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Synthesis and Structure of Mononuclear Zinc Complexes with Pyridine-2-Aldoxime

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Abstract—Three mononuclear different-ligand Zn(II) complexes, $[Zn(CH_3COO)_2(PaoH)_2]$ (**I**), $[Zn(PaoH)_2(DMSO)_2][BF_4]_2$ (**II**), and $[Zn(NCS)_2(PaoH)_2]$ (**III**) (DMSO = dimethylsulfoxide) were prepared by the reaction of zinc acetate and tetrafluoroborate with pyridine-2-aldoxime (PaoH). The composition and structure of the complexes were confirmed by IR spectroscopy and X-ray diffraction. All compounds crystallize in the monoclinic system, compounds **I** and **II** have space group $P2_1/n$, while compound **III** has space group $C2/c$. In all compounds, the Zn coordination polyhedron is a distorted octahedron, which is formed by the N_4O_2 sets of donor atoms in **I** and **II** and by N_6 in **III**. Complex **I** in the optimal concentration of 5–10 mg/L was found to stimulate the biosynthesis of standard (pH 4.7) amylases by the micromycete *Aspergillus niger* CNMN FD 06.

Keywords: coordination compounds, crystal structure, zinc cation, pyridine-2-aldoxime, stimulation of biosynthesis, amylolytic activity

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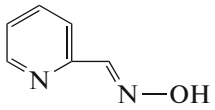
INTRODUCTION

The last decades are characterized by vigorous progress in the synthesis and studies of complexes based on pyridine-*n*-aldoxime ligands ($n = 2, 3, 4$) [1]. Of particular interest is the manufacture of new materials with useful properties: molecular magnets [2–6], photoluminescent materials [7], catalysts for cleavage of carboxylic acid esters [8], stimulatory agents for biological processes [9] and so on. Both homo- and heterometallic coordination compounds with pyridine-*n*-aldoximes are known [10–12]. Previously, we studied some discrete complexes and coordination polymers of zinc, cadmium, manganese(II), and copper(II) with pyridine-4-aldoxime and pyridine-2-aldoxime [13–16]. The advantage of pyridine-2-aldoxime (PaoH) over the two other positional isomers is the possibility to form strong metal chelates via simultaneous coordination of both the pyridine nitrogen and oxime nitrogen/oxygen atoms to the metal.



PaoH

The literature contains data for mono- [13, 17, 18], bis- [19, 20], and tris-oxime [21–23] mononuclear complexes based on pyridine-2-aldoxime and polynuclear homo- and heterometallic [24, 25] clusters with magnetic properties [2–6, 26] induced by the bridging coordination of this ligand to metal cations. The various possible coordination modes of the ligand, coordination capacities of transition metals, and conditions of synthesis and the addition of other chelating ligands may increase the structural diversity of the resulting complexes [27]. A bridging coordination of the PaoH ligand to the metal is also possible [20, 28].

This communication describes the synthesis and structure of three mononuclear zinc complexes with pyridine-2-aldoxime, $[Zn(CH_3COO)_2(PaoH)_2]$ (**I**), $[Zn(PaoH)_2(DMSO)_2][BF_4]_2$ (**II**), and $[Zn(NCS)_2(PaoH)_2]$ (**III**), and presents data on the biological activity of compound **I**.

EXPERIMENTAL

Synthesis of I. Pyridine-2-aldoxime (24.00 mg, 0.2 mmol) was added to a solution of $Zn(CH_3COO)_2 \cdot 2H_2O$ (21.9 mg, 0.1 mmol) in 30 mL of a CH_3OH–DMF mixture (5 : 1), where DMF is dimethylforma-

mide. The resulting solution was heated with stirring for 10 min. On slow spontaneous evaporation, colorless crystals precipitated from the transparent solution. The yield was ~67%. The compound was soluble in DMSO, DMF, methanol, and ethanol and slightly soluble in water.

For $C_{16}H_{18}N_4O_6Zn$

anal. calcd., %:	C, 45.03;	H, 4.25;	N, 13.13.
Found, %:	C, 44.76;	H, 3.94;	N, 13.02.

Synthesis of II. Pyridine-2-aldoxime (24.00 mg, 0.2 mmol) was added to a solution of $Zn(BF_4)_2 \cdot xH_2O$ (23.9 mg, 0.1 mmol) in 40 mL of a CH_3OH–DMF–DMSO mixture (6 : 1 : 1). The resulting solution was heated with stirring for 10 min. On slow evaporation, colorless crystals precipitated from the transparent solution. The yield was ~36%. The compound was soluble in DMSO, DMF, methanol, and ethanol and slightly soluble in water.

For $C_{16}H_{18}N_4O_4S_2B_2F_8Zn$

anal. calcd., %:	C, 30.10;	H, 3.79;	N, 8.78.
Found, %:	C, 29.82;	H, 3.68;	N, 8.53.

Synthesis of III. Pyridine-2-aldoxime (24.00 mg, 0.2 mmol) and NH_4NCS (7.6 mg, 0.1 mmol) were added to a solution of $Zn(BF_4)_2 \cdot xH_2O$ (23.9 mg. 0.1 mmol) in 30 mL of a CH_3OH–DMF mixture (4 : 1). The resulting solution was heated with stirring for 10 min. On slow evaporation, colorless crystals precipitated from the transparent solution. The yield was ~31%. The compound was soluble in DMSO, DMF, methanol, and ethanol and slightly soluble in water.

For $C_{14}H_{12}N_6O_2S_2Zn$

anal. calcd., %:	C, 39.59;	H, 2.85;	N, 19.79.
Found, %:	C, 39.37;	H, 2.71;	N, 19.52.

Physical methods. The compositions and structures of compounds **I**–**III** were established on the basis of elemental analysis, IR and NMR spectroscopy, and X-ray diffraction. IR spectra were measured on a Perkin-Elmer Spectrum 100 FT-IR spectrometer in mineral oil in the 4000–400 cm^{-1} range and the ATR (attenuated total reflection) spectra were measured in the 4000–650 cm^{-1} range.

X-ray diffraction. The data for **I**–**III** were collected at room temperature on an Xcalibur CCD Oxford Diffraction diffractometer (MoK_α radiation, λ = 0.71073 Å, graphite monochromator, ω scan mode). The unit cell parameters were refined for the whole array of experimental data. The crystal structures were solved by direct methods and refined by least squares in the full-matrix anisotropic approximation for non-hydrogen atoms (SHELX-97) [29]. The hydrogen atom positions were calculated geometrically and refined isotropically in the rigid-body approximation. In **II**, the dimethylsulfoxide moiety of one DMSO molecule is disordered over two positions with occupancies of 0.840(5) and 0.160(5). In one tetrafluoroborate anion, the fluorine atoms are disordered over two positions with occupancies of 0.786(6) and 0.214(6). The crystal data and X-ray experiment details for **I**–**III** are summarized in Table 1, the interatomic distances and bond angles are in Table 2, and the geometric parameters of hydrogen bonds are presented in Table 3. The CIF files containing full data for these structure are deposited with the Cambridge Crystallographic Data Centre (CCDC) (no. 487386 (**I**), 487387 (**II**), and 1487388 (**III**); www.ccdc.cam.ac.uk/data_request/cif).

Biological methods. The biological properties of the complexes were tested considering the degree of their influence on the enzyme formation by the micromycete *Aspergillus niger* CNMN FD 06, referring to the class of "black aspergilli" actively producing amylolytic enzymes, which hydrolyze starch-containing substrates both under usual conditions (pH 4.7) and under extremely acidic conditions (pH 2.5).

A producer strain was cultured by the submerged culture method in a medium with the previously selected composition [30] (pH 5.0, culturing temperature of 28–30°C) with continuous stirring on a shaker with rotation at 180–200 rpm. The complexes were inserted into the sterile culture medium in concentrations of 5, 10, or 15 mg/L simultaneously with the seed material. The medium without a complex added served as the control. The effect of complexes on the amylase activity of the micromycete *Aspergillus niger* CNMN FD 06 was measured over time on the 5th and 6th day of culturing, which corresponds to the period of maximum biosynthesis for this strain under the classic culturing conditions.

The amylolytic activity was measured by the photocolorimetric method based on the degree of starch degradation to dextrins wih various molecular masses under standard (pH 4.7) and extremely acidic (pH 2.5) conditions [31].

RESULTS AND DISCUSSION

The IR spectra of **I**–**III** exhibit bands inherent in the PaoH ligand. The band at ~1650 cm^{-1} corresponds to the $\nu(C{=}N)_{oxime}$ mode, the band at ~1600 cm^{-1} is due to pyridine ring vibrations, that at ~1060 cm^{-1} is the $\nu(N{-}O)_{oxime}$ mode, and the ~638 cm^{-1} band is caused by out-of-plane distortion of the pyridine ring. The medium-intensity bands at 1545 and 1411 cm^{-1} for **I** correspond to carboxyl group vibrations, $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$. The strong band at 2047 cm^{-1} in the spectrum of **III** attests to N-bound isothiocyanate anion.

Table 1. Crystallographic data and X-ray experiment details for compounds **I**–**III**

Parameter	Value		
	I	**II**	**III**
M	427.71	639.50	425.79
System	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$C2/c$
a, Å	8.763(2)	10.7939(3)	14.0272(16)
b, Å	13.649(4)	14.3612(5)	10.5441(7)
c, Å	15.566(4)	17.5865(6)	14.4254(15)
β, deg.	90.51(2)	96.194(3)	118.480(14)
V, Å^3	1861.7(9)	2710.23(15)	1875.4(3)
Z	4	4	4
ρ(calcd.), g/cm^3	1.526	1.567	1.508
μ, mm^{-1}	1.360	1.145	1.552
F(000)	880	1296	864
Crystal size, mm	0.4 × 0.2 × 0.1	0.2 × 0.17 × 0.12	0.15 × 0.12 × 0.09
Range of θ, deg	2.98–25.00	3.07–26.00	3.21–25.00
Ranges of reflection indices	$-10 \le h \le 10$, $-15 \le k \le 10$, $-9 \le l \le 18$	$-13 \le h \le 13$, $-9 \le k \le 17$, $-11 \le l \le 21$	$-7 \le h \le 16$, $-12 \le k \le 5$, $-16 \le l \le 14$
Number of measured/unique reflections (R_{int})	6275/3266 (0.0529)	9523/5270 (0.0419)	1954/1506 (0.0260)
Number of reflections with $I > 2\sigma(I)$	2100	3136	1123
The number of refined parameters	247	369	114
GOOF	1.000	1.009	1.000
R_1, wR_2 factor ($I > 2\sigma(I)$)	0.0573, 0.1109	0.0600, 0.1209	0.0529, 0.1019
R_1, wR_2 factor (for the whole array)	0.0981, 0.1373	0.1128, 0.1574	0.0788, 0.1167
$\Delta\rho_{max}$, $\Delta\rho_{min}$, eÅ^{-3}	0.376, –0.409	0.395, –0.371	0.350, –0.381

The reaction of zinc acetate with PaoH in 1 : 2 ratio in a CH_3OH–DMF mixture (5 : 1) gave non-electrolytic complex **I**. The independent part of the unit cell contains a zinc cation, two acetate anions, and two PaoH ligands (Fig. 1a). The Zn coordination polyhedron is a distorted octahedron formed by the N_4O_2 set of donor atoms. Zn ions is chelated by two pyridine-2-aldoxime molecules via the pyridine and oxime group nitrogen atoms and coordinates two acetate ions in the monodentate fashion via one oxygen atom of the carboxyl group. Each of the two chelating PaoH ligands forms a five-membered chelate ring with the NZnN endocyclic angles of 74.49(19)° and 73.71(17)° and Zn–N distances in the 2.151(5)–2.262(5) Å range (Table 2). In complex **I**, two PaoH ligands occupy *cis*-positions in virtually mutually perpendicular planes: the dihedral angle between their five-membered chelate rings is 89.07° (Fig. 1). Two acetate anions are coordinated in the monodentate fashion via the O(3) and O(5) atoms, the Zn–O distances are 2.031(4) and 2.044(5) Å, and the OZnO angle is 92.39(19)°. The oxygen atoms of the acetate anions that are not coordinated to the metal are involved in intramolecular hydrogen bonds, O–H···O, with oxime groups (Table 3). Analysis of the CCDC data unambiguously attests to stabilization of the transition metal coordination polyhedron by two hydrogen bonds involving carboxylate anions in mononuclear and polymeric analogues of compound **I** [7, 14, 32–37]. The structure of the complex is similar to those of mononuclear cadmium, manganese, and zinc acetates studied previously [38–44].

In order to eliminate the carboxylate anion from the complex formation, zinc tetrafluoroborate with readily leaving tetrafluoroborate anion was taken as the starting salt. The reaction of $Zn(BF_4)_2 \cdot xH_2O$ with PaoH in 1 : 2 ratio in a CH_3OH–DMSO mixture (5 : 1) gave compound **II** composed of $[Zn(PaoH)_2(DMSO)_2]^{2+}$ complex cations and the $[BF_4]^-$ outer-sphere anions. The independent part of

Table 2. Selected interatomic distances and bond angles in compounds **I**–**III***

Bond	*d*, Å	Bond	*d*, Å
		I	
Zn(1)–O(3)	2.031(4)	Zn(1)–N(2)	2.161(5)
Zn(1)–O(5)	2.044(5)	Zn(1)–N(3)	2.262(5)
Zn(1)–N(1)	2.212(5)	Zn(1)–N(4)	2.151(5)
		II	
Zn(1)–O(3)	2.091(3)	Zn(1)–N(2)	2.120(4)
Zn(1)–O(4)	2.052(3)	Zn(1)–N(3)	2.173(4)
Zn(1)–N(1)	2.293(4)	Zn(1)–N(4)	2.130(4)
		III	
Zn(1)–N(1)	2.121(3)	Zn(1)–N(3)	2.045(4)
Zn(1)–N(2)	2.329(4)		
Angle	ω, deg	Angle	ω, deg
		I	
O(3)Zn(1)O(5)	92.39(19)	N(4)Zn(1)N(1)	91.99(18)
O(3)Zn(1)N(4)	102.52(18)	N(2)Zn(1)N(1)	74.49(19)
O(5)Zn(1)N(4)	90.44(18)	O(3)Zn(1)N(3)	175.47(18)
O(3)Zn(1)N(2)	94.14(17)	O(5)Zn(1)N(3)	90.17(18)
O(5)Zn(1)N(2)	102.08(19)	N(4)Zn(1)N(3)	73.71(17)
N(4)Zn(1)N(2)	158.75(19)	N(2)Zn(1)N(3)	88.98(17)
O(3)Zn(1)N(1)	90.77(18)	N(1)Zn(1)N(3)	86.89(17)
O(5)Zn(1)N(1)	175.51(19)		
		II	
O(4)Zn(1)O(3)	91.47(13)	N(2)Zn(1)N(3)	172.34(16)
O(4)Zn(1)N(2)	95.20(15)	N(4)Zn(1)N(3)	75.19(14)
O(3)Zn(1)N(2)	101.25(14)	O(4)Zn(1)N(1)	169.50(14)
O(4)Zn(1)N(4)	96.44(14)	O(3)Zn(1)N(1)	88.51(15)
O(3)Zn(1)N(4)	156.72(14)	N(2)Zn(1)N(1)	74.52(15)
N(2)Zn(1)N(4)	99.79(15)	N(4)Zn(1)N(1)	87.60(15)
O(4)Zn(1)N(3)	91.15(14)	N(3)Zn(1)N(1)	99.27(14)
O(3)Zn(1)N(3)	82.82(14)		
		III	
N(3)Zn(1)N(3)	94.7(3)	N(1)Zn(1)N(2)$^{\#}$	93.12(14)
N(3)Zn(1)N(1)$^{\#}$	95.43(16)	N(3)Zn(1)N(2)	92.42(17)
N(3)Zn(1)N(1)	96.67(15)	N(1)Zn(1)N(2)	73.25(14)
N(1)$^{\#}$Zn(1)N(1)	162.1(2)	N(2)$^{\#}$Zn(1)N(2)	82.6(2)
N(3)Zn(1)N(2)$^{\#}$	167.26(15)		

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

Table 3. Geometric parameters of the hydrogen bonds in structures **I**–**III**

D–H···A	Distance, Å		DHA angle, deg	Symmetry codes for A
	H···A	D···A		
		I		
O(1)–H(1)···O(6)	1.69	2.511(7)	175	x, y, z
O(2)–H(2)···O(4)	1.68	2.474(6)	163	x, y, z
		II		
O(1)–H(1)···F(2)	1.93	2.703(5)	157	$x + 1, y, z$
O(2)–H(2)···F(8)	2.06	2.737(6)	139	$x + 1, y, z$
O(2)–H(2)···F(6*A*)	2.20	2.771(18)	127	$x + 1, y, z$
O(2)–H(2)···O(3)	2.41	2.982(5)	128	x, y, z
		III		
O(1)–H(1)···S(1)	2.48	3.188(4)	150	$1/2 - x, y - 1/2, 1/2 - z$

the unit cell contains a zinc cation, two tetrafluoroborate anions, two PaoH ligands, and two DMSO molecules (Fig. 1b). The structure of the complex cation in **II** is similar to that of **I** with two acetate anions being replaced by DMSO molecules. The PaoH molecules form two metallacycles (Zn–N, 2.120(4)–2.293(5) Å; NZnN, 74.52(15)° and 75.19(14)°; Zn–O, 2.091(3) and 2.052(3) Å). The absence of a stabilizing action of acetate anions results in a higher conformational freedom of the metal-coordinated neutral ligands, as indicated by rotation of one PaoH ligand and somewhat reduced dihedral angle between the metallacycle planes (85.2°). The $[BF_4]^-$ anions are held in the crystal lattice by the O–H···F hydrogen bonds (Table 3, Fig. 2a).

To eliminate the possibility of coordination of solvent molecules (as in **II**) and to study the anion exchange reactions, it was decided to add bidentate inorganic anions that could potentially occupy two sites in the Zn(II) coordination polyhedron. The use of ambident inorganic ligands such as isothiocyanate, which can be coordinated via two donor atoms (nitrogen and sulfur) pursued several goals: elucidation of the possible coordination of the isothiocyanate anion to the complexing atom under competition with other potential ligands and creation of conditions for this anion to behave as a bridging ligand for the assembly of coordination polymers. The reaction of zinc tetrafluoroborate with PaoH and NH_4SCN gave mononuclear non-electrolytic complex **III**. The neutral complex occupies a position on a twofold axis. The independent part of the unit cell contains half of the Zn^{2+} cation, one isothiocyanate anion, and one PaoH ligand (Fig. 1c). The Zn(II) coordination polyhedron is an N_6 octahedron. The Zn–N distances are in the range of 2.045(4)–2.329(4) Å and the endocyclic NZnN angle is 73.25(14)° (Table 2). In **III**, two PaoH ligands connected by a twofold axis are located almost in *trans*-positions, thus demonstrating even higher mobility; the dihedral angle between the planes of metallacycles is decreased to 79.61°. Unlike **I**, in the case of **III**, the intermolecular OH···S hydrogen bonds involving the terminal sulfur atom of NCS^- link the complex molecules to form infinite layers (Fig. 2b, Table 3).

Thus, the structural diversity of monomolecular heteroligand Zn(II) complexes with the chelating pyridine-2-aldoxime ligand was supplemented by three new complexes, which demonstrated a substantial contribution of the second ligand (acetate or isothiocyanate anion or DMSO) to the geometry of the metal coordination polyhedron.

Compound **I** was tested as an agent enhancing the amylolytic activity of the biotechnological producer strain *Aspergillus niger* CNMN FD 06. The presence of zinc, which is a vital nutrition element for microorganisms, suggests that the complex could affect the physiological processes of the micromycete [45, 46].

The results show that during culturing of the strain under classic conditions (control), the maximum enzymatic activity of both standard (50.68 U/mL, pH 4.7) and acid-resistant (56.56 U/mL, pH 2.5) amylases is observed on the 5th day of culturing. On the 6th day of culturing, the activity of both types of amylases sharply decreases: 20.44 U/mL (pH 4.7) and 38.08 U/mL (pH 2.5) (Table 4).

The introduction of the complex into the culture medium has a stimulating effect, which amounts to

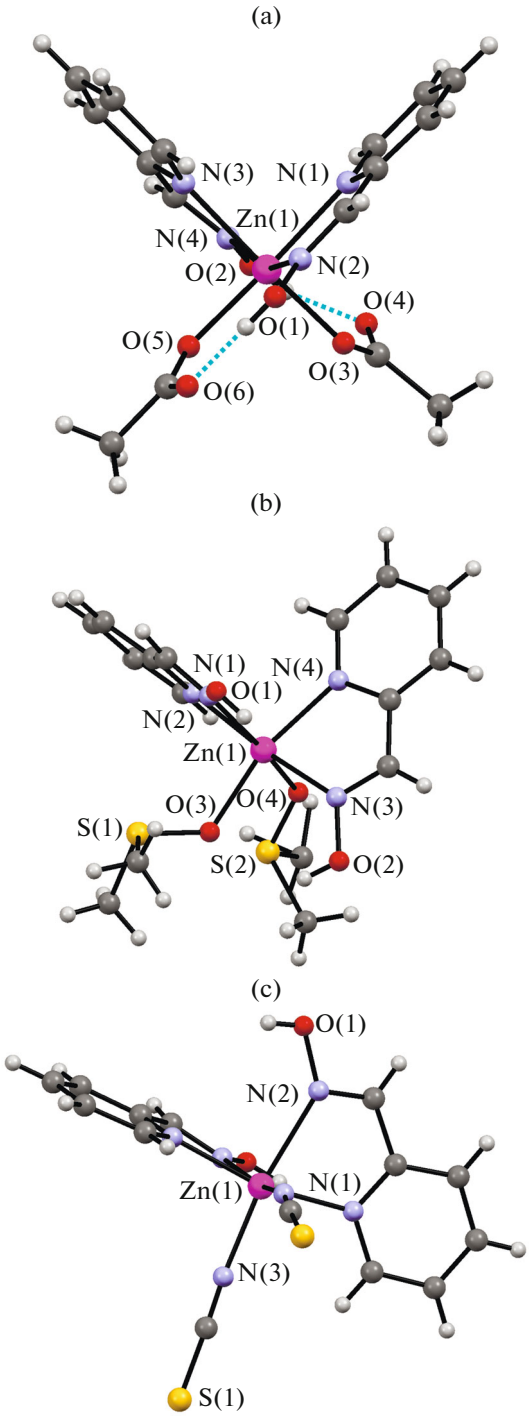


Fig. 1. Structures of (a) complex **I**, (b) $[Zn(PaoH)_2(DMSO)_2]^{2+}$ cation in **II**, and (c) complex **III** with partial atom numbering.

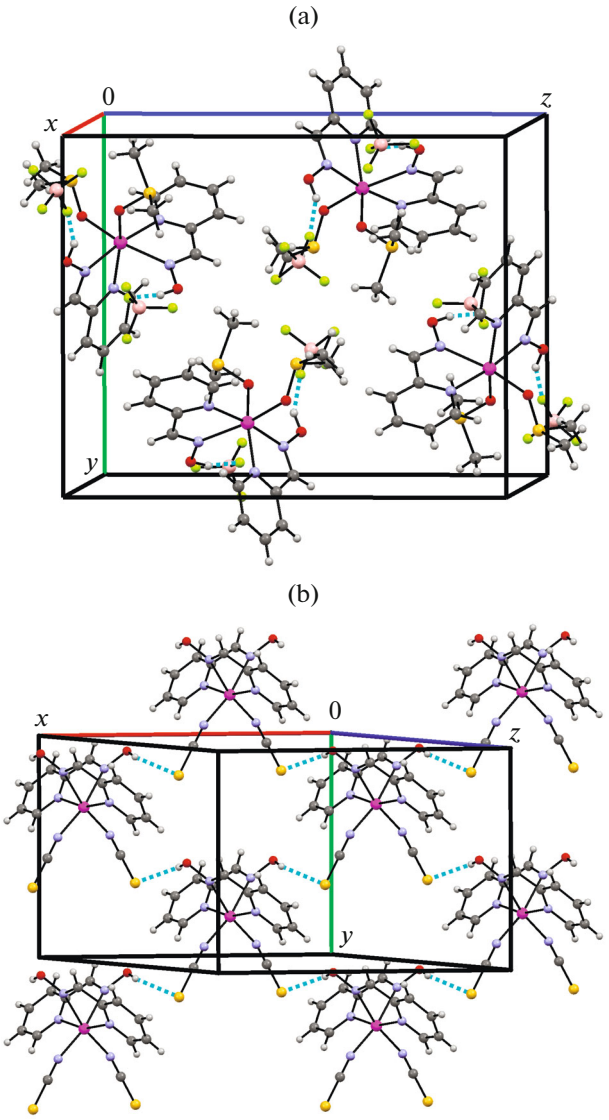


Fig. 2. Fragment of packing in the crystals of (a) **II** and (b) **III**.

35.63% (5th day) and 33.85% (6th day) for standard amylases and to 7.32 and 6.22%, respectively, for acid-resistant amylases. In the case of acid-labile amylases, the stimulation effect was stable within the concentrations range of 5–15 mg/L, being higher than the control level at any of the tested concentrations both on the 5th and 6th days. The stimulation effect for acid-resistant amylases is much less pronounced and is manifested at low concentrations of the complex (5 mg/L). As the concentration increases, the effect becomes unstable and at 15 mg/L, it becomes negative. The addition of the complex to the strain culture medium does not affect the micromycete development phases, the maximum amylase biosynthesis being observed on the 5th day of culturing, which coincides with that for the control.

Thus, it was found that zinc complex with pyridine-2-aldoxime, $[Zn(CH_3COO)_2(PaoH)_2]$ (**I**), in the optimal concentration of 5–10 mg/L can be used for stimulation of the biosynthesis of standard (pH 4.7) amylases of the micromycete *Aspergillus niger* CNMN FD 06. The presence of the complex in the

Table 4. Change in the enzymatic activity of amylases of the micromycete *Aspergillus niger* CNMN FD 06 induced by $[Zn(CH_3COO)_2(PaoH)_2]$ (**I**)

Concentration, mg/L	Standard amylases (pH 4.7)				Acid-resistant amylases (pH 2.5)			
	5th day		6th day		5th day		6th day	
	U/mL	%	U/mL	%	U/mL	%	U/mL	%
5	68.74	135.63	27.36	133.85	60.82	107.32	40.45	106.22
10	68.74	135.63	25.64	125.44	57.97	102.50	40.45	106.22
15	65.11	128.47	23.91	116.98	46.58	82.35	34.13	89.62
Control	50.68	100.0	20.44	100.0	56.56	100.0	38.08	100.0

medium does not affect the duration of culturing of the producer strain.

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