Synthesis, Structure, and Biological Activity of Copper(II), Nickel(II), Cobalt(III), and Iron(III) Coordination Compounds with 2-{2-[(Prop-2-en-1-yl)carbamothioyl]hydrazinylidene}propanoic Acid

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Abstract—2-Oxopropanoic acid reacts in ethanol with N-(prop-2-en-1-yl)hydrazinecarbothioamide in a 1 : 1 mole ratio to form thiosemicarbazone H_2L. Coordination compounds Cu(HL)X [X = Cl⁻, Br⁻, NO$_3^-$], Cu(H₂O)(L), Ni(HL)₂, Co(HL)₂X [X = Cl⁻, Br⁻], and Fe(HL)₂X [X = NO$_3^-$, Br⁻] are formed in the reactions of H_2L with copper(II), nickel(II), cobalt(II), and iron(III) salts. The reactions of Cu(H₂O)(L) with imidazole (Im) and 3,4-dimethylpyridine (3,4-Lut) result in mixed-ligand complexes Cu(A)(L) [A = Im, 3,4-Lut]. The structures of two copper complexes were determined by single crystal X-ray diffraction analysis. The synthesized complexes exhibit selective antimicrobial and antifungal activity in the concentration range of 15.62–1000 μg/mL. The introduction of amines into the inner sphere of copper complexes leads to an increase in the antimicrobial activity.

Keywords: coordination compounds, pyruvic acid 4-allylthiosemicarbazone, antimicrobial activity, antifungal activity

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Thiosemicarbazones and coordination compounds of transition metals with them are an important class of biologically active compounds [1–4]. The introduction of various substituents in the composition of thiosemicarbazones leads to a change in the mode of their coordination to the central metal atom, affects their biological activity, and increases the selectivity of their action. Previously, the coordination compounds of thiosemicarbazones of oxocarboxylic acids and their derivatives were found to have antimicrobial, antifungal [5, 6] and anticancer [7, 8] properties. Since the biological activity of such substances is often consistent with their structure [9], the introduction of amines into the inner sphere of copper complexes can lead to changes in their biological properties [3, 10, 11].

We have synthesized and studied new coordination compounds of copper(II), nickel(II), cobalt(III), and iron(III) with 2-{2-[(prop-2-en-1-yl)carbamothioyl]-hydrazinylidene}propanoic acid (H₂L, Scheme 1).

Thiosemicarbazone H₂L was obtained by the reaction of N-(prop-2-en-1-yl)hydrazinecarbothioamide (4-allylthiosemicarbazide) with 2-oxopropanoic acid (pyruvic acid), taken in a molar ratio of 1 : 1, in ethanol. Its structure was confirmed by ¹H and ¹³C NMR.
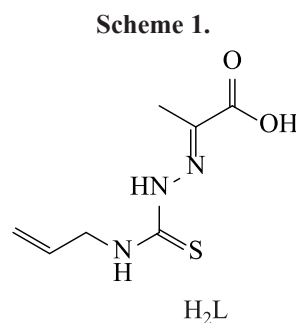
Scheme 1.

H₂L

Table 1. Physical and chemical characteristics of copper, nickel, cobalt, and iron coordination compounds with 2-{2-[(prop-2-en-1-yl)carbamothioyl]hydrazinylidene}propanoic acid

Comp. no.	Yield, %	μ_{ef},[a] BM	$æ$,[a] $\Omega^{-1}\,cm^2\,mol^{-1}$	Found, %			Formula	Calculated, %		
				M[b]	N	S		M[b]	N	S
1	82	1.94	86	20.96	13.99	10.87	$C_7H_{10}ClCuN_3O_2S$	21.24	14.04	10.72
2	79	1.85	89	18.72	12.41	9.03	$C_7H_{10}BrCuN_3O_2S$	18.49	12.23	9.33
3	86	1.24	87	19.75	17.46	9.70	$C_7H_{10}CuN_4O_5S$	19.51	17.20	9.84
4	72	0.65	10	22.88	14.68	11.45	$C_7H_{11}CuN_3O_3S$	22.63	14.96	11.42
5	83	1.18	9	19.52	21.12	9.45	$C_{10}H_{13}CuN_5O_2S$	19.21	21.17	9.69
6	81	0.96	8	17.42	15.11	8.72	$C_{14}H_{18}CuN_4O_2S$	17.18	15.15	8.67
7	81	2.84	13	12.83	12.76	13.86	$C_{14}H_{20}N_6NiO_4S_2$	12.78	12.78	13.97
8	84	c	76	11.64	16.96	13.11	$C_{14}H_{20}ClCoN_6O_4S_2$	11.91	16.98	12.96
9	75	c	62	11.05	15.49	11.81	$C_{14}H_{20}BrCoN_6O_4S_2$	10.93	15.58	11.89
10	68	5.96	64	10.42	19.19	12.15	$C_{14}H_{20}FeN_7O_7S_2$	10.77	18.92	12.37
11	78	5.80	61	10.64	15.84	12.25	$C_{14}H_{20}BrFeN_6O_4S_2$	10.41	15.67	11.96

[a] At 293 K.
[b] M—metal.
[c] Diamagnetic.

The reaction of a hot (50–55°C) ethanol solution of thiosemicarbazone H_2L with ethanol solutions of copper(II) chloride, bromide, or nitrate in a molar ratio of 1 : 1 results in fine–crystalline complexes Cu(HL)X **1–3**, where X = Cl⁻ (**1**), Br⁻ (**2**), NO_3^- (**3**). When an ethanol solution of H_2L reacts with copper(II) acetate hydrate, $Cu(H_2O)(L)$ **4** compound is formed. The reaction of an H_2L solution with nickel acetate tetrahydrate, as well as with solutions of cobalt(II) and iron(III) chlorides, bromides, or nitrates in a molar ratio of 2 : 1 leads to complexes Ni(HL)₂ **7**, Co(HL)₂X **8**, **9** [X = Cl⁻ (**8**), Br⁻ (**9**)], Fe(HL)₂X **10**, **11** [X = NO_3^- (**10**), Br⁻ (**11**)].

In order to obtain copper complexes with heteroaromatic amines included in their composition, ethanol solutions of complex **4** were reacted with imidazole (Im) and 3,4-dimethylpyridine (3,4-lutidine, 3,4-Lut) in a molar ratio of 1 : 1. Resulting complexes **5** and **6** have the composition Cu(A)(L), where A = Im (**5**), 3,4-Lut (**6**).

Coordination compounds **1–11** are insoluble in diethyl ether, slightly soluble in water, better—in alcohols, well soluble in DMF and DMSO. According to the data on the molar electrical conductivity (æ) of the complexes in DMF, compounds **1–3** and **8–11** are binary electrolytes, 1 : 1, (æ = 61–89 $\Omega^{-1}\,cm^2\,mol^{-1}$), and complexes **4–7** are non–electrolytes (æ = 8–13 $\Omega^{-1}\,cm^2\,mol^{-1}$) (Table 1).

A magnetochemical study of the synthesized coordination compounds has shown that copper complexes **1** and **2** have effective magnetic moments characteristic of a single unpaired electron, which suggests that they have a monomeric structure. Complexes **3-6** have an underestimated effective magnetic moment compared to the pure spin value for a single unpaired electron, which points to their poly-nuclear structure. The effective magnetic moment of nickel complex **7** (μ_{ef} = 2.84 BM) points to its octahedral structure. Cobalt complexes **8** and **9** are diamagnetic, hence they have an octahedral structure; during the synthesis, the cobalt(II) ion was oxidized to cobalt(III) by air oxygen. The effective magnetic moment of iron complexes **10** and **11** is characteristic of five unpaired electrons, hence the iron ion is in a high-spin state. As cobalt complexes are low-spin and iron complexes are high-spin, the studied thiosemicarbazone H_2L is a medium-field ligand.

To determine the mode of the ligand coordination to the central atoms, a comparative analysis of the IR spectra of H_2L and complexes **1–11** was performed. The IR spectra contain absorption bands of stretching vibrations of coordinated ligand molecules in the regions of 3400–3100, 1630–1560, and 870–790 cm^{-1}. The absorption band ν(O–H) in the region of 3400–3300 cm^{-1} disappears from the spectra of all complexes, which points to the proton replacement in the ligand molecule. In addition, in the spectra of complexes **1–3, 7–11** the band ν(C=N) is shifted to the low–frequency region by 12–43 cm^{-1} and the band ν(C=S)—to the high-frequency region by 1–26 cm^{-1}. This points to the H_2L coordination to the central atom via a deprotonated carboxylic oxygen atom, an azomethine nitrogen atom, and a sulfur atom in the thion form. In the spectra of complexes **4-6**, the absorption band ν(C=S) is absent and the band ν(C=N) appears, which points to the H_2L conversion to the thiol form. In the IR spectra of all

Table 2. Crystallographic characteristics, experimental data, and refinement of the structure of complexes **1a** and **6**

Parameter	1a	6
Formula	$C_7H_{14}ClCuN_3O_4S$	$C_{28}H_{36}Cu_2N_8O_4S_2$
M	335.26	739.85
Syngony	Monoclinic	Monoclinic
Space group	$I2/c$	$C2/c$
Z	8	4
a, Å	12.6727(6)	16.5934(8)
b, Å	5.5548(4)	16.6627(6)
c, Å	36.920(2)	12.3321(6)
β, deg	93.821(5)	101.648(4)
V, Å^3	2593.2(3)	3339.5(3)
D_{calc}, g/cm^3	1.717	1.472
μ, cm^{-1}	2.057	1.444
$F(000)$	1368	1528
Crystal size, mm	0.60×0.10×0.03	0.75×0.50×0.40
θ_{max}, deg	25.05	25.05
Index ranges	$-15 \le h \le 15,$	$-19 \le h \le 19,$
	$-6 \le k \le 6,$	$-14 \le k \le 19,$
	$-39 \le l \le 43$	$-14 \le l \le 12$
Number of measured/independent reflections	6432/2295 [R_{int} = 0.0286]	5999/2948 [R_{int} = 0.0275]
Number of reflections with $I > 2\sigma(I)$	1945	2262
Number of parameters	162	206
GOOF	1.004	1.005
R-Factors [$I > 2\sigma(I)$]	R_1 = 0.0303,	R_1 = 0.0390,
	wR_2 = 0.0760	wR_2 = 0.1026
R-Factors (all data)	R_1 = 0.0396,	R_1 = 0.0569,
	wR_2 = 0.0811	wR_2 = 0.1110
$\Delta\rho_{max}/\Delta\rho_{min}$, e/Å	0.281/–0.348	0.459/–0.377

complexes, a number of new absorption bands caused by ν(M–N), ν(M–O), and ν(M–S) vibrations appear in the region of 550–405 cm^{-1}.

Recrystallization of complex **1** from water and complex **6** from ethanol resulted in single crystals. Their structure was determined by X-ray structural analysis.
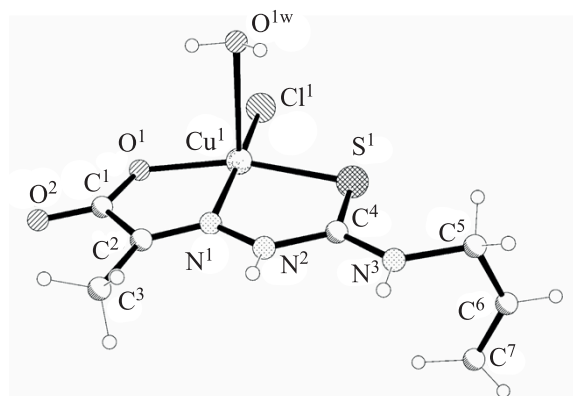

Fig. 1. General view of the molecule of Cu(II) complex **1a** in a crystal.

The recrystallization of green complex **1** from water resulted in blue single crystals of complex **1a**.

Crystals of complex **1a** belong to the space group $I2/c$ of the monoclinic syngony (Table 2); mononuclear molecular complexes [Cu(H$_2$O)(HL)Cl] include molecules of crystallization water. The coordination number of the central Cu(I) atom is five, and its coordination polyhedron is a distorted square pyramid. In the complex the tridentate monodeprotonated HL$^-$ ligand is coordinated to the central atom by O, N, and S donor atoms to form two five-membered metallocycles. A strong disordering of the electron density was found in the thiometallocycle, whereas the interatomic distances S–C and N–C, d = 1.702(3) and 1.316(3) Å, point to stabilization of the ligand thion form (Table 3). A similar phenomenon was previously observed in the Cu(II) polymer complex with 4-methylthiosemicarbazone of α-ketoglutaric acid [8]. The fourth coordination site at the base of the metal pyramidal coordination polyhedron in complex **1a** is occupied by the Cl$^-$ anion, and the axial

Table 3. Some interatomic distances and valence angles in molecules of complexes **1a** and **6**

| Bond	d, Å		Angle	ω, deg	
	1a	**6**		**1a**	**6**
Cu^1-N^1	1.960(2)	1.944(2)	$N^1Cu^1O^1$	80.88(9)	82.03(9)
Cu^1-O^1	1.975(2)	1.969(2)	$N^1Cu^1Cl^1/N^4$	173.19(7)	174.45(10)
Cu^1-S^1	2.2575(8)	2.2773(8)	$N^1Cu^1S^1$	85.41(7)	83.40(7)
Cu^1-Cl^1/N^4	2.2005(8)	1.995(3)	$N^1Cu^1O^{1w}/S^{1*}$	92.6	100.8(4
Cu^1-O^{1w}/S^{1*}	2.571(5)	2.943(3)	$O^1Cu^1Cl^1/N^4$	94.48(7)	93.83(10)
N^1-N^2	1.365(3)	1.365(3)	$O^1Cu^1S^1$	163.81(7)	164.21(7)
N^2-C^4	1.362(3)	1.327(4)	$O^1Cu^1O^{1w}/S^{1*}$	99.3	94.5(9)
N^3-C^4	1.316(3)	1.330(3)	$Cl^1/N^4Cu^1S^1$	98.36(3)	100.29(8)
S^1-C^4	1.702(3)	1.752(3)	$Cl^1/N^4Cu^1O^{1w}/S^{1*}$	93.1	83.2(10)
			$S^1Cu^1O^{1w}/S^{1*}$	89.9	94.2(9)
			$N^1N^2C^4$	116.5(2)	110.7(2)
			$N^2C^4N^3$	116.9(2)	118.1(3)
			$N^2C^4S^1$	121.42(19)	125.0(2)
			$N^3C^4S^1$	121.7(2)	116.9(2)

position is occupied by the oxygen atom of the water molecule (Fig. 1).

Interatomic distances $Cu-O^1$, $Cu-N^1$ and $Cu-S^1$ [$d =$ 1.975(2), 1.960(2), and 2.2575(8) Å] are shortened relative to those found in [8], and the distances $Cu-Cl^1$ and $Cu-O^{1w}$ are equal to 2.2005(8) and 2.571(4) Å (Table 3).

Coordination compound **6** crystallizes in the $C2/c$ space group of the monoclinic syngony (Table 2). The independent part of the unit cell of the crystal of the [Cu(3,4-Lut)(L)] complex contains is one copper atom and L^{2-} and 3,4-Lut organic ligands. The complex is combined into the binuclear compound by means of two interatomic $Cu-S^{1*}$ bonds, where S* is the atom of the second ligand L^{2-}. The final chemical formula of compound **6** is [Cu(3,4-Lut)(L)]$_2$. The coordination polyhedron of copper atoms in complex **6** is a distorted square pyramid, which is formed by the organic ligand L^{2-} coordinated to the central metal atom in the same way as in complex **1a** through a set of donor atoms O, N, S; the nitrogen atom of 3,4-dimethylpyridine is located at the base of the pyramid. Since the H$_2$L ligand is involved in the complex as a bridging twice-deprotonated L^{2-} ligand, the sulfur atom of the second similar ligand is located in the axial position of the metal polyhedron. A similar ligand coordination mode was found in Cu(II) complexes with 4-methyl-and 4-ethylthiosemicarbazones of pyruvic acid [12, 13]. Interatomic distances $Cu-O^1$, $Cu-N^1$, and $Cu-S^1$ in complex **6** [d = 1.969(2), 1.944(2), and 2.2773(8) Å] (Table 3) are similar to those found in [12] and slightly different from those found in [13], whereas the interatomic distances $Cu-N^4$ and $Cu-S^1$ in complex **6**

are 1.995(3) and 2.943(2) Å (–x + 1, y, –z + 3/2). Analysis of interatomic distances in the thiometallocycle points to stabilization of the ligand thiol form, so the C–S bond [d = 1.752(3)] is longer than the shortened bond in complex **1a** [d = 1.702(3) Å] (Table 3) and is comparable with those found in Cu(II) (Fig. 2) complexes with other pyruvic acid thiosemicarbazones [12, 13]. The geometric parameters of dimethylpyridine correspond to those in copper complexes with a similar ligand given in the Cambridge structural data base [14].

Different degrees of the organic ligand deprotonation in complexes **1a** and **6** and the presence of both coordinated water molecules and water of crystallization in complex **1a** led to the formation of different systems of hydrogen bonds in the crystals of these compounds. In the crystal of complex **1a**, the hydrogen bonds $N^2-H\cdots O^{1w}$ and $N^3-H\cdots Cl^1$ bind the molecules in infinite chains along
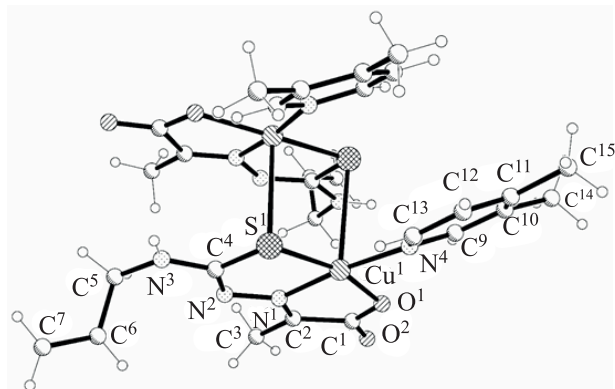
Fig. 2. General view of the molecule of binuclear Cu(II) complex **6** in a crystal.
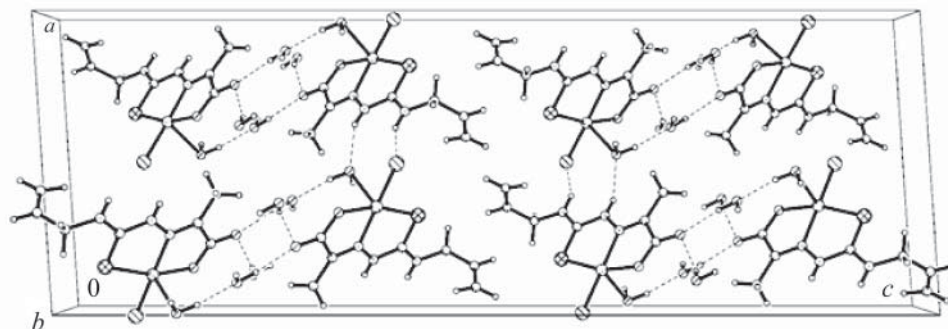
Fig. 3. Fragment of the crystal packing of complex **1a**.

the *a* axis (Table 4, Fig. 3). These chains combine with the centrosymmetric complexes of neighboring chains via the O^{1w}–H···O^{2w} and O^{2w}–H···O^2 hydrogen bonds to form centrosymmetric dimers. The remaining intermolecular hydrogen bonds, involving both coordinated and crystallization water molecules as proton donors, combine the complexes into O^{1w}–H···Cl^1 and O^{2w3}–H···O^2 layers. These layers are stabilized by C^5–H···Cl^1 weak hydrogen bonds and are associated with each other only by C^3–H···S^1 weak hydrogen bonds.

In the crystal structure of complex **6** we can distinguish chains formed along the *a* axis by binuclear complexes associated by N^3–H···O^2 hydrogen bonds and stabilized by weak C^5–H···O^1 bonds (Table 4, Fig. 4). The complexes themselves are stabilized by intramolecular hydrogen bonds C^{13}–H···S^1 and C^9–H···O^1.

The obtained physical and chemical data allow us to present the distribution of chemical bonds in the molecules of complexes **1**–**11** in the following form (Scheme 2).

The *in vitro* study of the antimicrobial and antifungal activity of H_2L and coordination compounds **1**–**11** against standard strains of gram-positive *Staphylococcus aureus* bacteria (ATCC 25923), gram-negative *Escherichia coli* coliform bacteria (ATCC 25922), and a representative of the yeast-like fungi *Candida albicans* (ATCC 10231) showed that uncoordinated H_2L does not exhibit antimicrobial activity in the studied concentration range and inhibits growth of *Candida albicans* only at a concentration of 500 µg/mL. Coordination of H_2L to 3*d*-metal ions leads to a change in the biological activity. The synthesized coordination compounds exhibit

Table 4. Geometric parameters of hydrogen bonds in crystals of complex **1a** and **6**

Contact D–H···A	Distance, Å				Angle DHA, deg	
	D–H	H···A	D···A			
1a						
N^2–H^2···O^{1w}	0.86	2.08	2.877(3)	155		x–1/2, –y+3/2, z
N^3–H^3···Cl^1	0.86	2.52	3.213(6)	139		x–1/2, –y+3/2, z
O^{1w}–H^1···O^{2w}	0.88	1.82	2.688(4)	170		x, y, z
O^{1w}–H^1···O^{3w}	0.88	1.82	2.688(4)	170		x, y, z
O^{1w}–H^2···Cl^1	0.92	2.94	3.508(2)	122		x, y+1, z
O^{1w}–H^2···O^1	0.92	2.10	2.996(3)	165		x, y+1, z
O^{2w}–H^1···O^2	0.88	2.03	2.816(5)	148		x, y+1, z
O^{2w}–H^2···O^2	0.96	1.91	2.789(4)	152		–x+3/2, –y+1/2, –z+1/2
O^{3w}–H^1···O^2	0.90	2.12	2.96(2)	155		–x+3/2, –y+1/2, –z+1/2
O^{3w}–H^2···O2w	0.82	2.14	2.96(2)	177		–x+2, y, –z+1/2
C^5–H^5···Cl^1	0.97	2.92	3.465(3)	117		x–1/2, –y+3/2, z
O^6–H^6···S^1	0.93	3.02	3.904(3)			–x+3/2, y+1/2, –z+1
6						
N^3–H^4···O^2	0.86	1.97	2.798(3)	160		x–1/2, –y+2/2, z–1/2
C^5–H^{5B}···O^1	0.97	2.60	3.403(4)	140		x–1/2, –y+2/2, z–1/2
C^9–H^9···O^1	0.93	2.47	2.999(4)	116		x, y, z
C^{13}–H^{13}···S^1	0.93	2.86	3.387(3)	117		x, y, z

Scheme 2.

1, 2 **3** **4–6**

7 **8–11**
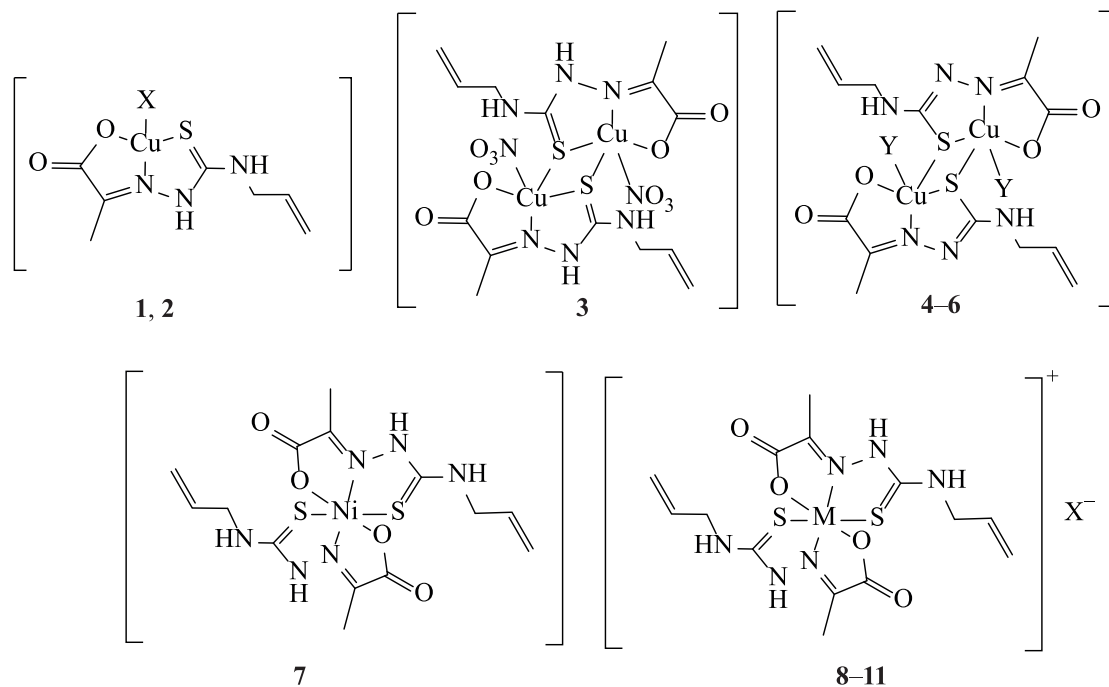
X = Cl⁻, Br⁻ (**1**, **2**); Y = H_2O, Im, 3,4-Lut (**4–6**); M = Co^{3+}, Fe^{3+}, X = Cl⁻, Br⁻, NO_3^- (**8–11**).

antimicrobial and antifungal activity and have a minimal inhibitory concentration (MIC) and a minimal bactericidal concentration (MBC) in the range of 15.62–1000 μg/mL (Table 5). The nature of the central atom makes the main influence on antimicrobial activity. Antimicrobial activity is significantly enhanced in copper(II) complexes **1–6**. Among the compounds of this group, complexes **5** and **6** stand out due to their higher antimicrobial activity against *Staphylococcus aureus* and *Eschirichia coli*.

The obtained data on the antimicrobial activity point to the prospects for further search for selective antimicrobial substances among copper coordination compounds with thiosemicarbazones of ketoacids and also copper mixed-ligand amine complexes.

EXPERIMENTAL

X-ray structural analysis. Experimental data for complexes **1a** and **6** were obtained at room temperature of 293(2) K on an Xcalibur e diffractometer with MoK_α radiation and a graphite monochromator. The unit
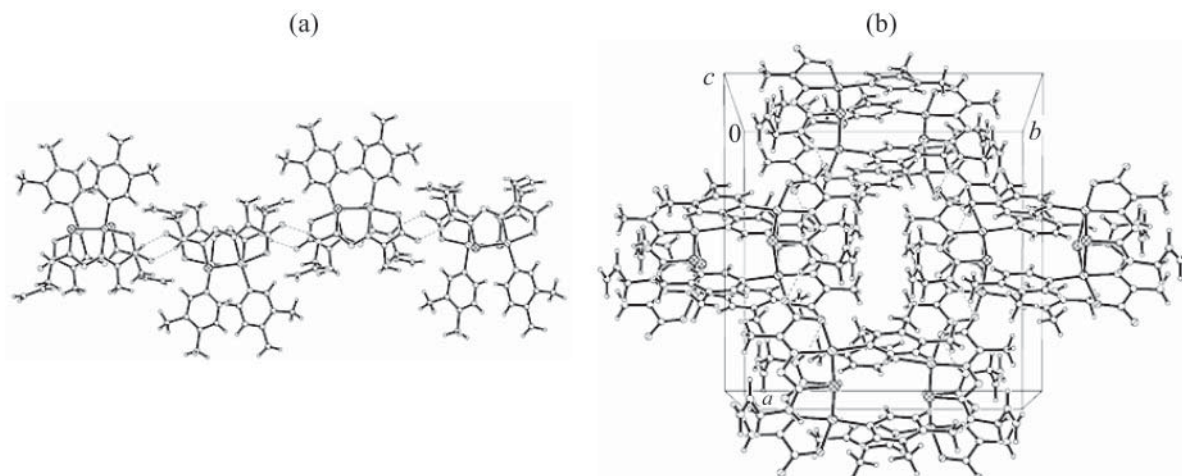
(a) (b)

Fig. 4. (a) Chain formation in the crystal of complex **6**; (b) fragment of the crystal packaging of complex **6**.

Table 5. Minimal inhibitory (MIC) and bactericidal (MBC) concentrations (µg/mL) of coordination compounds **1–11** in relation to test microbes

Compound	Eschirichia coli ATCC 25922		Staphylococcus aureus ATCC 25923		Candida albicans ATCC 10231	
	MIC	MBC	MIC	MBC	MIC	MBC
Initial salts[a]	>1000	>1000	>1000	>1000	>1000	>1000
H_2L	>1000	>1000	>1000	>1000	500	>1000
1	125	250	62.5	125	125	500
2	>1000	>1000	>1000	500	31.25	62.5
3	125	250	62.5	125	125	>1000
4	125	250	31.25	62.5	62.5	250
5	31.25	62.5	15.62	31.25	31.25	62.5
6	15.62	31.25	15.62	31.25	125	250
7	500	>1000	250	>1000	250	>1000
8	>1000	>1000	>1000	>1000	62.5	250
9	500	>1000	250	500	125	500
10	>1000	>1000	>1000	>1000	62.5	250
11	>1000	>1000	>1000	>1000	125	500

[a] $CuCl_2 \cdot 2H_2O$, $CuBr_2$, $Cu(NO_3)_2 \cdot 3H_2O$, $Cu(CH_3COO)_2 \cdot H_2O$, $Ni(CH_3COO)_2 \cdot 4H_2O$, $CoCl_2 \cdot 6H_2O$, $CoBr_2 \cdot 6H_2O$, $Fe(NO_3)_2 \cdot 6H_2O$, $FeBr_3$.

cell parameters refined over the entire array and other experimental data were obtained using the CrysAlis Oxford Diffraction software package [15]. The structures were solved by direct methods and refined by LSM in the anisotropic approximation for non-hydrogen atoms using the SHELX-97 program [16]. Hydrogen atoms are included in the refinement in geometrically calculated positions, and their temperature factors U_H were assumed to be 1.2 or 1.5 times greater than those of the associated carbon, nitrogen, and oxygen atoms. Molecules of crystallization water in complex **1A** are localized in two positions with filling coefficients 0.85 and 0.15. In complex **6**, the allyl fragment of the L^{2-} ligand is localized in two positions with a filling factor of 0.5. The main experimental parameters, solution, and refinement of structures are shown in Table 2, and some interatomic distances, valence angles, and hydrogen bonds are given in Tables 3 and 4. The coordinates of the base atoms of the studied structures are deposited in the Cambridge data Bank (CCDC 2010166-2010167).

The resistance of solutions of complexes **1-11** in DMF (20°C, $c = 0.001$ M) was measured using a P-38 rheochord bridge. The IR spectra of substances were recorded on a Bruker ALPHA spectrophotometer (4000–400 cm^{-1}). The effective magnetic moments of compounds **1–11** were determined by the Gouy method. The calculation of the molar magnetic susceptibility adjusted for diamagnetism was based on the theoretical values of the magnetic susceptibility of organic compounds.

Antimicrobial and antifungal activities were studied using the standard methods [17, 18].

2-{2-[(Prop-2-en-1-yl)carbamothioyl]hydra-zinylidene}propanoic acid (H₂L). A hot (55–60°C) solution of 10 mmol of pyruvic acid in 15 mL of ethanol was mixed with a solution of 10 mmol of 4-allylthiosemicarbazide in 20 mL of ethanol. When the reaction mixture was cooled, a light yellow precipitate fell out, which was filtered out on a glass filter, washed with a small amount of alcohol, and dried in air. Yield 95%, mp 150–152°C. It is well dissolved in DMA, DMSO, and when heated—in alcohols. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.09 s (3H, CH$_3$), 4.26 t (2H, C$\underline{H}_2$NH, $J = 5.6$ Hz), 5.16 d.d (2H, CH$_2$, $J = 1.7$ Hz), 5.89 m (1H, CH$_2$=C), 9.33 br. s (1H, NH), 10.78 br. s (1H, NH), 12.17 br. s (1H, OH). ^{13}C NMR spectrum (DMSO-d_6), δ$_C$, ppm: 12.63 (CH$_3$), 46.54 (CH$_2$N), 116.54 (CH$_2$=), 134.76 (CH$_{allyl}$), 139.03 (C=N), 165.31 (C=O), 179.00 (C=S).

{2-[2-(Prop-2-en-1-ilcarbamothioyl)gerineldo]-propanoate}chlorocopper (1). A solution of 10 mmol of copper(II) chloride dihydrate in 20 mL of ethanol was added with continuous stirring and heating (50–55°C) to an ethanol solution of thiosemicarbazone H₂L in 20 mL of ethanol. The reaction mixture was heated for 50–60 min. After cooling to room temperature, a fine crystalline substance fell out, which was filtered out, washed with a small amount of ethanol and ether, and dried in air to a constant weight.

Similarly, using copper(II) bromide, copper(II) nitrate trihydrate, and copper(II) acetate hydrate instead of copper(II) chloride dihydrate, compounds **2–4** were synthesized. Complexes **7–11** were synthesized similarly by reacting nickel(II) acetate hydrates, cobalt(II) chloride and bromide, and iron(III) nitrate and bromide with thiosemicarbazone H_2L in a molar ratio of 1 : 2.

{2-[2-(Prop-2-en-1-ilcarbamothioyl)hydrazinilidene]propanoate}imidazolocopper (5). To 20 mL of a hot (50–55°C) ethanol solution of 10 mmol of complex **4**, 10 mmol of imidazole was added, and stirred under heating for 40–50 min. When cooled, a precipitate was formed, which was filtered out, washed with a small amount of ethanol, and air-dried.

Similarly, using 3,4-dimethylpyridine instead of imidazole, compound **6** was synthesized. Yields and physicochemical characteristics of obtained complexes **1–11** are shown in Table 1.

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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