Coordination Compounds of Copper(II) Nitrate with Products of Aminotris(hydroxymethyl)methane Condensation with Salicyl- and 5-Nitrosalicylaldehydes: Synthesis and Crystal Structures

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Abstract—The crystal structures of copper(II) nitrate complexes with 2-(2-hydroxybenzylideneamino)-2-hydroxymethylpropane-1,3-diol (HL) and 2-hydroxymethyl-2-(2-hydroxy-5-nitrobenzylideneamino)propane-1,3-diol (HL^1) were determined. The resulting complexes were formulated as $[Cu_3OL_3(H_2O)_2]NO_3 \cdot 3H_2O$ (**I**) and $[Cu(H_2O)L^1]NO_3$ (**II**). The crystals of **I** are monoclinic, $a = 17.809(4)$ Å, $b = 30.549(6)$ Å, $c = 18.962(4)$ Å, $\beta = 115.36(3)°$, space group Cc, $Z = 8$, $R = 0.0482$. Complex **I** is composed of two independent three-dimensional μ_3-oxo complexes; the coordination polyhedron of the copper atoms in both compounds is an elongated tetragonal bipyramid. The coordination polyhedron of the third Cu atom is a tetragonal pyramid. The bases of the pyramids are composed of the oxygen atoms of the phenol and alcohol OH groups, the imine N atom of ligand L, and μ_3-oxo atoms. The phenol and water O atoms serve as the apices in both the tetragonal bipyramids. The crystals of **II** are triclinic, $a = 6.062(1)$ Å, $b = 7.701(2)$ Å, $c = 16.162(3)$ Å, $\alpha = 88.15(3)°$, $\beta = 84.94(3)°$, $\gamma = 78.13(3)°$, space group $P\bar{1}$, $Z = 2$, $R = 0.0272$. Complex **II** is composed of polymer chains formed by coordination bonds between the copper atom and two O atoms of the amino alcohol in the azomethine of the neighboring complex connected to the initial one by translation along the x axis. These chains are linked through hydrogen bonds involving the oxygen atoms of the NO_2 groups. The benzene rings of the azomethine ligands of the adjoining complexes from different chains are antiparallel to each other. The coordination polyhedron of the central atom is an elongated tetragonal bipyramid. Its equatorial plane is formed by the phenol O atom, one of the alcohol O atoms, the N atom of ligand L^1, and the O atom of the amino alcohol in the neighboring complex. The apices are the O atom of the water molecule and the O atom of the amino alcohol in the neighboring azomethine molecule. In complexes **I** and **II**, the outer-sphere nitrato group mainly serves to unite trimers and polymers in the crystal by means of hydrogen bonds.

Earlier [1], 3*d*-element salts were found to react with the products of aminotris(hydroxymethyl)methane condensation with salicylaldehyde or its derivatives to give a variety of coordination compounds with fungicidal properties. Depending on the synthesis conditions and the nature of the starting reagents, mono- or polynuclear complexes can be obtained. Because only halides and acetates were used as starting salts, it was interesting to find out how the compositions and structures of the resulting coordination compounds would be affected by replacement of the above acid residues by the nitrate ion. In connection with this, we synthe-

sized complexes $[Cu_3OL_3(H_2O)_2]NO_3 \cdot 3H_2O$ (**I**) and $[Cu(H_2O)L^1]NO_3$ (**II**) and determined their crystal structures by X-ray diffraction analysis

(HL) ; (HL^1)
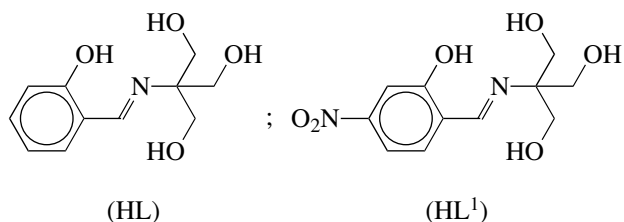
EXPERIMENTAL

The starting 2-(2-hydroxybenzylideneamino)-2-hydroxymethylpropane-1,3-diol (HL) and 2-hydroxymethyl-2-(2-hydroxy-5-nitrobenzylideneamino)propane-1,3-diol (HL^1) were prepared as described in [2].

Synthesis of complex I. A solution of HL (10 mmol) in ethanol (30 ml) and a solution of KOH (6.67 mmol) in ethanol (20 ml) were added at 50 to 55°C to a continuously stirred solution of cupric nitrate trihydrate (10 mmol) in ethanol (50 ml). The reaction mixture was refluxed for 50 to 60 min. After two to three days, the dark green crystals that formed were filtered off on a glass filter, washed with small amounts of ethanol and ether, and dried in air. Complex I is well soluble in DMF and DMSO, but poorly soluble in water and alcohols and virtually insoluble in ether. The composition of complex I was determined from elemental analysis data.

For $C_{33}H_{52}Cu_3N_4O_{21}$

anal. calcd. (%): C, 38.37; H, 5.04; Cu, 18.60; N, 5.43.

Found (%): C, 38.18; H, 4.97; Cu, 18.49; N, 5.31.

IR (cm^{-1}): 3590 ($\nu(H_2O)$), 3290–3270 ($\nu(OH)_{alc}$), 1615 ($\nu(C=N)$), 1590 ($\delta(H_2O)$), 1540 ($\nu(C–O)_{phenol}$), 1055–1050 ($\nu(C–O)_{alc}$), 900 ($\gamma(H_2O)$), 600 ($\nu(Cu_3O)$), 510 and 405 ($\nu(Cu–N)$), 470–460 ($\nu(Cu–O)$).

At room temperature (291 K), the effective magnetic moment of complex I is 1.64 μ_B (per paramagnetic ion).

The derivatogram of complex I shows two endothermic peaks (70 to 90°C and 110 to 130°C) and an exothermic peak at 270 to 290°C. The first two steps of the thermolysis of complex I are its dehydration and deaquation, while the last step is thermooxidative destruction of coordinated azomethines.

The room-temperature ^{1}H NMR spectrum of complex I contains very broad signals, which are not very informative; as the temperature decreases, these signals become narrower. At 270 K and below, slow (on the NMR scale) intramolecular ligand exchange was detected. The paramagnetic ^{1}H shifts appear at δ 15 to 80 ppm. The presence of comparatively narrow resonance signals indicates that complex I in solution retains its original polynuclear structure. The spin relaxation of the electron in this complex ($\tau_e \leq 10^{-8}$ s) differs from that characteristic of monomeric copper complexes whose spectra contain broad lines. The temperature dependence of the contact shifts was used to estimate the spin–spin coupling constant A/h, which is negative from –0.13 to 0.76 MHz for the γ-protons and positive from 0.46 to 0.82 MHz for the other protons in the system.

Synthesis of complex II. Complex II was obtained as described for complex I from an equimolar mixture of $Cu(NO_3)_2 \cdot 3H_2O$ and HL^1 in ethanol. The composition of complex II was determined from elemental analysis data.

For $C_{11}H_{15}CuN_3O_{10}$

anal. calcd. (%): C, 32.01; H, 3.66; Cu, 15.39; N, 10.18.

Found (%): C, 31.89; H, 3.45; Cu, 15.11; N, 9.85.

IR (cm^{-1}): 3585 ($\nu(H_2O)$), 3270–3265 ($\nu(OH)_{alc}$), 1605 ($\nu(C=N)$), 1585 ($\delta(H_2O)$), 1535 ($\nu(C–O)_{phenol}$), 1055–1050 ($\nu(C–O)_{alc}$), 918 ($\gamma(H_2O)$), 525 and 415 ($\nu(Cu–N)$), 490 ($\nu(Cu–O)$).

At room temperature (293 K), the effective magnetic moment of complex II is 1.71 μ_B.

The thermolysis of complex II involves deaquation (175–230°C) and complete thermal decomposition (545–580°C).

The IR spectra of the complexes preliminarily dried in a desiccator at 105°C to constant weights were recorded on a Specord M80 spectrophotometer (suspensions in Vaseline and fluorinated oils).

The effective magnetic moments of the complexes were determined by the Gouy method. The molar magnetic susceptibilities corrected for diamagnetism were calculated from the theoretical magnetic susceptibilities of organic compounds.

The derivatograms of the complexes were recorded on a Paulik-Paulik-Erdey derivatograph over the 20–1000°C range in a corundum crucible in air with Al_2O_3 as a standard.

The ^{1}H NMR spectra of complex I were recorded on a Bruker DPX400 spectrometer (400.2 MHz) in methanol in the 398–230 K range. Samples of complex I were weighed in a 5-mm tube and then CD$_3$OD (0.6 ml) was added. The concentration of complex I was 2.5 mmol/l. Chemical shifts were referenced to Me$_4$Si as the internal standard. The temperature was maintained to within ±0.1 K with the use of a Bruker BVT300 attachment.

X-ray diffraction analyses of complexes I and II were performed on Bruker AXS Smart (CCD detector) and Siemens P3/PC diffractometers (MoK_α radiation, $\lambda = 0.71073$ Å, 293(2) K), respectively. Absorption correction was applied only for complex I with the SHELXTL-NT V5.1 programs [3]. The structures of complexes I and II were solved by the direct methods and refined by the least-squares method with the SHELX97 programs [4] in the anisotropic approximation for non-hydrogen atoms and in the isotropic approximation for H atoms. The latter were located from electron-density difference maps.

Selected crystallographic parameters and a summary of data collection are given in Table 1. The coordinates of basic atoms of the complexes studied were deposited with the Cambridge Crystallographic Data Collection (CCDC 252509&252510). Selected bond lengths and angles in structures I and II are given in Tables 2 and 3. In Table 2, n in the atomic index denotes the number of the complex in structure I.

Table 1. Crystallographic parameters and a summary of data collection for structures **I** and **II**

Parameter	Value	
	I	**II**
Complex	**I**	**II**
M	1013.39	825.60
Crystal system	Monoclinic	Triclinic
Space group	Cc	$P\bar{1}$
Unit cell parameters		
a, Å	17.809(4)	6.062(1)
b, Å	30.549(6)	7.701(2)
c, Å	18.962(4)	16.162(3)
α, deg	90	88.15(3)
β, deg	115.36(3)	84.94(3)
γ, deg	90	78.13(3)
V, Å^3	9323(3)	735.4(3)
Z	8	2
ρ(calcd), g/cm^3	1.454	1.864
$\mu_{аó}$, mm^{-1}	1.433	1.550
Crystal size, mm	$0.5 \times 0.3 \times 0.2$	$0.6 \times 0.3 \times 0.1$
θ scan range, deg	2.26–28.30	2.53–27.47
Number of measured reflections	49374	5983
Number of independent reflections	20217 (R_{int} = 0.0265)	3298 (R_{int} = 0.0155)
Number of parameters refined	1173	289
GOOF on F^2	1.000	1.042
R factors for reflections with ($I > 2\sigma(I)$)	R_1 = 0.0482, wR_2 = 0.1265	R_1 = 0.0272, wR_2 = 0.0711
R factors for all reflections	R_1 = 0.0573, wR_2 = 0.13112	R_1 = 0.0293, wR_2 = 0.0724
$\Delta\rho_{max}$ and $\Delta\rho_{min}$, e Å^{-3}	1.543 and −0.429	0.395 and −0.531

RESULTS AND DISCUSSION

The crystal of complex **I** is composed of two independent μ_3-oxo complexes *A* and *A'* (Fig. 1); in either oxo complex, the coordination polyhedron of two copper atoms ($n = 2$ and $n = 3$) is an elongated tetragonal bipyramid (TBP). The coordination polyhedron of the third Cu atom ($n = 1$) is a tetragonal pyramid (TP). The bases of the pyramids include the O atoms of the phenol and alcohol OH groups, the N atom of the imino group of ligand L and the μ_3-oxo atoms. In trimer *A*, the Cu(11), Cu(12), and Cu(13) atoms deviate from the mean-square planes of the donating atoms in the pyramid bases by 0.097, 0.122, and 0.091 Å, respectively. The corresponding values for trimer *A'* are 0.091, 0.017, and 0.059 Å. In the structure with $n = 1$ of trimer *A* (*A'*), the phenol O(12) (O(12)') atom of the neighboring complex serves as the TP apex for the Cu(11) (Cu(11)') atom (Cu(11)–O(12) 2.478(7) Å, Cu(11)'–O(12)' 2.407 Å). The angles between these bonds and the TP base are 73.3(3)° to 108.8(3)° and 75.0(3)° to 107.0(3)°

in complexes *A* and *A'*, respectively. The sixth coordination positions of the Cu(11) and Cu(11)' atoms are occupied by the O(4S) atom of the nitrato group and the O(8w) atom of the water molecule; the Cu···O distances are 3.64 and 3.09 Å, respectively. However, according to [5], these distances exceed the maximum possible length of the Cu···O coordination bond (3.07 Å) and thus cannot be regarded as coordination bonds. The TBP apices for the Cu(12) atom are the O(1S) atom of the nitrato group and the O(13) atom of the phenol OH group, while the TBP apices for the Cu(12)' atom are the O(5w) and O(13)' atoms of the water molecule. The Cu(12)–O(1S), Cu(12)–O(13), Cu(12)'–O(5w), and Cu(12)'–O(13)' distances are 2.96(1), 2.396(7), 2.664(9), and 2.452(8) Å, respectively. The angles between these bonds and the equatorial plane of the TBP are 82.6(3)° to 105.2(2)°, 73.80(3)° to 114.5(4)°, 86.2(3)° to 96.9(3)°, and 75.0(3)° to 107.0(3)°, respectively. The apices of the TBPs of the Cu(13) and Cu(13)' atoms are the O atoms of the phenol OH groups

Table 2. Selected bond lengths and angles in structure **I**

Bond	d, Å			Bond	d, Å		
	$n = 1$	$n = 2$	$n = 3$		$n = 1$	$n = 2$	$n = 3$
Cu(1n)–O(1n)	1.889(14)	1.893(15)	1.888(15)	Cu(1n)'–O(1n)'	1.885(15)	1.876(15)	1.889(15)
Cu(1n)–O(1)	1.976(15)	2.017(14)	1.988(14)	Cu(1n)'–O(1)'	1.982(14)	1.986(13)	1.999(14)
Cu(1n)–O(2n)	1.979(15)	1.993(17)	1.940(16)	Cu(1n)'–O(2n)'	1.991(16)	1.990(15)	1.990(16)
Cu(1n)–N(1n)	1.927(18)	1.93(2)	1.937(17)	Cu(1n)'–N(1n)'	1.938(18)	1.937(16)	1.929(19)
N(1n)–C(1n)	1.30(3)	1.26(3)	1.28(3)	N(1n)'–C(1n)'	1.28(3)	1.27(3)	1.28(3)
N(1n)–C(8n)	1.48(3)	1.51(3)	1.47(3)	N(1n)'–C(8n)'	1.50(3)	1.49(3)	1.51(3)
O(1n)–C(3n)	1.32(3)	1.31(3)	1.32(3)	O(1n)'–C(3n)'	1.33(3)	1.33(2)	1.33(3)
O(2n)–C(9n)	1.43(3)	1.45(3)	1.47(3)	O(2n)'–C(9n)'	1.45(3)	1.46(3)	1.44(3)
O(3n)–C(10n)	1.42(3)	1.39(5)	1.41(3)	O(3n)'–C(10n)'	1.41(4)	1.42(3)	1.37(4)
O(4n)–C(11n)	1.42(3)	1.40(5)	1.40(3)	O(4n)'–C(11n)'	1.43(3)	1.39(4)	1.43(3)
C(1n)–C(2n)	1.44(3)	1.44(4)	1.44(3)	C(1n)'–C(2n)'	1.45(3)	1.46(3)	1.44(3)
C(2n)–C(3n)	1.43(3)	1.41(3)	1.44(3)	C(2n)'–C(3n)'	1.43(3)	1.40(3)	1.41(3)
C(2n)–C(7n)	1.40(3)	1.44(3)	1.42(3)	C(2n)'–C(7n)'	1.38(3)	1.40(3)	1.44(3)
C(3n)–C(4n)	1.41(3)	1.43(3)	1.44(3)	C(3n)'–C(4n)'	1.38(3)	1.40(3)	1.40(3)
C(4n)–C(5n)	1.35(3)	1.36(4)	1.36(4)	C(4n)'–C(5n)'	1.38(4)	1.37(3)	1.36(4)
C(5n)–C(6n)	1.42(4)	1.41(5)	1.35(4)	C(5n)'–C(6n)'	1.39(4)	1.39(4)	1.42(4)
C(6n)–C(7n)	1.36(3)	1.37(4)	1.37(4)	C(6n)'–C(7n)'	1.37(4)	1.37(3)	1.34(4)
C(8n)–C(9n)	1.53(3)	1.54(4)	1.50(3)	C(8n)'–C(9n)'	1.50(4)	1.55(3)	1.54(3)
C(8n)–C(10n)	1.51(3)	1.53(5)	1.53(3)	C(8n)'–C(10n)'	1.54(4)	1.54(3)	1.56(4)
C(8n)–C(11n)	1.52(3)	1.49(5)	1.52(3)	C(8n)'–C(11n)'	1.53(4)	1.48(4)	1.53(4)
Angle	ω, deg	ω, deg	ω, deg	Angle	ω, deg	ω, deg	ω, deg
O(1n)Cu(1n)N(1n)	96.1(7)	95.8(8)	97.0(7)	O(1n)Cu(1n)N(1n)	96.1(7)	95.8(8)	97.0(7)
O(1n)Cu(1n)O(1)	87.3(6)	87.6(6)	85.9(6)	O(1n)Cu(1n)O(1)	87.3(6)	87.6(6)	85.9(6)
N(1n)Cu(1n)O(1)	175.2(7)	170.0(8)	176.8(7)	N(1n)Cu(1n)O(1)	175.2(7)	170.0(8)	176.8(7)
O(1n)Cu(1n)O(2n)	170.7(7)	175.4(7)	166.9(8)	O(1n)Cu(1n)O(2n)	170.7(7)	175.4(7)	166.9(8)
N(1n)Cu(1n)O(2n)	82.4(7)	83.0(8)	83.5(7)	N(1n)Cu(1n)O(2n)	82.4(7)	83.0(8)	83.5(7)
O(1)Cu(1n)O(2n)	93.7(6)	92.9(7)	94.0(6)	O(1)Cu(1n)O(2n)	93.7(6)	92.9(7)	94.0(6)
O(1n)'Cu(1n)'N(1n)'	96.1(7)	95.7(7)	94.9(7)	O(1n)'Cu(1n)'N(1n)'	96.1(7)	95.7(7)	94.9(7)
O(1n)'Cu(1n)'O(1)'	87.6(6)	87.5(6)	87.4(6)	O(1n)'Cu(1n)'O(1)'	87.6(6)	87.5(6)	87.4(6)
N(1n)'Cu(1n)'O(1)'	175.4(7)	175.6(7)	176.6(7)	N(1n)'Cu(1n)'O(1)'	175.4(7)	175.6(7)	176.6(7)
O(1n)'Cu(1n)'O(2n)'	171.7(7)	174.8(8)	175.2(8)	O(1n)'Cu(1n)'O(2n)'	171.7(7)	174.8(8)	175.2(8)
N(1n)'Cu(1n)'O(2n)'	82.8(7)	83.4(6)	83.5(7)	N(1n)'Cu(1n)'O(2n)'	82.8(7)	83.4(6)	83.5(7)
O(1)'Cu(1n)'O(2n)'	93.1(6)	93.7(6)	94.1(6)	O(1)'Cu(1n)'O(2n)'	93.1(6)	93.7(6)	94.1(6)

Table 3. Selected bond lengths and angles in structure **II***

Bond	d, Å	Bond	d, Å
Cu(1)–O(1)	1.909(1)	O(9)–C(11)	1.426(2)
Cu(1)–N(1)	1.959(2)	N(1)–C(1)	1.283(2)
Cu(1)–O(9)	1.984(1)	N(1)–C(8)	1.486(2)
Cu(1)–O(2)	2.006(1)	N(2)–C(6)	1.438(2)
Cu(1)–O(9)'	2.328(2)	C(1)–C(2)	1.455(2)
Cu(1)–O(3)'	2.456(2)	C(2)–C(7)	1.397(2)
O(1)–C(3)	1.282(2)	C(2)–C(3)	1.442(2)
O(2)–C(9)	1.440(2)	C(3)–C(4)	1.426(2)
O(3)–C(10)	1.431(2)	C(4)–C(5)	1.364(2)
O(4)–N(2)	1.241(2)	C(5)–C(6)	1.404(2)
O(5)–N(2)	1.232(2)	C(6)–C(7)	1.384(2)
O(6)–N(3)	1.270(2)	C(8)–C(10)	1.539(2)
O(7)–N(3)	1.258(2)	C(8)–C(9)	1.544(2)
O(8)–N(3)	1.235(2)	C(8)–C(11)	1.539(2)

Angle	ω, deg	Angle	ω, deg
O(1)Cu(1)N(1)	94.8(1)	C(7)C(2)C(3)	119.5(2)
O(1)Cu(1)O(9)'	86.8(1)	C(7)C(2)C(1)	116.9(2)
N(1)Cu(1)O(9)'	177.4(1)	C(4)C(5)C(6)	119.2(2)
O(1)Cu(1)O(2)	173.7(1)	C(7)C(6)C(5)	121.1(2)
N(1)Cu(1)O(2)	84.0(1)	C(7)C(6)N(2)	119.4(2)
O(9)Cu(1)O(2)	94.1(1)	C(5)C(6)N(2)	119.5(2)
O(1)Cu(1)O(9)'	95.8(1)	C(6)C(7)C(2)	120.6(2)
N(1)Cu(1)O(1w)	98.0(1)	N(1)C(8)C(10)	114.2(2)
O(9)Cu(1)O(1w)	83.9(1)	N(1)C(8)C(9)	105.7(1)
O(2)Cu(1)O(1w)	90.5(1)	C(10)C(8)C(9)	106.2(2)
O(3)'Cu(1)O(2)	81.89(5)	N(1)C(8)C(11)	109.2(1)
O(3)'Cu(1)N(1)	102.03(5)	C(11)C(8)C(10)	113.0(2)
O(3)'Cu(1)O(1)	92.31(6)	C(9)C(8)C(11)	108.0(2)
O(3)'Cu(1)O(9)'	75.82(5)	O(2)C(9)C(8)	110.9(2)
C(3)O(1)Cu(1)	127.0(1)	O(3)C(10)C(8)	113.1(2)
C(9)O(2)Cu(1)	109.8(1)	O(5)N(2)O(4)	121.7(2)
C(11)'O(9)'Cu(1)	127.6(1)	O(5)N(2)C(6)	119.6(2)
C(1)N(1)C(8)	120.8(2)	O(4)N(2)C(6)	118.7(2)
C(1)N(1)Cu(1)	124.7(1)	O(9)C(11)C(8)	112.5(2)
C(8)N(1)Cu(1)	114.4(1)	C(5)C(4)C(3)	122.2(2)
O(8)N(3)O(7)	120.9(2)	C(4)C(3)C(2)	117.3(2)
O(8)N(3)O(6)	121.2(2)	O(1)C(3)C(2)	124.5(2)
O(7)N(3)O(6)	118.0(2)	O(1)C(3)C(4)	118.2(2)
N(1)C(1)C(2)	125.2(2)	C(3)C(2)C(1)	123.6(2)

* The coordinates of the O(3)', O(9)', and C(11)' were obtained by
the symmetry operation $x -1$, y, z.

and the O atoms of water molecules. The Cu(13)–O(11), Cu(13)–O(4w), Cu(13)'–O(11)', and Cu(13)'–O(9w) distances are 2.459(8), 2.822(9), 2.475(7), and 2.794(8) Å, respectively. The angles between these bonds and the equatorial plane of the TBP are 82.6(3)° to 105.2(2)°, 73.80(3)° to 114.5(4)°, 73.4(3)° to 102.0(3)°, and 82.3(3)° to 95.4(3)°, respectively.

In trimer *A*, the six-membered chelate Cu(13)O(13)C(13)C(23)C(33)N(13) is slightly folded along the O(13)⋯N(13) line: the dihedral angle between the Cu(13)O(13)N(13) and O(13)N(13)C(13)C(23)C(33) planes is 15.9°. In trimer *A*', the respective folding is somewhat smaller (9.1°). In trimers *A* and *A*', in the above six-membered chelate for $n = 1$ and 2, the dihedral angles between the planes intersecting in the O(1n)⋯N(1n) (O(1n)'⋯N(1n)') line are 4.4° and 6.2° and 4.3° and 5.4°, respectively. It should be noted that in related complexes such as di(μ-O$_{phenoxy}$)bis[nitrato-2-(2-hydroxyethyliminomethyl)phenoloimidazolecopper] [6], nitrato-2-(2-hydroxyethyliminomethyl)phenolo-3-picolinecopper [7], and 3-hydroxypropylsalicyl-aldiminatocopper [8], the analogous dihedral angle is 20.6°, 14.9°, and 22.7°, respectively. However, such a folding is absent from nitrato-2-(2-hydroxyethylimi-nomethyl)phenolocopper [9], nitrato-2-(2-hydroxyethyl-iminomethyl)phenolo-4-picolinecopper [10], and 2-(2-hydroxyethyliminomethyl)phenolocopper [11].

In structure **I**, the benzene rings C(2n)C(3n)C(4n)C(5n)C(6n)C(7n) (**B**) in trimer *A* are virtually coplanar with the fragments O(1n)N(1n)C(1n)C(2n)C(3n) (**C**) of the six-membered chelates. The angles between the planes *B* and *C* of the rings including the Cu(11), Cu(12), and Cu(13) atoms are 1.4°, 3.0°, and 7.2°, respectively; the corresponding angles in trimer *A*' are 0.4°, 2.6°, and 5.8°. The five-membered chelates in trimers *A* and *A*' occur in a sharply asymmetric *gauche*-conformation. The C(8n) and C(8n)' atoms deviate from the Cu(1n)O(2n)N(1n) and Cu(1n)'O(2n)'N(1n)' planes by 0.02–0.07 Å, while the deviations of the C(9n) and C(9n)' atoms from these planes range from 0.42 to –0.69 Å. This conformation of the chelate can also be described as a C(9n) enve-lope.

The parameters of the hydrogen bonds in the crystal of complex **I** are given in Table 4. In trimers *A* and *A*', the oxygen atoms of the alcohol OH groups in frag-ments 1 (1') and 2 (2') form hydrogen bonds 1–5 to water molecules and the nitrato group. In addition, tri-mers *A* and *A*' are connected by hydrogen bonds 6–10 through the NO$_3$ groups (Fig. 2). In the crystal, such structures are united by means of bonds of the types O–H⋯O (11–13, 16–18) and C–H⋯O (14, 15, 19). The parameters of the latter bond type agree with the crite-rion proposed in [12].

The crystal of complex **II** consists of polymer chains formed via coordination bonds between the Cu atom and two O(9) and O(3)' atoms of the amino alco-
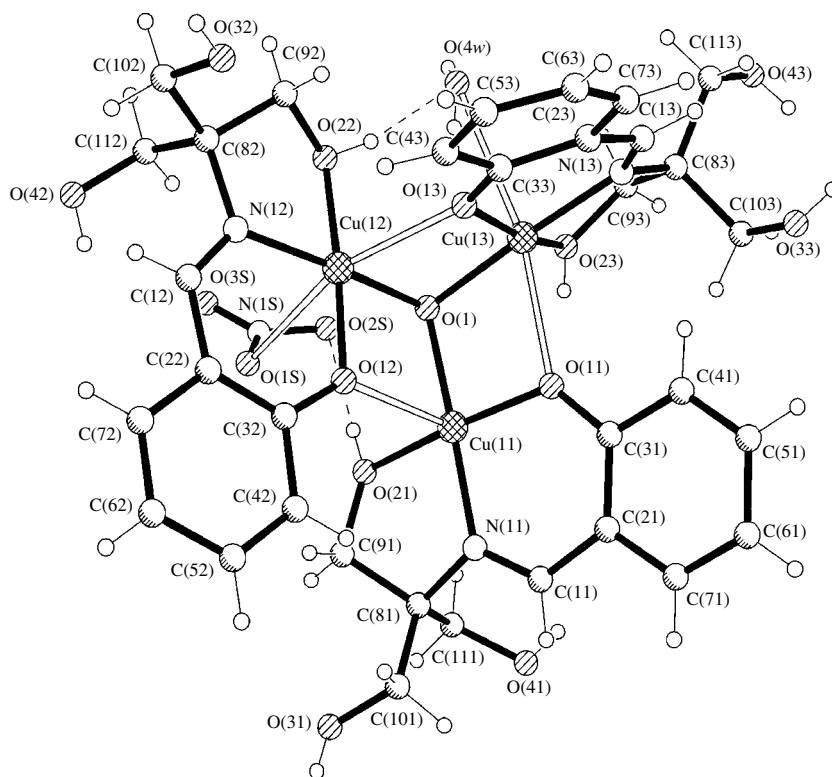
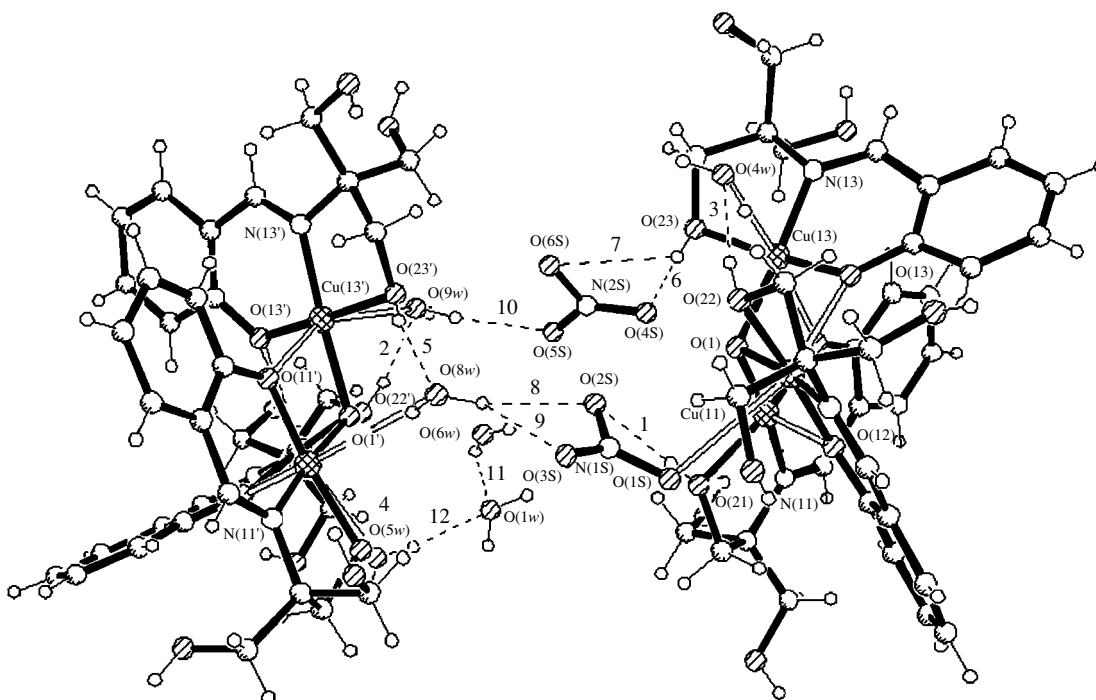**Fig. 1.** Structure of trimer *A* in complex **I**.

Fig. 2. Fragment of the packing of structural units in crystal **I**.

hol fragment of HL^1 in the neighboring complex connected to the initial one by translation along the *x* axis (Fig. 3). The polymer chains are united through hydrogen bonds 1–3 involving the O atoms of the nitrato groups (Table 5). Polymers together with nitrato groups form, by means of hydrogen bonds 4, 5, and 6, infinite

Table 4. Geometrical parameters of hydrogen bonds in structure **I**

No.	Bond D–H⋯A	Distance, Å		DHA angle, deg	Coordinates of atom A
		D⋯A	H⋯A		
1	O(21)–H(30)⋯O(2S)	3.02(3)	2.2(3)	180(2)	x, y, z
2	O(22)'–H(23)'⋯O(9w)	2.62(2)	1.8(1)	167(3)	x, y, z
3	O(22)–H(50)⋯O(4w)	2.61(3)	1.8(2)	166(1)	x, y, z
4	O(21)'–H(50)⋯O(5w)	2.63(3)	1.8(2)	178(1)	x, y, z
5	O(23)'–H(23)'⋯O(8w)	2.58(3)	1.9(2)	143(3)	x, y, z
6	O(23)–H(70)⋯O(4S)	2.55(3)	1.7(1)	167(3)	x, y, z
7	O(23)–H(70)⋯O(6S)	3.07(8)	2.5(2)	123(2)	x, y, z
8	O(8w)–H(1w8)⋯O(2S)	3.03(4)	2.2(1)	174(3)	x, y, z
9	O(8w)–H(1w8)⋯O(3S)	3.26(6)	2.7(2)	129(3)	x, y, z
10	O(9w)–H(1w9)⋯O(5S)	2.87(5)	2.13(2)	150(3)	x, y, z
11	O(6w)–H(1w6)⋯O(1w)	2.72(11)	2.1(2)	135(3)	x, y, z
12	O(5w)–H(1wH)⋯O(1w)	2.78(6)	2.0(3)	173(3)	x, y, z
13	O(42)–H(10A)⋯O(33)'	2.55(5)	1.9(2)	139(2)	$x + 1/2, -y + 3/2, z + 1/2$
14	O(41)–H(8A)⋯O(32)'	2.70(3)	2.1(4)	135(2)	$x, -y + 2, z + 1/2$
15	O(41)'–H(11D)⋯O(31)	2.67(3)	2.0(4)	135(2)	$x - 1/2, -y + 3/2, z - 1/2$
16	O(32)'–H(12C)⋯O(41)	2.70(3)	2.1(3)	127(1)	$x, -y + 2, z - 1/2$
17	O(32)–H(11A)⋯O(5w)	2.80(4)	2.2(4)	128(2)	$x - 1/2, -y + 3/2, z + 1/2$
18	O(31)'–H(10D)⋯O(4w)	2.72(3)	2.0(2)	150(1)	$x + 1/2, -y + 3/2, z - 1/2$
19	C(52)–H(16A)⋯O(2S)	3.37(4)	2.5(4)	156(1)	$x + 1/2, -y + 3/2, z + 1/2$
20	C(51)–H(5A)⋯O(5S)	3.47(4)	2.7(4)	147(1)	$x, -y + 2, z + 1/2$
21	C(61)'–H(15B)⋯O(6w)	3.43(6)	2.6(3)	154(1)	$x - 1/2, -y + 3/2, z - 1/2$

Table 5. Geometrical parameters of hydrogen bonds in structure **II**

No.	Bond D–H⋯A	Distance, Å		DHA angle, deg	Coordinates of atom A
		D⋯A	H⋯A		
1	O(1w)–H(13)⋯O(6)	2.831(3)	1.94(4)	161(3)	x, y, z
2	O(9)–H(11)⋯O(6)	2.653(2)	1.75(3)	171(3)	$x - 1, y, z$
3	O(1w)–H(12)⋯O(8)	2.866(2)	1.95(4)	172(3)	$x - 1, y, z$
4	O(2)–H(14)⋯O(7)	2.674(2)	1.75(3)	168(3)	$-x + 1, -y, -z + 1$
5	O(3)–H(15)⋯O(4)	2.872(2)	1.99(3)	158(3)	$-x + 2, -y, -z$
6	C(7)–H(7)⋯O(5)	3.209(3)	2.45(3)	141(2)	$-x + 2, -y, -z$
7	C(11)–H(5)⋯O(7)	3.364(2)	2.59(3)	157(2)	$-x, -y, -z + 1$

ribbons along the z axis. These ribbons are united through hydrogen bonds 7 along the y axis into a three-dimensional framework (Fig. 4). The nitrosalicylidene fragments of adjoining copper complexes from different polymer chains are antiparallel. The interplanar distances between them (3.45 to 3.46 Å) are characteristic of stacking interactions between molecules in the crystal [13].

The coordination polyhedron of the central atom in complex **II** is an elongated tetragonal bipyramid. The equatorial plane of the polyhedron is composed of the O(1), O(2), and N(1) atoms of its own organic ligand L^1 and the O(9) atom coming from a neighboring complex. The apices in the TBP are the O(1w) atom of a water molecule and the O(3)' atom of the alcohol OH group in the neighboring azomethine molecule
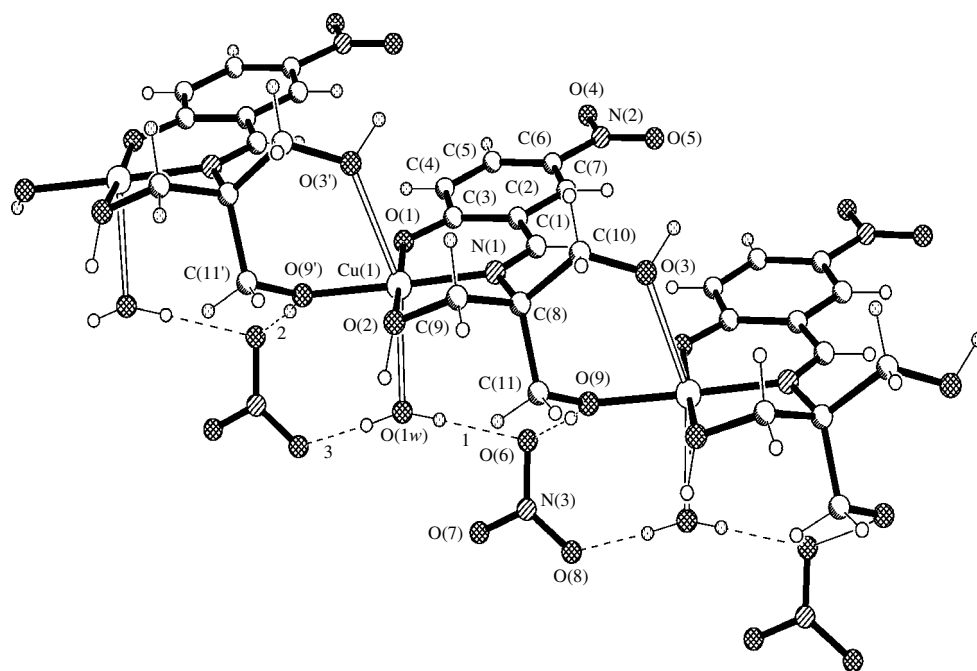
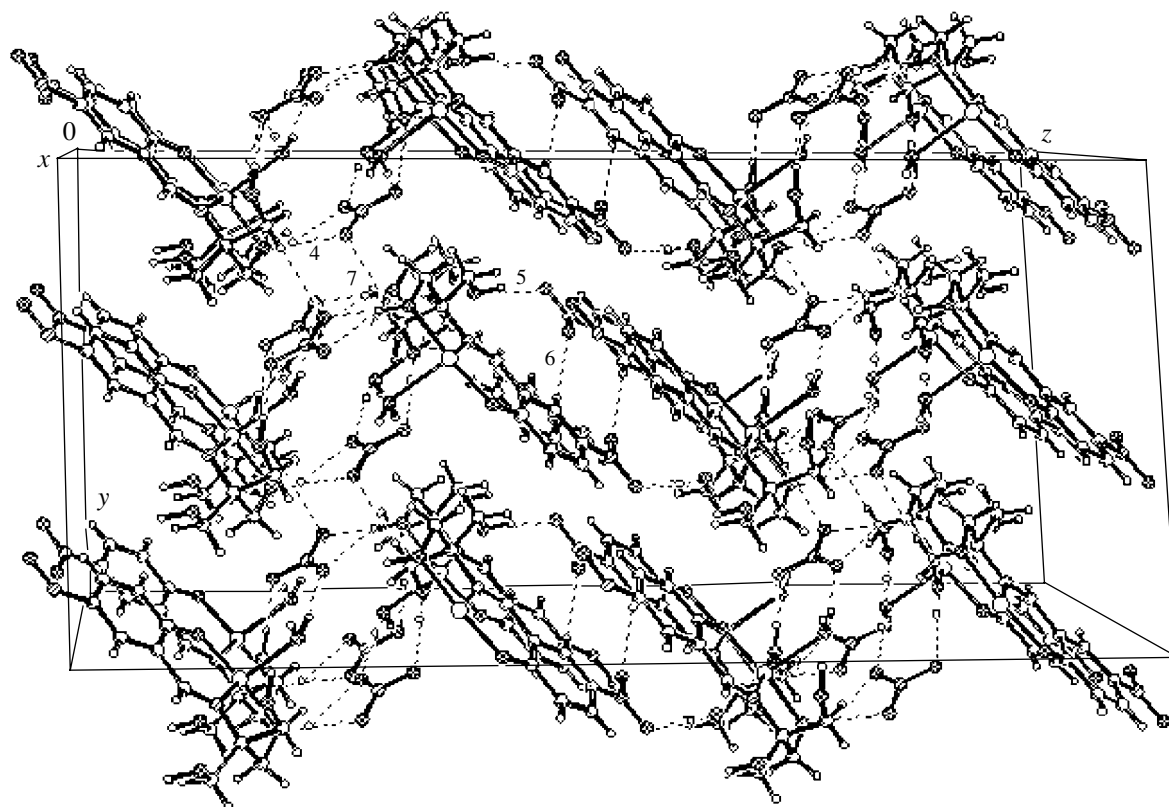**Fig. 3.** Fragment of the polymer chain in structure **II**.

Fig. 4. Fragment of the packing of structural units in crystal **II**.

(Cu(1)–O(1w) 2.326(2) Å, Cu(1)–O(3)' 2.453(2) Å). The angles between these bonds and the equatorial plane of the TBP range from 83.90(7)° to 97.99(7)° and from 75.71(6)° to 102.11(6)°, respectively. The Cu(1) atom deviates from the mean-square plane of the equatorial atoms by 0.07 Å toward the O(3)' atom.

In complex **II**, as in complexes described in [9–11], the folding along the O(1)···N(1) line is very small: the dihedral angle between the Cu(1)O(1)N(1) and O(1)N(1)C(1)C(2)C(3) planes in structure **II** is only 2.0°. The benzene ring C(2)C(3)C(4)C(5)C(6)C(7) (***D***) is virtually coplanar with the O(1)N(1)C(1)C(2)C(3) fragment (***E***) of the six-membered chelate: the dihedral *D/E* angle is 1.9°. As in complex **I**, the five-membered chelate in complex **II** has an asymmetric *gauche*-conformation; the deviations of the C(8) and C(9) atoms from the Cu(1)O(2)N(1) plane are 0.16 and –0.40 Å, respectively.

Thus, in the complexes **I** and **II** studied, the nitrato group mainly serves to unite trimers and polymers in the crystal through hydrogen bonding. Only in the molecule with $n = 2$ of trimer *A* is one of the oxygen atoms of the NO$_3$ group included in the coordination sphere of the Cu atom. Introduction of a NO$_2$ group into the *para*-position of the benzene ring of the tridentate organic ligand seems to favor the formation of polymer chains in the crystal of complex **II** by means of stacking and hydrogen bonding.

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