ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2008, Vol. 34, No. 1, pp. 44–52. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © Yu.M. Chumakov, E. Janneau, N.P. Bezhenar', V.I. Tsapkov, A.P. Gulya, 2008, published in Koordinatsionnaya Khimiya, 2008, Vol. 34, No. 1, pp. 46–54.

Crystal Structure of Copper Sulfate and Thiocyanate Complexes with 5-Bromo- and 5-Nitrosalicylaldehyde Thiosemicarbazones

Yu. M. Chumakov[a], E. Janneau[b], N. P. Bejenari[c], V. I. Tsapkov[c], and A. P. Gulea[c]

[a] *Institute of Applied Physics, Academy of Sciences of Moldova, Chisinau, Moldova*

[b] *Claude Bernard University, Lyon, France*

[c] *Moldova State University, ul. Matteevicha 60, Chisinau, 277009 Moldova*

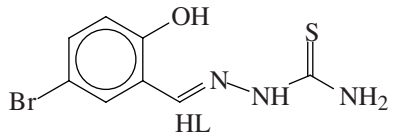
E-mail: vtsapkov@usm.md

Received December 20, 2006

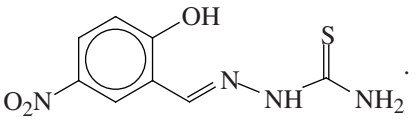
Abstract—The crystal structures of (5-bromosalicylidenethiosemicarbazido)aquacopper(II) sulfato(5-bromosalicylidenethiosemicarbazido)aquacuprate(II) tetrahydrate (**I**), (5-nitrosalicylidenethiosemicarbazido)dimethylsulfoxide(methanol)copper(II) sulfate (**II**), and catena(μ-thiocyanato)(5-nitrosalicylidenethiosemicarbazido)copper(II) (**III**) were determined. In structure **I**, the independent part of the unit cell contains four water molecules of crystallization and the cation–anion complex $[Cu(H_2O)(L)][Cu(H_2O)(L)(SO_4)]$ containing two nonequivalent copper complexes (*A* and *B*). In these, the metal atom coordinates monodeprotonated 5-bromosalicylaldehyde thiosemicarbazone (HL) and water molecules, and in anion *B* also a sulfate ion. In complex ions *A* and *B*, sulfur, azomethine nitrogen, and phenolic oxygen of the salicylidene thiosemicarbazone fragment, and also water molecule form a distorted planar square around the metal atom. The axial vertex of the pyramid in anion *B* is occupied by the oxygen atom of the monodentate sulfate anion. In structure **II**, the independent part of the unit cell contains the (5-nitrosalicylidenethiosemicarbazido)dimethylsulfoxide(methanol)copper(II) complex cation and the sulfate anion. The coordination polyhedron of the central atom is a slightly distorted tetragonal pyramid whose base is formed by sulfur, azomethine nitrogen, phenolic oxygen of thiosemicarbazone, and dimethyl sulfoxide oxygen. The axial position is occupied by the methanol oxygen atom. In structure **III**, the copper atom coordinates 5-nitrosalicylaldehyde thiosemicarbazone and the thiocyanate ion, which combines complexes into infinite polymer chains along the [010] direction. The copper coordination polyhedron in **III** is a slightly distorted tetragonal pyramid whose base is formed by sulfur, azomethine nitrogen, phenolic oxygen of thiosemicarbazone, and nitrogen of thiocyanate ion, the axial vertex is occupied by sulfur of thiocyanate ion of the neighboring complex.

DOI: 10.1134/S1070328408010089

Thiosemicarbazide derivatives are widely used in medicine for treatment of various diseases [1, 2]. They all contain a set of donor atoms and are bound to metal ions to form coordination compounds with diverse composition, structure, and properties. In many cases, the biological activity of drugs is correlated with their complexation capacity [3–5]. The structural features of the biologically active transition metal complexes with thiosemicarbazones of aromatic hydroxyaldehydes have been studied rather comprehensively [6–8]. However, since these compounds have mainly been synthesized from thiosemicarbazides of unsubstituted aromatic aldehydes, it appeared pertinent to elucidate the effect of substituents of different nature introduced in the salicylidene fragment of azomethine on the structure and properties of the resulting complexes.



HL



HL[1]

The purpose of this study is to prepare (5-bromosalicylidenethiosemicarbazido)aquacopper(II) sulfato(5-bromosalicylidenethiosemicarbazido)aquacuprate(II) tetrahydrate (**I**), (5-nitrosalicylidenethiosemicarbazido)dimethylsulfoxide(methanol)copper(II) sulfate (**II**), and catena(μ-thiocyanato)(5-nitrosalicylidenethi-

osemicarbazido)copper(II) [Cu(L^1)(NCS)] (**III**) and study their crystal structures by X-ray diffraction.

EXPERIMENTAL

Synthesis of I. A solution containing copper(II) sulfate pentahydrate (2.5 g, 10 mmol) in distilled water (30 ml) was added with continuous magnetic stirring and heating (50–55°C) to a solution containing 5-bromosalicylaldehyde thiosemicarbazone (2.74 g, 10 mmol) in methanol (50 ml). Then the reaction mixture was heated at reflux for 50–60 min. On cooling, dark green crystals precipitated from the solution. These were collected on a filter, washed with small amounts of ethanol and ether, and dried in air. The yield of complex **I** was 71%.

For $C_{16}H_{26}Br_2Cu_2N_6O_{12}S_3$

anal. calcd. (%): C, 21.90; H, 2.99; Br, 18.21; Cu, 14.48; N, 9.58; S, 10.96.

Found (%): C, 21.69; H, 2.75; Br, 18.10; Cu, 14.21; N, 9.41; S, 10.79.

IR (ν, cm^{-1}): 1590 ν(C=N), 1215 ν(C–O), 1180 and 1115 δ(C–N), 1115 ν(C=S), 1045 $\nu_3(SO_4^{2-})_{monodentate}$, 985 and 945 ν(C–N), 975 $\nu_1(SO_4^{2-})_{monodentate}$, 640 $\nu_4(SO_4^{2-})_{monodentate}$, 515 and 420 ν(Cu–N), 470 ν(Cu–O), 455 ν(Cu–S), 435 $\nu_2(SO_4^{2-})_{monodentate}$.

At room temperature (294 K), the effective magnetic moment μ_{eff} of compound **I** equals 1.85 μ_B (per paramagnetic ion).

Synthesis of II. The complex was prepared in 60% yield by the reaction of copper(II) sulfate pentahydrate in methanol with 5-nitrosalicylaldehyde thiosemicarbazone in 1 : 1 ratio in DMSO according to the above-described procedure.

For $C_{22}H_{34}Cu_2N_8O_{14}S_5$

anal. calcd. (%): C, 28.66; H, 3.72; Cu, 13.7; N, 12.15; S, 17.39.

Found (%): C, 28.49; H, 3.50; Cu, 13.64; N, 12.25; S, 17.19.

IR (ν, cm^{-1}): 3625 $\nu(OH)_{alc}$, 1595 ν(C=N), 1260 $\nu(OH)_{alc}$, 1220 ν(C–O), 1180 and 1120 δ(C–N), 1135 $\nu_3(SO_4^{2-})$, 1115 ν(C=S), 1075 $\nu(S{=}O)_{DMSO}$, 1040 $\nu(C{-}O)_{alc}$, 615 $\nu_4(SO_4^{2-})$, 530 and 415 ν(Cu–N), 460 ν(Cu–O), 445 ν(Cu–S).

At room temperature (292 K), the effective magnetic moment μ_{eff} of compound **II** equals 1.94 μ_B.

Complex III was prepared by a procedure similar to that described above from a suspension of copper(II) sulfate pentahydrate in methanol and 5-nitrosalicylal dehyde thiosemicarbazone in DMSO in the presence of potassium thiocyanate (1 : 1 : 1 molar ratio). The product **III** was formed as a dark green solid in 77% yield.

For $C_9H_7CuN_5O_3S_2$

anal. calcd. (%): C, 29.96; H, 1.96; Cu, 17.61; N, 19.41; S, 17.17.

Found (%): C, 29.75; H, 2.09; Cu, 17.47; N, 19.20; S, 16.99.

IR (ν, cm^{-1}): 2110 $\nu(C{=}N)_{Cu-NCS-Cu}$, 1595 ν(C=N), 1220 ν(C–O), 1185 and 1120 δ(C–N), 1120 ν(C=S), 530 and 420 ν(Cu–N), 460 ν(Cu–O), 450 ν(Cu–S).

At room temperature (293 K), the effective magnetic moment μ_{eff} of compound **III** equals 1.75 μ_B.

Compounds **I–III** are readily soluble in DMF and DMSO, poorly soluble in water and alcohols, and almost insoluble in ether. Their single crystals suitable for X-ray crystallography were obtained by recrystallization from a methanol–DMSO (4 : 1) solution.

X-ray diffraction analysis of compounds **I–III** was carried out on a Nonius Kappa diffractometer with a CCD detector (MoK_α radiation, λ = 0.71069 Å) at room temperature (293(2) K). Analytical absorption correction was applied only for complex **III** [9]. The structures of complexes **I–III** were solved by the direct method using SHELX-86 [10] and SIR-97 [11] software and refined by least squares in the anisotropic approximation for nonhydrogen atoms (CRYSTALS) [12]. The hydrogen atoms were refined isotropically. In complex **I**, all hydrogen atoms were included in the refinement in geometrically calculated positions (except for water hydrogens, which were not located). In compounds **II** and **III**, the hydrogens attached to the carbon atoms were included in the refinement in geometrically calculated positions, while the other H atoms were located from the Fourier syntheses. In compound **II**, the phenolic hydroxyl and methanol atoms were not located. The C–H and N–H bond lengths varied in the 0.93–0.98 and 0.86–0.89 Å ranges, respectively. The thermal factors U_H were taken to be 1.2–1.5 times as high as the U_{eq} values of the carbon and nitrogen atoms bearing these hydrogens.

The key X-ray experiment details for **I–III** are presented in Table 1 and interatomic distances and bond angles are listed in Table 2. The coordinates of basis atoms are deposited with the Cambridge Crystallographical Data Center (CCDC No. 623449–623451). The geometric calculations and drawings were made with the PLATON program [13]; the drawings show only the hydrogen atoms involved in hydrogen bonds. The structures were analyzed using the CSDB data (version 5.27) [14, 15].

RESULTS AND DISCUSSION

The independent part of the crystal unit cell in structure **I** contains four water molecules of crystallization and the cation–anion complex [Cu(H_2O)(L)][Cu(H_2O)(L)(SO_4)] composed of two nonequivalent copper complexes (***A*** and ***B***).

Table 1. Crystal data and X-ray experiment and structure refinement details for structures **I–III**

Parameter	Value		
	I	**II**	**III**
M	873.77	919.94	359.93
System	Orthorhombic	Monoclinic	Orthorhombic
Space group	*Pcab*	*C*2/*c*	*Pbca*
a, Å	8.661(5)	18.954(5)	15.531(5)
b, Å	18.732(5)	17.345(5)	10.389(5)
c, Å	39.567(5)	13.483(5)	15.987(5)
β, deg	90	119.105(5)	90
V, Å^3	6419(4)	3873(2)	2580(2)
Z	8	4	8
ρ_{calcd}, g/cm^3	1.778	1.578	1.858
μ_{Mo}, mm^{-1}	4.069	1.436	2.031
Crystal size, mm	0.09 × 0.13 × 0.25	0.11 × 0.15 × 0.29	0.09 × 0.10 × 0.40
θ range, deg	1.03–24.43	1.7–28.16	2.55–27.86
Range of intensity measurements	$-10 \le h \le 6$, $-21 \le k \le 15$, $-45 \le l \le 43$	$-24 \le h \le 20$, $-19 \le k \le 22$, $-14 \le l \le 17$	$-20 \le h \le 18$, $-13 \le k \le 13$, $-21 \le l \le 20$
The number of measured reflections	22468	21090	23984
The number of independent reflections	5247 (R_{int} = 0.122)	4532 (R_{int} = 0.1041)	3071 (R_{int} = 0.111)
The number of reflections with $I > 2\sigma(I)$	2627	945	1834
The number of refined parameters	394	231	181
GOOF on F^2	1.07	1.0892	1.0696
R-factor [$I > 2\sigma(I)$]	R_1 = 0.0663, wR_2 = 0.0958	R_1 = 0.0764, wR_2 = 0.0808	R_1 = 0.0512, wR_2 = 0.0430
R-factor (for the whole array)	R_1 = 0.1280, wR_2 = 0.1312	R_1 = 0.2359, wR_2 = 0.1467	R_1 = 0.0973, wR_2 = 0.0636
$\Delta\rho_{(max)}$ and $\Delta\rho_{(min)}$, e Å^{-3}	1.29 and –0.67	0.81 and –0.92	0.68 and –0.39

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

Bond	*d*, Å			
	I		**II**	**III**
	A	*B*		
Cu(1)–S(1)	2.263(4)	2.276(5)	2.245(6)	2.291(2)
Cu(1)–O(1)	1.929(9)	1.921(8)	1.88(1)	1.937(3)
Cu(1)–O(2SN(5))	1.97(1)	1.99(1)	1.94(2)	1.928(5)
Cu(1)–O(3VS(2))		2.414(9)	2.44(2)	2.887(2)
Cu(1)–N(1)	1.94(1)	1.925(9)	1.95(2)	1.954(3)
S(1)–C(8)	1.69(1)	1.73(1)	1.71(3)	1.684(5)
O(1)–C(3)	1.32(1)	1.28(2)	1.29(3)	1.302(5)
N(1)–N(2)	1.40(2)	1.38 (1)	1.42(2)	1.389(4)
N(1)–C(1)	1.29(2)	1.29(2)	1.25(3)	1.288(6)
N(2)–C(8)	1.33(2)	1.35(2)	1.29(3)	1.345(6)
N(3)–C(8)	1.29(2)	1.35(2)	1.34(3)	1.328(7)
C(1)–C(2)	1.40(2)	1.45(2)	1.43(3)	1.438(7)
C(2)–C(3)	1.39(2)	1.39(2)	1.43(3)	1.422(6)
C(2)–C(7)	1.37(2)	1.46(2)	1.40(3)	1.399(6)
C(3)–C(4)	1.37(2)	1.39(2)	1.37(3)	1.422(7)
C(4)–C(5)	1.37(2)	1.32(2)	1.32(3)	1.346(7)
C(5)–C(6)	1.38(2)	1.41(3)	1.40(3)	1.397(7)
C(6)–C(7)	1.36(2)	1.39(2)	1.37(3)	1.372(7)
Angle	ω, deg			
S(1)Cu(1)O(1)	172.8(3)	173.0(3)	175.8(5)	168(1)
S(1)Cu(1)O(2SN(5))	91.4(3)	89.6(3)	89.3(5)	95(1)
S(1)Cu(1)O(3VS(2))		100.4(2)	101.6(5)	92.25(5)
S(1)Cu(1)N(1)	87.3(3)	86.1(3)	87.3(5)	86.3(1)
O(1)Cu(1)O(2SN(5))	89.8(4)	91.2(4)	91.2(6)	88.2(2)
O(1)Cu(1)O(3VS(2))		86.6(3)	82.5(6)	100.1(1)
O(1)Cu(1)N(1)	91.6(4)	92.5(4)	91.3(7)	90.5(1)
O(2SN(5)Cu(1)O(3VS(2))		84.8(4)	99.8(8)	90.98(14)
O(2S)Cu(1)N(1)	178.5(5)	173.4(4)	165.8(7)	175.83(17)
O(3V)Cu(1)N(1)		100.9(3)	94.5(7)	93.2(1)
Cu(1)S(1)-(8)	95.8(4)	96.0(5)	94.4(7)	95.7(2)
Cu(1)O(1)C(3)	127.7(7)	128.9(8)	131(1)	129.5(3)
Cu(1)(1)N(2)	115.2(8)	120.0(7)	116(1)	116.8(2)
Cu(1)N(1)C(1)	126.7(8)	125.8(8)	128(2)	127.7(3)
N(2)N(1)C(1)	118(1)	114(1)	115(2)	115.4(3)
N(1)N(2)C(8)	120(1)	117(1)	117(2)	118.9(4)
N(1)C(1)C(2)	126(1)	126(1)	123(2)	125.3(4)
C(1)C(2)C(3)	124(1)	123(1)	125(2)	122.3(4)
C(1)C(2)C(7)	116(1)	114(1)	117(2)	117.4(4)
C(3)C(2)C(7)	120(1)	123(1)	117(2)	120.2(4)
O(1)C(3)C(2)	1244(1)	124(1)	120(2)	123.6(4)
O(1)C(3)C(4)	117(1)	122(1)	121(2)	118.7(4)
C(2)C(3)C(4)	119(1)	114(1)	118(2)	117.7(4)
C(3)C(4)C(5)	122(1)	127(1)	124(2)	121.6(4)
C(4)C(5)C(6)	117(1)	119(1)	118(2)	119.4(4)
C(5)C(6)C(7)	122(1)	121(2)	121(2)	122.1(5)
C(2)C(7)C(6)	119(1)	116(1)	120(2)	118.9(4)
S(1)C(8)N(2)	120.9(9)	121(1)	124(2)	122.0(3)
S(1)C(8)N(3)	123(1)	121(1)	117(2)	122.6(4)
N(2)C(8)N(3)	116(1)	118(1)	119(2)	115.4(4)

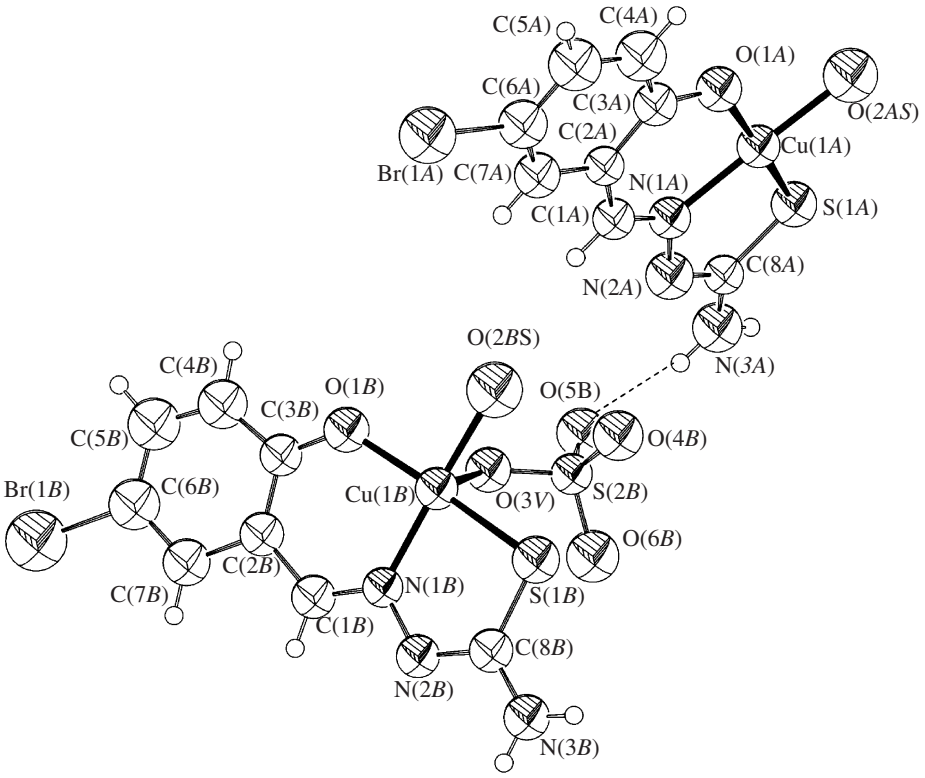


Fig. 1. Structure of complex **I**.

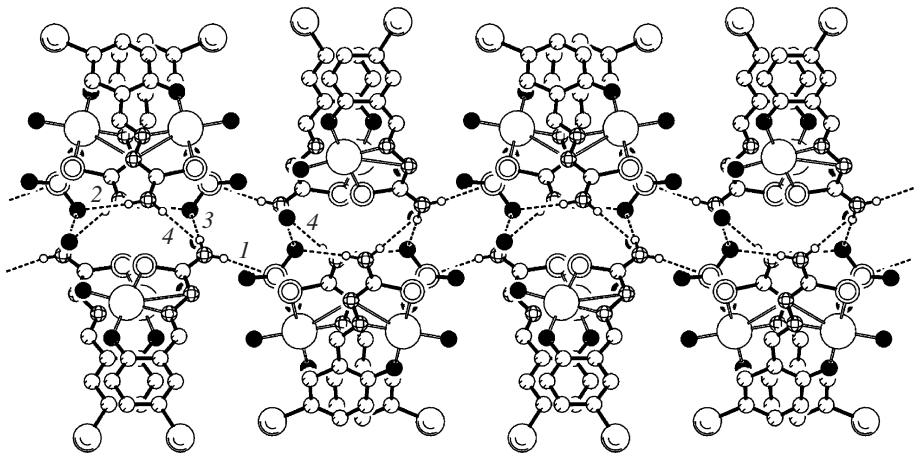


Fig. 2. Fragment of two-dimensional hydrogen bond network in structure **I**.

In cation *A*, the metal atom coordinates monodeprotonated 5-bromosalicylaldehyde thiosemicarbazone (HL) and water molecules, and in anion *B* also a sulfate ion (Fig. 1). In complex cation *A*, the S(1*A*) atom, the azomethine N(1*A*) atom, the phenolic O(1*A*) atom of the salicylidene fragment of thiosemicarbazone, and the O(2*A*S) atom of the water molecule form a distorted square around the metal atom (Cu–S(1*A*), Cu–O(1*A*), Cu–N(1*A*), Cu–O(2*A*S) are 2.263(4), 1.929(9), 1.94(1), and 1.97(1) Å, respectively; the OCuN, SCuN, and SCuO angles are 87.3(3)°–91.6(4)°, respectively. In cation *A*, the displacements of the donor atoms from the mean plane vary from –0.08 to 0.07 Å, the deviation of the copper atom from this plane equals 0.056 Å. To find out whether the metal coordination polyhedron in the complex anion *B* is a tetragonal pyramid or trigonal bipyramid, the index $\tau = (\beta - \alpha)/60$ [16] was used, where α and β are the greatest angles between the bonds formed by the central atom. If $\tau = 0$, the metal coordination polyhedron is described as a perfect tetragonal pyramid and $\tau = 1$ implies a perfect trigonal

Table 3. Geometric parameters of hydrogen bonds for compounds **I–III**

No.	D–H···A bond	Distance, Å			DHA angle, deg	Coordinates of A atom
		D···A	H···A	D–H		
			I			
1	N(3*A*)–H(32*A*)···O(5*B*)	2.93(2)	2.1	0.9	171	*x*, *y*, *z*
2	N(3*B*)–H(32*B*)···O(6*B*)	3.08(2)	2.3	0.9	159	1/2 + *x*, –3/2 – *y*, *z*
3	N(3*A*)–H(31*A*)···O(6*B*)	2.76(2)	1.9	0.9	179	–1/2 + *x*, –1 – *y*, 3/2 – *z*
4	N(3*B*)–H(31*B*)···O(1*w*)	3.08(2)	2.2	0.9	176	3/2 – *x*, –1 + *y*, 1/2 + *z*
			II			
5	N(3)–H(3a)···O(6)	2.83(2)	1.99	0.86	165	*x*, *y*, *z*
6	N(2)–H(2)···O(7)	2.79(3)	2.02	0.86	149	–*x*, *y*, 3/2 – *z*
7	N(3)–H(3b)···O(7)	3.08(2)	2.24	0.86	165	–*x*, –*y*, 1 – *z*
8	C(5)-H(5)···O(7)	3.32(2)	2.54	0.93	142	1/2 + *x*, 1/2 – *y*, 1/2 + *z*
9	C(1)–H(1)···O(7)	3.24(3)	2.55	0.93	131	–*x*, *y*, 3/2 – *z*
10	C(10)–H(10)···O(6)	3.36(3)	2.44	0.96	160	1/2 + *x*, 1/2 + *y*, *z*
			III			
11	N(3)–H(3b)···O(1)	2.971(6)	2.24	0.86	143	–1/2 + *x*, *y*, 1/2 – *z*
12	N(2)–H(2)···O(3)	2.867(6)	2.02	0.88	164	–1/2 + *x*, –1/2 – *y*, –*z*
13	N(3)–H(3a)···O(2)	3.049(6)	2.2	0.87	165	–1/2 + *x*, –1/2 – *y*, –*z*
14	C(1)–H(1)···O(3)	3.244(6)	2.41	0.95	147	–1/2 + *x*, –1/2 – *y*, –*z*

bipyramid. For anion *B* τ = 0.01; thus, the coordination polyhedron of copper is nearly a perfect tetragonal pyramid. The pyramid base is formed by the S(1*A*) atom, the azomethine N(1*B*) atom, the phenolic O(1*B*) atom of ligand L, and the O(2*B*S) atom of the water molecule. The displacements of these atoms from their mean plane vary from –0.02 to 0.02 Å; the deviation of the copper atom from this plane is 0.107 Å, which exceeds that in complex cation *A*. The bond lengths in the pyramid base in anion *B* are as follows: Cu(1*B*)–S(1*B*) 2.276(5), Cu(1*B*)–O(1*B*) 1.921(8), Cu(1*B*)–N(1*B*) 1.925(9), Cu(1*B*)–O(2*B*S) 1.99(1) Å. The axial vertex of the pyramid is occupied by the O(3V) atom of the monodentate sulfate ion (Cu(1*B*)–O(3V) 2.414(9) Å; the angles formed by this bond with the bonds of the pyramid base are in the range 84.8(4)°–100.9(3)°. In complexes *A* and *B*, the metal rings are nearly coplanar: the angles between the Cu(1)N(1)N(2)C(8)S(1) and Cu(1)N(1)C(1)C(2)C(3)O(1) planes are 4.5° and 4.6° and the angles between the planes of six-membered metal rings and the C(2)–C(7) salicylidene fragments of thiosemicarbazone are 1.6° and 1.8°.

In the crystal of **I**, complex ions *A* and *B* are combined by a hydrogen bond (**HB**) (Figs 1, 2; Table 3). Owing to HBs 2 and 3, theses pairs form two-dimensional networks parallel to (001) plane. The layers are connected by van der Waals contacts. Since water hydrogen atoms have not been located, Table 4 presents the intermolecular contacts that define the corresponding HB.

The independent part of the unit cell of **II** contains the (5-nitrosalicylidenethiosemicarbazido)dimethylsulfoxide(methanol)copper(II) complex cation and the sulfate anion. In the cation, the metal atom coordinates 5-nitrosalicylaldehyde thiosemicarbazone and methanol and dimethyl sulfoxide molecules. For the copper(II) coordination polyhedron in the crystal of **II**, τ = 0.17 [16], i.e., the coordination polyhedron of the metal atom is a slightly distorted tetragonal pyramid with the base formed by the S(1) atom, the azomethine N(1) atom, the phenolic O(1) atom of the organic ligand, and the O(3) atom of the dimethyl sulfoxide molecule. The displacements of these atoms from their mean plane are

Table 4. Short intermolecular contacts for water molecules in compound **I**

Contact	Distance, Å	Coordinates of the second atom
O(1*w*)···O(2*A*S)	2.66(1)	1/2 – *x*, 1/2 + *y*, 1 – *z*
O(1*w*)···O(4*B*)	2.80(1)	1 – *x*, –*y*, 1 – *z*
O(1*w*)···O(5*B*)	2.76(1)	1/2 – *x*, 1 + *y*, –1/2 + *z*
O(2*w*)···O(3*w*)	2.66(2)	–1 + *x*, *y*, *z*
O(2*w*)···O(2*A*S)	2.72(2)	1/2 – *x*, 1/2 + *y*, 1 – *z*
O(2*w*)···O(1*A*)	2.76(1)	1/2 – *x*, 1/2 + *y*, 1 – *z*
O(2*w*)···O(2*B*S)	2.67(1)	1 – *x*, –*y*, 1 – *z*

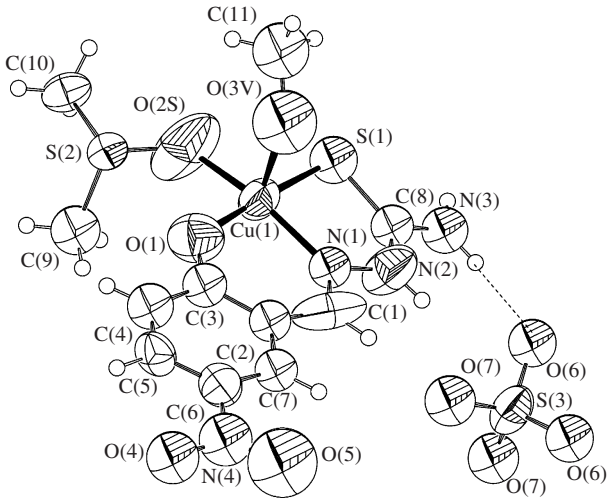


Fig. 3. Structure of complex **II**.

in the range from –0.08 to 0.09 Å; the deviation of the copper atom from this plane (0.154 Å) is greater than that in **I**. The bond lengths are as follows: Cu(1)–S(1), 2.245(6) Å; Cu(1)–O(1), 1.88(1) Å; Cu(1)–N(1), 1.95(2) Å; and Cu(1)–O(2S), 1.94(2) Å. The axial position in the pyramid is occupied by the O(3V) atom of the methanol molecule (Cu(1)–O(3V) is 2.44(2) Å; the angles formed by this bond with the bonds of the coordination pyramid base are 82.5(6)°–101.6(5)°). The metal rings in structure **II** lie almost in one plane; the angle between the Cu(1)N(1)N(2)C(8)S(1) and Cu(1)N(1)C(1)C(2)C(3)O(1) planes is 7.2° and the angle between the planes of six-membered metal ring and C(2)–C(7) salicylidene fragment of thiosemicarbazone is 4.6°.

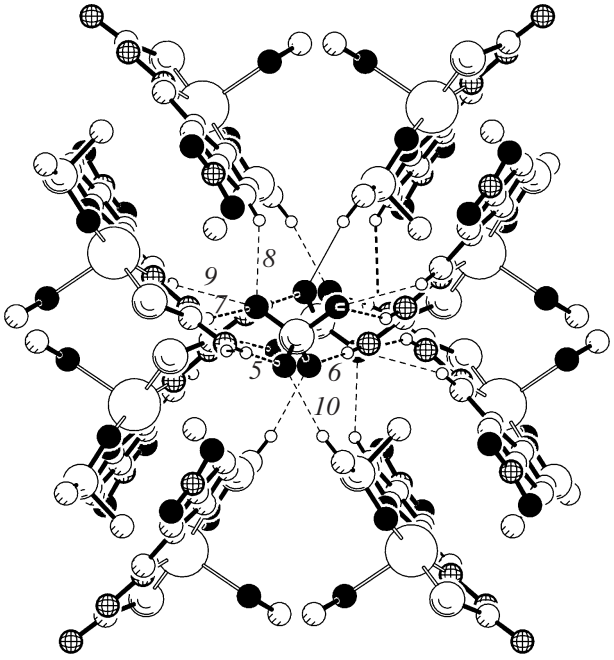


Fig. 4. Fragment of the packing of compound **II**.

In the crystal of **II**, the molecules are united by HB 5 (Figs. 3, 4; Table 3). Owing to HBs 6–10, these pairs form a three-dimensional HB motif (Fig. 4, Table 3).

In structure **III**, as in **I** or **II**, the copper atom coordinates 5-nitrosalicylaldehyde thiosemicarbazone and the thiocyanate ion NCS^-. The ion combines complexes **III** related by the glide plane *y* into infinite polymer chains along the [010] direction (Fig. 5). The coordination polyhedron of copper is a slightly distorted tetrag-

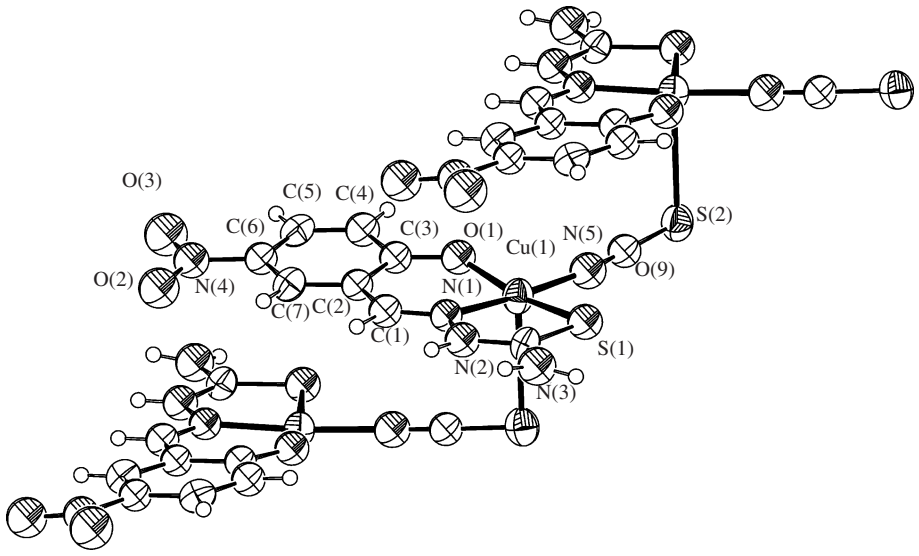


Fig. 5. Structure of the polymeric chain in compound **III**.

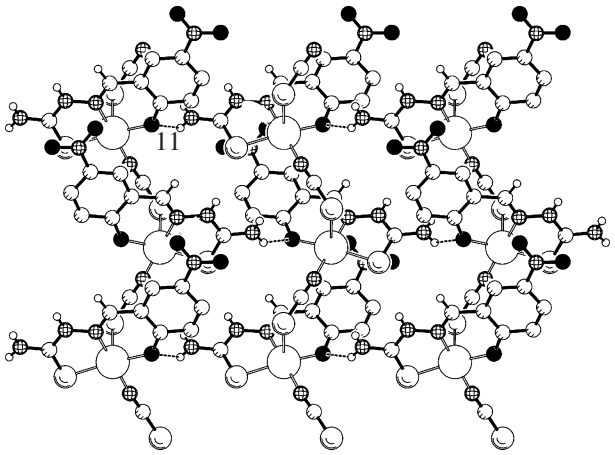


Fig. 6. Fragment of two-dimensional hydrogen bond network in structure **III**.

onal pyramid (τ = 0.14 [16]). The pyramid base is formed by the S(1) atom, the azomethine N(1) atom, the thiosemicarbazone phenolic O(1) atom, and the N(5) atom of thiocyanate. The displacements of these atoms from their mean plane vary from –0.09 to 0.08 Å; the deviation of the copper atom from this plane (0.147 Å) is greater than that in **I** and similar to that in **II**. The bond lengths are as follows: Cu(1)–S(1), 2.291(2) Å; Cu(1)–O(1), 1.937(3) Å; Cu(1)–N(1), 1.954(3) Å; and Cu(1)–N(5), 1.928(5) Å. The axial position in the pyramid is occupied by the S(2) atom of the neighboring complex related to the initial complex by plane *y* (Cu(1)–S(2) is 2.887(2) Å; the angles formed by this bond with the bonds of the coordination pyramid base are 90.5(1)°–100.1(1)°). The metal rings in structure **III** lie almost in one plane; the angle between the Cu(1)N(1)N(2)C(8)S(1) and Cu(1)N(1)C(1)C(2)C(3)O(1) planes is 7.1° and the angle between the planes of six-membered metal ring and the C(2)C(3)C(4)C(5)C(6)C(7) salicylidene fragment of thiosemicarbazone is 4.0°.

In the crystal of **III**, the polymer chains are combined by HB 11 (Fig. 6; Table 3) to form two-dimensional layers parallel to the (001) plane. Owing to HBs 12–14, these layers are combined into a three-dimensional HB motif (Fig. 7, Table 3).

The bond lengths in compounds **I**–**III** almost coincide with published data [17, 18]. An exception is the distance from the copper atom to the sulfur atom of the thioamide fragment. The Cu(1)–S(2) bond length in **III** (2.291(2) Å) exceeds that in I*A* and in **II** by 0.028 and 0.046, respectively, and is markedly longer than similar distances in binuclear copper complexes with 2-hydroxyacetophenone hexamethyleneiminothiosemicarbazone [17] (2.200(2) Å) and with 5-methyl-2-hydroxyacetophenone N(4)-dimethylthiosemicarbazone [18] (2.206(2) Å).

Our study demonstrated that coordination of tridentate thiosemicarbazones of substituted aromatic hydroxy aldehydes by the copper atom affords five- and six-membered metal rings, which lie virtually in one plane. However, the type of the complex crystal lattice depends on the nature of the substituent in the salicylidene fragment of thiosemicarbazone, on the nature of the acid residue, and on the synthesis conditions.

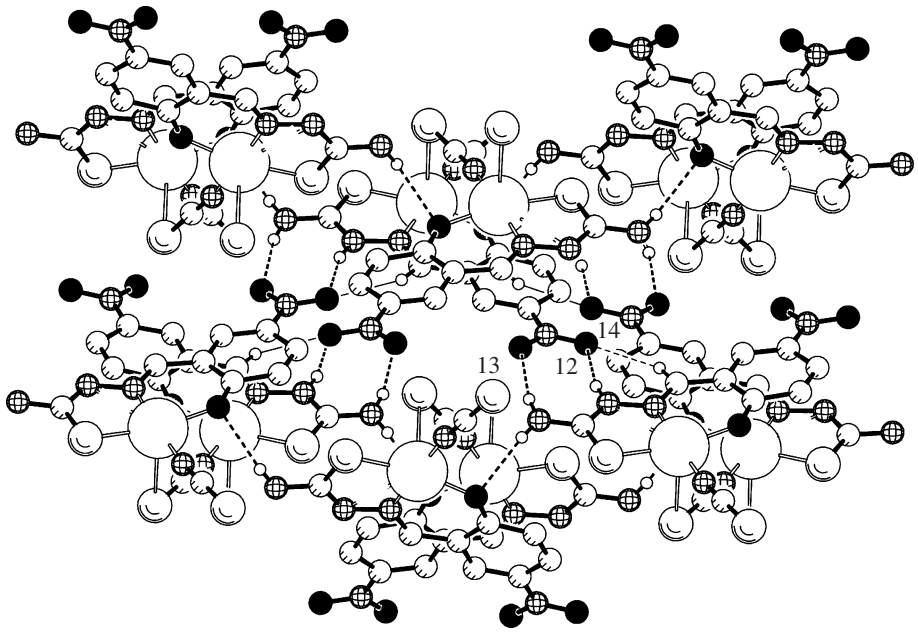


Fig. 7. Fragment of the packing of compound **III**.

REFERENCES

1. Mashkovskii, M.D., *Lekarstvennye sredstva* (Pharmaceuticals), Minsk: Belarus', 1987, vol. 2.
2. Zhungietu, G.I. and Granik, V.G., *Osnovnye printsipy konstruirovaniya lekarstv* (Main Principles of Drug Design), Chisinau: MoldGU, 2000.
3. Zelenin, K.N., Kuznetsova, O.B., Saminskaya, A.G., et al., *Khim.-Farm. Zh.*, 1994, vol. 31, no. 2, p. 34.
4. Ovsepyan, T.R., Gabrielyan, G.E., Simonyan, G.K., et al., *Khim.-Farm. Zh.,* 2000, vol. 34, no. 5, p. 21.
5. Prisakar', V.I., Tsapkov, V.I., Buracheva, S.A., et al., *Khim.-Farm. Zh.*, 2005, vol. 39, no. 5, p. 93.
6. Valdes-Martinez, J., Toscano, R.A., Zentella-Sehesa, A., et al., *Polyhedron,* 1996, vol. 15, p. 427.
7. Wang, D., Ebet, M., Schulzke, C., et al., *Eur. J. Inorg. Chem.*, 2001, p. 935.
8. Labisbal, E., Haslow, K.D., Sousa-Pedrares, A., et al., *Polyhedron*, 2003, vol. 22, p. 2831.
9. De Meulenaer, J. and Tomp, H., *Acta Crystallogr.*, 1965, vol. 19, p. 1014.
10. Sheldrick, G.M., *SHELX-86. Program for the Solution and Refinememt of Crystal Structure*, Göttingen (Germany): Univ. of Göttingen, 1986.
11. Altomare, A., Burla, M.C., Camalli, M., et al., *J. Appl. Crystallogr.*, 1999, vol. 32, p. 115.
12. Betteridge, P.W., Carruthers, J.R., Cooper, R.I., et al., *J. Appl. Crystallogr.*, 2003, vol. 36, p. 1487.
13. Spek, A.L., *J. Appl. Crystallogr.*, 2003, vol. 36, p. 7.
14. Bruno, I.J., Cole, J.C., Edginton, P.R., et al., *Acta Crysallogr., Sect. B: Struct. Sci.*, 2002, vol. 58, p. 389.
15. Allen, F.H., *Acta Crystallogr., Sect. B: Struct. Sci.*, 2002, vol. 58, p. 380.
16. Addison, A.W., Rao, J., Reedijk, J., et al., *J. Chem. Soc., Dalton Trans.*, 1984, p. 1349.
17. West, D.X., Yang, Y., Klein, T.L., et al., *Polyhedron*, 1995, vol. 14, no. 12, p. 1681.
18. Labisbal, E., Haslow, K.D., Sousa-Pedrares, A., et al., *Polyhedron*, 2003, vol. 22, p. 2831.