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Crystal Structures of Nitrato-{4-Bromo-2-[(2-Hydroxyethylimino)methyl]phenolo}-(3,5-Dibromopyridine)copper and Nitrato-{2,4-Dibromo-6-[(2-Hydroxyethylimino)methyl]phenolo}-(3,5-Dibromopyridine)copper

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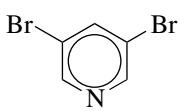
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Abstract—The crystal structures of nitrato-{4-bromo-2-[(2-hydroxyethylimino)methyl]phenolo}-(3,5-dibromopyridine)copper (**I**) and nitrato-{2,4-dibromo-6-[(2-hydroxyethylimino)methyl]phenolo}-(3,5-dibromopyridine)copper (**II**) are determined. The crystals of compound **I** are orthorhombic: a = 14.157(3) Å, b = 15.420(3) Å, c = 17.494(4) Å, space group $Pbca$, Z = 8, R = 0.067. The crystals of compound **II** are monoclinic: a = 10.675 Å, b = 13.973 Å, c = 14.007 Å, β = 111.92°, space group $P2_1/n$, Z = 4, R = 0.0464. In the structures of compounds **I** and **II**, the copper atom coordinates, correspondingly, singly deprotonated 4-bromo-2-[(2-hydroxyethylimino)methyl]phenol and 2,4-dibromo-6-[(2-hydroxyethylimino)methyl]phenol molecules, and 3,5-dibromopyridine, and the nitrate ion. The coordination polyhedron of the copper ion in complexes **I** and **II** is a slightly distorted tetragonal pyramid. The bases of the pyramids are formed by the imine and pyridine nitrogen atoms and the phenolic and alcoholic oxygen atoms, and the axial vertices are occupied by the oxygen atoms of the monodentate nitrato groups. In the complexes under study, the six-membered metallocycles are slightly bent along the phenolic oxygen–azomethine nitrogen lines. The five-membered metallocycles have asymmetric *gauche* conformation. In crystal, complexes **I** are united, due to the slip plane a, through bifurcate hydrogen bonds into infinite chains along the direction [100]. Complexes **II** in crystal form two-dimensional networks by means of hydrogen bonds.

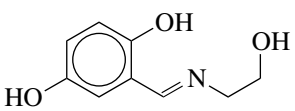
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INTRODUCTION

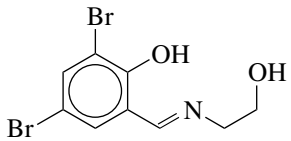
It has been shown previously in [1, 2] that copper(II) nitrate with 2-[2-(hydroxyethylimino)methyl]phenol, pyridine, and its derivatives forms polynuclear coordination compounds showing antimicrobial activity. The structures of these substances, dentate character of the nitrato group, and physicochemical and antimicrobial properties are determined by the nature of amine in the composition of the complex. Since only salicylic aldehyde was used in the syntheses as the initial substance, it was of interest to establish the influence of various substituents introduced into the composition of the salicylidene fragment of azomethine on the structures and properties of the complexes. Therefore, we synthesized nitrato-{4-bromo-2-[(2-hydroxyethylimino)methyl]phenolo}-(3,5-dibromopyridine)copper [$CuALNO_3$] (**I**) and nitrato-{2,4-dibromo-6-[(2-hydroxyethylimino)methyl]phenolo}-(3,5-dibromopyridine)copper [$CuAL^1NO_3$] (**II**) and determined their structures by X-ray diffraction analysis.



A



HL



HL^1

EXPERIMENTAL

Synthesis of complex I. A solution containing 4-bromo-2-[(2-hydroxyethylamino)methyl]phenol (10 mmol) and 3,5-dibromopyridine (10 mmol) in ethanol (30 ml) was added with continuous magnetic stirring and heating (50–55°C) to a solution of copper(II) nitrate trihydrate (10 mmol) in ethanol (20 ml). Then the reaction mixture was heated with a reflux condenser for 45–50 min. Dark green crystals precipitated on cooling from the resulting solution were filtered on a glass filter, washed with small amounts of ethanol and ether, and dried in air. The yield of complex **I** was 66%. Complex **I** is well soluble in dimethylformamide (DMF) and dimethyl sulfoxide, slightly soluble in water and alcohols, and almost insoluble in ether.

For $C_{14}H_{12}Br_3CuN_3O_5$

anal. calcd. (%): C 27.77, H 2.00, Br 39.58, Cu 10.49, N 6.94.

Found (%): C 27.54, H 1.85, Br 39.40, Cu 10.25, N 6.79.

Synthesis of complex II. The complex was synthesized according to a procedure similar to that described for complex **I**, using copper(II) nitrate trihydrate, 2,4-dibromo-6-[(2-hydroxyethylimino)methyl]phenol, and 3,5-dibromopyridine taken in a molar ratio of 1 : 1 : 1. The yield of complex **II** was 78%.

For $C_{14}H_{11}Br_4CuN_3O_5$

anal. calcd. (%): C 24.57, H 1.62, Br 46.70 Cu 9.29, N 6.14.

Found (%): C 24.39, H 1.50, Br 46.70 Cu 9.17, N 6.01.

Single crystals of compounds **I** and **II** suitable for X-ray diffraction analysis were prepared by the recrystallization of the studied substances from an ethanol–DMF (3 : 1) mixture.

X-ray diffraction analyses of complexes **I** and **II** were carried out on Philips PW1100 and Nonius Kappa CCD diffractometers (MoK_α radiation, $\lambda = 0.71073$ Å). An absorption correction was applied only for complex **I** using the SHELXTL-NT V. 5.1 programs [3]. The structures of compounds **I** and **II** were solved by direct methods using the SHELX-97 [4] and SIR92 [5] programs and refined by the least-squares method using the SHELX-97 [5] and CRYSTALS [6] programs, respectively, in the anisotropic approximation for non-hydrogen atoms and in the isotropic approximation for hydrogen atoms. Hydrogen atoms in complexes **I** and **II** were included in the refinement in the geometrically calculated positions, and their temperature factors U_H were taken to be 1.5 times higher than those of the carbon and oxygen atoms bonded to these hydrogen atoms.

The experimental details for complexes **I** and **II** are given in Table 1. Selected interatomic distances and bond angles are presented in Table 2. The coordinates of basal atoms in the structures under study were deposited with the Cambridge Structural Database (CCDC 288827 and 288828). Geometric calculations and figure plots were made using the PLATON program [7]. The materials from the Cambridge Structural Database (V. 5.26) [8, 9] were used for analyses of the obtained structures.

Table 1. Crystallographic data and details of the experiment and refinement of structures **I** and **II**

Parameter	Value	
	I	**II**
Empirical formula	$C_{14}H_{12}Br_3CuN_3O_5$	$C_{14}H_{11}Br_4CuN_3O_5$
M	605.54	684.42
Temperature, K	293(2)	293 (2)
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	$P2_1/n$
Cell parameters		
a, Å	14.157(3)	10.675
b, Å	15.420(3)	13.973
c, Å	17.494(4)	14.007
β, deg		111.92°
V, Å^3	3819.0(13)	1938.26
Z	8	4
ρ(calc), g/cm^3	2.106	2.345
μ_{Mo}, mm^{-1}	7.451	9.404
Crystal sizes, mm	0.4 × 0.2 × 0.2	0.2 × 0.1 × 0.05
θ range, deg	3.04–27.02	2.1–26.9
Number of measured reflections	4118	14662
Number of independent parameters	4118	3529 (R_{int} = 0.131)
Number of refined parameters	235	245
Goodness-of-fit for F_2	0.843	0.975
Final R factor [$I > 2\sigma(I)$]	R_1 = 0.0574, wR_2 = 0.1434	R_1 = 0.045, wR_2 = 0.0586
R factor (over the whole set)	R_1 = 0.067, wR_2 = 0.1906	R_1 = 0.0464, wR_2 = 0.0604
$\Delta\rho_{max}$ and $\Delta\rho_{min}$, e A^{-3}	0.862 and –0.878	1.16 and –1.97

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

Bond	**I**	**II**
	d, Å	
Cu(1)-O(1)	1.870(6)	1.889(3)
Cu(1)–O(2)	2.033(6)	2.005(3)
Cu(1)–O(3)	2.425(7)	2.412(4)
Cu(1)–N(1)	1.936(7)	1.947(4)
Cu(1)–N(2)	2.040(7)	2.017(4)
O(1)–C(7)	1.319(10)	1.299(5)
O(2)–C(9)	1.429(10)	1.429(7)
N(1)–C(1)	1.292(10)	1.270(6)
N(1)–C(8)	1.456(10)	1.467(7)
C(1)–C(2)	1.407(12)	1.452(6)
C(2)–C(3)	1.439(11)	1.403(6)
C(2)–C(7)	1.442(12)	1.421(6)
C(3)–C(4)	1.316(12)	1.365(6)
C(4)–C(5)	1.396(12)	1.388(6)
C(5)–C(6)	1.390(11)	1.384(6)
C(6)–C(7)	1.374(12)	1.414(6)
C(8)–C(9)	1.502(13)	1.518(8)
Angle	ω, deg	
O(1)Cu(1)O(2)	165.0(3)	171.9(1)
O(1)Cu(1)O(3)	111.4(3)	96.6(1)
O(1)Cu(1)N(1)	94.2(3)	93.5(2)
O(1)Cu(1)N(2)	90.2(3)	90.6(2)
O(2)Cu(1)O(3)	83.6(2)	90.1(1)
O(2)Cu(1)N1	81.9(3)	83.1(2)
O(2)Cu(1)N(2)	92.7(3)	92.3(2)
O3Cu(1)N(1)	99.8(3)	81.7(2)
O3Cu(1)N(2)	82.7(3)	104.5(2)
N(1)Cu(1)N(2)	173.7(3)	172.3(2)
Cu(1)O(1)C7	128.0(6)	127.2(3)
Cu(1)O(1)C(9)	112.2(5)	109.8(3)
Cu(1)O(3)N(3)	120.7(6)	127.2(3)
Cu(1)N(1)C(1)	125.5(6)	125.8(3)
Cu(1)N(1)C(8)	112.1(6)	114.3(3)
C(1)N(1)C(8)	122.5(8)	119.8(4)
Cu(1)N(2)C(10)	121.0(8)	120.9(3)
C(10)N(2)C(14)	121.4(7)	119.4(4)
Cu(1)N(2)C(14)	116.6(6)	119.6(3)
N(1)C(1)C(2)	124.7(9)	124.9(4)
C(3)C(2)C(7)	116.7(8)	120.5(4)
C(1)C(2)C(3)	118.6(8)	116.8(4)
C(1)C(2)C(7)	124.7(8)	122.5(4)
C(2)C(3)C(4)	122.0(9)	120.9(4)
C(3)C(4)C(5)	121.6(8)	120.8(4)
C(4)C(5)C6	118.9(9)	118.6(4)
C(5)C6C(7)	121.8(9)	123.3(4)
C(2)C(7)C(6)	119.1(8)	115.9(4)
O(1)C(7)C(6)	119.0(8)	119.3(4)
O(1)C(7)C(2)	121.9(8)	124.8(4)
N(1)C(8)C(9)	107.3(8)	107.5(4)
O(2)C(9)C(8)	107.8(8)	109.2(5)

RESULTS AND DISCUSSION

In structures **I** (Fig. 1) and **II** (Fig. 2), the copper atom coordinates the singly deprotonated 4-bromo-2-[(2-hydroxyethylimino)methyl]phenol (**L**) and 2,4-dibromo-6-[(2-hydroxyethylimino)methyl]phenol ($\mathbf{L^1}$) molecules, 3,5-dibromopyridine (A), and the nitrate ion. To answer the question whether the coordination polyhedron of the metal atom is a tetragonal pyramid (TP) or a trigonal bipyramid (TBP), we used the τ index proposed in [10]: $\tau = (\beta - \alpha)/60$, where α and β are two maximum angles between the bonds formed by the central atom. If $\tau = 0$, then the coordination polyhedron of the metal atom is described as an ideal TP, whereas for $\tau = 1$ it is an ideal TBP. For compounds **I** and **II**, τ is 0.145 and 0.017, respectively; in other words, the coordination polyhedron of the copper atom in them, according to the criterion proposed in [10], is a slightly distorted TP and an almost ideal tetragonal pyramid, respectively. The base of the TP is formed by the imine and pyridine N(1) and N(2) atoms and the phenolic and alcoholic O(1) and O(2) atoms. In compound **I**, the displacements of these atoms from their mean plane are 0.095, 0.085, –0.090, and –0.090 Å, respectively, and the deviation of the Cu atom from this plane is 0.157 Å. In compound **II**, similar values are 0.010, 0.009, –0.010, –0.009, and 0.118 Å. The bond lengths of the metal with the donor atoms in the pyramid base in complex **I** are the following: Cu(1)–O(1) 1.870(6) (1.889(3)), Cu(1)–O(2) 2.033(6) (2.005(3)), Cu(1)–N(1) 1.936(7) (1.947(4)), and Cu(1)–N(2) 2.040(7) (2.017(4)) Å. In the complexes under study, the axial vertices of the TP are occupied by the O(3) atoms of the monodentate nitrato groups (Cu(1)–O(3) 2.425(7) Å in **I** and 2.412(4) Å in **II**). In complexes **I** and **II**, the angles formed by the Cu(1)–O(3) bonds with the atoms of the base of the coordination polyhedron are within 82.7°–111.4° and 81.7°–101.5°, respectively.

The complexes under study exhibit a slight bent of the six-membered metallocycles Cu(1)O(1)C(1)C(2)C(3)N(1) along the O(1)···N(1) lines; the dihedral angles between the Cu(1)O(1)N(1) and O(1)N(1)C(1)C(2)C(3) planes in complexes **I** and **II** are equal to 8.2° and 9.6°, respectively. Note that in the related compounds di(μ-$O_{phenoxy}$)-bis{nitrato-2-[2-(hydroxyethylimino)methyl]phenoloimidazolecopper(II)} [11], nitrato-2-[2-(hydroxyethylimino)methyl]phenolo-3-pico-linecopper(II) [12], and 3-hydroxypropylsalicylaldiminatocopper [13], the values of the similar dihedral angle are 20.6°, 14.9°, and 22.7°, respectively. This bent is not observed for nitrato-2-[2-(hydroxyethylimino)methyl]-phenolocopper [14], nitrato-2-[2-(hydroxyethylimino)-methyl]phenolo-4-picolinecopper [15], and 2-[2-(hydroxyethylimino)methyl]phenolocopper [16]. In compounds **I** and **II**, the benzene rings lie almost in the planes of the six-membered metallocycles; the angle between the corresponding root-mean-square planes is equal to 5.5° and 3.7°, respectively. The five-membered metallocycles in

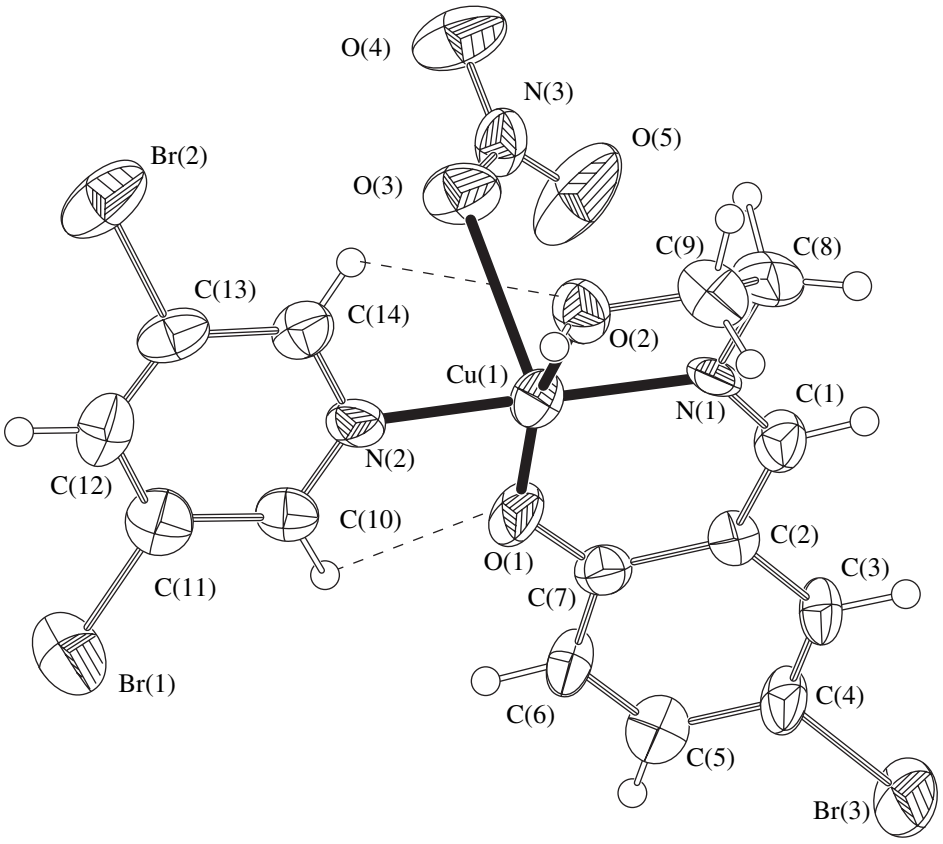


Fig. 1. Structure of complex **I**.

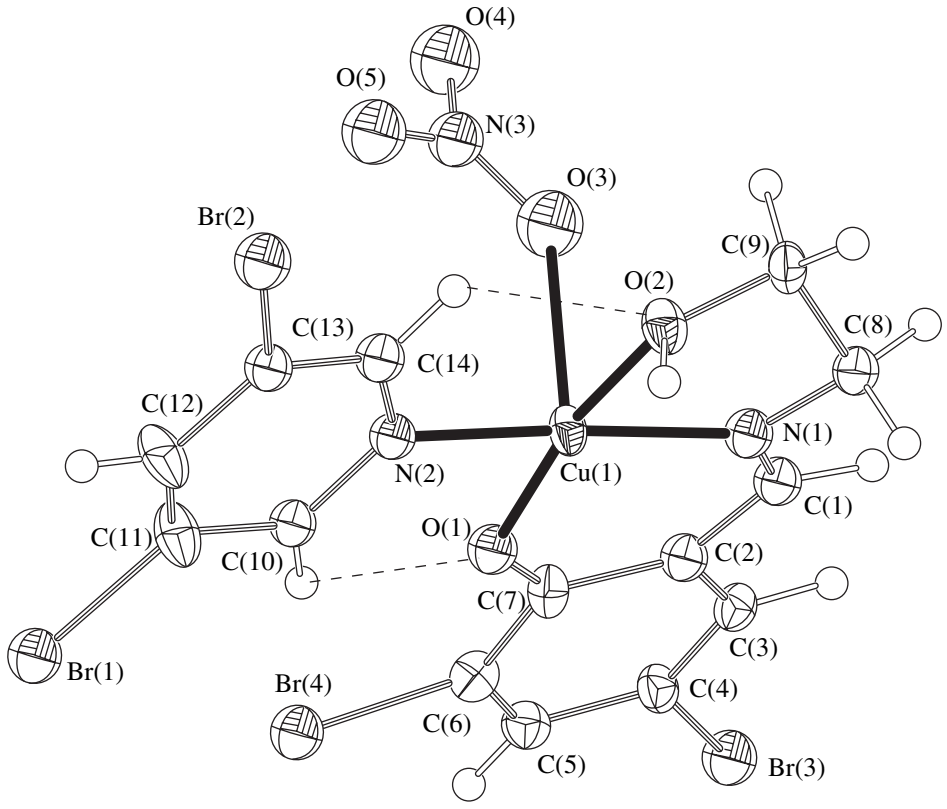


Fig. 2. Structure of complex **II**.

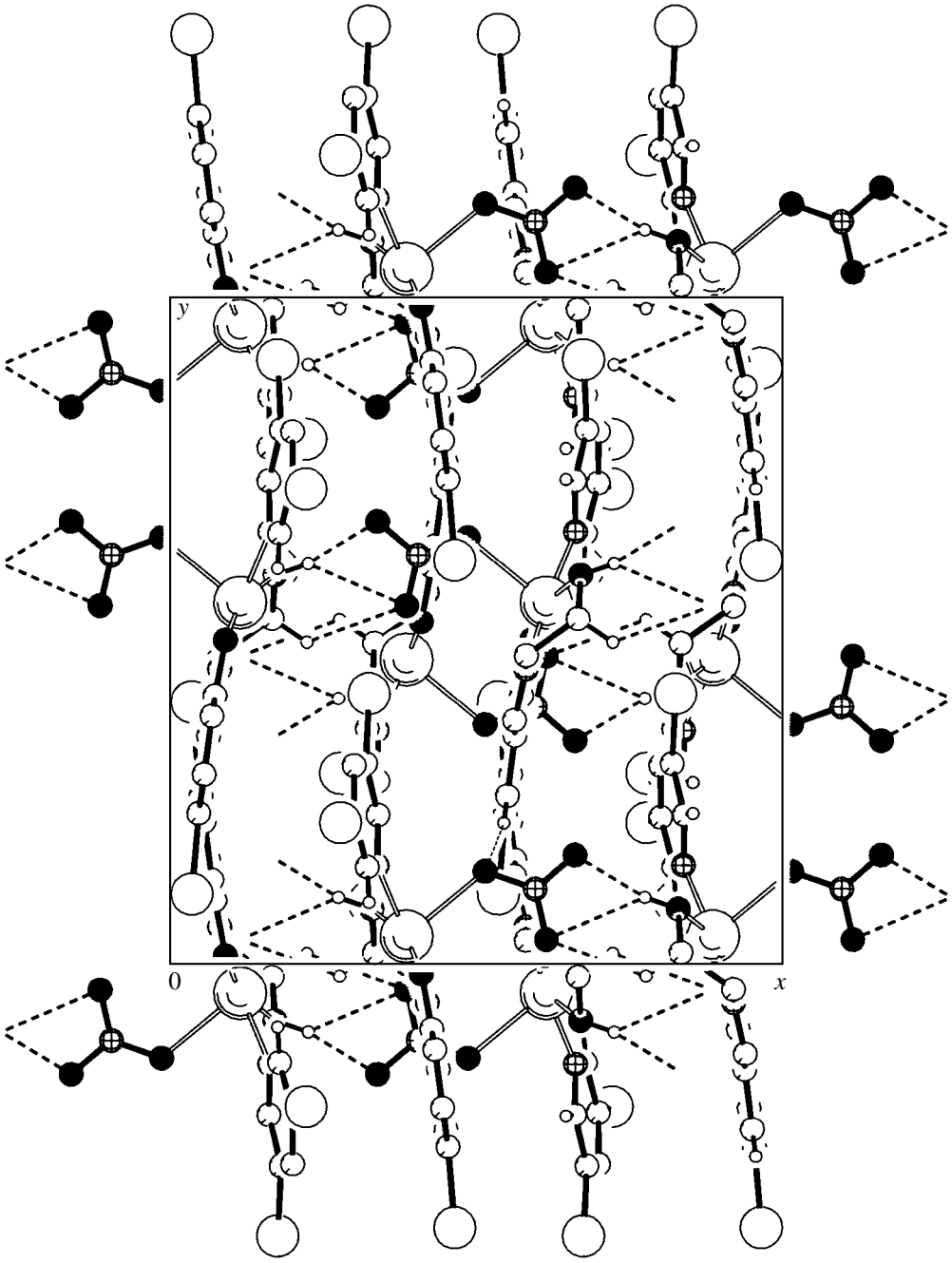


Fig. 3. Packing fragment in compound **I**.

the complexes under study have an asymmetric *gauche* conformation; the deviations of the C(8) and C(9) atoms from the Cu(1)O(2)N(1) planes in **I** and **II** being 0.47, –0.15 and 0.49, –0.06 Å, respectively.

Complexes **I** in crystal are linked due to the slip plane *a* by the bifurcate hydrogen bonds O(2)–H(2)···O(4) and O(2)–H(2)···O(5) and the C(9)–H(9)···O(5) H-bond into infinite chains along the direction [100] (Fig. 3, Table 3). These chains are linked through the C(3)–H(3)···O(3) H-bond. According to the criterion proposed in [7], the π–π-stacking interaction [17] is observed between the phenylic C(2)–C(7) and pyridinic N(2),C(10)–C(14) rings of the adjacent complexes bonded through the slip plane *b*. The distance between the centroids of these fragments is 3.97 Å. Complexes **II** in crystal are connected by the C(12)–H(12)···Br(3) hydrogen bond due to translation along the *y* axis to form infinite chains. In turn, these chains are multiplied by the plane *n* and united by the O(2)–H(2)···O(4)

Table 3. Hydrogen bond geometry for compounds **I** and **II**

Bond D–H···A	Distance, Å			Angle DHA, deg	Coordinates of A atom
	D···A	H···A	D–H		
			I		
O(2)–H(2)···O(5)	3.16(1)	2.53	0.82	135	$-1/2 + x, y, 3/2 - z$
O(2)–H(2)···O(4)	2.688(9)	1.88	0.82	167	$-1/2 + x, y, 3/2 - z$
C(9)–H(9)···O(5)	3.18(1)	2.52	0.97	125	$-1/2 + x, y, 3/2 - z$
C(3)–H(3)···O(3)	3.59(1)	2.69	0.97	125	$2 - x, -1/2 + y, 3/2 - z$
C(10)–H(10)···O(1)	2.85(1)	2.34	0.93	114	x, y, z
C(14)–H(14)···O(2)	3.03(1)	2.53	0.93	114	x, y, z
			II		
O(2)–H(2)···O(4)	2.583(5)	1.69	0.92	163	$-1/2 + x, 1/2 - y, -1/2 + z$
C(12)–H(12)···Br(3)	3.723(4)	2.77	1.00	160	$x, -1 + y, z$
C(8)–H(8)···O(3)	3.621(7)	2.66	1.00	161	$2 - x, 1 - y, 2 - z$
C(10)–H(10)···O(1)	2.831(5)	2.26	1.00	115	x, y, z
C(14)–H(14)···O(2)	2.892(5)	2.30	1.00	117	x, y, z

H-bonds to form two-dimensional networks (Fig. 4, Table 3). The C(8)–H(8)···O(3) hydrogen bonds are formed dye to the symmetry center between these networks. Complexes **I** and **II** also contain intramolecular H-bonds C(10)–H(10)···O(1) and C(14)–H(14)···O(2) (Figs. 1, 2; Table 3).

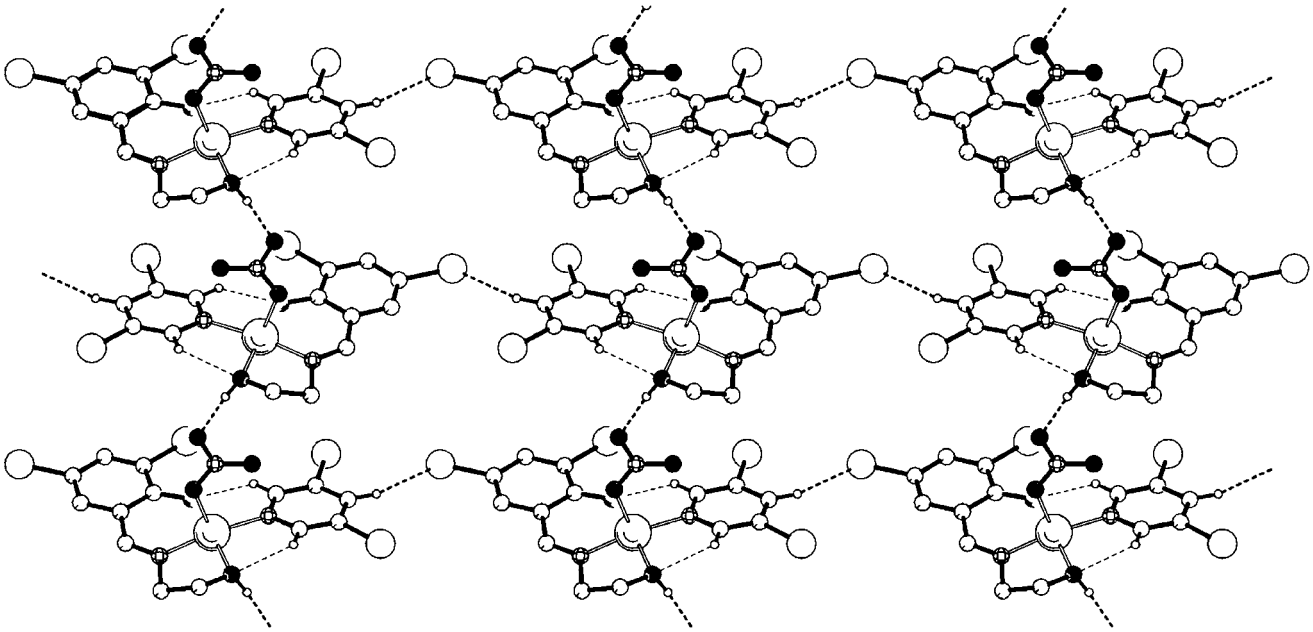


Fig. 4. Packing fragment in compound **II**.

Thus, as a result of the introduction of any number of bromine atoms into the salicylidene fragment of 2-[2-(hydroxyethylimino)methyl]phenol, copper nitrate forms with this ligand L (L^1) monomeric complexes in the crystalline state. In addition, bromine in position 3 of the ligand L^1 in complex **II** induces the formation of two-dimensional networks in its crystal, while in the structure of compound **I**, infinite chains are formed.

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