.С., Березин Б.Д. В кн.: Порфирины: структура, свойства, синтез (Ениколопян Н.С., ред.). М.: Наука, 1985. 205–212].