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Synthesis and Crystal Structure of $[Co(DmgH)_2(Thio)_2]_2F[PF_6]$. The Effect of Fluorine-Containing Co(III) Dioximates on the Physiological Processes of the Microalga *Porphyridium cruentum*

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Abstract—New fluorine-containing cobalt(III) dioximates $[Co(DmgH)_2(Thio)_2]_2F[PF_6]$ (**I**) and $[Co(DmgH)_2(Sam)_2]_2[TiF_6] \cdot 4H_2O$ (**II**) (DmgH = dimethylglyoxime monoanion, Thio = thiourea, Sam = sulfanilamide) were obtained. The structure of **I** was determined by X-ray diffraction (CIF file CCDC no. 1852216). The crystals are cubic, space group $Pn\bar{3}n$. The octahedral coordination polyhedron of the metal is formed by the N_4S_2 set of donor atoms of two $DmgH^-$ ligands and two Thio molecules. The effect of compounds **I** and **II** and two previously described compounds of this class with fluorine anions, $[Co(DmgH)_2(Thio)_2]_2[TiF_6] \cdot 2H_2O$ (**III**) and $[Co(DmgH)_2(An)_2]_2[ZrF_6]$ (**IV**) (An = aniline), on the physiological processes of the red microalga *Porphyridium cruentum* was studied. Complex **III** in concentration of 20 mg/L increased the microalga productivity by 20% and lipid biosynthesis by 17% and can be proposed for biotechnology applications.

Keywords: Co(III) dioximates, crystal structure, red microalga *Porphyridium cruentum*, biomass accumulation, lipid synthesis

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INTRODUCTION

The preparation of chemical compounds as biological models and study of their effect on metabolic processes of microorganisms is a promising trend in the targeted synthesis of biologically active molecules. Especially attractive in this respect are transition metal complexes [1], which are characterized by diverse compositions and structures. The trace elements involved in the metabolic activity of organisms via catalysis, redox reactions, hydration, and hydrolysis often influence the enzyme activity [2]. Cobalt, which activates most of kinases and synthetases and participates in B12-dependent metabolic reactions [3], together with other metals, is vitally important for microorganisms.

The properties of coordination compounds, although dictated primarily by the metal atom, depend also on the nature of ligands, which are complexed with transition metal ions owing to the broad set of donor atoms and form stable complexes with different composition, structure and properties [4, 5]. Biologically active molecules or species incorporated in metal complexes as ligands increase their efficiency [4]. Thus it was found that transition metal dioximates are biologically active and can be considered as vitamin B_{12} models [5, 6]. These compounds are investigated at the boundary between classical coordination chemistry, organometallic chemistry, and biochemistry. We have described a series of fluorine-containing Co(III) dioximates [7–13], including those stimulating the vitamin B_{12} biosynthesis [14] and functioning as hydrolytic enzymes of some microscopic fungi [15–18].

It is also pertinent to study the effect of this type of complexes on microalgae, including the red microalga *Porphyridium cruentum,* which is applied in biotechnology as a producer of polyene fatty acids, phycobilins, and sulfated polysaccharides [19]. The known growth technologies for this microalga include the use of organic and inorganic agents stimulating the growth and biosynthetic activity, in particular, coordination compounds, which are perceived by cells as xenobiotics [20]. Being an eukaryotic organism, *Porphyridium cruentum* possesses stability systems and mechanisms against xenobiotics. The application of coordination compounds of metals often induces a selective increase in the amount of biomass and biologically active compounds in the biomass depending on the metal and ligand natures in the compound used [1].

In order to elucidate the degree of influence of fluorine-containing cobalt(III) dioximates on the physiological processes of red microalga *Porphyridium cruentum* and to identify the roles of various coordination compounds, we decided to test a number of Co(III) complexes with identical equatorial moiety, but different axial ligands and outer-sphere anions: $[Co(DmgH)_2(Thio)_2]_2F[PF_6]$ (**I**), $[Co(DmgH)_2(Sam)_2]_2[TiF_6] \cdot 4H_2O$ (**II**), $[Co(DmgH)_2(Thio)_2]_2[TiF_6] \cdot 2H_2O$ (**III**), and $[Co(DmgH)_2(An)_2]_2[ZrF_6]$ (**IV**) (DmgH = dimethylglyoxime monoanion, Thio = thiourea, Sam = sulfanilamide, An = aniline). The synthesis and structure of complexes **III** and **IV** were reported previously [11, 21]; compounds **I** and **II** were newly prepared in this work. The crystal structure of **I** was determined by X-ray diffraction. In the case of **II**, single crystals suitable for X-ray diffraction could not be obtained.

EXPERIMENTAL

Synthesis of I. $[Co(DmgH)_2(Thio)_2]F \cdot 3H_2O$ (0.5 g, 0.001 mol) was dissolved in methanol (20 mL). After filtration, an aqueous solution (15 mL) containing KPF_6 (0.2 g, 0.001 mol) was added to the filtrate, and then thiourea (0.015 g, 0.002 mol) in water (10 mL) was added to prevent the thiourea replacement by water in the complex cation. The solution was stirred for ~5 min at ~40°C, filtered, and left for slow evaporation at room temperature. Fine cherry-colored pyramidal crystals were formed; they were separated by filtration and dried in air. The product yield was ~55%. The compound was sparingly soluble in water, methanol, and ethanol.

For $C_{20}H_{44}N_{16}O_8F_7S_4P_1Co_2$

Anal. calcd., %	C, 22.95	H, 4.24	N, 21.41	Co, 11.26
Found, %	C, 22.73	H, 4.21	N, 21.32	Co, 11.08

Complex **I** was also obtained from the $CoF_2 \cdot 4H_2O–2DmgH_2–2Thio–KPF_6$ system.

Synthesis of II. Dimethylglyoxime (0.23 g, 2 mol) in methanol (40 mL) and sulfanilamide (0.35 g, 0.002 mol) in methanol (30 mL) were added to a solution of $CoTiF_6 \cdot 6H_2O$ (0.33 g, 0.001 mol) in water (30 mL). The resulting solution was heated on a water bath at 60°C for 10 min. Slow evaporation of the dark brown solution afforded a brown powder. The product yield was 37%. The compound was soluble in DMSO, DMF, and alcohols and less soluble in water.

For $C_{40}H_{68}N_{16}O_{20}F_6S_4TiCo_2$

Anal. calcd., %	C, 32.00	H, 4.57	N, 14.93	Co, 7.85
Found, %	C, 31.89	H, 4.41	N, 14.78	Co, 7.66

X-ray diffraction. The experimental data for **I** were collected on a STOE IPDS diffractometer at room temperature (MoK_α radiation, graphite monochromator). The structure was solved by direct methods and refined by least-squares calculations in the full-matrix anisotropic approximation for non-hydrogen atoms (SHELX-97) [22]. The central atom of the $[Co(DmgH)_2(Thio)_2]^+$ complex cation occurs on a twofold axis and the central atom of the $[PF_6]^-$ anion is on a fourfold axis. The F^- ion occupies five positions with different occupancies, one being in the general position. The hydrogen atom positions were calculated geometrically and refined isotropically in the "rigid body" model with $U_{ef} = 1.2\ U_{eq}$ or $1.5\ U_{eq}$ of the corresponding O, N, and C atoms. The crystallographic data and X-ray experiment details for **I** are summarized in Table 1, selected interatomic distances and bond angles are in Table 2, and geometric parameters of hydrogen bonds are given in Table 3.

The positional and thermal parameters for structure **I** are deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1852216); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

Biological assays. The CNMN-AR-01 strain of marine red microalga *Porphyridium cruentum* from the National Collection of Non-Pathogenic Microorganisms of the Institute of Microbiology and Biotechnology was used in the study. The microalgae were cultured on a mineral medium [20] in 100-mL Erlenmayer flasks with 50 mL experimental volume. The experiment proceeded for 14 days under permanent illumination at 22°C. The productivity under these conditions was 2.2–2.5 g/L. The biomass thus formed contained up to 27–32% proteins and 12–14% lipids.

For measurement of the biological effect, the coordination compounds were added to the culture medium on the first day of microalga culturing in two concentrations, 10 and 20 mg/L.

The amount of biomass was determined by spectrophotometry using the calibration curve for the absorbance of the culture at 545 nm vs. the amount of biomass in the medium. The protein content in the algae biomass was determined by the Lowry assay using the Folin–Ciocalteu reagent [23]. The amount of lipids in the biomass was determined using the phospho-vanillin reagent after preliminary extraction into chloroform [24]. The experiment and the measurements were performed in triplicate. The results

Table 1. Crystallographic data and X-ray diffraction experiment details for compound **I**

Parameter	Value
M	1046.78
System	Cubic
Space group	$Pn\bar{3}n$
a, Å	23.3960(10)
V, Å^3	12806.3(9)
Z	12
ρ(calcd.), g/cm^3	1.629
μ, mm^{-1}	1.101
F(000)	6432
Crystal size, mm	0.30 × 0.20 × 0.15
Range of θ, deg	2.46–25.24
Ranges of reflection indices	$-25 \leq h \leq 28$, $-24 \leq k \leq 26$, $-23 \leq l \leq 28$
Number of measured/unique reflections ($R_{\rm int}$)	38570/1943 (0.1003)
Completeness, %	99.7
Number of reflections with $I > 2\sigma(I)$	1524
Number of refined parameters	169
GOOF	1.004
R factor ($I > 2\sigma(I)$)	0.0486, 0.1224
R, wR_2 (all data)	0.0649, 0.1303
$\Delta\rho_{\rm max}/\rho_{\rm min}$, e Å^{-3}	0.775/–0.418

were statistically processed according to procedures commonly used for biological assays [25].

RESULTS AND DISCUSSION

The DmgH$^-$ coordination to the central atom in **I** and **II** is confirmed by the IR bands at 1230–1245 ν_{as}(NO) and 1080–1095 cm^{-1} ν_s(NO), which are missing in the IR spectrum of uncoordinated dimethylglyoxime. The presence of dioxime monoanions is also confirmed by the bands at 1560–1580 ν(CN), 505–525 ν_{as}(Co–N), and 425–440 cm^{-1} ν_s(Co–N). The presence of a coordinated thiourea molecule in **I** and **III** is indicated by the band at 3312–3327 ν_{as}(NH), 3215–3221 ν_s(NH), 1617–1621 δ(NH$_2$), and 1408 cm^{-1} ν(C=S). The Co(III) dioximates containing sulfanilamide molecules in the 1.6 coordinate (**II**) also have absorption bands at 1580–1610 ν_{as}(CC) + δ(CCH), 1480–1495 ν_s(CC) + δ(CCH), 1310–1340 ν_{as}(SO), 1150–1170 cm^{-1} ν_s(SO), and the bending modes of the aromatic *para*-substituted ring δ(CH) at 670–740 cm^{-1}. The coordination of aniline molecules in 1.6 coordinates of the [Co(DmgH)$_2$(An)$_2$]$^+$ octahedron in **IV** is confirmed by the absorption bands at 3068–3135 ν(CH) and 1590–1602 cm^{-1} ν(CC) + δ(CCH) and by the 670–770 cm^{-1} δ(CH) bands, which are typical of a monosubstituted aromatic ring [26].

Compound **I** supplements the series of fluorinated dioximates described in our previous publications [7–13], which were studied by X-ray diffraction. In the ionic structure of **I**, like in the dioximates obtained earlier [12, 13], [PF$_6$]$^-$ serves as the outer-sphere anion; however, the CCDC [27] includes two more transition metal dioximates (mainly hetero compounds) with the same anion [28–32]. In the crystal structure of **I**, an unusual arrangement and packing of structural units was identified, which is dictated by the cubic system of crystallization. The special position of the central atom of cobalt (on a twofold axis of symmetry) implies that a unit cell of the crystal includes 24 [Co(DmgH)$_2$(Thio)$_2$]$^+$ cations. The octahedral environment of the Co(III) atom is formed by four nitrogen atoms of two monodeprotonated bidentate chelating DmgH$^-$ ligands and by two sulfur atoms of two neutral monodentate Thio ligands (Fig. 1). The interatomic distances in the coordination polyhedron are as follows: Co(1)–N(1), 1.876(3); Co(1)–N(2), 1.924(3); and Co(1)–S(1), 2.2876(9) Å (Table 2). Two DmgH$^-$ ligands are located in the equatorial plane of

Table 2. Interatomic distances and bond angles in **I***

Bond	*d*, Å	Bond	*d*, Å
Co(1)–N(1)	1.876(3)	C(1)–C(1)$^{\#1}$	1.459(8)
Co(1)–N(2)	1.924(3)	C(1)–C(3)	1.500(6)
Co(1)–S(1)	2.2876(9)	C(2)–C(2)$^{\#1}$	1.462(10)
O(1)–N(1)	1.335(4)	C(2)–C(4)	1.491(6)
O(2)–N(2)	1.358(4)	S(1)–C(5)	1.741(4)
N(1)–C(1)	1.293(5)	N(3)–C(5)	1.309(5)
N(2)–C(2)	1.283(5)	N(4)–C(5)	1.317(5)
Angle	ω, deg	Angle	ω, deg
N(1)Co(1)N(2)	99.4(1)	C(2)N(2)Co(1)	117.1(3)
N(1)Co(1)N(1)$^{\#1}$	81.4(2)	O(2)N(2)Co(1)	124.0(3)
N(1)Co(1)N(2)$^{\#1}$	178.2(1)	N(1)C(1)C(1)$^{\#1}$	112.5(2)
N(1)Co(1)S(1)	88.61(9)	N(1)C(1)C(3)	122.6(4)
N(1)Co(1)S(1)$^{\#1}$	97.13(9)	C(3)C(1)C(1)$^{\#1}$	124.9(3)
N(2)Co(1)N(2)$^{\#1}$	79.7(2)	N(2)C(2)C(2)$^{\#1}$	113.0(3)
N(2)Co(1)S(1)	84.53(10)	N(2)C(2)C(4)	124.4(5)
N(2)Co(1)S(1)$^{\#1}$	89.68(10)	C(4)C(2)C(2)$^{\#1}$	122.5(4)
S(1)Co(1)S(1)$^{\#1}$	172.45(6)	C(5)S(1)Co(1)	115.2(1)
C(1)N(1)O(1)	121.9(3)	N(3)C(5)N(4)	119.7(4)
C(1)N(1)Co(1)	116.8(3)	N(3)C(5)S(1)	115.6(3)
O(1)N(1)Co(1)	121.3(2)	N(4)C(5)S(1)	124.7(3)
C(2)N(2)O(2)	118.8(4)		

* Symmetry codes: $^{\#1}$ $-x + 3/2, z, y$.

Table 3. Geometric parameters of hydrogen bonds in **I**

D–H···A	Distance, Å			DHA angle, deg	Symmetry code for A
	D–H	H···A	D···A		
O(2)–H(1)···O(1)	0.82	1.77	2.547(4)	158	x, y, z
N(3)–H(1)···O(1)	0.80	2.23	2.953(5)	150	$x + 1, y - 1, z$
N(3)–H(2)···F(4)	0.87	1.96	2.829(4)	173	x, y, z
N(4)–H(1)···F(1)	0.89	2.49	3.213(6)	139	x, y, z
N(4)–H(1)···F(2*A*)	0.89	2.48	3.16(3)	134	x, y, z
N(4)–H(1)···O(1)	0.89	2.21	2.956(5)	141	$x + 1, y - 1, z$
N(4)–H(2)···O(1)	0.84	2.25	2.977(5)	146	$-x + 3/2, z, y$

the metal coordination polyhedron and are linked by two O–H···O intramolecular hydrogen bonds (O···O, 2.547(4) Å, Table 3), while the axial positions are occupied by Thio molecules; this is consistent with earlier data for Co(III) dioximates containing Thio in $[Co(DmgH)_2(Thio)_2]_3F[SiF_6] \cdot 1.5H_2O$ [7], $[Co(DmgH)_2(Thio)_2]_2[SiF_6] \cdot 2H_2O \cdot C_2H_5OH$ [8], $[Co(DmgH)_2(Thio)_2]_3[AlF_6] \cdot 2H_2O$ [9], $[Co(DmgH)_2(Thio)_2]_2[ZrF_6] \cdot H_2O$ [10], $[Co(DmgH)_2(Thio)_2]_2[TiF_6] \cdot 2H_2O$ [11], and $[Co(NioxH)_2(Thio)_2]_2[PF_6] \cdot DMF \cdot 1/2H_2O$ [12] ($NioxH_2$ = 1,2-cyclohexadione dioxime). The $DmgH^-$ coordination to the Co^{3+} ion gives two nearly coplanar metallacycles, as the dihedral angle between the planes through the metallacycle atoms is 2.8°. It was found that coordinated thiourea molecules present in dioximates [7–12] can be arranged in the complex cation at right angle to the equatorial plane, be virtually parallel to this plane, or occupy an intermediate position. As a result, the intramolecular interactions between

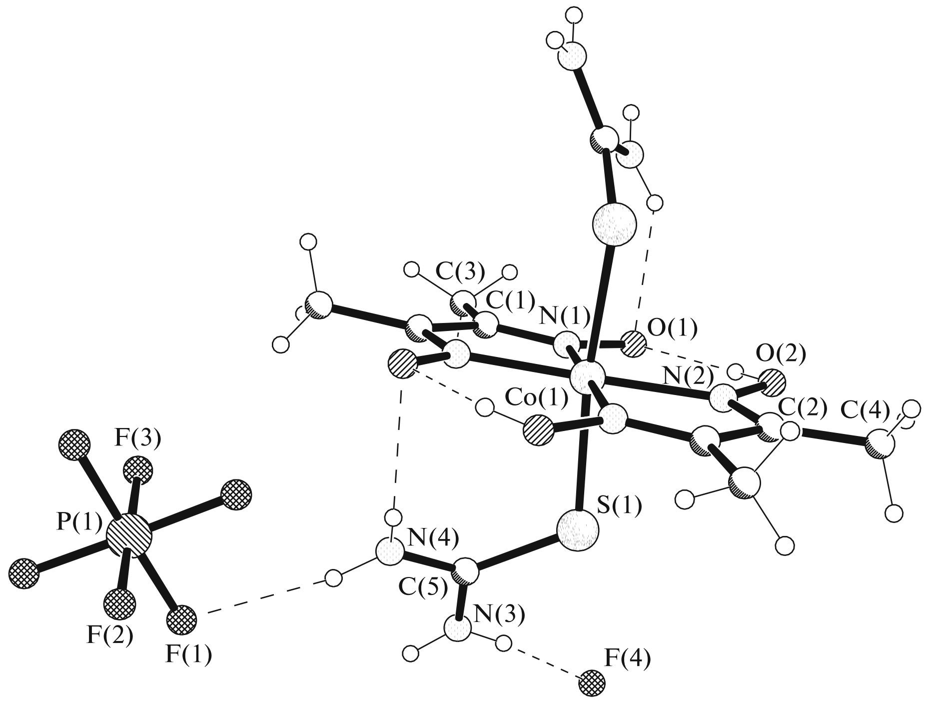

Fig. 1. Structure of $[Co(DmgH)_2(Thio)_2]_2F[PF_6]$ with numbering of crystallographically independent atoms.

organic ligands in the complex cation may also be different: (a) $DmgH^-$ and Thio are linked by the N–H···O hydroge bonds, in which the Thio amine groups are proton donors and $DmgH^-$ oxygen atoms are proton acceptors; or (b) weak π–π interactions act between the Thio molecules and the metallacycles formed upon $DmgH^-$ chelation. It was found that the $[Co(DmgH)_2(Thio)_2]^+$ cation in **I** is stabilized by two symmetrical intramolecular N–H···O hydrogen bonds (Fig. 1): N(4)···O(1) ($-x + 3/2, z, y$), 2.977(5); H···O(1), 2.25 Å; NHO angle, 146° (Table 3), which is in line with the data reported for the compounds described in [7–12].

In the crystal of **I**, the components are joined by hydrogen bonds in which the Thio amine groups of the complex cations are proton donors and both oxime oxygen atoms of neighboring cations and the F^- ions and fluorine atoms of $[PF_6]^-$ function as proton acceptors. As a result, the crystal comprises cationic networks (Figs. 2 and 3) formed, to a considerable extent, via two N–H···O intermolecular hydrogen bonds: N(3)···O(1) ($x + 1, y - 1, z$) and N(4)···O(1) ($x + 1, y - 1, z$), 2.953(5) and 2.956(5); N(3)–H(2), 0.80; H(2)···O(1), 2.23 Å; NHO angle, 150°; and N(4)–H(1), 0.89; H(1)···O(1), 2.21 Å; NHO angle, 141°.

The packing mode of the structural units in crystal **I** is also determined by the positions of $[PF_6]^-$ and F^- anions in the crystal. Each $[PF_6]^-$ anion located on a fourfold symmetry axis is involved in four N–H···F hydrogen bonds (Fig. 2b) only via the F(1) atom located in the general position: N(4)···F(1), 3.213(6); N(4)–H(1), 0.89; H(1)···F(1), 2.49 Å; NHF, 139°. The F···F interactions were detected between the F(2) atoms of two $[PF_6]^-$ anions in the special positions with different occupancies. Whereas F(2*A*) (0.25 occupancy) is involved in one N–H···F hydrogen bond (N(4)···F(2*A*), 3.16(3); N(4)–H(1), 0.89; H(1)···F(2*A*), 2.48 Å; NHF angle, 134°), the F(2) atom (0.75 occupancy) participates in only one weak contact: F(2)···F(2) ($x, -y - 1/2, -z + 1/2$), 2.638 Å (Fig. 2b). The F(3) atoms are not involved in the interactions between the crystal components. The CCDC [27] was found to include compounds with similar types of F···F contacts [33, 34], but they are weaker than those in **I**. The F^- ion (F(4)) located at the center of symmetry is involved in hydrogen bonding with six complex cations interrelated by an inversion threefold axis (Fig. 3) (N(3)···F(4), 2.829(4); N(3)–H(1), 0.87; H(1)···F(4), 1.96 Å; NHF angle, 173°), while the F^- ion (F(6)) located on a threefold axis is involved only in weak C–H···F hydrogen bonds (C(3)···F(6) ($x, -y - 1/2, -z - 1/2$), 3.42(2); C(3)–H(2), 0.96; H(2)···F(6), 2.84 Å; NHF angle, 119°).

As a result, the hydrogen-bonded $[Co(DH)_2(Thio)_2]^+$ cations form a 3D lattice, with the cavities being occupied by F^- and $[PF_6]^-$ anions.

A key parameter indicating the tolerance of microorganisms to xenobiotics that enter from the environment is biomass accumulation. Therefore, first of all,

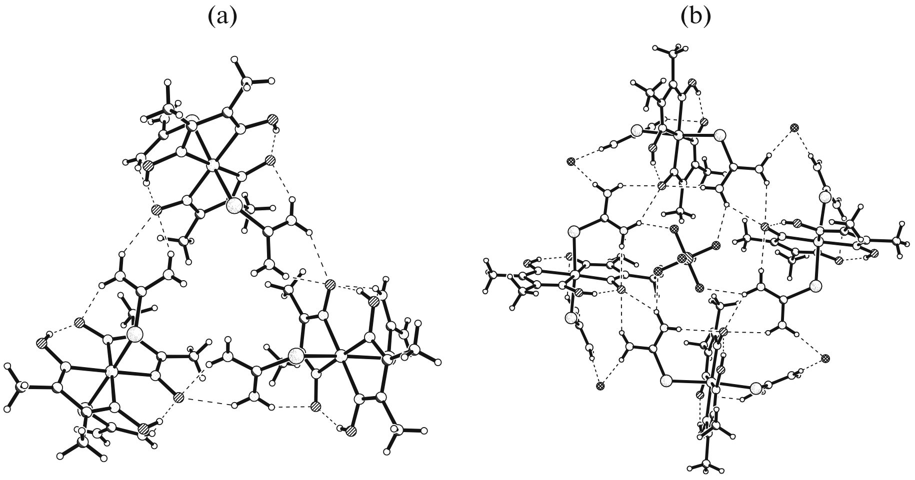

Fig. 2. (a) Fragment of the cationic network in **I**; (b) tunnels formed by the complex cations and occupied by the $[PF_6]^-$ anions.

we determined the effect of coordination compounds on the growth of the porphyridium culture.

The addition of complexes in 10 mg/L concentration to the culture medium did not induce substantial changes in the accumulation of the microalga *P. cruentum* biomass (Fig. 4). In the presence of complexes **II** and **IV** in the medium, the amount of microalgae biomass slightly changed (by 7%). When the concentration of complexes was 20 mg/L, the *P. cruentum* biomass accumulation changed. The presence of 20 mg/L of complex **III** in the culture medium increased the biomass amount by 20%. The addition of compound **II** decreased the amount of porphyridium biomass by 15%, while the addition of 20 mg/L of **IV** induced the same response of microalgae culture as 10 mg/L concentration.

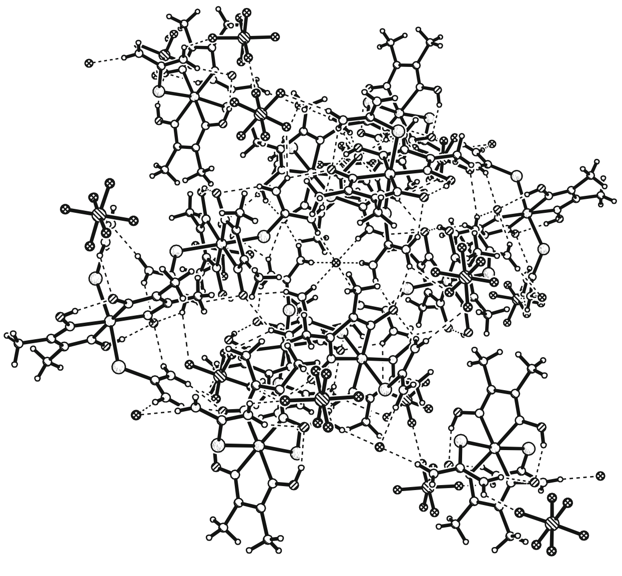

Fig. 3. Supramolecular architecture of the complex with the F^- ions in the tunnels.

The accumulation of proteins in the biomass is an important indication of the biosynthetic activity of microalgae.

When the concentration of the compounds was 10 mg/L, the protein content in the porphyridium biomass increased (Fig. 5). Indeed, compounds **I** and **III**, which did not inhibit the growth of microalgae, increased the protein content in the biomass by 64–80% compared with the control. A increase in the protein content by 38% was also observed in experiments with complex **IV**, whereas compound **II** in the same concentration (10 mg/L) did not change the protein content in the biomass. Compounds **I–III** present in concentration of 20 mg/L inhibited the protein biosynthesis, resulting in a 20–30% lower protein content in the biomass than in the control, whereas compound **IV** in the same concentration did not change the protein content in the biomass.

The stimulation effect on the protein biosynthesis is also accompanied by a change in other biosynthetic parameters of microalgae. A 17% increase in the lipid content in the porphyridium biomass was induced by

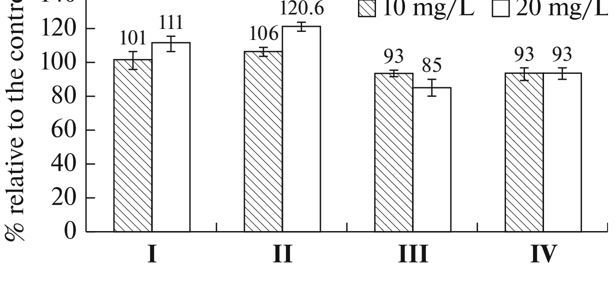

Fig. 4. Microalga *P. cruentum* biomass (% relative to the control) grown in the presence of cobalt complexes.

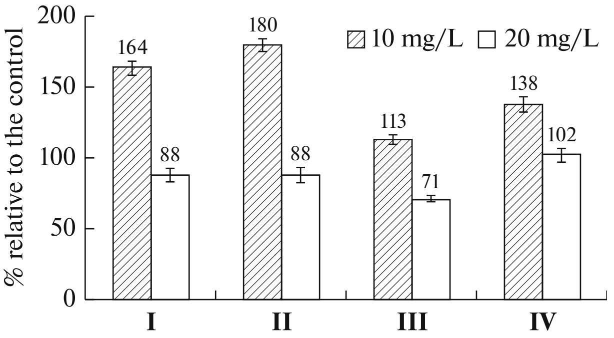

Fig. 5. Protein content (% relative to the control) in the *P. cruentum* biomass grown in the presence of cobalt complexes.

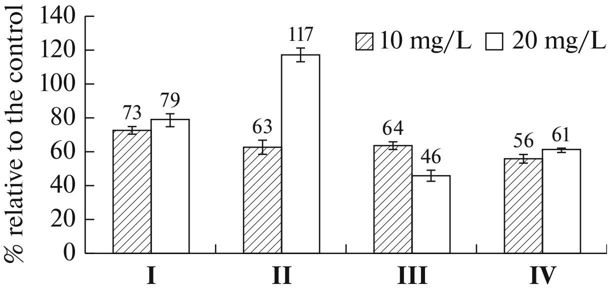

Fig. 6. Lipid content (% relative to the control) in the *P. cruentum* biomass grown in the presence of cobalt complexes.

addition of complex **III** in concentration of 20 mg/L into the culture medium (Fig. 6). When this compound was added in 10 mg/L concentration, the lipid content, conversely, decreased by 37% relative to the control. The addition of compound **I** (10 and 20 mg/L) to the culture medium led to decreasing lipid content by 19–27% relative to the control.

A considerable decrease in the lipid content in the porphyridium biomass (by more than 30%) was detected in experiments with compounds **II** and **IV**; in the case of **IV**, the decrease in the lipid content did not depend on the concentration of the compound in the culture medium.

Thus, new dioximates **I** and **II** were prepared; the structure was studied for complex **I** in which the charge of the complex cation is counterbalanced simultaneously by two different fluorine-containing anions, F^- and $[PF_6]^-$. The results of assays of the effects of these compounds and compounds **III** and **IV** on the physiological processes of red microalga *Porphyridium cruentum* showed that complex **III** in concentration of 20 mg/L stimulates the production of microalgae biomass (by 20%) and increases the lipid content in the biomass (by 17%); this compound can be proposed as a specific growth stimulant for porphyridium-culturing biotechnology.

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