

STRUCTURE OF ORGANIC COMPOUNDS

Crystal Structures of Nitrate-{2-[2-(1-pyridine-2-ylethylidene)hydrazine]-1,3-benzothiazolo}aquacopper and Chloro-{2-[2-phenyl(pyridine-2-ylethylidene)hydrazine]-1,3-benzothiazolo}copper

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Abstract—Two crystal modifications of nitrate-{2-[2-(1-pyridine-2-ylethylidene)hydrazine]-1,3-benzothiazolo}aquacopper (**I** and **II**) and two modifications of chloro-{2-[2-phenyl(pyridine-2-ylethylidene)hydrazine]-1,3-benzothiazolo}copper (**III** and **IV**) have been synthesized and studied by X-ray diffraction. In structures **I** and **II**, the copper atoms coordinate a monodeprotonated molecule of the organic ligand, nitrate ions, and a water molecule. In crystals of **I**, the complexes are monomeric, whereas complexes **II** are linked via nitrate ions to form polymeric chains. In both structures the coordination polyhedron of the copper atom can be described as a distorted tetragonal bipyramid—(4 + 1 + 1) in **I** and (4 + 2) in **II**. These coordination polyhedra have different compositions. In structures **III** and **IV**, the metal atoms coordinate a monodeprotonated {2-[2-phenyl(pyridine-2-ylethylidene)hydrazine]-1,3-benzothiazolo} molecule and chloride ions. In **III** the complex-forming ion has square-planar coordination geometry, whereas structure **IV** consists of centrosymmetric dimers with two bridging chlorine atoms. It was found that nitrate-{2-[2-(1-pyridine-2-ylethylidene)hydrazine]-1,3-benzothiazolo}aquacopper possesses antitumor activity.

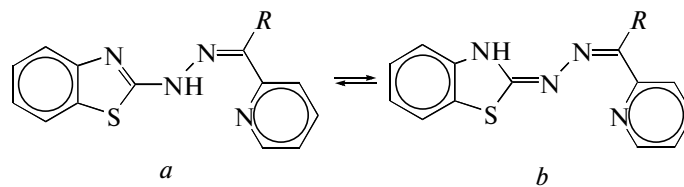
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INTRODUCTION

It is known [1–3] that Schiff bases are considered an important class of biologically active compounds. Thiazole and benzothiazole hydrazones belonging to this class of compounds exhibit anticonvulsant, anti-tuberculosis, anti-inflammatory, antibacterial, and fungicidal activities [4–8]. Bimetallic complexes with such Schiff bases exhibit higher antimicrobial and fungicidal activities when compared to the starting ligands [9]. In many cases, the biological activity of such compounds agrees well with their structures. Therefore, the synthesis and investigation of structural features of

new compounds of this type are both of theoretical and applied interest.

In the present work, we report on the synthesis and X-ray diffraction studies of two crystal modifications of nitrate-{2-[2-(1-pyridine-2-ylethylidene)hydrazine]-1,3-benzothiazolo}aquacopper (**I** and **II**) of the general formula $[\text{CuL}^1(\text{H}_2\text{O})\text{NO}_3] \cdot n\text{H}_2\text{O}$ [$n = 0$ (**I**) and 1 (**II**)] and two modifications of chloro-{2-[2-phenyl(pyridine-2-ylethylidene)hydrazine]-1,3-benzothiazolo}copper (**III** and **IV**) of the general formula $[\text{CuL}^2\text{Cl}]$.



HL¹⁻²

HL¹: R = CH₃; HL²: R = C₆H₅

Table 1. Crystallographic characteristics and the X-ray-data-collection and structure-refinement statistics for $C_{14}H_{13}CuN_5O_4S$ (**I**) and $C_{14}H_{15}CuN_5O_5S$ (**II**)

| Compound | I | II |
|--|---|---|
| <i>M</i> | 410.89 | 428.91 |
| Crystal system, sp. gr., <i>Z</i> | Monoclinic, $P2_1/c$, 4 | |
| <i>a</i> , <i>b</i> , <i>c</i> , Å | 7.2709(8), 15.1311(7), 15.7118(9) | 6.9599(2), 13.9136(3), 17.8236(4) |
| β , deg | 108.384(6) | 97.993(2) |
| <i>V</i> , Å ³ | 1640.3(2) | 1709.22(7) |
| <i>D_x</i> , g/cm ³ | 1.664 | 1.667 |
| Radiation; λ , Å | MoK α , 0.71073 | |
| μ , cm ⁻¹ | 1.490 | 1.438 |
| <i>T</i> , K | 293(2) | |
| Crystal dimensions, mm | 0.23 × 0.30 × 0.20 | 0.40 × 0.30 × 0.05 |
| Diffractometer | Xcalibur | |
| Scan mode | ω | |
| θ_{max} , deg | 29.30 | 29.02 |
| <i>h</i> , <i>k</i> , <i>l</i> ranges | -9 ≤ <i>h</i> ≤ 9, -19 ≤ <i>k</i> ≤ 18, -21 ≤ <i>l</i> ≤ 17 | -4 ≤ <i>h</i> ≤ 9, -16 ≤ <i>k</i> ≤ 17, -22 ≤ <i>l</i> ≤ 23 |
| Number of reflections: measured/unique (<i>N</i> ₁), <i>R</i> _{int} /with <i>I</i> > 2 σ (<i>I</i>) (<i>N</i> ₂) | 7619/3761, 0.0229/2848 | 7499/3905, 0.0215/3099 |
| Refinement method | Full-matrix least-squares based on <i>F</i> ² | |
| Number of parameters | 227 | 236 |
| <i>R</i> ₁ / <i>wR</i> ₂ based on <i>N</i> ₁ | 0.0577/0.0875 | 0.0534/0.0898 |
| <i>R</i> ₁ / <i>wR</i> ₂ based on <i>N</i> ₂ | 0.0376/0.0787 | 0.0371/0.0829 |
| <i>S</i> | 0.993 | 1.028 |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$, e/Å ³ | 0.379, -0.483 | 0.507, -0.348 |
| Programs | CrysAlisPro [10], SHELX97 [11], PLATON [12] | |

EXPERIMENTAL

Synthesis

Compounds **I** and **II** were synthesized according to the following procedure. A solution of copper(2+) nitrate trihydrate (5 mmol) in ethanol (10 mL) was added to a hot (50–55°C) ethanol solution (15 mL) containing 5-hydrazinobenzothiazole (5 mmol) and 2-acetylpyridine (5 mmol). The reaction mixture was refluxed with continuous magnetic stirring for 40–50 min. After the resulting brown solution cooled, a dark brown finely crystalline compound precipitated (in 80% yield). This compound was filtered off on a glass filter, washed with ethanol and diethyl ether, and dried in air. The recrystallization of this compound from ethanol gave a mixture of two types of crystals (**I** and **II**). Dark green single crystals **I** have a distorted octahedral shape, whereas green-brown single crystals **II** are square prisms. Their compositions were determined by elemental analysis.

For $C_{14}H_{13}N_5O_4CuS$ (**I**) anal. calcd. (%): C, 40.92; H, 3.44; N, 17.05; Cu, 15.46; S, 7.80.

Found (%): C, 40.82; H, 3.4; N, 16.95; Cu, 15.38; S, 7.78.

For $C_{14}H_{15}N_5O_5CuS$ (**II**) anal. calcd. (%): C, 39.20; H, 3.77; N, 16.33; Cu, 14.81; S, 7.47.

Found (%): C, 39.10; H, 3.73; N, 16.23; Cu, 14.71; S, 7.45.

Compounds **III** and **IV** were synthesized in a 70% yield of the theoretical value calculated for the reaction of ethanol solutions of benzoylpyridine with 2-hydrazinobenzothiazole and copper(2+) chloride hydrate in a molar ratio of 1 : 1 : 1. The recrystallization of this compound from ethanol gave a mixture of two types of green crystals (**III** and **IV**). These crystals have different habits—hexagonal and tetragonal-prismatic, respectively. Their compositions were determined by elemental analysis.

For $C_{19}H_{13}N_4CuSCl$ (**III**) anal. calcd. (%): C, 53.27; H, 3.30; N, 13.08; Cu, 14.83; S, 7.48; Cl, 8.28.

Found (%): C, 53.17; H, 3.26; N, 12.98; Cu, 14.73; S, 7.45; Cl, 8.18.

For $C_{38}H_{26}N_8Cu_2S_2Cl_2$ (**IV**) anal. calcd. (%): C, 53.27; H, 3.30; N, 13.08; Cu, 14.83; S, 7.48; Cl, 8.28.

Found (%): C, 53.17; H, 3.26; N, 12.98; Cu, 14.73; S, 7.45; Cl, 8.18.

The complexes are readily soluble in dimethylformamide and dimethyl sulfoxide, slightly soluble in alcohols, and almost insoluble in diethyl ether. Single crystals of the complexes suitable for X-ray diffraction studies were obtained by recrystallization from ethanol solutions.

X-ray Diffraction Study of **I–IV**

The crystallographic characteristics and the X-ray-data-collection and structure-refinement statistics are given in Tables 1 and 2. The structures were solved by

Table 2. Crystallographic characteristics and the X-ray-data-collection and structure-refinement statistics for $C_{19}H_{13}ClCuN_4S$ (**III**) and $C_{38}H_{26}Cl_2Cu_2N_8S_2$ (**IV**)

| Compound | III | IV |
|--|---|--|
| <i>M</i> | 428.38 | 856.77 |
| Crystal system, sp. gr., <i>Z</i> | Monoclinic, <i>C2/c</i> , 8 | Monoclinic, <i>P2₁/c</i> , 2 |
| <i>a</i> , <i>b</i> , <i>c</i> , Å | 24.890(3), 7.7015(7), 18.9701(16) | 10.1482(6), 7.7635(5), 23.168(2) |
| β , deg | 113.245(12) | 109.928(8) |
| <i>V</i> , Å ³ | 3341.2(6) | 1716.0(2) |
| <i>D_x</i> , g/cm ³ | 1.703 | 1.658 |
| Radiation; λ , Å | | MoK α , 0.71073 |
| μ , cm ⁻¹ | 1.603 | 1.561 |
| <i>T</i> , K | | 293(2) |
| Crystal dimensions, mm | 0.20 × 0.15 × 0.08 | 0.50 × 0.09 × 0.03 |
| Diffractometer | | Xcalibur |
| Scan mode | | ω |
| θ_{\max} , deg | 29.19 | 29.10 |
| <i>h</i> , <i>k</i> , <i>l</i> ranges | -31 ≤ <i>h</i> ≤ 30, -8 ≤ <i>k</i> ≤ 9, -25 ≤ <i>l</i> ≤ 14 | -5 ≤ <i>h</i> ≤ 13, -9 ≤ <i>k</i> ≤ 9, -31 ≤ <i>l</i> ≤ 21 |
| Number of reflections: measured/unique (<i>N</i> ₁), <i>R</i> _{int} /with <i>I</i> > 2 σ (<i>I</i>) (<i>N</i> ₂) | 7600/3840, 0.028/2946 | 6842/3904, 0.0499/2538 |
| Refinement method | | Full-matrix least-squares based on <i>F</i> ² |
| Number of parameters | | 235 |
| <i>R</i> ₁ / <i>wR</i> ₂ based on <i>N</i> ₁ | 0.0595/0.0882 | 0.0918/0.0920 |
| <i>R</i> ₁ / <i>wR</i> ₂ based on <i>N</i> ₂ | 0.0394/0.0790 | 0.0499/0.0757 |
| <i>S</i> | 1.025 | 1.029 |
| $\Delta\rho_{(\max)}$, $\Delta\rho_{(\min)}$, e/Å ³ | 0.409, -0.340 | 0.414, -0.349 |
| Programs | CrysAlisPro [10], SHELX97 [11], PLATON [12] | |

direct methods and refined with anisotropic displacement parameters for non-hydrogen atoms. The hydrogen atoms were positioned geometrically and refined with the temperature factors U_H , which were 1.2 times larger than those of the attached carbon and oxygen atoms. Selected interatomic distances and bond angles are listed in Tables 3 and 4. The coordinates of the reference atoms of structures **I–IV** were deposited in the Cambridge Crystallographic Data Centre (CCDC nos. 926496–926499). In the figures presenting crystal packing motifs of structures **I–III**, only hydrogen atoms that are involved in the hydrogen bonding are shown. In the crystal packing of **IV**, the hydrogen atoms are not shown for the sake of clarity. The structures were analyzed using the data retrieved from the Cambridge Structural Database (Version 5.30) [13, 14].

RESULTS AND DISCUSSION

In structures **I–IV**, the monodeprotonated ligands L^{1-2} are coordinated to the copper atoms through the

donor nitrogen atoms N1, N2, and N3 (Figs. 1–3). The C1–N4 bond is rather short (1.331–1.344 Å) and is largely double in character, which indicates that form *b* makes the major contribution to the structure. In the thiazole and hydrazine moieties, the S–C, C–N, and N–N bonds are delocalized and are 1.5-order bonds (Tables 3 and 4). However, the N2 and C13 atoms in **I–IV** form a double bond (C–N, 1.285–1.301 Å).

The coordinated azomethine ligands L^{1-2} (except for the phenyl substituent in **III** and **IV**) are nearly planar. The angles between the five-membered metallocycles (Cu1N1N2N4C1) and (Cu1N2N3C12C13) are 2.1°, 2.4°, 1.6°, and 1.1° in **I–IV**, respectively. The dihedral angles between these metallocycles and the adjacent benzothiazole and pyridine moieties (S1N1C1–C7) and (N3C8–C12) are 1.5°, 3.0°, 1.8°, 3.0°, 1.1°, 5.4° and 5.3°, 3.1°, respectively. In **III** and **IV** the dihedral angles between the phenyl ring (C14–C19) and the abovementioned metallocycles are 63.4°, 61.1° and 59.4°, 60.8°.

Table 3. Selected interatomic distances d (Å) and bond angles ω (deg) in structures **I** and **II**

| Bond | d | | Angle | ω | |
|-----------------|-----------|-----------|------------------|------------|------------|
| | I | II | | I | II |
| Cu1–N2 | 1.953(2) | 1.948(2) | N1–Cu1–O3 [O3A]* | 86.09(9) | 92.65(8) |
| Cu1–N1 | 1.965(2) | 1.973(2) | N2–Cu1–O3 [O3A]* | 114.34(9) | 91.86(9) |
| Cu1–O1 | 2.214(2) | 1.956(2) | N1–Cu1–O1 | 95.93(8) | 100.23(7) |
| Cu1–N3 | 2.010(2) | 2.016(2) | N3–Cu1–O1 | 93.13(8) | 99.38(8) |
| Cu1–O2 | 2.017(2) | 2.581(2) | N3–Cu1–O3 [O3A]* | 99.78(8) | 91.42(7) |
| Cu1–O3 | 2.762(2) | 2.546(2) | O2–Cu1–O1 | 84.43(7) | 85.56(8) |
| N3–C12 | 1.358(2) | 1.355(3) | O2–Cu1–O3 [O3A]* | 50.88(8) | 165.08(8) |
| S1–C1 | 1.739(3) | 1.745(2) | N4–N2–Cu1 | 118.0(2) | 118.20(15) |
| S1–C2 | 1.748(4) | 1.749(2) | C12–N3–Cu1 | 112.94(19) | 112.29(16) |
| N2–C13 | 1.285(4) | 1.294(3) | C1–N1–Cu1 | 108.8(2) | 109.57(16) |
| N2–N4 | 1.371(3) | 1.366(3) | C13–N2–Cu1 | 118.8(2) | 118.42(16) |
| N4–C1 | 1.331(4) | 1.344(3) | C7–N1–Cu1 | 138.72(18) | 138.41(16) |
| N1–C1 | 1.345(3) | 1.329(3) | N5–O2–Cu1 | 112.92(14) | 156.14(8) |
| N1–C7 | 1.376(4) | 1.392(3) | C8–N3–Cu1 | 128.54(18) | 128.55(7) |
| C7–C2 | 1.413(4) | 1.409(3) | C1–S1–C2 | 89.99(15) | 89.22(11) |
| C12–C13 | 1.475(4) | 1.479(3) | C7–C2–S1 | 109.7(3) | 110.30(18) |
| Angle | ω | ω | N1–C1–S1 | 113.8(3) | 114.88(18) |
| N2–Cu1–N1 | 80.38(11) | 79.99(8) | C1–N1–C7 | 112.4(2) | 111.9(2) |
| N2–Cu1–O1 | 110.69(8) | 173.18(8) | N4–C1–N1 | 125.8(3) | 124.9(2) |
| N2–Cu1–N3 | 80.18(10) | 80.61(8) | N3–C12–C13 | 114.8(3) | 115.4(2) |
| N1–Cu1–N3 | 160.41(9) | 160.29(8) | N1–C7–C2 | 114.0(3) | 113.6(2) |
| N1–Cu1–O2 [O1]* | 100.42(8) | 100.28(8) | C1–N4–N2 | 107.0(2) | 107.34(19) |
| N3–Cu1–O2 [O1]* | 97.71(8) | 99.39(8) | N2–C13–C12 | 113.2(2) | 112.9(2) |
| N2–Cu1–O2 | 164.77(8) | 101.21(8) | | | |

* The corresponding atom name in crystal structure **II** is given in brackets.

In structures **I** and **II**, the copper atoms are coordinated also by nitrate ions and water molecules. In crystals **I** the complexes are monomeric, whereas the complexes in **II** are linked by the bridging nitrate groups to form polymeric chains along the [100] direction (Fig. 2). In both structures, the coordination polyhedron of the Cu1 atom can be described as a distorted tetragonal bipyramid, but these bipyramids have different compositions in **I** and **II**. Both in **I** and **II**, the nitrogen atoms N1, N2, and N3 of the organic ligand L^1 lie in the equatorial plane of the bipyramids. However, the fourth vertex of the equatorial plane in **I** is occupied by the oxygen atom O2 of the nitrate

group, whereas this position in **II** is occupied by the oxygen atom O2 of the water molecule. The deviations of these donor atoms from the mean planes formed by these atoms are 0.087, 0.103, -0.081 , and 0.071 Å in **I** and -0.078 , 0.091 , -0.076 , and 0.064 Å in **II**. The axial positions of the bipyramid in complex **I** are occupied by the water molecule O1 and the second oxygen atom (O3) of the bidentate-chelate nitrate group. The copper atom is displaced by 0.175 Å from the equatorial plane of the bipyramid toward the oxygen atom O1 of the water molecule. The corresponding Cu1–O1 and Cu1–O3 distances are $2.214(2)$ and $2.762(3)$ Å, respectively. Therefore, this bipyramid can be

Table 4. Selected interatomic distances d (Å) and bond angles ω (deg) in structures **III** and **IV**

| Bond | d | | Angle | ω | |
|-----------------|------------|------------|-----------------|------------|------------|
| | III | IV | | III | IV |
| Cu1–N2 | 1.975(2) | 1.966(3) | N2–Cu1–Cl1 | 176.75(7) | 176.72(9) |
| Cu1–N1 | 1.976(2) | 1.978(3) | N4[N3]*–Cu1–Cl1 | 97.38(6) | 96.36(9) |
| Cu1–N4 [N3]* | 2.030(2) | 2.013(3) | N1–Cu1–Cl1A | | 90.85(9) |
| Cu1–Cl1 | 2.2036(8) | 2.217(1) | N3–Cu1–Cl1A | | 89.79(10) |
| Cu1–Cl1A | | 2.959(2) | Cl1–Cu1–Cl1A | | 100.26(11) |
| S1–C1 | 1.741(3) | 1.747(3) | C1–N1–Cu1 | 109.58(17) | 108.9(2) |
| S1–C2 | 1.748(3) | 1.747(4) | C7–N1–Cu1 | 138.86(18) | 138.9(2) |
| N1–C1 | 1.344(3) | 1.332(4) | C13–N2–Cu1 | 118.00(17) | 117.6(2) |
| N2–C13 | 1.301(3) | 1.296(4) | N4–N2–Cu1 | 118.90(16) | 118.0(2) |
| N1–C7 | 1.403(3) | 1.393(4) | C12–N3–Cu1 | 113.20(17) | 112.9(2) |
| N3–C12 | 1.361(3) | 1.354(4) | C8–N3–Cu1 | 127.99(19) | 128.26(2) |
| N2–N4 | 1.357(3) | 1.356(4) | N1–C1–S1 | 114.9(2) | 114.4(3) |
| N4–C1 | 1.340(3) | 1.335(4) | C1–S1–C2 | 89.53(13) | 89.59(17) |
| C7–C2 | 1.397(4) | 1.401(5) | C7–C2–S1 | 110.4(2) | 110.1(3) |
| C13–C12 | 1.476(3) | 1.485(5) | C1–N1–C7 | 110.9(2) | 111.7(3) |
| Angle | ω | ω | C1–N4–N2 | 106.8(2) | 107.4(3) |
| N1Cu1–N2 | 79.21(9) | 79.58(12) | N1–C1–N4 | 125.4(2) | 125.6(3) |
| N1–Cu1–N4 [N3]* | 159.20(9) | 159.47(12) | C2–C7–N1 | 114.3(2) | 114.2(3) |
| N2–Cu1–N4 [N3]* | 80.00(9) | 80.36(12) | N2–C13–C12 | 113.8(2) | 113.0(3) |
| N1–Cu1–Cl1 | 103.39(7) | 103.69(9) | | | |

* The corresponding atom name in crystal structure **IV** is given in brackets.

described as (4 + 1 + 1). In complex **II** the axial positions of the bipyramid are occupied by the O2 and O3 atoms of the bridging nitrate group. The copper atom is displaced by 0.039 Å from the equatorial plane of the bipyramid toward the oxygen atom O3 of the nitrate group. The corresponding Cu1–O2 and Cu1–O3 distances are 2.583(2) and 2.549(2) Å, respectively; i.e., they substantially differ from those in complex **I**. This bipyramid can be described as (4 + 2). The angles between these bonds and the atoms lying in equatorial plane of the bipyramids in **I** and **II** fall in the ranges of 50.9°–114.3°, 84.4°–110.7° and 83.4°–101.13°, 81.4°–91.8°, respectively. The O1–Cu1–O3 and O2'–Cu1–O3 angles are 134.6° and 165.6°. The volumes of the coordination bipyramids of the copper atoms in these complexes are 11.496 and 12.966 Å³, respectively.

In crystal **I** the translation-related complexes are linked by O1–H1...O3 hydrogen bonds to form infinite chains along the [100] direction. The chains are linked to each other by “nonclassical” [15] C10–H11...O3 and C3–H10...O3 hydrogen bonds to form layers parallel to the (001) plane. In the crystals the layers are, in turn, linked to each other by O1–H2...O2 hydrogen bonds related via inversion centers (Fig. 4, Table 5). According to the criterion proposed in [12, 16] ($Cg \cdots Cg < 6.0$ Å, $\beta < 60.0^\circ$, where β is the angle between the CgICgJ vector and the normal to the aromatic ring CgI), there are π – π stacking interactions between the rings Cg1(N3C8–C12) and Cg2(C2–C7) in the layers. The Cg1...Cg2 ($2 - x, 1/2 + y, 1/2 - z$) distance between the centroids of these moieties is 3.778 Å, and the β angle is 8.3°.

In crystal **II** the polymeric chains are linked to each other by O5–H13...N4 and O1–H2...O5 hydrogen

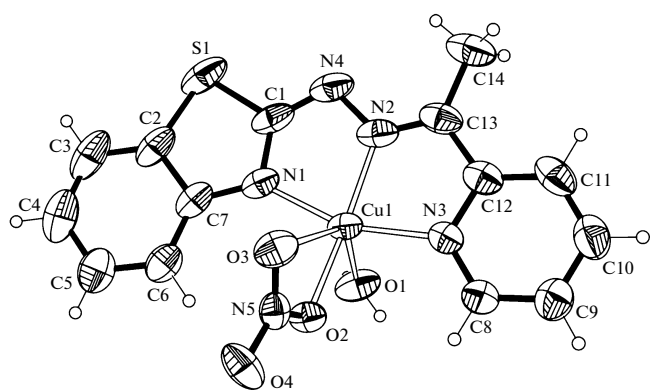


Fig. 1. Atomic numbering scheme for complex I.

bonds involving outer-sphere water molecules. Within the chains the nitrate groups form O1–H1...O4 and O5–H12...O4 hydrogen bonds with both water molecules (Fig. 5, Table 5). In the crystal the polymeric chains are linked together via both π – π stacking interactions between the rings and X –H...Cg(π -ring) interactions. The Cg(S1N1C1C2C7)...Cg(N3C8–C12) ($2 - x, 1/2 + y, 1/2 - z$) distance is 3.883 Å, and $\beta = 23.5^\circ$. For the C14–H9...Cg(C8–C12) ($2 - x, 1/2 + y, 1/2 - z$) and C14–H10...Cg(C8–C12) ($1 - x, 1/2 + y, 1/2 - z$) interactions, the H...Cg distances are 2.69 and 2.80 Å, respectively; γ are -7.5° and 13.7° .

Compounds **III** and **IV** are polymorphic. In **III** the copper atom has square-planar coordination geometry, whereas structure **IV** consists of centrosymmetric dimers with bridging chlorine atoms (Fig. 3). In complex **III** the chlorine atom is in the terminal position. The shortest intermolecular contacts involving this atom are as follows: C11...H12–C8 ($-x, y, -1/2 - z$) 2.81 Å (this contact can be considered a hydrogen bond); C11–C1, C11...C1 ($x, 2 - y, -z$) 3.556 Å. In crystal **IV** the coordination polyhedron of the central atom can be described as a distorted tetragonal pyra-

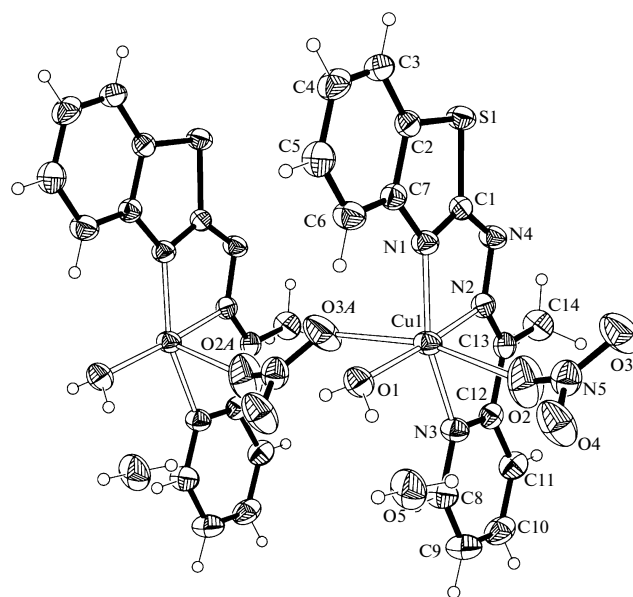


Fig. 2. Formation of the polymeric chain in structure II.

mid. This interpretation is supported by the criterion $\tau = (\beta - \alpha)/60$ proposed in [17], where α and β are the largest angles between the bonds formed by the central atom. If τ is 0, the coordination polyhedron of the metal atom is described as an ideal tetragonal pyramid; if τ is 1, the coordination polyhedron is considered an ideal trigonal bipyramid. In structure $\tau = (176.72 - 159.47)/60 = 0.29$, which confirms our conclusion that the coordination polyhedron of the copper atom can be considered a distorted tetragonal pyramid. In structure **III** the deviations of the donor atoms N1, N2, N3, and C11, which lie in the base of the pyramid, from the mean plane passing through these atoms are 0.01, -0.013 , 0.01, and -0.008 Å, respectively. The deviation of the copper atom from this plane is 0.025 Å. In structure **IV** the corresponding

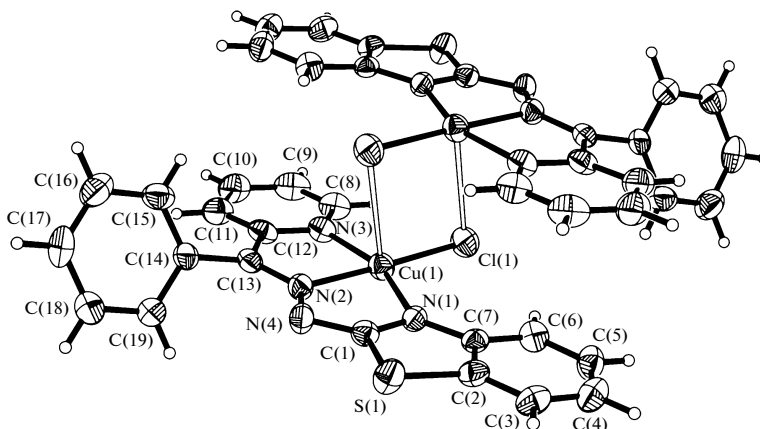


Fig. 3. Structure of the dimer in structure IV. The atomic numbering scheme is given for complexes **III** and **IV**.

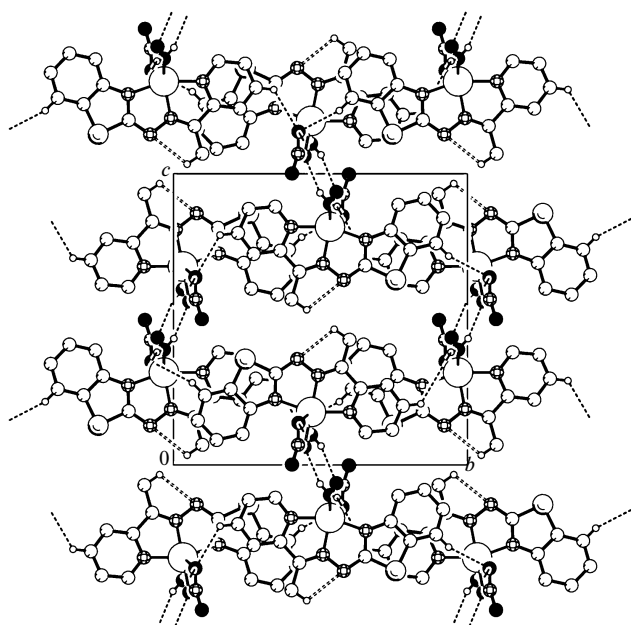


Fig. 4. Fragment of the molecular packing in crystal I.

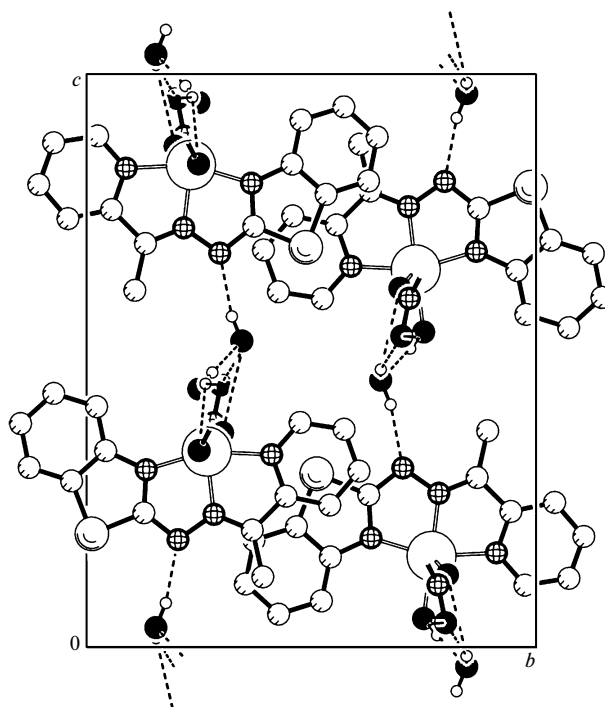


Fig. 5. Fragment of the crystal packing in structure II.

deviations are -0.035 , 0.044 , -0.036 , 0.028 , and 0.038 Å. The apical vertex of the coordination pyramid of the Cu1 atom in IV is occupied by the chlorine atom of the adjacent complex related to the initial complex by an inversion center with a distance of $2.259(3)$ Å. The angles between this bond and the atoms of the base of the tetragonal pyramid are in the range of 79.8° – 100.3° . The volume of the coordination pyramid of the Cu1 atom is 8.17 Å³.

In crystal III the complexes related by twofold axes are linked in pairs via the C8–H12...C11 hydrogen bonds (Fig. 6, Table 5). There are π – π stacking interactions between the rings Cg1(Cu1,N1,N2,N4,C1) and Cg2(C2–C7) of the complexes. The Cg1...Cg2 ($-x, 1-y, -z$) distance is 3.569 Å, and $\beta = 14.5^\circ$. In

Table 5. Geometric parameters of the hydrogen bonds in compounds I–III

| <i>D</i> –H... <i>A</i> bond | Distance, Å | | | <i>DHA</i> , angle, deg | Coordinates of the atom <i>A</i> |
|------------------------------|-------------|---------------|-----------------------|-------------------------|----------------------------------|
| | <i>D</i> –H | H... <i>A</i> | <i>D</i> ... <i>A</i> | | |
| I | | | | | |
| O1–H1...O3 | 0.72 | 2.23 | 2.902 | 157 | $-1 + x, y, z$ |
| O1–H2...O2 | 0.78 | 2.08 | 2.826 | 161 | $1 - x, 1 - y, -z$ |
| C3–H10...O3 | 0.93 | 2.56 | 3.367 | 145 | $2 - x, -1/2 + y, 1/2 - z$ |
| C10–H11...O3 | 0.93 | 2.58 | 3.212 | 126 | $2 - x, 1/2 + y, 1/2 - z$ |
| II | | | | | |
| O1–H1...O4 | 0.82 | 1.96 | 2.762 | 168 | $1 + x, y, z$ |
| O1–H2...O5 | 0.83 | 1.77 | 2.606 | 175 | $x, 1/2 - y, 1/2 + z$ |
| O5–H12...O4 | 0.82 | 2.21 | 3.003 | 162 | $x, 1/2 - y, -1/2 + z$ |
| O5–H13...N4 | 0.82 | 1.99 | 2.793 | 168 | x, y, z |
| III | | | | | |
| C8–H12...C11 | 0.93 | 2.81 | 3.453 | 127 | $-x, y, -1/2 - z$ |

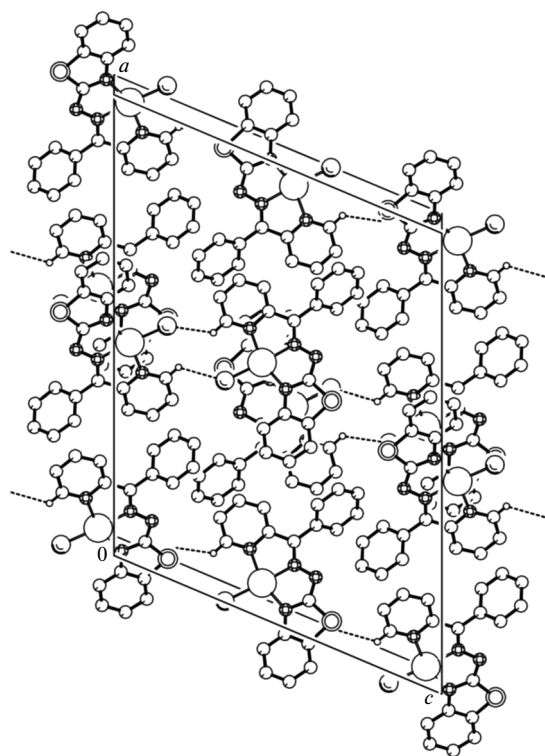


Fig. 6. Fragment of the crystal packing in structure III.

In addition, there is the metal $\cdots\pi$ ring interaction. The Cu \cdots Cg2 ($-x, 2 - y, -z$) distance is 3.537 Å, $\gamma = 18.5^\circ$. In the crystal structure there are also X-H \cdots Cg and Y-X \cdots Cg (π -ring) interactions. For Cu1-C11 \cdots Cg1 ($-x, 2 - y, -z$), the C11 \cdots Cg distance is 3.78 Å and the γ angle is 25.1°. For C18-H \cdots Cg3 (C14-C19) ($1/2 - x, 1/2 + y, 1/2 - z$), the H \cdots Cg distance is 2.79 Å and $\gamma = 14.0^\circ$.

In crystal IV there are no hydrogen bonds between the dimers (Fig. 7). The complexes are linked by the π - π stacking interaction Cg1(Cu1, N1, N2, N4, C1) \cdots Cg2(Cu1, N2, N3, C12C13) (the Cg1 \cdots Cg2

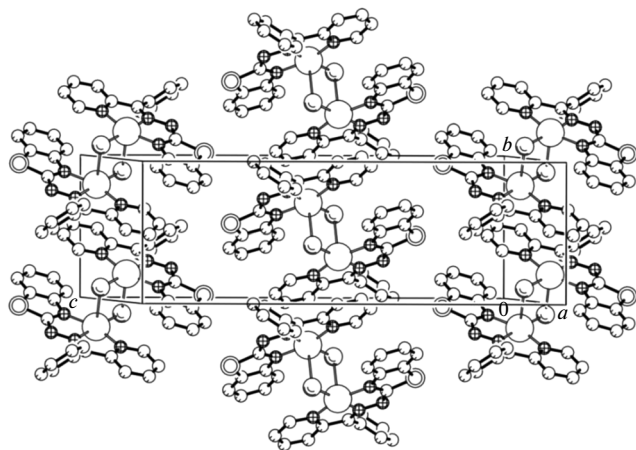


Fig. 7. Fragment of the crystal packing in structure IV.

($1 - x, 2 - y, -z$) distance is 3.424 Å, $\beta = 56.7^\circ$), the metal $\cdots\pi$ -ring interaction (the Cu1 \cdots Cg(N3C8-C12) ($1 - x, 1 - y, -z$) distance is 3.424 Å, $\gamma = 9.7^\circ$), and the C18-H \cdots Cg(C14-C19) ($2 - x, -1/2 + y, 1/2 - z$) interaction (H \cdots Cg 2.8 Å, $\gamma = 10.2^\circ$).

It was shown [18–20] that bimetallic coordination compounds with sulfur-containing Schiff bases can exhibit selective anticancer activity. Hence, we studied the in vitro anticancer activity of the complex compounds [CuL(H₂O)NO₃] \cdot nH₂O [*n* = 0 (I), 1 (II)] using the human myeloid leukemia cells HL-60. It was found that the compounds under study inhibit the growth of this type of cancer cells as efficiently as chemotherapeutic agents used in medicine for the prophylaxis and treatment of leukemia. At a concentration of 10⁻⁵ mol/L, these compounds inhibit the growth and progression of 90.7% of cancer cells; at a concentration of 10⁻⁶ mol/L, 98.3% of cancer cells are inhibited.

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