

CRYSTAL STRUCTURES OF [*N'*-(2- OXIDOBENZYLIDENE)-*N*-(PROP-2-EN-1-YL)- CARBAMOHDRAZONOTHIOATO(2-)](1,10- PHENANTHROLINE)COPPER AND [*N'*-(2- OXIDOBENZYLIDENE)-*N*-(PROP-2-EN-1-YL)- CARBAMOHDRAZONOTHIOATO(2-)](2,2'- BIPYRIDINE)COPPER HEMIHYDRATES

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The crystal structures and biological properties of [*N'*-(2-oxidobenzylidene)-*N*-(prop-2-en-1-yl)-carbamohydrazonothioato(2-)](1,10-phenanthroline)copper hemihydrate [Cu(1,10-Phen)(L)]·0.5H₂O (**I**) and [*N'*-(2-oxidobenzylidene)-*N*-(prop-2-en-1-yl)-carbamohydrazonothioato(2-)](2,2'-bipyridine)copper hemihydrate [Cu(2,2'-BPY)(L)]·0.5H₂O (**II**), where H₂L is 2-(2-hydroxybenzylidene)-*N*-(prop-2-en-1-yl)hydrazinecarbothioamide, are determined. The asymmetric unit of the unit cell in the crystal structures of **I** and **II** contains a copper complex with bidentate amine and a ligand coordinated by the azomethine nitrogen atom, the deprotonated phenolic oxygen atom, and the sulfur atom in the thiol form. The coordination polyhedron of the copper atom in compounds **I** and **II** is a distorted tetragonal pyramid. Obtained coordination compounds **I** and **II** exhibit antimicrobial and antifungal activities and have minimum inhibitory concentration and bactericidal concentration values in a range of 1.5-500 µg/mL. The study of the antioxidant activity shows that compounds **I** and **II** are less active than uncoordinated thiosemicarbazone H₂L, but more active than trolox used in medical practice.

DOI: 10.1134/S0022476622060075

Keywords: Cu(II) complexes, salicylaldehyde 4-allylthiosemicarbazone, mixed-ligand amine-containing complexes, antimicrobial, antifungal, and antioxidant activities.

INTRODUCTION

Mixed-ligand transition metal complexes containing donor nitrogen, oxygen, sulfur atoms often exhibit biological properties which directly depend on the structures of these compounds. One of these ligands are thiosemicarbazones. They

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are able to form stable complexes with transition metal ions [1]. The biological activity of these substances is greatly influenced by the nature of the central atom and the substituent in the thiosemicarbazone N₄ position [2].

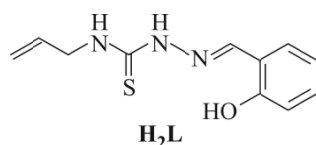
Among transition metals, copper is one of the main microelements affecting nerve cells and the immune system [3]. Copper(II) complexes with thiosemicarbazones exhibit biological activities: antifungal, antimicrobial [4], and anticancer [5].

Copper coordination compounds with salicylaldehyde 4-allylthiosemicarbazone (2-(2-hydroxybenzylidene)-*N*-(prop-2-en-1-yl)hydrazinecarbothioamide, H₂L) were previously described in [6].

The introduction of heteroaromatic amines into the inner sphere of these complexes changes their biological activity [7-9].

Previously, we published the results of the synthesis and study of the biological activity of copper(II) complexes with salicylaldehyde 4-allylthiosemicarbazone and monodentate heteroaromatic amines in the inner sphere (imidazole, 4-methylpyridine, 3,5-dibromopyridine) [10]. The obtained coordination compounds exhibited antimicrobial, antifungal, antioxidant, and anticancer biological activities. Therefore, it is of interest to study how bidentate amine substitution for monodentate amine affects the structures of mixed-ligand coordination compounds formed and their biological properties.

The work aims to synthesize and establish the structural features and biological properties of [*N'*-(2-oxidobenzylidene)-*N*-prop-2-en-1-yl-carbamohydrazonothioato(2-)](1,10-phenanthroline)copper hemihydrate [Cu(1,10-Phen)(L)]·0.5H₂O (**I**) and [*N'*-(2-oxidobenzylidene)-*N*-(prop-2-en-1-yl)-carbamohydrazonothioato(2-)](2,2'-bipyridine)copper hemihydrate [Cu(2,2'-BPY)(L)]·0.5H₂O (**II**), where H₂L is 2-(2-hydroxybenzylidene)-*N*-(prop-2-en-1-yl)hydrazinecarbothioamide (Scheme 1).



Scheme 1. Structural formula of salicylaldehyde 4-allylthiosemicarbazone.

EXPERIMENTAL

2-(2-Hydroxybenzylidene)-*N*-(prop-2-en-1-yl)hydrazinecarbothioamide was obtained by the previously described procedure [11].

Synthesis of compound **I**. A solution containing 10 mmol of 2-(2-hydroxybenzylidene)-*N*-(prop-2-en-1-yl)hydrazinecarbothioamide and 10 mmol of copper(II) acetate monohydrate in 30 mL of ethanol was stirred on heating for 40-50 min. After filtering off and drying in the air, the resulting complex was dissolved in a mixture of methanol and acetonitrile. To the reaction mixture 10 mmol of 1,10-phenanthroline were added and the obtained mixture was stirred for 30 min. As a result, fine crystalline green substance formed (yield of 90%), which was filtered off, washed with a small amount of methanol, and dried in the air.

Compound **II** was synthesized in a similar way, using 2,2'-bipyridine instead of 1,10-phenanthroline.

The elemental analysis was carried out according to the procedures described in [12].

The resistance of solutions of the complexes in methanol (20 °C, *c* of 0.001 mol/L) was measured using an R-38 rheochord measuring bridge (Table 1).

To determine the effective magnetic moments of compounds **I** and **II** the Gouy method was applied. The diamagnetism-corrected molar magnetic susceptibility was calculated from theoretical values of the magnetic susceptibility of organic compounds.

IR absorption spectra were recorded on a Bruker ALPHA spectrometer (4000-400 cm⁻¹).

TABLE 1. Physicochemical Characteristics of Copper Coordination Compounds **I** and **II** with 2-(2-hydroxybenzylidene)-*N*-(prop-2-en-1-yl)hydrazinecarbothioamide (H₂L)

No.	Yield, %	μ_{eff} (at 293 K), μ_{B}	χ (at 293 K), $\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$	Found, %			Formula	Calculated, %		
				Cu	N	S		Cu	N	S
I	90	1.88	8	13.02	14.58	6.71	C ₂₃ H ₁₉ CuN ₅ OS·0.5H ₂ O	13.07	14.41	6.60
II	87	1.92	10	13.78	15.28	7.08	C ₂₁ H ₁₉ CuN ₅ OS·0.5H ₂ O	13.75	15.16	6.94

Single crystal X-ray diffraction (XRD) of complexes **I** and **II** was performed on an Oxford Diffraction Xcalibur diffractometer [13]. The structures were solved by a direct method and refined by the least squares method in the anisotropic approximation for non-hydrogen atoms using the SHELX-97 programs [14] (Table 2). The hydrogen atoms were included in the refinement in geometrically calculated positions and their thermal factors U_{H} were taken 1.2 times larger than those of carbon and oxygen atoms bonded to them. Selected interatomic distances and bond angles, as well as hydrogen bonds are given in Tables 3 and 4; coordinates of the basis atoms of the studied structures have been deposited with the Cambridge

TABLE 2. Crystallographic Characteristics, Experiment and Refinement Data for the Structures of **I** and **II**

Parameter	I	II
	C ₄₆ H ₄₀ Cu ₂ N ₁₀ O ₃ S ₂	C ₄₂ H ₄₀ Cu ₂ N ₁₀ O ₃ S ₂
M	972.1	924.04
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Z	2	2
$a, b, c, \text{Å}$	10.3860(6), 12.4156(8), 16.7644(11)	10.5446(4), 11.5937(10), 16.962(1)
$\alpha, \beta, \gamma, \text{deg}$	87.922(6), 86.309(5), 89.798(5)	85.502(6), 86.587(4), 88.353(5)
$V, \text{Å}^3$	2155.8(2)	2063.0(2)
$D_x, \text{g/cm}^3$	1.499	1.488
Radiation: MoK α , $\lambda, \text{Å}$	0.71073	0.71073
μ, cm^{-1}	1.139	1.185
T, K	293(2)	293(2)
Sample size, mm	0.3×0.2×0.1	0.35×0.3×0.152
Diffractometer	XCalibur	XCalibur
Scanning mode	$\theta/2\theta$	$\theta/2\theta$
$\theta_{\text{max}}, \text{deg}$	25	25
h, k, l intervals	$-12 \leq h \leq 12, -14 \leq k \leq 14,$ $-19 \leq l \leq 19$	$-12 \leq h \leq 12, -12 \leq k \leq 13,$ $-20 \leq l \leq 20$
Reflections: measured / independent (N_1) / with $I > 2\sigma(I)$ (N_2)	7577 / 7577 / 6076	9957 / 9957 / 6911
Refinement method	LSM	LSM
Parameters	572	536
$R_1 / wR_2 (N_1)$	0.0742 / 0.1674	0.0608 / 0.078
$R_1 / wR_2 (N_2)$	0.0588 / 0.1576	0.0368 / 0.073
S	1.08	0.86
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}, \text{e/Å}^3$	1.75, -0.95	0.50, -0.40
Programs	SHELX-97	SHELX-97

TABLE 3. Selected Interatomic Distances and Bond Angles for Independent Complexes in **I (IA)** and **II (IIA)**

Parameter	I	IA	II	IIA
Bond	<i>d</i> , Å			
Cu1–N1	1.940(4)	1.947(4)	1.950(3)	1.958(3)
Cu1–O1	1.941(3)	1.941(3)	1.949(2)	1.936(2)
Cu1–N4	2.019(4)	2.021(4)	2.042(3)	2.033(3)
Cu1–S1	2.270(1)	2.279(1)	2.279(1)	2.282(1)
Cu1–N3	2.279(4)	2.286(4)	2.224(3)	2.210(3)
S1–C1	1.733(5)	1.739(5)	1.736(3)	1.744(3)
O1–C4	1.320(6)	1.314(6)	1.310(4)	1.318(4)
N1–C2	1.293(6)	1.287(6)	1.287(4)	1.282(3)
N1–N2	1.391(5)	1.386(5)	1.391(3)	1.394(3)
N2–C1	1.316(6)	1.322(6)	1.310(4)	1.314(4)
C3–C2	1.435(7)	1.433(7)	1.435(4)	1.445(4)
C4–C3	1.414(7)	1.423(7)	1.416(4)	1.422(4)
Angle	ω , deg			
N1–Cu1–O1	94.6(2)	94.4(2)	93.9(1)	94.5(0)
N1–Cu1–N4	175.9(2)	177.2(2)	176.1(1)	173.8(1)
O1–Cu1–N4	88.2(2)	88.3(1)	89.7(1)	89.1(1)
N1–Cu1–S1	85.0(1)	97.4(2)	84.8(1)	84.4(18)
O1–Cu1–S1	159.2(1)	161.3(1)	160.6(1)	155.4(1)
N4–Cu1–S1	93.4(1)	92.4(1)	92.4(1)	94.3(1)
N1–Cu1–N3	98.9(2)	100.7(2)	101.6(1)	97.5(1)
O1–Cu1–N3	99.3(2)	85.4(1)	89.7(1)	89.1(1)
N4–Cu1–N3	77.7(2)	77.0(2)	101.6(1)	97.5(1)
S1–Cu1–N3	101.2(1)	100.0(1)	103.1(1)	103.4(1)
C1–S1–Cu1	93.4(2)	93.8(2)	94.1(1)	93.4(1)
C4–O1–Cu1	126.1(3)	126.5(3)	126.3(2)	125.8(2)
C2–N1–N2	115.2(4)	115.1(4)	114.6(3)	115.8(3)
C2–N1–Cu1	124.5(3)	124.7(3)	124.9(2)	124.0(2)
N2–N1–Cu1	120.2(3)	120.3(3)	120.5(2)	120.0(2)
C1–N2–N1	113.4(4)	114.1(4)	113.7(3)	112.8(3)
N1–C2–C3	126.1(5)	125.9(5)	126.3(3)	126.7(3)
O1–C4–C3	123.3(4)	123.3(4)	124.2(3)	124.3(3)
C4–C3–C2	124.9(4)	124.7(5)	124.0(3)	124.3(3)
N2–C1–S1	124.8(4)	124.4(4)	124.7(3)	125.7(3)

Crystallographic Data Centre (CCDC 2116848-2116849). The geometrical calculations were performed and the figures were drawn using the PLATON program [15].

The antimicrobial, antifungal, and antioxidant activities were studied using the standard procedures described in [16, 17].

TABLE 4. Geometric Parameters of the Hydrogen Bonds of Compounds **I** and **II**

<i>D</i> –H··· <i>A</i> bond	Distance, Å			$\angle DHA$, deg	Coordinates of the <i>A</i> atom
	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>		
Compound I					
O1W–H···O1	0.85	2.18	3.014(6)	166	<i>x</i> , <i>y</i> , <i>z</i>
O1W–H···O1A	0.85	2.17	3.008(6)	171	<i>x</i> , <i>y</i> , 1+ <i>z</i>
N5A–H···N2	0.86	2.28	3.092(6)	157	<i>x</i> , <i>y</i> , <i>z</i>
N5–H···N2A	0.86	2.22	3.045(6)	161	<i>x</i> , <i>y</i> , <i>z</i>
Compound II					
N5A–H···N2	0.86	2.22	3.035(4)	158	1– <i>x</i> , 1– <i>y</i> , 2– <i>z</i>
O1W–H···O1	0.85	2.12	2.967(3)	174	<i>x</i> , <i>y</i> , <i>z</i>
O1W–H···1A	0.85	2.11	2.960(3)	173	1– <i>x</i> , 1– <i>y</i> , 1– <i>z</i>
N5–H···N2A	0.86	2.38	3.151(3)	149	1– <i>x</i> , 1– <i>y</i> , 2– <i>z</i>
C12–H···O1W	0.93	2.5	3.365(6)	155	– <i>x</i> , 1– <i>y</i> , 1– <i>z</i>
C12A–H···O1W	0.93	2.5	3.325(5)	148	<i>x</i> , <i>y</i> , <i>z</i>

RESULTS AND DISCUSSION

By the interaction of 2-(2-hydroxybenzylidene)-*N*-(prop-2-en-1-yl)hydrazinecarbothioamide with copper(II) acetate monohydrate and heteroaromatic amines (1,10-phenanthroline, 2,2'-bipyridine) complexes **I** and **II** were obtained and their compositions were determined from the elemental analysis data (Table 1).

Compounds **I** and **II** are very soluble in dimethyl formamide and dimethyl sulfoxide, soluble on heating in alcohol, poorly soluble in water.

The determination of the molar electrical conductivity (κ) of the synthesized complexes in methanol showed that compounds **I** and **II** were nonelectrolytes ($\kappa = 8\text{--}10 \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$) (Table 1).

The magnetochemical study of these compounds showed that they had the magnetic moment characteristic of one unpaired electron, which indicated their monomeric structure.

To determine the coordination pattern of thiosemicarbazone to copper(II) ions the comparative analysis of the IR spectra of H₂L and complexes **I**, **II** was performed. In the IR spectra of the synthesized compounds there are absorption bands in the ranges of 3380–3100 cm⁻¹, 1630–1570 cm⁻¹, 1400–1100 cm⁻¹, which characterize stretching vibrations of coordinated molecules of the respective ligands. In the 3380–3100 cm⁻¹ range of the IR spectra of compounds **I** and **II**, the $\nu(\text{O–H})$ absorption band of the phenol group disappears, and in the 1330 cm⁻¹ range, the $\nu(\text{C=S})$ absorption band disappears, from which it can be concluded that the H₂L ligand is doubly deprotonated. Moreover, there is a low-frequency shift of the $\nu(\text{C=N})$ absorption band by 18–59 cm⁻¹ in the spectra. This suggests that H₂L is coordinated to the central atoms by the deprotonated phenolic oxygen atom, the azomethine nitrogen atom, and the sulfur atom in the thiol form.

Single crystals suitable for XRD were obtained by recrystallization of the titled substances from ethanol.

The asymmetric unit of the unit cell in each of the crystal structures of **I** and **II** contains two copper complexes with bidentate amine and the L²⁻ ligand coordinated by the azomethine nitrogen atom, which is deprotonated by the phenolic oxygen atom and the sulfur atom in the thiol form (Figs. 1–4). In the outer sphere of these coordination compounds there are crystal water molecules. In the titled complexes, the coordination polyhedron of the copper atom is a distorted tetragonal pyramid whose base is composed of O1, S1 and N1 and N4 atoms. The apical vertices of the pyramids are occupied by N3 atoms with Cu1–N3 distances in a range of 2.210(3)–2.286(4) Å (Table 3). The displacements of the pyramid base atoms of **I** and **II** from the mean planes they define do not exceed 0.232 Å and 0.288 Å respectively, and the minimum deviations of

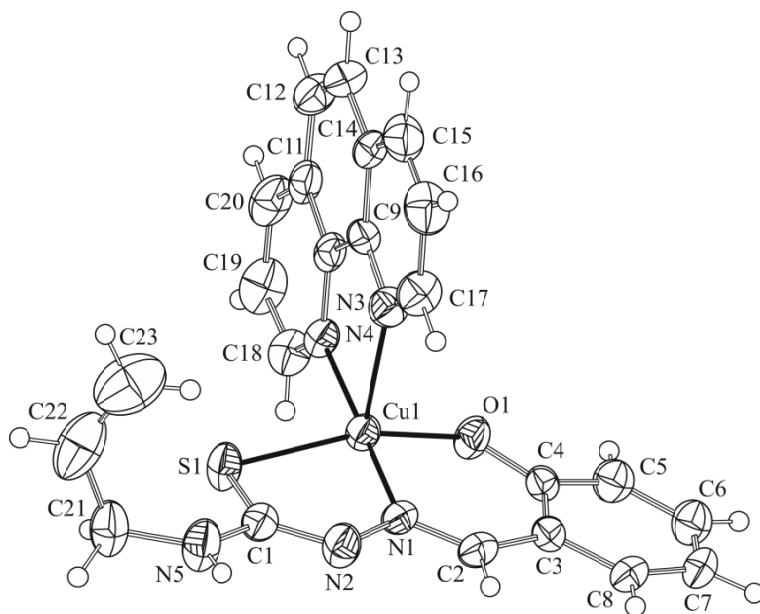


Fig. 1. Atomic numbering in the complex of compound **I**.

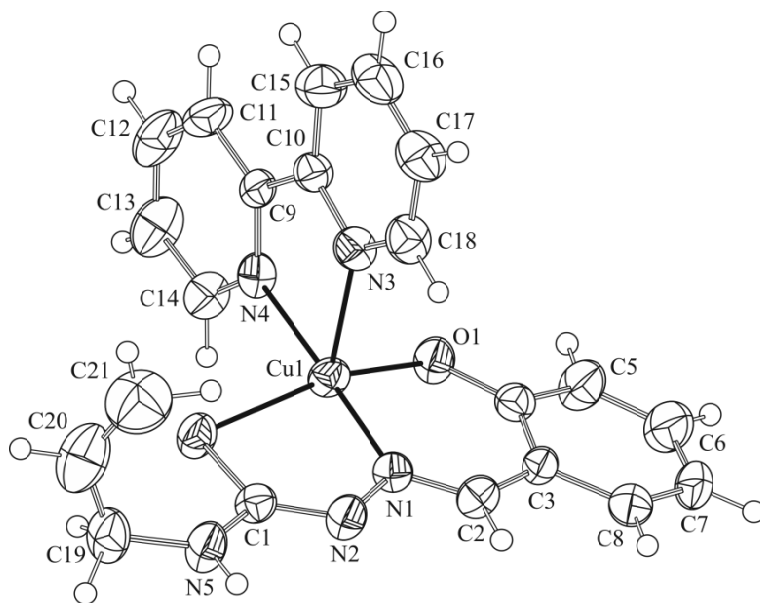


Fig. 2. Atomic numbering in the complex of compound **II**.

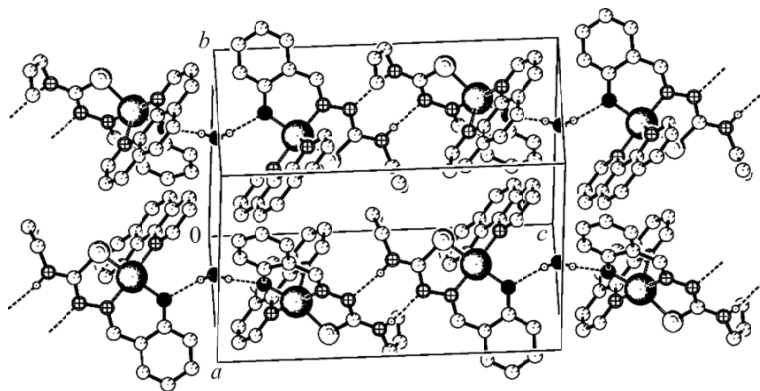


Fig. 3. Fragment of packing in complex **I**.

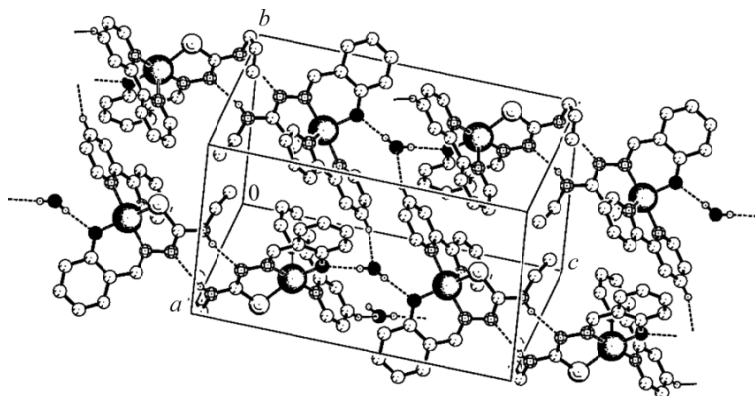


Fig. 4. Fragment of packing in complex II.

copper atoms from these planes toward the N3 atom are 0.156 Å and 0.172 Å. Therewith, the volumes of the coordination polyhedra of I and II are 7.147 Å³, 7.091 Å³, 6.968 Å³, and 7.146 Å³.

In the crystals of compounds I and II, water molecules and N5A–H...N2, N5–H...N2A hydrogen bonds link the complexes in chains along the *c* axis. In I there is a Van der Waals interaction between the chains, whereas in II, the chains are linked together by C12–H...O1W and C12A–H...O1W hydrogen bonds (Figs. 3, 4, Table 4). In compounds I and II, according to the criterion proposed in [13] ($CgI \cdots CgJ < 6.0 \text{ \AA}$, $\beta < 60.0^\circ$, where β is the angle between the $CgI \cdots CgJ$ vector and the normal to the aromatic ring CgI), there is a π – π -stacking interaction between amine fragments $Cg1(N3AC10AC11AC20AC19AC18A)$ and $Cg2(N3C10C9C14C13C12C11C20)$ ($1-x, 1-y, 1-z$), as well as $Cg3(N4AC9AC11AC12AC14)$ and $Cg4(N3C10C15C16C17C18)$ (x, y, z) respectively. The distances between the centroids of the indicated fragments are 3.574(3) Å and 3.619(3) Å, and the β values are 9.5° and 14.1°. In compound I there is also π – π -stacking between the other fragments of the aromatic systems, such as $Cg5(N3C9C14C15C16C17)$ and $Cg6(C9AC10AC11AC12AC13AC14A)$ ($-x, 1-y, 1-z$), $Cg7(N4AC10AC11AC20AC19AC18A)$ and $Cg8(N4C10C11C20C19C18)$ ($1-x, 1-y, 1-z$) with the intercentroid distances and the β angles of 3.791 Å, 23.4 Å and 3.772 Å, 28.8° respectively.

The *in vitro* study of the antimicrobial and antifungal activities of coordination compounds I and II against standard strains of Gram-positive (*Staphylococcus aureus* (ATCC 25923)), Gram-negative (*Escherichia coli* (ATCC 25922), *Klebsiella pneumoniae* (ATCC 13883)) bacteria, and the fungus representative *Candida albicans* (ATCC 10231) showed that coordination compounds I and II exhibited antimicrobial and antifungal activities and had the values of the minimum inhibitory concentration (MIC) and the minimum bactericidal concentration (MBC) in a range of 1.5–500 µg/mL. Compound I shows the lowest inhibitory concentration of 1.5 mcg/mL against *Staphylococcus aureus* and *Candida albicans* (Table 5).

The results of studying the antiradical activity of the synthesized compounds with respect to ABTS⁺ radical cations (Table 6) demonstrated that complexes I and II exhibited this type of the activity and outperform trolox used in medical practice. However, the activities of complexes I and II are lower than those of thiosemicarbazone H₂L.

TABLE 5. Minimum Inhibitory (MIC) and Minimum Bactericidal/Fungicidal (MBC/MFC) Concentrations of H₂L and Complexes I and II Against Microorganisms and Fungi (µg/mL)

Compound	<i>Escherichia coli</i> (ATCC 25922)		<i>Klebsiella pneumoniae</i> (ATCC 13883)		<i>Staphylococcus aureus</i> (ATCC 25923)		<i>Candida albicans</i> (ATCC 10231)	
	MIC	MBC	MIC	MBC	MIC	MBC	MIC	MFC
H ₂ L [10]	>1000	>1000	-	-	7	60	>1000	>1000
I	500	500	500	500	1.5	30	1.5	30
II	500	500	250	500	30	30	30	30

TABLE 6. Antioxidant Activity of Compounds H₂L and **I** and **II** Against ABTS^{•+} Radical Cations

Compound	IC ₅₀ , μM
H ₂ L [10]	9.0
I	22.7
II	10.2
Trolox	33

CONCLUSIONS

The asymmetric unit of the unit cells of crystal structures of **I** and **II** contains copper complexes in which the coordination polyhedron of the central atom is a distorted tetragonal pyramid. The pyramid base consists of the azomethine nitrogen atom, the deprotonated phenolic oxygen atom, the sulfur atom in the thiol form, and one of nitrogen atoms of bidentate amine, while the second nitrogen atom of this ligand occupies the pyramid vertex. In the outer sphere of the titled compounds are crystal water molecules. In the crystals of compounds **I** and **II**, water molecules and N–H...N hydrogen bonds link the complexes in chains along the *c* axis. In these compounds, the complexes are also linked by π – π stacking along the [1 0 1] direction, forming a layered packing.

The study of the antimicrobial and antifungal activities showed that complexes **I** and **II** exhibited it in a concentration range of 1.5-500 μg/mL. Moreover, the investigation of the antiradical activity of the synthesized compounds with respect to ABTS^{•+} radical cations allowed us to state that complexes **I** and **II** were more active than trolox. Compared to the previously described copper(II) complexes with salicylaldehyde 4-allylthiosemicarbazone and monodentate amines [10] in the inner sphere, it may be noted that the replacement of monodentate heteroaromatic amines with bidentate ones diminishes the antioxidant activity. The antioxidant activity of the complexes with monodentate amines [10] outperforms that of H₂L in all cases, and complexes **I** and **II** show a lower antioxidant activity than H₂L. The minimum inhibitory and bactericidal concentrations of complexes **I** and **II** against *Escherichia coli* have 4-167 times higher values than those of the complexes with monodentate amines [10] while these two series of amine-containing compounds have similar MIC, MBC, and MFC against other studied microorganisms they. Thus, the replacement of monodentate amines with bidentate ones did not enhance the biological activity of copper coordination compounds.

ACKNOWLEDGMENTS

The authors are grateful to G. G. Balan and O. S. Burdunyk for assistance in conducting biological tests of the synthesized compounds.

FUNDING

The work was performed within State Programs of the Republic of Moldova (projects 20.80009.5007.10 and 20.80009.5007.15).

CONFLICT OF INTERESTS

The authors declare that they have no conflicts of interests.

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