ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2017, Vol. 43, No. 7, pp. 433–440. © Pleiades Publishing, Ltd., 2017.
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Synthesis and Structure of Some Zinc and Cadmium 1,2-Cyclohexanedione Dioximines

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Received October 2, 2016

Abstract—The complexes $[Zn(CH_3COO)_2(NioxH_2)(DMF)(H_2O)]$ (**I**), $[Cd(CH_3COO)_2(NioxH_2)(DMF)(H_2O)]$ (**II**), $[Zn(CH_3COO)_2(NioxH_2)(S\text{-}Nia)(H_2O)] \cdot DMF$ (**III**), $[Zn(CH_3COO)_2(NioxH_2)(Nia)(H_2O)]$ (**IV**), and $[Zn(CH_3COO)_2(NioxH_2)(INia)(H_2O)]$ (**V**), where $NioxH_2$ is 1,2-cyclohexanedione dioxime, S-Nia is thionicotinamide, Nia is nicotinamide, and INia is *iso*-nicotinamide, were prepared and investigated. Compounds **I**–**III** were studied by X-ray diffraction (CCDC nos. 1505280–1505282 for **I**–**III**, respectively). Testing of zinc complexes containing various ligands demonstrated that at the optimized concentration (5 mg/L), they can be used for stimulating biosynthesis of both standard (57.14%, pH 4.7) and acid-labile (17.63%, pH 2.5) amylases by the micromycete *Aspergillus niger* CNMN FD 06 without affecting the duration of producer culturing.

Keywords: coordination compounds, crystal structure, d^{10}-metals, 1,2-cyclohexanedione dioxime
DOI: 10.1134/S1070328417070053

INTRODUCTION

Although dioxime-based coordination compounds have been studied in detail [1], published data on zinc and cadmium compounds are scarce [2–4]; meanwhile, complexes of diverse composition and molecular structure can be prepared with these metals. Mononuclear Zn and Cd complexes obtained in the presence of organic and inorganic anions have been reported [5–7]. Trinuclear heterometal zinc compounds with dioximes are of interest for the production of monomolecular magnets [8–10] based on Cr(III)Zn(II)Cr(III) and Mn(IV)Zn(II)Mn(IV) complexes containing oximate anions as bridging ligands. In a study of the interaction of 3*d* metals with 1,2-cyclohexanedione dioxime ($NioxH_2$) in strongly acidic solutions, tris-dioximines and their structural analogs, transition metal *cis*-dioximines, have been prepared [11, 12].

The structural diversity of zinc and cadmium 1,2-cyclohexanedione dioximines/1,2-cyclohexanedione dioximates is formed by mono- and binuclear compounds as well as coordination polymers with bipyridine and dicarboxyl bridging ligands [13–16]. For some of these compounds, a relationship has been established between the nature of the anion in the initial salt and the architecture of the resulting coordination compound. Coordination compounds containing complex cations and metallate anions have been prepared [17, 18]. Compounds with different dioximes coordinated to the complexing metal have been reported [19]. *d*-Metal tris-dioximate clathrochelates of various structural types are of interest [20]. Dioximates can be used for electrocatalytic production of hydrogen [21]. Several tris-dioximate clathrochelates have been prepared as potential agents for the therapy of cancer. The self-assembly of clathrochelates and their interaction with nucleic acids can be employed in immunology and molecular biology [22, 23].

Since Zn(II) and Cd(II) dioximates have been poorly studied and the classical dioximes as bidentate ligands are convenient objects for the formation of stable chelates, we decided to synthesize a series of complexes based on these ligands. We attempted to prepare complexes with various classical dioximes (dimethylglyoxime, 1,2-cyclohexanedione dioxime, diphenyldioxime), but succeeded in the synthesis of only $NioxH_2$-based complexes, namely,

$[Zn(CH_3COO)_2(NioxH_2)(DMF)(H_2O)]$ (**I**), $[Cd(CH_3COO)_2(NioxH_2)(DMF)(H_2O)]$ (**II**), $[Zn(CH_3COO)_2(NioxH_2)(S\text{-}Nia)(H_2O)] \cdot DMF$ (**III**), $[Zn(CH_3COO)_2(NioxH_2)(Nia)(H_2O)]$ (**IV**), and $[Zn(CH_3COO)_2(NioxH_2)(INia)(H_2O)]$ (**V**), where S-Nia is thionicotinamide, Nia is nicotinamide, INia is *iso*-nicotinamide. Compounds **I**–**III** were studied by X-ray diffraction.

EXPERIMENTAL

Synthesis of I. $NioxH_2$ (21.00 mg, 0.15 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). The solution was heated with magnetic stirring for 10 min. On slow evaporation of the yellowish transparent solution, colorless crystals of prismatic habitus precipitated. Yield, ~32%. The product was soluble in DMSO, DMF, methanol, and ethanol and poorly soluble in water.

For $C_{13}H_{25}N_3O_8Zn$

anal. calcd., %:	C, 37.46;	H, 6.05;	N, 10.08.
Found, %:	C, 37.18;	H, 5.72;	N, 9.81.

Synthesis of II. The complex was prepared similarly to **I** from $Cd(CH_3COO)_2 \cdot 2H_2O$. On slow evaporation of the yellowish transparent solution, colorless crystals precipitated. Yield, ~27%. The product was soluble in DMSO, DMF, methanol, and ethanol and poorly soluble in water.

For $C_{13}H_{25}N_3O_8Cd$

anal. calcd, %:	C, 33.67;	H, 5.43;	N, 9.06.
Found, %:	C, 33.42;	H, 5.27;	N, 8.93.

Synthesis of III. $NioxH_2$ (21.00 mg, 0.15 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). The resulting solution was heated with magnetic stirring for 10 min, and thionicotinamide (28.0 mg, 0.2 mmol) was added. On slow evaporation of the yellowish transparent solution, yellow crystals precipitated. Yield, ~18%. The product was soluble in DMSO, DMF, methanol, and ethanol and poorly soluble in water.

For $C_{16}H_{24}N_4O_7ZnS$

anal. calcd, %:	C, 39.88;	H, 5.02;	N, 11.63.
Found, %:	C, 39.71;	H, 4.87;	N, 11.42.

Syntheses of IV and V were performed similarly to the synthesis of **III** with the difference that nicotinamide (**IV**) or *iso*-nicotinamide (**V**) was added instead of thionicotinamide. Complexes **IV** and **V** have the same empirical formula.

For $C_{16}H_{24}N_4O_8Zn$

anal. calcd., %:	C, 41.25;	H, 5.19;	N, 12.04.
Found, %:	C, 40.83;	H, 5.06;	N, 11.97 (**IV**).
	C, 41.02;	H, 5.11;	N, 11.93 (**V**).

IR spectra were recorded on a FT-IR Perkin-Elmer Spectrum 100 instrument in mineral oil in the 4000–400 cm^{-1} range and in the ATR mode 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 the least-squares method in the full-matrix anisotropic approximation for non-hydrogen atoms (SHELX-97) [24]. The positions of hydrogen atoms of oxime groups and water molecules were found from difference Fourier maps, the other were calculated geometrically and refined isotropically in the "rigid body" model. The DMF molecule in **III** is disordered over two sites and refined in the anisotropic approximation with occupancies of 0.65(2) and 0.35(2). The crystal data and X-ray experiment details for **I**–**III** are summarized in Table 1, the interatomic distances and bond angles are listed in Table 2, and the geometric parameters of hydrogen bonds (HBs) are given in Table 3.

The positional and thermal parameters of **I**–**III** are deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 1505280–1505282, respectively; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Biological methods. The biological properties of the complexes were tested by the degree of their influence on the enzyme formation by the micromycete *Aspergillus niger* CNMN FD 06. Black aspergilli are active producers of amylolytic enzymes, which hydrolyze starch-containing substrates both under usual conditions (pH 4.7) and under extremely acidic conditions (pH 2.5).

The producer was cultured by the submerged culture method in a medium with the previously selected composition [25] (pH 5.0, culturing temperature of 28–30°C) with continuous stirring on a shaker with rotation at 180–200 rpm. The tested complexes were inserted into the sterile culture medium in concentrations of 5, 10, or 15 mg/L simultaneously with the seed material. The medium in which no complex was added served as the control. The effect of complexes on the activity of micromycete amylases was measured over time on the 5th and 6th day of culturing, which corresponds to the period of maximum biosynthesis for the

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

Parameter	Value		
	I	**II**	**III**
M	416.73	463.76	554.92
System	Orthorhombic	Triclinic	Monoclinic
Space group	*Pnma*	$P\bar{1}$	$P2_1/n$
a, Å	15.778(3)	9.6497(7)	16.1857(11)
b, Å	11.394(2)	9.8708(7)	8.0387(4)
c, Å	10.510(2)	11.0641(8)	20.0836(13)
α, deg	90	66.463(7)	90
β, deg	90	77.976(6)	100.130(7)
γ, deg	90	89.621(6)	90
V, Å^3	1889.4(7)	941.53(13)	2572.4(3)
Z	4	2	4
ρ(calcd.), g/cm^3	1.465	1.636	1.433
μ, mm^{-1}	1.343	1.203	1.087
F(000)	872	472	1160
Crystal size, mm	0.2 × 0.06 × 0.04	0.35 × 0.3 × 0.2	0.25 × 0.12 × 0.05
Range of θ, deg	2.936–25.493	2.993–26.00	2.942–25.00
Ranges of reflection indices	$-16 \le h \le 19$, $-6 \le k \le 13$, $-12 \le l \le 8$	$-11 \le h \le 11$, $-11 \le k \le 12$, $-8 \le l \le 13$	$-19 \le h \le 18$, $-9 \le k \le 5$, $-11 \le l \le 23$
Number of measured/ unique reflections (R_{int})	4274/1838 (0.0415)	5405/3654 (0.0299)	7924/4493 (0.0855)
Number of reflections with $I > 2\sigma(I)$	1301	3162	1972
Number of refined parameters	135	238	341
GOOF	0.999	1.000	0.857
R_1-, wR_2-factor ($I > 2\sigma(I)$)	0.0512, 0.1232	0.0366, 0.0731	0.0673, 0.0800
R_1-, wR_2- factor (for the whole array)	0.0819, 0.1404	0.0454, 0.0787	0.1751, 0.1132
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e Å^{-3}	0.426, –0.389	0.471, –0.456	0.510, –0.453

Aspergillus niger CNMN FD 06 strain under the classic culturing conditions.

The amylolytic activity was measured by the photocolorimetric method based on the degree of starch degradation to dextrins with various molecular masses under standard (pH 4.7) and extremely acidic (pH 2.5) conditions [26].

RESULTS AND DISCUSSION

The IR spectra of complexes **I**–**V** contain bands at 1662–1646 cm^{-1} corresponding to the $\nu(C{=}N)_{oxime}$ mode and at 1076–1063 cm^{-1} due to the $\nu(N{-}O)_{oxime}$ mode. In the case of **III**–**V**, the band at 1616–1603 cm^{-1} corresponds to the pyridine ring vibrations. The strong bands at 1554–1543 and 1415–1401 cm^{-1} are caused by carboxyl group vibrations, $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$. The presence of acetate ions is also indicated by the $\nu_{as}(CH_3)$ (2951–2938 cm^{-1}) and $\nu_s(CH_3)$ (2875–2860 cm^{-1}) bands. The bands at 3328 (**III**), 3306 (**IV**), 3298 (**V**) cm^{-1} and 3161 (**III**), 3174 (**IV**), 3177 (**V**) cm^{-1} attest to the presence of valence-bonded NH_2 group. The strong band at 1032 cm^{-1} in the spectrum of **III** may correspond to C=S vibrations.

The isomorphous compounds **I** and **II** differ only by the metal cation (Fig. 1). The mononuclear complexes **I** and **II** are prepared in like manners by the reaction of the corresponding metal acetate with $NioxH_2$ in 1 : 1.5 ratio in a CH_3OH–DMF solution. Complex **I** occupies a special position in mirror plane *m*; **II** is in a general position. The metal cation is chelated by $NioxH_2$ via the oxime nitrogen atoms and also coordinated by two monodentate acetate anions and water and DMF molecules (Fig. 1). The coordi-

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

Bond	*d*, Å	Bond	*d*, Å
	I		
Zn(1)–O(1)	2.042(3)	Zn(1)–O(1*w*)	2.083(4)
Zn(1)–O(3)	2.139(4)	Zn(1)–N(1)	2.208(3)
	II		
Cd(1)–O(1*w*)	2.304(3)	Cd(1)–O(7)	2.327(2)
Cd(1)–O(3)	2.221(3)	Cd(1)–N(1)	2.385(3)
Cd(1)–O(5)	2.214(2)	Cd(1)–N(2)	2.383(3)
	III		
Zn(1)–O(1*w*)	2.135(4)	Zn(1)–N(1)	2.173(5)
Zn(1)–O(3)	2.036(4)	Zn(1)–N(2)	2.194(5)
Zn(1)–O(5)	2.053(4)	Zn(1)–N(3)	2.181(5)
Angle	ω, deg	Angle	ω, deg
	I		
O(1)*Zn(1)O(1)	88.87(17)	O(1)Zn(1)N(1)	99.74(12)
O(1)Zn(1)O(1*w*)	93.43(12)	O(1*w*)Zn(1)N(1)	89.64(13)
O(1)Zn(1)O(3)	90.02(12)	O(3)Zn(1)N(1)	86.43(13)
O(1*w*)Zn(1)O(3)	175.16(18)	N(1)*Zn(1)N(1)	71.45(17)
O(1)Zn(1)N(1)*	170.67(12)		
	II		
O(5)Cd(1)O(3)	94.44(10)	O(1*w*)Cd(1)N(2)	95.24(10)
O(5)Cd(1)O(1*w*)	89.08(10)	O(7)Cd(1)N(2)	85.97(9)
O(3)Cd(1)O(1*w*)	91.21(10)	O(5)Cd(1)N(1)	163.40(10)
O(5)Cd(1)O(7)	90.55(9)	O(3)Cd(1)N(1)	101.38(10)
O(3)Cd(1)O(7)	87.66(10)	O(1*w*)Cd(1)N(1)	85.64(10)
O(1*w*)Cd(1)O(7)	178.77(10)	O(7)Cd(1)N(1)	95.05(9)
O(5)Cd(1)N(2)	97.65(10)	N(2)Cd(1)N(1)	67.27(9)
O(3)Cd(1)N(2)	166.37(10)	O(1*w*)Cd(1)N(2)	95.24(10)
	III		
O(3)Zn(1)O(5)	87.35(18)	O(1*w*)Zn(1)N(3)	177.71(18)
O(3)Zn(1)O(1*w*)	91.88(18)	N(1)Zn(1)N(3)	92.63(19)
O(5)Zn(1)O(1*w*)	89.38(19)	O(3)Zn(1)N(2)	172.38(19)
O(3)Zn(1)N(1)	100.30(19)	O(5)Zn(1)N(2)	99.66(19)
O(5)Zn(1)N(1)	172.11(19)	O(1*w*)Zn(1)N(2)	85.25(19)
O(1*w*)Zn(1)N(1)	88.42(19)	N(1)Zn(1)N(2)	72.61(19)
O(3)Zn(1)N(3)	89.94(18)	N(3)Zn(1)N(2)	93.11(19)
O(5)Zn(1)N(3)	89.31(18)		

* Symmetry code: $x, -y + 1/2, z$.

nation polyhedra of metal atoms are distorted octahedra formed by the N_2O_4 group of donor atoms. The $NioxH_2$ ligand forms a five-membered chelate ring with NMN endocyclic angle of 71.45(17)° in **I** and 67.27(9)° in **II** and M–N distances of 2.208(3) Å in **I** and 2.385(3) and 2.383(3) Å in **II** (Table 2). All oxygen-containing ligands are coordinated to metal atoms in the monodentate fashion. Two acetate anions complete the equatorial plane and the solvent molecules (water and DMF) occupy the axial positions. The metal–O distances in the coordination polyhedra are 2.042(3)–2.139(4) Å in **I** and 2.214(2)–2.327(2) Å in **II**.

The oxygen atoms of acetate anions that are not metal coordinated are involved in the intramolecular O–H···O HBs with oxime groups (Table 3). The

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

D–H···A	Distance, Å		DHA angle, deg	Symmetry codes for the acceptor
	H···A	D···A		
		I		
O(1*w*)–H(1*w*)···O(2)	1.78(4)	2.731(4)	175(4)	$-x, -y, 1-z$
O(5)–H(1O5)···O(2)	1.67(6)	2.548(5)	169(5)	x, y, z
		II		
O(1*w*)–H(2*w*)···O(4)	1.858(18)	2.710(4)	177(4)	$2-x, 1-y, 1-z$
O(1*w*)–H(1*w*)···O(6)	1.909(18)	2.756(4)	178(4)	$2-x, 2-y, -z$
O(2)–H(2)···O(6)	1.81	2.584(4)	157.4	x, y, z
O(1)–H(1)···O(4)	1.79	2.608(4)	170.8	x, y, z
		III		
N(4)–H(1N4)···O(6)	1.970(12)	2.812(7)	166(4)	$3/2-x, y+1/2, 3/2-z$
N(4)–H(2N4)···S(1)	2.566(17)	3.391(6)	161(4)	$2-x, 1-y, 2-z$
O(1)–H(1)···O(4)	1.76	2.576(6)	175.6	x, y, z
O(2)–H(2)···O(6)	1.77	2.585(6)	175.6	x, y, z
O(1*w*)–H(1*w*)···O(4)	1.877(13)	2.723(6)	167(5)	$1-x, -y, 2-z$

mononuclear complexes in the crystals are associated via O–H···O HBs involving water molecules and acetate anions. The complexes related by the inversion center are joined via two OH···O HBs to form identical centrosymmetrical chains along the [010] direction in **I** and [1–1–1] direction in **II** (Table 3, Fig. 2). Only van der Waals interactions occur between the chains in the crystals.

In order to study the structural diversity and exchange reactions at the metal cation, additional ligands were introduced in the system. In the case of heterofunctional ligands, this provides the possibility to monitor the competitiveness of various functional groups during complex formation. The reaction of zinc acetate with $NioxH_2$ and S-Nia in 1 : 1.5 : 2 ratio in a CH_3OH–DMF–H_2O mixture (3 : 1 : 1) gave complex **III** in which the zinc ion is coordinated to two acetate anions and $NioxH_2$, S-Nia, and water molecules (Fig. 3). Comparison of the coordination

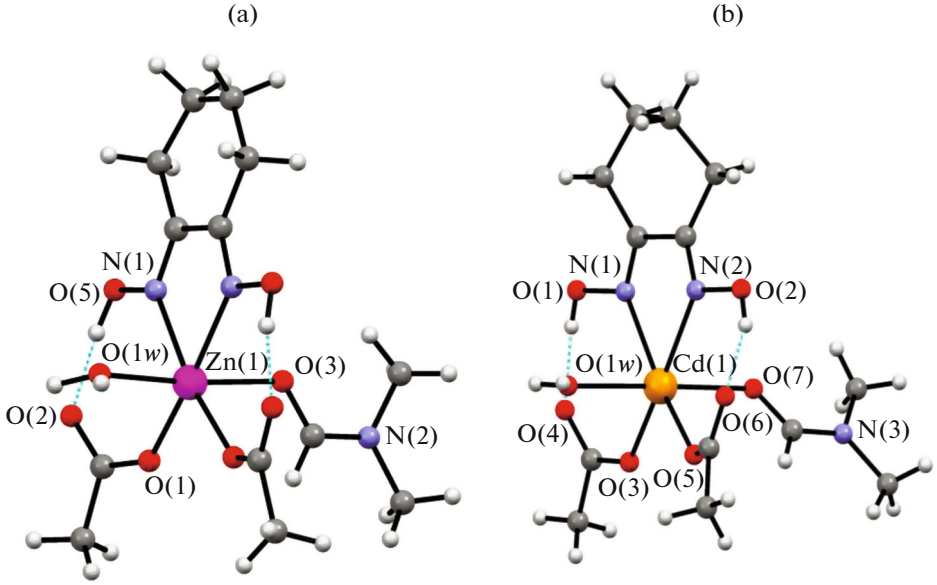

Fig. 1. Structures of mononuclear complexes (a) **I** and (b) **II** with partial atom numbering and indication of intramolecular hydrogen bonds.

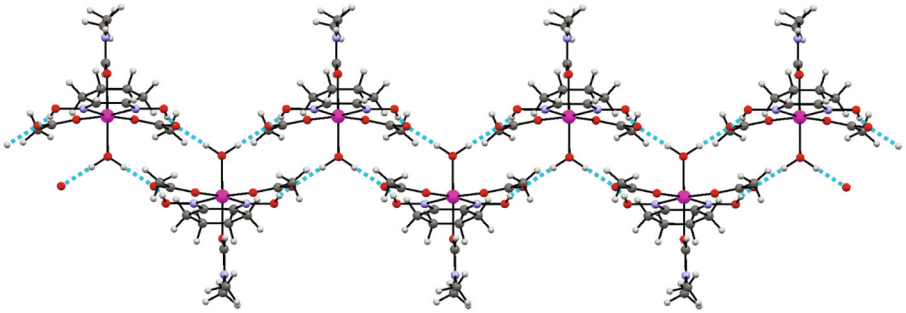

Fig. 2. Fragment of H-bonded chain in **I**.

environment in **III** with those in **I** and **II** attests to the replacement of the DMF molecule by S-Nia in the metal coordination polyhedron. Similarly to **I** and **II**, the zinc coordination polyhedron in **III** is a distorted octahedron formed by the N_3O_3 group of donor atoms. The $NioxH_2$ ligand forms a five-membered chelate ring with the N–Zn–N endocyclic angle of 72.61(19)° and Zn–N distances of 2.173(5) and 2.194(5) Å. The axial S-Nia ligand coordinates the metal atom in the monodentate fashion via heterocycle nitrogen (Zn–N 2.181(5) Å). All oxygen-containing ligands coordinate the metal atom in the monodentate fashion. Two acetate anions complete the equatorial plane and the water molecule occupies the second axial position.

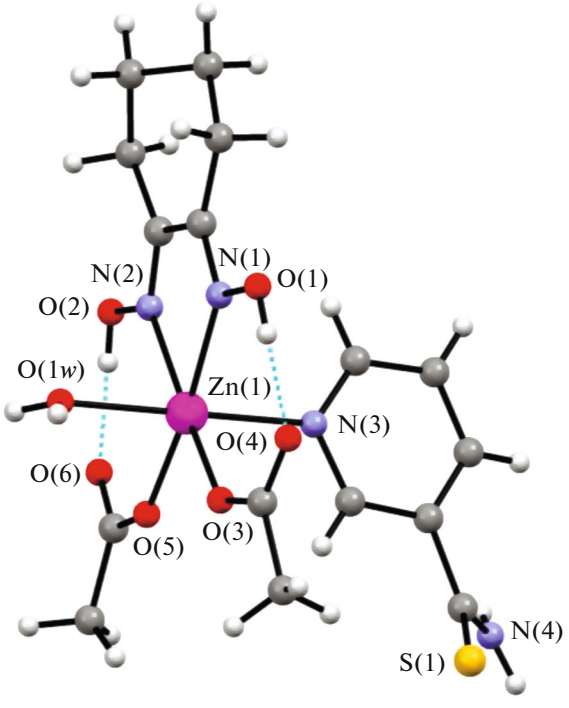

Fig. 3. Structure of mononuclear complex **III** with partial atom numbering and indication of intramolecular hydrogen bonds.

The Zn–O distances are in the 2.036(4)–2.135(4) Å range. The replacement of the axial ligand gives rise to diverse intermolecular HBs; apart from the O–H···O contacts, which are also present in **I** and **II**, the hydrogen bonds in **III** include also N–H···S and N–H···O bonds (Table 3) and combine the complexes into a three-dimensional H-bonded network with inclusion of outer-sphere DMF molecules (Fig. 4).

In recent years, it was found that transition metal complexes play a considerable role in processes taking place in living organisms, exhibiting either stimulatory or inhibitory (antiviral, antimicrobial, antitumor, etc.) action on their growth and development. Complexes were found to stimulate the growth and productivity of some microalgae (*Spirulina platensis* (*Nordst*) Geitl and *Dunaliella salina* Teod.) promising for industrial culturing and the growth and rooting of some plants for the preparation of pharmaceuticals [27, 28]. They also act as regulators of biosynthesis of biologically active compounds, including extracellular enzymes, and a broad range of microorganisms [29, 30].

Investigation of the biological activities of new coordination compounds with metals is a topical issue in view of their possible practical use and the search for new applications. Elucidation of the causes behind their high biological activity and understanding of the fundamental role of these complexes in the living cell metabolism can serve as theoretical grounds for the targeted synthesis of compounds with specified properties.

The ability of the complexes to affect the physiological properties of microorganisms was studied by testing compounds **III**–**V** as potential biostimulators of the amylolytic activity of the producer strain *Aspergillus niger* CNMN FD 06.

From the biological standpoint, the good prospects of these complexes are attributable, first of all, to the presence of nutrition elements, many of which (including zinc) in trace amounts are vital for living organisms [31–34].

The results (Table 4) show that the maximum enzymatic activity of both standard (50.68 U/mL, pH 4.7) and acid-resistant (56.56 U/mL, pH 2.5)

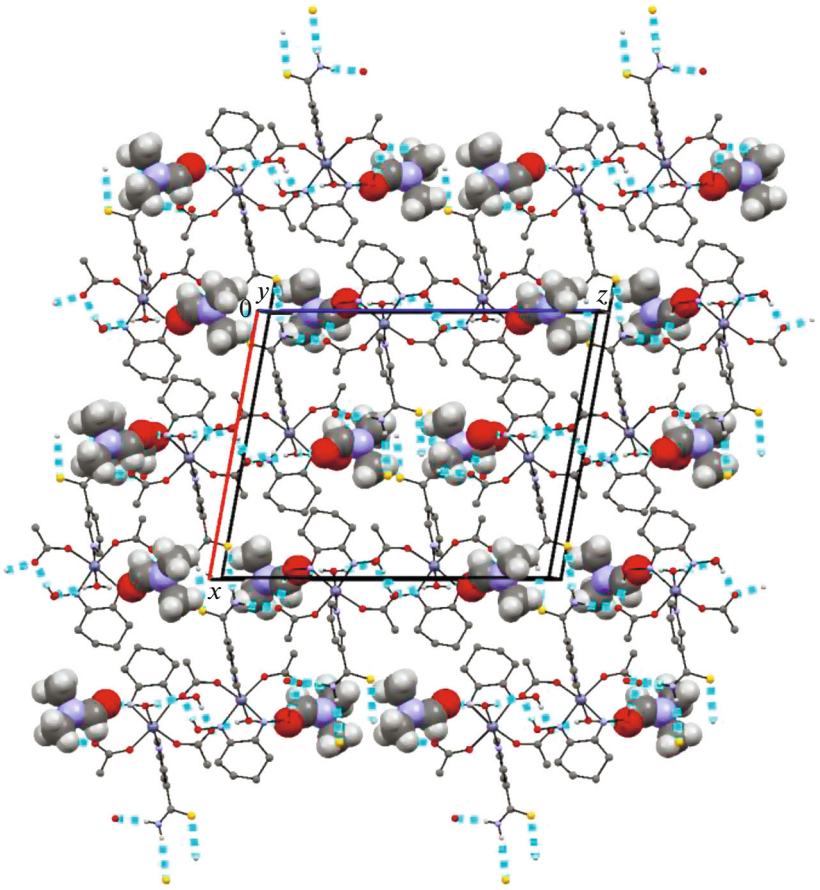

Fig. 4. Fragment of packing in **III** with indication of hydrogen bonds and outer-sphere DMF molecules.

Table 4. Change in the enzymatic activity of standard (pH 4.7) and aid-resistant (pH 2.5) amylases of the micromycete *Aspergillus niger* CNMN FD 06 induced by zinc complexes with various ligands

Complex	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	%
III	5	76.01	149.98	29.09	142.32	66.53	117.63	37.16	97.58
	10	65.11	128.47	29.09	142.32	52.29	92.45	27.82	73.06
	15	65.11	128.47	27.36	133.85	52.29	92.45	26.24	68.91
IV	5	79.64	157.14	32.55	159.24	66.53	117.63	38.87	102.07
	10	70.56	139.22	27.36	133.85	49.43	87.39	37.16	97.58
	15	66.92	132.05	27.36	133.85	46.59	82.37	30.97	81.33
V	5	72.37	142.79	29.09	142.32	63.67	112.57	37.16	97.58
	10	68.74	135.63	29.09	142.32	63.67	112.57	30.97	81.33
	15	57.84	114.13	25.64	125.44	43.74	77.33	27.82	73.06
Control		50.68	100.0	20.44	100.0	56.56	100.0	38.08	100.0

amylases is observed on the 5th day of culturing. On the 6th day of culturing, the activity of both types of amylases sharply decreases down to 20.44 U/mL (pH 4.7) and 38.08 U/mL (pH 2.5).

Further analysis of the results indicates that the given strain is sensitive to the addition of zinc complexes to the culture medium. They affect most noticeably the enzymatic activity of amylases, which hydrolyze starch-containing materials at pH 4.7. Their activity is much higher in the optimized media than in control ones. For example, with the zinc nicotinamide complex (**IV**), the enzymatic activity in the test run is 79.64, 70.56, or 66.92 U/mL, depending on the concentration used vs. 50.68 U/mL in the control run.

Compounds **III**–**V** are roughly equal in the efficiency. The concentration of 5 mg/L, which provides high stimulatory effect (42.79–57.14%; 5th day of culturing), can be considered to be the optimal. On the 6th day of culturing of the producer, the stimulatory effect is retained at approximately the same level, being 42.32–59.24% of the control level of the same day.

The effect of the test complexes on the activity of acid-resistant amylases proved to be less pronounced. As in the case of acid-labile amylases, the stimulatory effect is manifested on the 5th day of culturing at the same concentration (5 mg/L) and amounts to 17.63 (**III**), 17.63 (**IV**), and 12.57% (**V**).

Thus, testing of zinc complexes with various ligands demonstrated that at the optimized concentration of 5 mg/L, they can be used for stimulation of the biosynthesis of both standard (57.14%, pH 4.7) and acid-resistant (17.63%, pH 2.5) amylases by the micromycete *Aspergillus niger* CNMN FD 06.

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Translated by Z. Svitanko