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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(NBiI) with frequencies 150–165 cm^{-1}, deformation vibrations of δ[BiN4] 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 этиопорфирина II, ДМЭ протопорфирина IX и трех производных тетрафенилпорфина, в которых в качестве экстралиганда выступает атом йода. Полученные соединения охарактеризованы 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 электронов атомов азота выровнены. Изучены ИК спектры поглощения свободных оснований порфиринов и их висмутовых комплексов. Сравнение

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ИК спектров поглощения исходных порфиринов показывает, что существенных различий в колебаниях азотно-углеродного циклов не наблюдается. При переходе к висмутовым комплексам в длинноволновых областях спектров появляются полосы колебаний связей висмут-йод ν(Bi-I) при 90–130 см$^{-1}$, а также деформационных колебаний с участием атомов висмута, йода и азота δ(NBiI) с частотами 150–165 см$^{-1}$, деформационных колебаний пирамиды δ[BiN$_4$] при ~300 см$^{-1}$ и в области 335–375 см$^{-1}$ полосы валентных колебаний этого фрагмента комплекса с участием деформаций азотно-углеродного кольца. Выполнены квантовохимические расчеты, в том числе рассчитаны колебательные спектры, дипольные моменты и распределение зарядов на атомах (по Малликену). Наиболее полярным из полученных соединений является комплекс йодида висмута с этиопорфирином II.

Ключевые слова: Висмут, порфирин, металлокомплексы, ИК-спектроскопия, РФЭС, квантовохимические расчеты.

Introduction

Interest towards bismuth containing complexes to a large degree is due to their use in medicine. First reports about application of bismuth containing salts for treatment of dyspepsia appeared in 1786.[1] Currently, such medicinal compounds of bismuth as de-nol, desmol, tribimol, vicair, vikalin and *etc*., are well-known for treatment of gastritis and peptic ulcer disease.[2,3] Recently, antitumor effectiveness of bismuth complex with diethylenetriaminepentaacetic acid was demonstrated in binary radiation therapy.[4]

First syntheses of bismuth complexes with porphyrins were described by A. Treibs in 1969.[5] The bismuth ion insertions into mesoporphyrin IX dimethyl ester and etioporphyrin II were carried out in pyridine in the presence of bismuth nitrate. However, the complexes structures were not fully established.

Later, Buchler[6] described the synthesis of bismuth octaethylporphyrin (OEP) complex also in pyridine with bismuth nitrate. The authors attributed to bismuth in OEP-Bi(O)NO$_2$ the oxidation state (V). The complex was found to be decomposing upon recrystallization or treatment with dilute hydrochloric acid.

Subsequently, complexes of Bi(III) with substituted tolyl- and methoxy-derivatives of tetraphenylporphyrin (TPP) in chloroform with bismuth chloride were synthesized.[7] At the same time, dimeric porphyrin structures bound together by Bi$_2$Cl$_6$ fragment were isolated.

The bismuth(III) ion insertion into porphyrin macrocycle in dimethylformamide and pyridine was carried out using bismuth nitrate and bismuth triflate.[8] OEP, TPP, tetramesityl- and tetra(4-tolyl)porphyrins were chosen as free bases. It turned out that complexes with nitro group are more stable than chlorides and bromides, the latter complexes are not stable and sensitive to light and water. The use of bismuth triflate led to increase in complexes stability and syntheses yield (75% – OEP, 50% – TPP, 70% – tolylporphyrin). This is due to steric protection provided by relatively large triflate ligand.

In recent years, bismuth(III) compounds containing radioactive isotopes ^{212}Bi (t$_{1/2}$=60 min) and ^{213}Bi (t$_{1/2}$=45 min), have been used in cancer therapy.[9-11] Bismuth drugs in the form of porphyrins complexes have found application as chemotherapeutic agents for leishmania treatment.[12]

Bi^{III}NO$_3$ complexes with TPP and 5,10,15,20-tetrakis (4-methoxycarbonylphenyl)porphyrin have been studied. The compounds were characterized by UV-vis, ^{1}H NMR spectroscopy, mass spectrometry and elemental analysis.

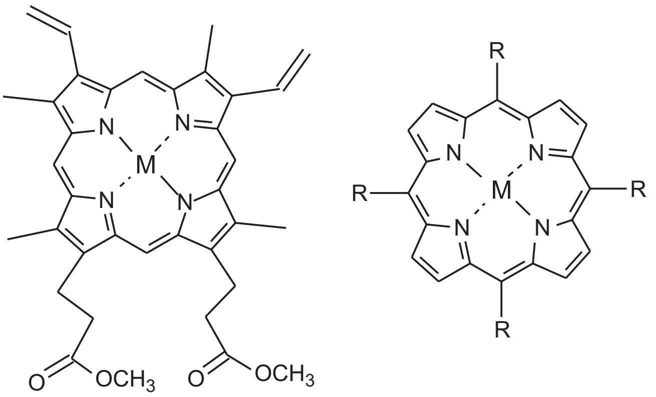
Along with hydrophobic bismuth complexes, kinetically labile complexes with tetrasulfophenylporphyrin in an anion form and 5,10,15,20-tetrakis(1-methyl-4-pyridyl)porphyrin in a cation form were synthesized.[13]

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 «apix» metal-ligand bond - promising elements for a new electronic materials design. From this point of view bismuth(III) compounds with its spatially localized 6s^2 orbital are the perspective targets. The problem solution involves the synthesis of various Bi^{III}I-porphyrins 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,[14] protoporphyrin IX dimethyl ester (PP IX DME) (**1**) and three tetraphenylporphyrin 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 ^{1}H 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-acetonitrile (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 (hν=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=BiI

2. a: R=(4-CO_2MePh); M=2H
b: R=(4-CO_2MePh); M=BiI

3. a: R=mesytyl; M=2H
b: R=mesytyl; M=BiI

4. a: R=C_6F_5; M=2H
b: R=C_6F_5; M=BiI

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

range (4000–700 cm^{-1}) the samples were prepared in the form of a powder with KBr and spectra were recorded using a diffuse reflection attachment EasiDiffTM Diffuse Reflectance Accessory (PIKE Technologies, Inc.). For study in the far-IR range (700–50 cm^{-1}) the samples were prepared in the form of a suspension in vaseline on windows of high-density polyethylene. The spectra were processed using OPUS6.0 software.

The geometry optimization and the absorption frequencies calculation were performed with the Priroda 16 software package[15-17] using the density functional method: dft/pbe/L1 in the full-electron scalar-relativistic Dyall Modified Dirac approximation. The optimized geometric structure image was prepared with the Chemcraft software.

General methods of bismuth iodide porphyrin complexes synthesis

Protoporphyrin IX DME (PP IX DME) (**1a**) was obtained from blood hemin following the previously described method.[18] Porphyrin **2a** was synthesized from pyrrole and 4-formylbenzoic acid methyl ester by Rothemund method in propionic acid.[19] 5,10,15,20-Tetrakis-mesitylporphyrin (TMP) (**3a**) and pentafluorophenylporphyrin ($TPPF_{20}$) (**4a**) were prepared by Lindsey method.[20]

To a boiling porphyrin pyridine solution in argon stream, a 5–10 fold excess of bismuth iodide was added, and the mixture was boiled for 3–7 hours. The reaction was monitored spectrophotometrically and by TLC on Silufol plates. At the end of the reaction, the solvent was evaporated to dryness in vacuum. The isolated red-brown solid was treated with chloroform. The bismuth iodide and bismuth oxoiodide precipitate was filtered off, washed with chloroform and discarded. The green color mother liquor was concentrated and chromatographed on a silica gel column using solution of CH_2Cl_2 and petroleum ether (3:2). At this step the unreacted free porphyrin base was separated. The bismuth complexes were eluted with solution of CH_2Cl_2-*i*-PrOH (20:1), evaporated and recrystallized from methylene chloride-methanol.

*BiI-PP IX DME (**1b**)*. Yield 28 %. UV-vis ($CHCl_3$) λ_{max} nm (lgε): 477(4.85), 586 (4.07). *m/z* 797.468 [M-I]$^+$. Calculated for $C_{36}H_{36}N_4O_4Bi$ 797.686.

*BiI-TPP(4-COOCH$_3$Ph) (**2b**)*. Yield 63 %. UV-vis (DMSO) λ_{max} nm (lgε): 472 (5.03), 600 (3.87), 646 (3.96). *m/z* 1053.281 [M-I]$^+$. Calculated for $C_{52}H_{36}N_4O_8Bi$ 1053.862. ^{1}H NMR ppm: 8.89 (8H, s, β–H), 8.4 (8H, m, o-C_6H_5). 8.17 (8H, br. s , m-C_6H_5), 4.2 (12H, s, $COOCH_3$). HPLC: RT 17.856 min; complex content 98.33 %.

*BiI-TMP (**3b**)*. Yield 50.7 %. UV-vis ($CHCl_3$) λ_{max} nm (lgε): 474 (5.17), 605 (3.91), 653 (4.01). *m/z* 989.008 [M-I]$^+$. Calculated for $C_{56}H_{52}N_4Bi$ 990.064. ^{1}H NMR ppm: 8.98 (8H, s, β-H), 7.38 (4H, s, m-H-C_6H_5), 7.28 (4H, s, m-H-C_6H_5), 2.65 (12H, s, o-CH_3-Ph), 2.15 (12H, s, o-CH_3-Ph), 1.27 (12H, s, p-CH_3-Ph).

*BiITPPF$_{20}$ (**4b**)*. Yield 16.4 %. UV-vis ($CHCl_3$) λ_{max} nm (lgε): 473 (5.18), 589 (4.13). *m/z* 1180.550 [M-I]$^+$. Calculated for $C_{44}H_8N_4F_{20}Bi$ 1181.51. ^{1}H NMR ppm: 9.0 (8H, s, β-H).

Results and Discussion

Analysis of the results of chemical syntheses of bismuth porphyrin complexes indicates that derivatives of tetraarylporphyrins have higher metallocomplexes yields than protoporphyrin containing two labile vinyl groups. The yield of etioporphyrin II (36.8 %) occupies an intermediate position.[14] The presence of ester groups in *meso*-tetraarylporphyrin increases its stability and, accordingly, leads to higher yield of the bismuth complex. The use of the bismuth pentafluorophenylporphyrin (**4b**) complex seems to be the least promising because of its spatially distorted configuration and lower stability.

Table 1. The binding energies of the core electrons of bismuth triiodide molecules, porphyrins and their iodide complexes with bismuth (eV).

Compound	Elements (photoelectron line)			
	N1s	C1s	Bi4f	I3d
BiI_3			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-COOMePh)	400.1; 398.0	287.8; 284.8		
BiI-TPP(4-COOMePh)	398.6	284.8	164.7; 159.3	630.3; 618.8
$TPPF_{20}$	400.02; 398.2	284.6; 285.8; 288		
BiI-$TPPF_{20}$	398.8	284.7; 284.4; 288	164.7; 159.5	630.3; 618.7

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 $6s^2$ 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.[14] The latter is compensated by a large negative charge on oxygen. But the hydroxy-group 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$_{20}$.

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.

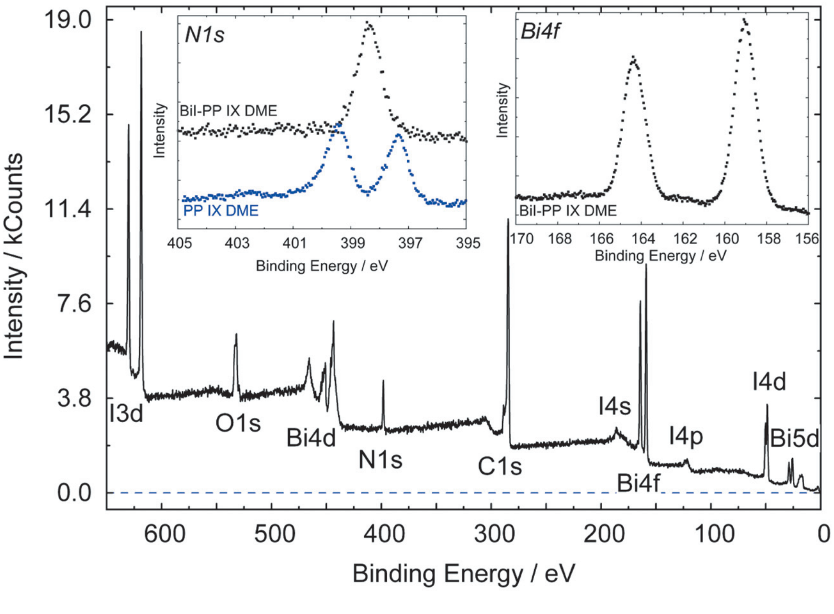


Figure 2. XPS spectra of BiI-PP IX DME (black) and PP IX DME (blue).

Table 2. The vibrational frequencies of bismuth porphyrins complexes in the region of porphyrin cycle oscillations (cm^{-1}).

BiI-PP IX DME ν, cm^{-1}	BiI-TMP ν, cm^{-1}	BiI-TPPF$_{20}$ ν, cm^{-1}	BiI-TPP(4-COOMePh) ν, cm^{-1}	BiI-EP II[14] ν, cm^{-1}	Assignment*
110	117	91 103	80	101	ν(BiI)+ν$_{as}$(BiN)
132	134	122 137	120 137	125	δ(IBiNC)+ν(BiN)+ν(BiI)
165	161	153	–	156	ν(BiI)+ν(BiN)+δ(BiNC)
	182	176	175	173	ν(BiN)+δ(BiNC)+δ(IBiN)
226 248	217 236	202 212 247	204 242	228	δ(BiNC)+δ(IBiN)
226	260	267	253	277	δ(BiNC)
248 300	290 314	280 302	280 293 305	301	δ(NBiN)+δ(ring)
348 362	336 375	340 368 372	346	346 373	ν(BiN)+δ(BiNC)
427	419 443	397 416 443	396 421 443	399 418	δ(CNC)+δ(ring)+δ(NBiN)
500	470 487	471 504 523	467 490	461 492	δ(CNC)+(δring)+δ(NBiN)
568	569	566 582	572	561	δ(CNC)+δ(ring)
643 687	640 667 690	646 670 682	637 650 684	624 662 679	δ(CNC)+δ(ring)

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

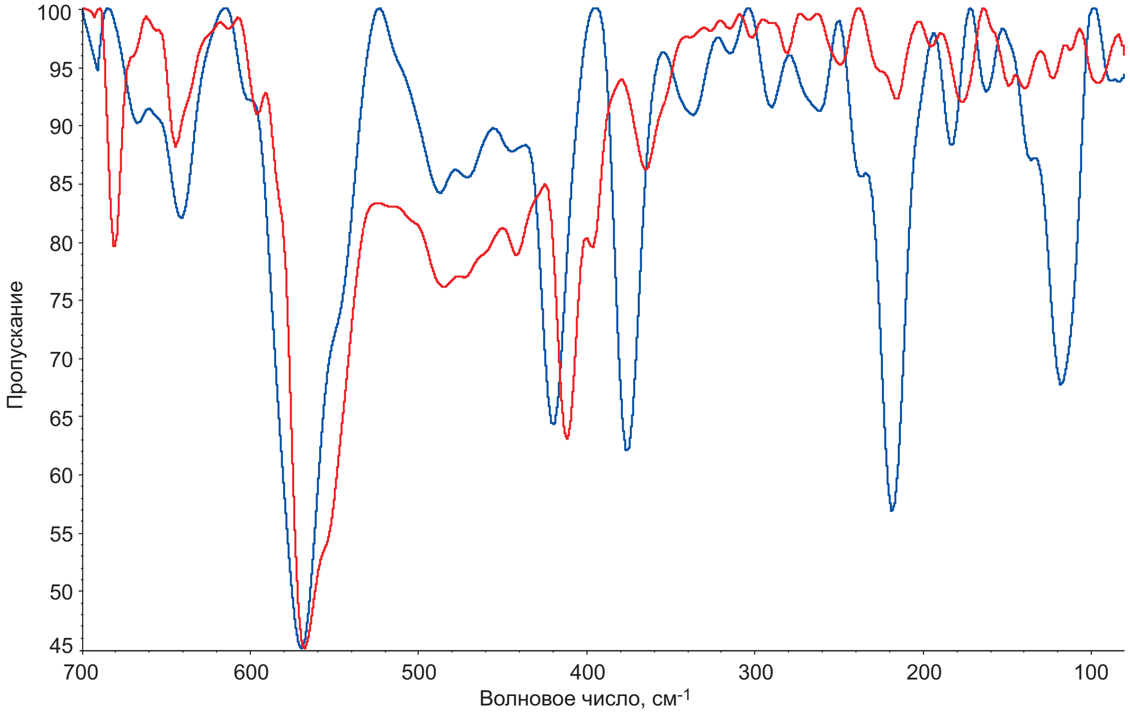


Figure 3. The FT-IR spectra of TMP (**3a**) (red) and BiI-TMP complex (**3b**) (blue) in the frequency range of porphyrin cycle oscillations.

Table 3. Values of Mulliken charges on porphyrin cycle atoms (e).

EP II		BiI-EP II		BiOH-EP II		$TPPF_{20}$		BiI-$TPPF_{20}$	
atom	charge	atom	charge	atom	charge	atom	charge	atom	charge
N1	-0.4267	N1	-0.6838	N1	-0.6815	N1	-0.4209	N1	-0.6451
C4	0.1549	C4	0.2187	C4	0.2070	C3	0.1864	C3	0.2789
C5	0.1606	C5	0.2293	C5	0.2156	C4	0.1880	C4	0.2638
N2	-0.4258	N2	-0.6525	N2	-0.6212	N2	-0.4210	N2	-0.6778
C7	0.1544	C7	0.2395	C7	0.2315	C6	0.1880	C6	0.2504
C8	0.1624	C8	0.2621	C8	0.2681	C7	0.1862	C7	0.2439
C10	0.1554	C10	0.2623	C10	0.2697	C9	0.1862	C9	0.2408
N3	-0.4259	N3	-0.6838	N3	-0.6821	N3	-0.4208	N3	-0.6383
C14	0.1614	C14	0.2399	C14	0.2333	C12	0.1879	C12	0.2446
C16	0.1546	C16	0.2295	C16	0.2167	C14	0.1881	C14	0.2607
N4	-0.4260	N4	-0.6529	N4	-0.6229	N4	-0.4210	N4	-0.6780
C24	0.1613	C24	0.2187	C24	0.2074	C17	0.1864	C17	0.2777
		Bi1	1.5332	Bi1	1.5813			Bi1	1.5280
		I1	-0.6503	O1	-0.7985			I1	-0.5685
				H37	0.2201				

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.

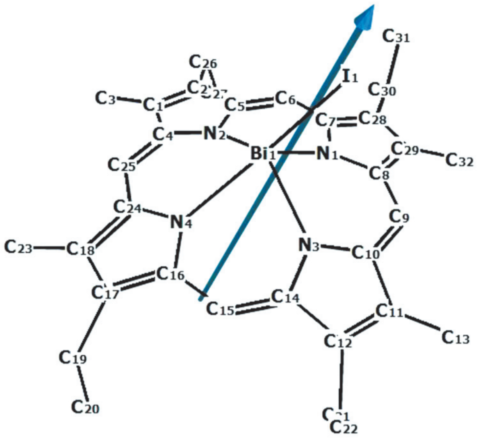


Figure 4. Optimized geometry of bismuth(III) iodide complex with etioporphyrin II (the dipole moment vector is indicated).

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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