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Supramolecular Structure Organization and the Biological Properties of $[Co(DH)_2(PP)_2][BF_4]$

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Abstract—The coordination compound $[Co(DH)_2(PP)_2][BF_4]_2 \cdot 2H_2O$ (DH^- is the dimethylglyoxime residue, PP is nicotinamide) was synthesized and studied by X-ray diffraction. The equatorial plane of the octahedral Co(III) complex contains two DH^- residues combined by intramolecular hydrogen bonds O–H···O, while the apical positions are occupied by two PP molecules. A method for the optimal use of the complex for enhancement of the biosynthesis of standard and acid-stable amylases of the micromycete *Aspergillus niger* 33-19 CNMN FD 02A and lipases of the micromycete *Rhizopus arrhizus Fischer* CNMN FD 03L was depeloped. The introduction of the complex in a concentration of 1–5 mg/l into the culture medium of *Aspergillus niger* 33-19 CNMN FD 02A reduces the process cycle by 24 h. The stimulating effect of the introduction of the complex (5 mg/l) into the culture medium of the *Rhizopus arrhizus Fischer* CNMN FD 03L strain is 55.5%.

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The efficiency of biologically active compounds is considerably increased when they have been incorporated in metal complexes as ligands [1]. This is also true for transition metal dioximates that exhibit biological activity [2, 3] and are adequate models for vital systems such as vitamin B_{12} [4].

Many of cobalt(III) *trans*-dimethylglyoximates generally described as $[Co(DH)_2A_2]X$, which have octahedral structure where the *trans*-axial positions of the equatorial plane of the $Co(DH)_2$ group (DH^- is HO–N=C(CH_3)–C(CH_3)=N–O–) is occupied by two monodentate neutral ligands and the axial positions accommodate fluoride ion F^- or a fluorine-containing anion ($[BF_4]^-$, $[PF_6]^-$, $[SiF_6]^{2-}$, etc.) are also biologically active [5–8].

A Co(III) compound with DH_2 described as $[Co(DH)_2(PP)_2][BF_4] \cdot 2H_2O$ (**I**) was synthesized and studied by X-ray diffraction. Physiologically important nicotinamide (vitamin PP) is located in the apical coordinate of its octahedron as a ligand. The optimal conditions of the use of complex **I** for enhancement of the biosynthesis of standard and acid-resistant amylases of the micromycete *Aspergillus niger* 33-19 CNMN FD 02A and lipases of the micromycete *Rhizopus arrhizus Fischer* CNMN FD 03L were found.

EXPERIMENTAL

Synthesis of I. Dimethylglyoximate (0.23 g, 0.002 mol) in methanol (30 ml) and nicotinamide (0.25 g, 0.002 mol) were added to a solution of $Co(BF_4)_2 \cdot 6H_2O$ (0.34 g, 0.001 mol) in water (20 ml). The resulting solution was oxidized by air oxygen for ~30 min in a graphite crucible at 70°C. On slow cooling, brown crystals precipitated from the solution. Yield 25% (relative to $Co(BF_4)_2 \cdot 6H_2O$). The compound was soluble in water, methanol, and ethanol.

For $C_{20}H_{30}BF_4N_8O_8Co$				
anal. calcd., %:	Co, 8.57;	C, 36.42;	H, 4.53;	N, 16.93.
Found, %:	Co, 8.57;	C, 36.42;	H, 4.53;	N, 16.93.

The IR spectrum of compound **I** exhibits absorption bands (cm^{-1}): 3359 $\nu_{as}(NH_2)$, 3160 $\nu_s(NH_2)$, 1692 ν(C=O), 1637 $\delta(NH_2)$, 1609 ν(C=C) + δ(CCH), 1562 ν(C=N), 1444 $\delta_{as}(CH_3)$, 1097 ν(N=O), 1167 δ(CCH), 697 ρ(CH), 515, 429 $\nu(Co–N)_{DH}$, 459 $\nu(Co–N)_{PP}$P. The presence of the $[BF_4]^-$ anion in the complex is confirmed by the presence of absorption bands (cm^{-1}): 1085 $\nu_{as}(BF_4)$, 750 $\nu_s(BF_4)$, and 545 δ(F–B–F) [9, 10].

X-Ray diffraction. The unit cell parameters and the three-dimensional set of reflection intensities were measured at 100 K on a Nonius Kappa CCD diffractometer (MoK_α radiation, graphite monochromator, ω–

Table 1. Crystallographic data and X-ray experiment details for the structure $[Co(DH)_2(PP)_2][BF_4] \cdot 2H_2O$

Parameter	Value
M	656.26
System	Monoclinic
Space group	*C*2/*c*
Unit cell parameters:	
a, Å	27.218(5)
b, Å	7.426(2)
Ò, Å	16.077(3)
β, deg	119.74(3)
V, Å^3	2821.4(10)
Z	4
ρ(calcd.), g/cm^3	1.545
μ, mm^{-1}	0.693
F(000)	1352
Crystal size, mm	0.5 × 0.3 × 0.1
θ range, deg	3.41–25.50
Ranges of reflection indices	$-28 \le h \le 32$
	$-8 \le k \le 8$
	$-19 \le l \le 17$
he number of measured/independent reflections	7959/2606 (R_{int} = 0.0792)
The number of reflections with $I > 2\sigma(I)$	2113
The number of refined parameters	210
GOOF	1.044
R-factor ($I > 2\sigma(I)$)	R_1 = 0.0819, wR_2 = 0.2257
R-factor for the whole array	R_1 = 0.1023, wR_2 = 0.2399
$\Delta\rho_{max}$, $\Delta\rho_{min}$, *e* Å^{-3}	0.766, –0.663

2θ scan mode [11]). The intensities were integrated and brought to a common scale using the DENZO [12] and SKALEPACK [12 programs; absorption corrections were applied by the XEMP program [13]. The structure of compound **I** was solved by the direct method and refined by least squares in the anisotropic full matrix approximation for non-hydrogen atoms (SHELX-97) [14]. The hydrogen atoms in the complex cation were found objectively and refined in the rigid-body model. The oxygen atom of water is statistically disordered over three positions with population factors of 0.33; the $H(H_2O)$ atoms were not located.

The crystallographic data and X-ray experiment details for structure **I** are presented in Table 1, selected interatomic distances and bond angles are listed 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. 706634).

Biological studies. The biological studies were carried out for the micromycetes *Aspergillus niger* 33-19 CNMN FD 02A, which is an amylase producer, and *Rhizopus arrhizus Fischer* CNMN FD 03L, lipase producer [15, 16].

The producers were cultivated by submerged cultivation method with continuous stirring in media of specified composition without complex **I** (control) and with complex **I** present in concentrations of 1, 5, and 10 mg/l (test).

In culture liquids, the change in the enzymatic activity of the producers was determined. The amylolytic activity was determined by iodometric method based on cleavage of soluble starch to dextrins with different molecular weight under standard hydrolysis conditions at pH 4.7 for standard amylases and at pH 2.5 for acid-stable amylases [17, 18]. The lipolytic activity was determined from cleavage of olive oil to oleic acid using modified Ota–Yamada method [15, 19].

RESULTS AND DISCUSSION

The ionic structure of **I** is composed of the $[Co(DH)_2(PP)_2]^+$ cations, $[BF_4]^-$ anions, and water molecules of crystallization. The cation has C_i symmetry and the anion is C_2-symmetric. The octahedral Co(III) complex cation (Co–N(l), 1.908(4); Co–N(2), 1.890(5); Co–N(3), 1.974(4) Å (Table 2) is stabilized in the equatorial plane by an intramolecular hydrogen bond O–H···O, which combines two dimethylglyoxime residues DH^- into a stable pseudomacrocyclic system (Table 3, Fig. 1). This type of architecture is typical of all *trans*-octahedral transition metal complexes with α-dioximes [2, 20-23]. The apical nicotinamide ligand PP is coordinated to the central metal atom by the nitrogen atom of the aromatic heterocycle. On the basis of CCDC data [24], one can note that this type of coordination predominates in the coordination compounds with nicotinamide. For example, in the complex cation N,N'-bis(4-hydroxy-3-pent-2-enylidene)ethylene-1,2-diamine)-bis(pyridine-3-carboxamide)cobalt (III (**II**) [25], two PP molecules coordinated through nitrogen atoms are also located in apical coordinates (Co–N(PP), 1.974 and 1.942 Å). In complex **I**, the dihedral angle between the plane of the aromatic ring and the equatorial plane of the coordination polyhedron is 90.2°. The corresponding angles in the Co(III) complex cation of structure **II** are 89.2° and 92.5°. This type of arrangement of coordinated dimethylglyoxime mole-

cules and neutral nitrogen-containing ligands was also found in Co(III) complexes with Py [20–23]. However, in some transition metal complexes (mainly in Zn(II), Mn(II), and Cu(II) complexes) with pyridinecarboxylic acid amides), a different mode of coordination was found, in particular, bidentate coordination through nitrogen atoms of the heterocycle and the amide group. In this case, the crystals are formed by dimers (for example, in Zn(II) complexes with diethylnicotinamide [26] and Cu(II) complexes with nicotinamide [27]) or chains, as in Mn(II) and Cu(II) complexes with nicotinamide and its derivatives [28–31].

Fragments of the packing of complex cations in **I** are shown in Figs. 2 and 3. The neighboring complex cations $[Co(DH)_2(PP)_2]^+$ are involved in the formation of the synthon $R_2^2(8)$ through the amino groups of the coordinated PP molecules. This H-bond N(4)–H···O(3) is responsible for the formation of a one-dimensional chain directed along the *x*-axis of the crystal (Fig. 2). The chains of cations are combined to a framework by the H-bonds C–H···O (the methyl groups of the DH^- ligand are donors and the oxygen atoms of the DH^- and PP ligands are acceptors) thus forming channels directed along the *y*-axis of the crystal (Fig. 3). The $[BF_4]^-$ anions and water molecules combined by the H-bonds O(1*w*)–H···F (O···F 2.831(6) Å) are arranged in the channels. Using the second hydrogen atom of the amino groups of the PP ligands, the cations participate as donors in the N(4)–H···O(1*w*) H-bonding with water molecules. The other intermolecular contacts in structure **I** correspond to the sums of the van der Waals radii of the atoms.

Analysis of the obtained data (Table 4) on activity change for standard (pH 4.7) and acid-stable (pH 2.5) amylases of the micromycete *Aspergillus niger* 33-19, CNMN FD 02A during the cultivation dynamics (4 to 7 days) shows that the introduction of the new Co(III) dioximate to the nutrition medium enhances the amylase biosynthesis as soon as the fourth day of producer cultivation (26.1 and 36.2 %, respectively). The stimulating effect is higher at low concentrations (1–5 mg/l).

During the subsequent cultivation (5–6 day), the difference between the test and control samples decreases. These results suggest that the use of complex **I** accelerates the phases of microorganism development thus ensuring earlier arrival of the stationary phase, which is characterized by active metabolic processes, in particular, active amylase biosynthesis. This assumption is supported by microbiological studies, which demonstrate earlier formation of abundant and well-developed mycelium and active sporulation in the test run.

As a result of studies, the optimal conditions were selected for the use of complex **I** for acceleration and enhancement of the biosynthesis of standard and acid-stable amylases during submerged cultivation of the micromycete *Aspergillus niger* 33-19 CNMN FD 02A in the process conditions developed for the strain.

Table 2. Selected interatomic distances and bond angles in the structure $[Co(DH)_2(PP)_2][BF_4] \cdot 2H_2O$*

Bond	*d*, Å	Bond	*d*, Å
Co(1)–N(1)	1.908(4)	N(4)–C(10)	1.324(7)
Co(1)–N(2)	1.890(5)	C(1)–C(2)	1.474(8)
Co(1)–N(3)	1.974(4)	C(1)–C(4)	1.487(8)
O(1)–N(1)	1.345(6)	C(2)–C(3)	1.483(8)
O(2)–N(2)	1.346(6)	C(5)–C(6)	1.392(8)
O(3)–C(10)	1.232(7)	C(6)–C(7)	1.385(9)
N(1)–C(1)	1.302(7)	C(6)–C(10)	1.507(8)
N(2)–C(2)	1.299(7)	C(7)–C(8)	1.362(8)
N(3)–C(5)	1.339(7)	C(8)–C(9)	1.392(8)
N(3)–C(9)	1.346(7)		
B(1)–F(1)	1.36(2)	B(1)–F(2)	1.41(2)
Angle	ω, deg	Angle	ω, deg
N(1)Co(1)N(2)	81.0(2)	C(2)C(1)C(4)	124.7(5)
N(1)Co(1)N(3)	90.2(2)	N(2)C(2)C(1)	111.8(5)
N(2)Co(1)N(3)	89.9(2)	N(2)C(2)C(3)	123.5(5)
C(1)N(1)O(1)	120.9(5)	C(1)C(2)C(3)	124.7(5)
C(1)N(1)Co(1)	116.4(4)	N(3)C(5)C(6)	122.1(5)
O(1)N(1)Co(1)	122.7(4)	C(5)C(6)C(7)	118.5(5)
C(2)N(2)O(2)	121.1(5)	C(5)C(6)C(10)	115.9(5)
C(2)N(2)Co(1)	117.8(4)	C(7)C(6)C(10)	125.5(6)
O(2)N(2)Co(1)	121.1(4)	C(8)C(7)C(6)	119.5(5)
C(5)N(3)C(9)	118.9(5)	C(7)C(8)C(9)	119.4(5)
C(5)N(3)Co(1)	120.7(4)	N(3)C(9)C(8)	121.5(5)
C(9)N(3)Co(1)	120.4(4)	O(3)C(10)N(4)	123.9(5)
N(1)C(1)C(2)	113.0(5)	O(3)C(10)C(6)	119.2(5)
N(1)C(1)C(4)	122.4(5)	N(4)C(10)C(6)	116.9(6)
F(1)B(1)F(2)	109.7(6)	F(1)B(1)F(2)$^{\#1}$	109.1(4)
F(1)B(1)F(1)$^{\#1}$	113(3)	F(2)B(1)F(2)$^{\#1}$	107(3)

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

Table 3. Geometric parameters of intra- and intermolecular hydrogen bonds in the structure $[Co(DH)_2(PP)_2][BF_4] \cdot 2H_2O$

The D–H···A contact	Distances, Å			DHA angle, deg	Coordinates of A atoms
	D–H	H···A	D···A		
O(1)–H···O(2)	0.82	1.69	2.486(6)	162	$-x + 1/2, -y + 1/2, -z + 1$
N(4)–H(1)···O(3)	0.86	1.98	2.831(6)	170	$-x, -y, -z + 1$
N(4)–H(2)···O(1*w*)	0.86	2.42	3.14(4)	142	x, y, z
N(4)–H(2)···O(2*w*)	0.86	2.17	3.00(4)	162	x, y, z
N(4)–H(2)···O(3*w*)	0.86	2.12	2.78(3)	133	$-x, y, z$

Then we studied the effect of the complex on the enzymogenesis process of the micromycete *Rhizopus arrhizus Fischer* CNMN FD 03L, an active producer of lipases, which are key enzymes in the lipid metabolism of living organisms. They are vigorously studied due not only to the theoretical interest but also the possibility of extensive use in various industrial processes.

Data on the change in the lipolytic activity of the producer during its cultivation (1 to 3 days) are presented in Table 5. The stimulating effect was observed in the test run even in the first 24 h, the enzymatic activity being 11.1% higher than that in the control run for concentrations of 5 to 10 mg/l. The biosynthesis maximum is observed on the second day being 122.2–

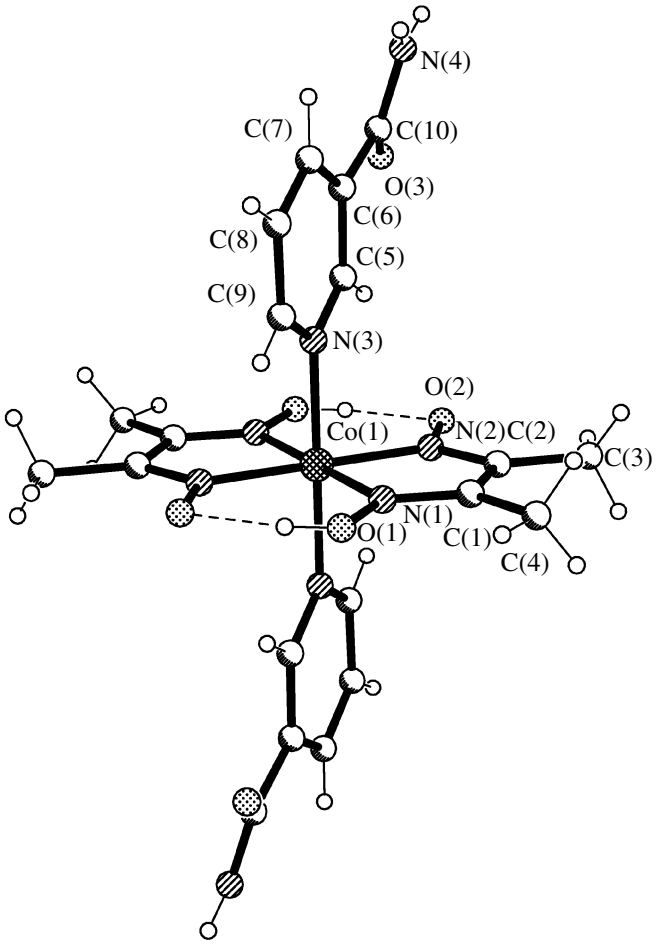

Fig. 1. Structure of the complex cation $[Co(DH)_2(PP)_2]^+$.

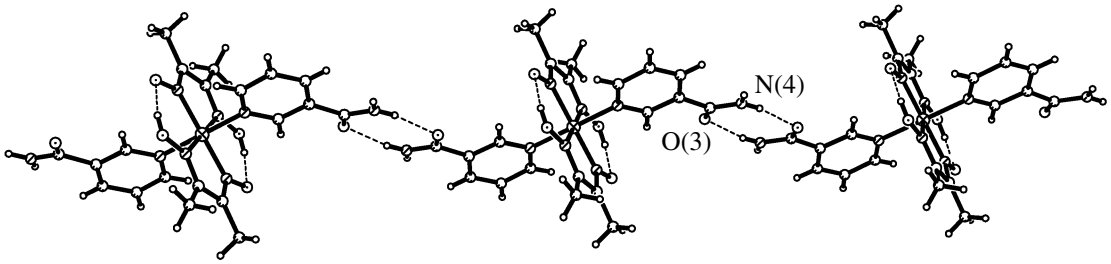

Fig. 2. Structure of the H-bonded chain composed of the cations $[Co(DH)_2(PP)_2]^+$.

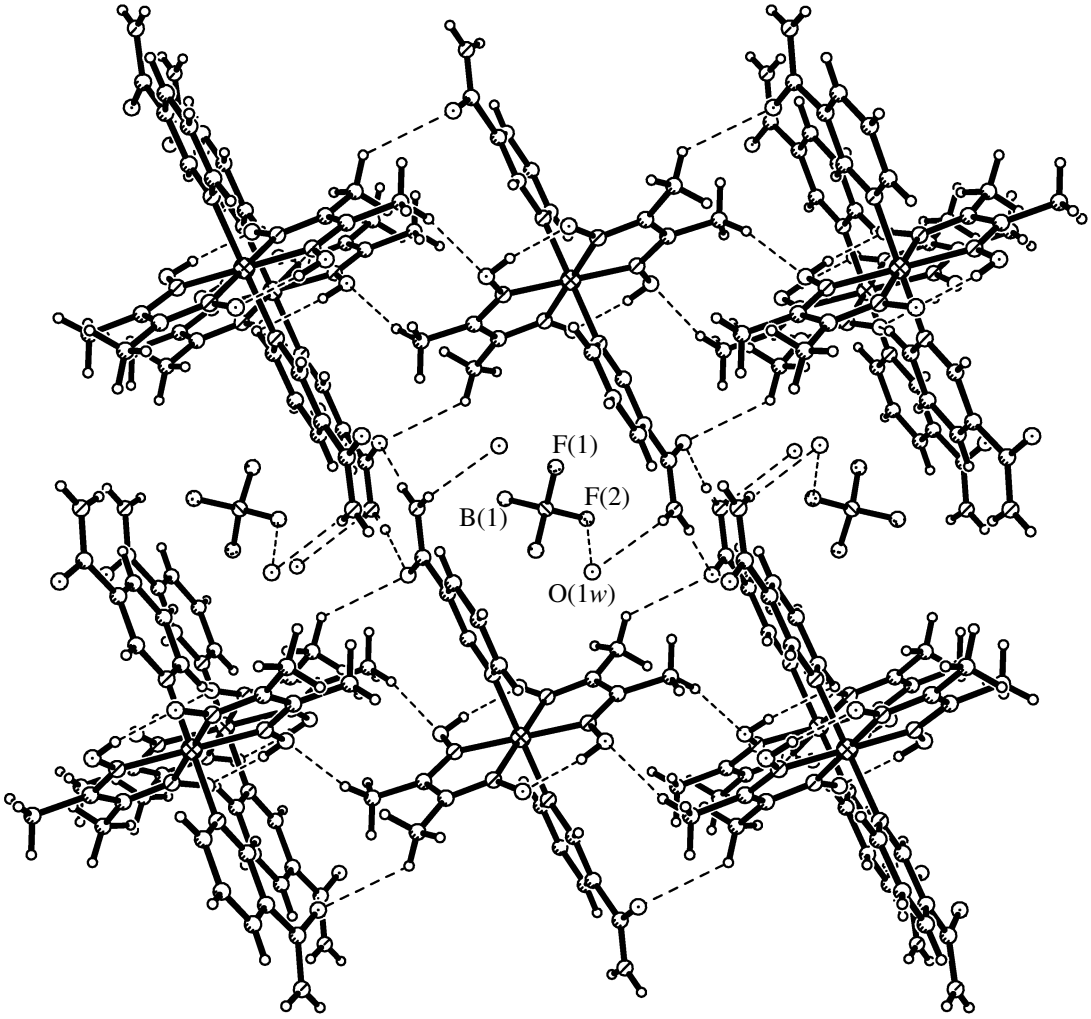

Fig. 3. Fragment of the crystal structure of $[Co(DH)_2(PP)_2][BF_4] \cdot 2H_2O$.

155.5% compared to the control run where the maximum biosynthesis is observed simultaneously.

Microscopic studies also did not reveal any acceleration of the culture development upon the use of test complex **I**. The reason is the short cycle of development of the strain *Rhizopus arrhizus Fischer* CNMN FD 03L (2 days) compared to the strain *Aspergillus niger* 33-19 CNMN FD 02A (6 days).

Thus, a method for the optimal use of the complex $[Co(DH)_2(PP)_2][BF_4] \cdot 2H_2O$ for the enhancement of biosynthesis of standard and acid-stable amylases of the strain *Aspergillus niger* 33-19 CNMN FD 02A and

Table 4. Change in the amylolytic activity of the micromycete *Aspergillus niger* 33-19 CNMN FD 02A under the action of the complex $[Co(DH)_2(PP)_2][BF_4] \cdot 2H_2O$

Compound	Concentration, mg/l	Activity					
		4 days		5 days		6 days	
		u./ml	percent of the control	u./ml	percent of the control	u./ml	percent of the control
Standard amylases (pH 4.7)							
$[Co(DH)_2(PP)_2][BF_4] \cdot 2H_2O$	1	171.7	126.1	188.7	109.0	142.6	80.1
	5	159.3	117.0	188.7	109.0	157.7	88.7
	10	151.0	110.8	167.9	97.0	172.8	97.2
Control		136.2	100	173.1	100	177.9	100
Acid-stable amylases (pH 2.5)							
$[Co(DH)_2(PP)_2][BF_4] \cdot 2H_2O$	1	293.4	136.2	307.5	117.5	210.8	70.8
	5	270.0	125.4	278.4	106.4	246.1	82.6
	10	248.8	115.4	271.2	103.6	264.8	88.9
Control		215.3	100	261.7	100	297.8	100

Table 5. Change in the lipolyrtic activity of the micromycete *Rhizopus arrhizus Fischer* CNMN FD 03 L under the action of the complex $[Co(DH)_2(PP)_2][BF_4] \cdot 2H_2O$

Compound	Concentration, mg/l	Lipolytic activity					
		24 h		2 days		2 days	
		u./ml	percent of the control	u./ml	percent of the control	u./ml	percent of the control
$[Co(DH)_2(PP)_2][BF_4] \cdot 2H_2O$	1	51500	100.0	68750	122.2	35000	77.8
	5	57500	111.1	87500	155.5	45000	100.0
	10	57500	111.1	68750	122.2	35000	77.8
Control		51750	100	56250	100	45000	100

lipases of the strain *Rhizopus arrhizus Fischer* CNMN FD 03L was developed. The introduction of this complex into the culture medium of the micromycete *Aspergillus niger* 33-19 CNMN FD 02A in a concentration of 1 to 5 mg/l reduces the process cycle by 24 h. The stimulating effect caused by the addition of the complex to the culture medium of the micromycete *Rhizopus arrhizus Fischer* CNMN FD 03L in a concentration of 5 mg/l is 55.5%.

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