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Coordination Compounds of Copper(II) with Substituted 3-{[(2-Hydroxyphenyl)methylidene]amino}propane-1,2-diols

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Abstract—3-{[(2-Hydroxyphenyl)methylidene]amino}propane-1,2-diol, its 5-chloro-,5-bromo-, 5-nitro-, 3-methoxy derivatives, and 3-{[(2-hydroxynaphthyl-1)methylidene]amino}propane-1,2-diol react with hydrates of copper(II) chloride, bromide and nitrate in ethanol to form coordination compounds $Cu(L)X\cdot nH_2O$. Template condensation reaction between 3-aminopropane-1,2-diol and 2,3-, 2,4- or 2,5-dihydroxybenzaldehyde in the presence of copper(II) nitrate trihydrate results in similar compounds $Cu(L)NO_3\cdot nH_2O$. Structure of some of the condensation products was identified by X-ray analysis. Thermolysis of the substances obtained occurs through the dehydration step (70–90°C) and complete thermal decomposition (290–560°C).

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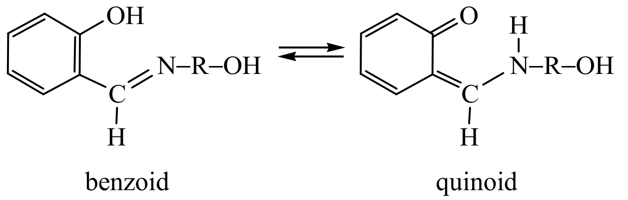
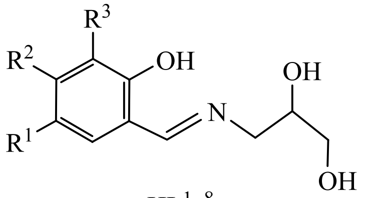
Salicylic aldehyde is known to react with alkanolamines to form the condensation products existing in two tautomeric forms in solution and in the solid [1–3].

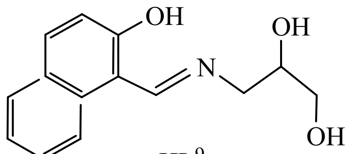


This equilibrium can be shifted towards one of the forms by changing the solvent nature, pH of the solution, or by introduction of various substituents into the benzene ring [4]. Both tautomeric forms contain several donor atoms and form biologically active coordination compounds of variable composition, structure, and properties with metal ions [5–7]. In many cases, the activity of these compounds is consistent with their composition and structure. Therefore, accumulation of experimental data on the synthesis of new complexes of this class, study their composition and structure is of both fundamental and practical interest.

The purpose of this work is finding the synthesis conditions and studying the structure and properties of the complexes of copper(II) with the products (HL^{1-9}) of 3-aminopropane-1,2-diol condensation with salicylic aldehyde (HL^1), 5-chloro- (HL^2), 5-bromo- (HL^3), 5-nitro- (HL^4), 3-methoxysalicylic aldehydes (HL^5), 2-hydroxy-1-naphthoic aldehyde (HL^9), 2,3-(HL^6), 2,4-(HL^7), and 2,5-dihydroxybenzaldehydes (HL^8).



HL^{1-8}



HL^9

HL^1, $R^1 = R^2 = R^3 = H$; HL^2, $R^1 = Cl$, $R^2 = R^3 = H$; HL^3, $R^1 = Br$, $R^2 = R^3 = H$; HL^4, $R^1 = NO_2$, $R^2 = R^3 = H$; HL^5, $R^1 = R^2 = H$, $R^3 = OCH_3$; HL^6, $R^1 = R^2 = H$, $R^3 = OH$; HL^7, $R^1 = R^3 = H$, $R^2 = OH$; HL^8, $R^1 = OH$, $R^2 = R^3 = H$.

Table 1. Physico-chemical characteristics of the coordination compounds of copper with substituted 3-{[(2-hydroxyphenyl)-methylidene]amino}propane-1,2-diol

Comp. no.	Yield, %	μ_{eff}, MB[a]	æ,[a] Ω^{-1} cm^2 mol^{-1}	Found, %		Formula	Calculated, %		Temperature of complete decomposition, °C
				Cu	N		Cu	N	
I	68	1.96	3	20.13	8.52	$C_{10}H_{12}CuN_2O_6$	19.87	8.76	330
II	67	1.80	2	21.66	4.75	$C_{10}H_{12}ClCuNO_3$	21.67	4.78	560
III	70	1.83	2	18.75	3.92	$C_{10}H_{12}BrCuNO_3$	18.82	4.15	540
IV	79	1.81	4	17.79	8.11	$C_{10}H_{11}ClCuN_2O_6$	17.94	7.91	305
V	70	1.78	3	19.43	4.35	$C_{10}H_{11}Cl_2CuNO_3$	19.39	4.27	535
VI	78	1.84	2	15.81	6.79	$C_{10}H_{11}BrCuN_2O_6$	15.94	7.03	320
VII	73	1.95	2	17.36	3.70	$C_{10}H_{11}BrClCuNO_3$	17.08	3.76	555
VIII	77	1.75	3	14.97	3.59	$C_{10}H_{11}Br_2CuNO_3$	15.26	3.36	540
IX	79	1.81	4	17.66	11.56	$C_{10}H_{11}CuN_3O_8$	17.42	11.52	280
X	82	1.86	2	18.90	8.45	$C_{10}H_{11}ClCuN_2O_5$	18.79	8.28	510
XI	79	1.88	4	16.40	7.27	$C_{10}H_{11}BrCuN_2O_5$	16.61	7.32	505
XII	73	1.94	3	18.06	7.79	$C_{11}H_{14}CuN_2O_7$	18.17	8.01	320
XIII	67	1.91	5	19.82	4.19	$C_{11}H_{14}ClCuNO_4$	19.66	4.33	530
XIV	74	1.94	2	16.72	3.80	$C_{11}H_{16}BrCuNO_5$	16.48	3.63	560
XV	83	1.87	4	17.28	7.78	$C_{10}H_{16}CuN_2O_9$	17.09	7.53	290
XVI	86	2.10	5	16.15	7.02	$C_{10}H_{18}CuN_2O_{10}$	16.30	7.19	290
XVII	81	2.04	4	18.96	8.16	$C_{10}H_{12}CuN_2O_7$	18.93	8.34	295
XVIII	79	1.87	2	16.89	7.70	$C_{14}H_{14}CuN_2O_6$	17.18	7.57	270
XIX	73	1.89	3	18.30	4.22	$C_{14}H_{14}ClCuNO_3$	18.51	4.08	530

[a] At 294 K.

Interaction of hot (50–55°C) ethanol solutions of the condensation products HL^{1-5} and HL^9 with hydrates of copper(II) chloride, bromide and nitrate taken in a 1:1 molar ratio resulted in fine-crystalline substances **I**–**XIV**, **XVIII**, and **XIX**. According to the elemental analysis data (Table 1) their composition was as follows: $Cu(L^{1-5})X\cdot nH_2O$ and $Cu(L^9)X\cdot nH_2O$ [L^1 (**I**–**III**), L^2 (**IV**, **V**), L^3 (**VI**–**VIII**), L^4 (**IX**–**XI**), L^5 (**XII**–**XIV**), L^9 (**XVIII**, **XIX**); X = Cl^- (**II**, **V**, **VII**, **X**, **XIII**, **XIX**), Br^- (**III**, **VIII**, **XI**, **XIV**), NO_3^- (**I**, **IV**, **VI**, **IX**, **XII**); $n = 0$ (**I**–**XIII**), $n = 1$ (**XIV**)]. Since we failed to isolate the products HL^{6-8} of 3-amino-1,2-propanediol condensation with 2,3-, 2,4- or 2,5-dihydroxybenzaldehyde, the complexes **XV**–**XVII** of the composition $Cu(L^{6-8})NO_3\cdot nH_2O$ were obtained by template condensation between 3-aminopropane-1,2-diol and 2,3-, 2,4-, or 2,5-dihydroxybenzaldehyde in the presence of copper(II) nitrate trihydrate [L^6 (**XV**), L^7 (**XVI**), L^8 (**XVII**); $n = 0$ (**XVII**), 2 (**XV**), 3 (**XVI**)].

The coordination compounds **I**–**XIX** were insoluble in diethyl ether, soluble in water and alcohols, and very soluble in dimethylformamide, dimethyl sulfoxide and acetonitrile. Their yields and physico-chemical characteristics are given in Table 1.

Recrystallization of the studied compounds from ethanol succeeded in growing single crystals of the condensation products HL^1 and HL^4, the structure of which was confirmed by X-ray analysis.

Table 2. Crystallographic data, experimental data, and refinement of the structures of HL^1 and HL^4

Parameter	HL^1	HL^4
Formula	$C_{10}H_{13}NO_3$	$C_{10}H_{12}N_2O_5$
M	195.21	240.22
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Z	4	4
a, Å	19.428(5)	7.063(3)
b, Å	6.092(4)	14.371(3)
c, Å	8.278(5)	10.864(2)
α, deg	90	90
β, deg	100.66(3)	92.89(2)
γ, deg	90	90
V, $Å^3$	963(1)	1101.4(5)
D_x, g cm^{-3}	1.347	1.449
λ, Å	MoK_α, 0.7107	MoK_α, 0.7107
μ, cm^{-1}	0.1	0.118
T, K	293(2)	293(2)
Crystal size, mm	0.10×0.30×0.35	0.25×0.20×0.15
Scanning type	$\theta/2\theta$	$\theta/2\theta$
θ_{max}, deg	25.0	25.18
h, k, l	$-21 \le h \le 23$, $-7 \le k \le 7$, $-9 \le l \le 9$	$-8 \le h \le 8$, $-17 \le k \le 17$, $-12 \le l \le 12$
Reflections number: measured/independent (N_1),R_{int}/ with $I > 2\sigma(I)$	3268/1436, 0.0257/1436	6697/1775, 0.0543/1775
Refinement method	Least square method	Least square method
Weight scheme	K_1 0.0839, K_2 0.0	K_1 0.0434, K_2 0.0
Parameters number	127	158
R_1/wR_2 N_1	0.066/0.1453	0.0425/0.0849
R_1/wR_2 N_2	0.1337/0.163	0.1585/0.1084
S	0.914	0.819
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e $Å^{-3}$	0.388, –0.164	0.134, –0.14

In the solid both compounds existed in the quinoid tautomeric form (Tables 2, 3, Figs 1, 2). In the molecules of both HL^1 and HL^4, the N^1–C^1 bond was located almost in the planes of phenolic rings. The torsion angles $N^1C^1C^2C^3$ and $N^1C^1C^2C^7$ in the condensation products HL^1 and HL^4 were of 1.4, 178.5 and 2.69, 176.5°, respectively. Thus, those molecules were not flat; atoms C^9, C^{10}, O^2, and O^3 deviated from the phenolic rings by 1.91–2.89 and 0.19–0.66 Å. The determined interatomic distances and bond angles were consistent with the literature data.

Due to hydrogen bonding, in the crystal, the molecules of HL^1 and HL^4 formed two-dimensional layers parallel to the (100) plane (Table 4, Fig. 3). However, in contrast with HL^1, in the crystal of HL^4

Table 3. Some interatomic distances (Å) and bond angles (deg) for compounds HL^1 and HL^4

Bond, angle	HL^1	HL^4	Bond, angle	HL^1	HL^4
$O^1–C^3$	1.296(5)	1.278(3)	$C^9–C^{10}$	1.502(5)	1.523(4)
$O^2–C^9$	1.415(4)	1.430(4)	$C^{10}–O^3$	1.422(6)	1.410(4)
$N^1–C^1$	1.286(5)	1.286(4)	$C^1N^1C^8$	125.3(3)	123.0(3)
$N^1–C^8$	1.434(5)	1.478(4)	$N^1C^1C^2$	124.7(3)	124.4(3)
$C^1–C^2$	1.416(5)	1.415(4)	$C^1C^2C^7$	119.5(3)	117.2(3)
$C^2–C^3$	1.432(5)	1.439(4)	$C^3C^2C^7$	119.2(4)	120.5(3)
$C^3–C^4$	1.391(6)	1.439(4)	$C^1C^2C^3$	121.1(3)	122.3(3)
$C^4–C^5$	1.358(7)	1.354(4)	$N^1C^8C^9$	111.8(3)	112.6(3)
$C^6–C^5$	1.388(6)	1.396(4)	$O^2C^9C^{10}$	109.6(3)	113.7(3)
$C^7–C^6$	1.357(6)	1.369(4)	$C^8C^9C^{10}$	111.5(3)	111.8(3)
$C^2–C^7$	1.409(5)	1.398(4)	$O^3C^{10}C^9$	118.6(4)	113.3(3)
$C^9–C^8$	1.503(5)	1.464(4)			

such layers were interconnected by $O^2–H\cdots O^3$ bond (Figs. 4, 5). In the molecule of HL^1, besides the van der Waals interaction, the $X–H\cdots Cg$ (π-ring) interaction was operative ($H\cdots Cg < 3.0$ Å, $\gamma < 30.0°$, γ being the angle between the vector HCg and the normal to the aromatic ring [8]). For example, in the case of inter-action $C^1–H^1\cdots Cg$ ($C^2C^3C^4C^5C^6C^7$) (x, 3/2 – y, 1/2 + z), distances between the hydrogen H^1 atom and centroid of phenolic cycle was 2.95 Å, and γ equaled 9.3°. According to the criterion proposed in [8], $CgI\cdots CgJ < 6.0$ Å, $\beta < 60.0°$, β being the angle between the CgICgJ vector and the normal to the aromatic ring CgI, in HL^4 the π–π-stacking interactions between the phenolic rings were operative. The $Cg1\cdots Cg1$ distance ($1 - x$, $1 - y$, $1 - z$) between the centroids of those fragments was of 3.626 Å, β being of 35.0°. In addition to the mentioned π–π- interaction, in compound HL^4 the $Y–X\cdots Cg$ interaction (π-ring) was operative ($X\cdots Cg < 4.0$ Å, $\gamma < 30.0°$, γ being the angle between the XCg vector and the normal to the aromatic ring). For example, in the case of interaction $C^3–O^1\cdots Cg$ ($C^2C^3C^4C^5C^6C^7$) ($-x$, $1 - y$, $1 - z$), the distances between the oxygen atom O^1 and the centroid of phenolic cycle were of 3.378 Å, and γ was of 7.8°.

Thus, in crystals the studied compounds formed two-dimensional layers parallel to the (100) plane via hydrogen bonding. The introduction of NO_2 group into the phenolic ring of HL^4 led to binding of these layers by the $O–H\cdots O$ bonds.

Composition and structure of the complexes **I**–**XIX** were determined by elemental and thermal analyzes data, molar conductivity, IR spectroscopy and magnetochemistry methods.

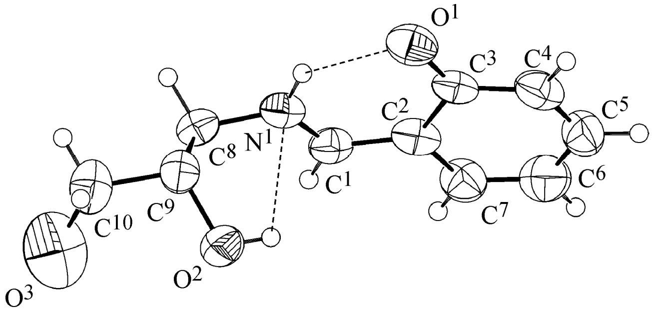


Fig. 1. Crystallographically independent part in the molecule of HL^1.

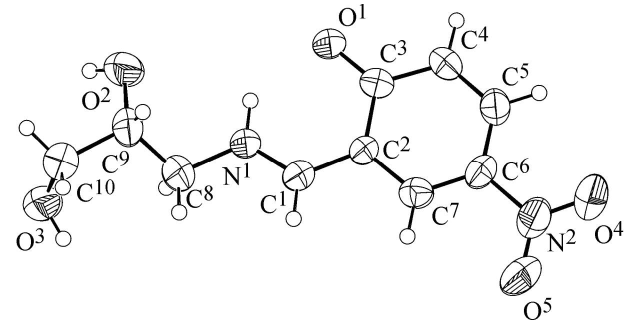


Fig. 2. Crystallographically independent part in the molecule of HL^4.

Table 4. The geometry parameters of the hydrogen bonds (Å) for compounds HL^1 and HL^4

D–H···A bond	D–H	H···A	D···A	DHA angle, deg	Coordination of the atom A
			HL^1		
$O^2–H^2\cdots N^1$	0.82	2.53	2.860(4)	106	x, y, z
$N^1–H^3\cdots O^1$	0.86	1.94	2.600(4)	133	x, y, z
$O^2–H^2\cdots N^1$	0.82	2.52	3.219(5)	144	$x, 3/2 - y, -1/2 + z$
$O^3–H^3\cdots O^2$	0.82	2.05	2.726(6)	140	$x, 5/2 - y, 1/2 + z$
$C^8–H^8\cdots O^2$	0.93	2.44	3.064(5)	124	$x, 3/2 - y, 1/2 + z$
			HL^4		
$N^1–H^1\cdots O^1$	0.89	1.99	2.674(5)	133	x, y, z
$O^2–H^2\cdots O^3$	0.82	1.93	2.744(5)	173	$-x, -y, 1 - z$
$O^3–H^3\cdots O^1$	0.82	1.96	2.739(5)	159	$x, 1/2 - y, -1/2 + z$
$C^1–H^1\cdots O^2$	0.93	2.36	3.154(5)	143	$x, 1/2 - y, -1/2 + z$
$C^5–H^5\cdots O^5$	0.93	2.54	3.389(6)	152	$-x, 3/2 - y, 1/2 + z$

From the values of the molar conductivity (æ) of the synthesized compounds in DMF (Table 1), all of them were non-electrolytes (æ = 2–4 Ω^{-1} cm^2 mol^{-1}).

Magneto-chemical measurements of the complexes **I–XIX** at room temperature (294 K) showed (Table 1) that their effective magnetic moments (1.75–2.10 MB) were close to the spin values for one unpaired electron.

In order to determine the type of the ligands HL^{1-9} coordination to the central ion, we compared the IR spectra of the prepared complexes **I–XIX**, the condensation products HL^{1-5} and HL^9, and coordination compounds of transition metals with similar ligands described in [1–5]. In the studied complexes the azomethines HL^{1-9} were in benzenoid tautomeric form and behaved as tridentate monodeprotonated O,N,O ligands, coordinated to the complexing ion via the atoms of phenolic and alcoholic oxygens and azomethine nitrogen to form six- and five-membered metallocycles. This was supported by downfield shifting of the absorption bands ν(C=N) and $\nu(OH)_{alcohol}$ by 25–15 cm^{-1} as compared with those in the IR spectra of similar Schiff's bases [1–5]. Appearance of several absorption bands in the range of 550–400 cm^{-1} assigned to ν(Cu–N) (535–510 and 430–405 cm^{-1}) and ν(Cu–O) (490–450 cm^{-1}) in the IR spectra of the prepared complexes supported the above-described coordination of azomethines HL^{1-9}. Other functional groups of the con-

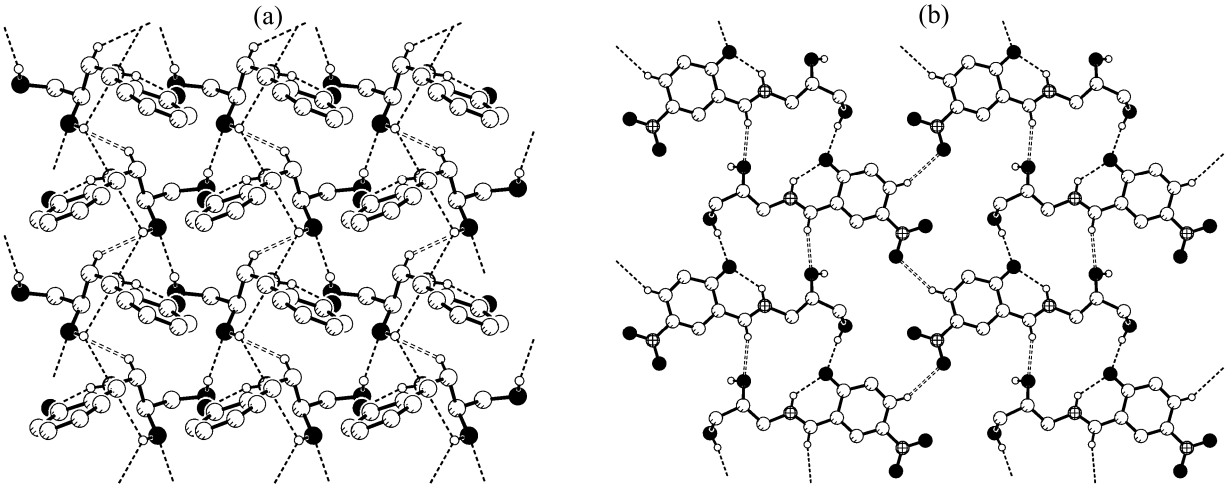


Fig. 3. Formation of two-dimensional hydrogen bonding layers parallel to the plane (100) in compounds HL^1 (a) and HL^4 (b).

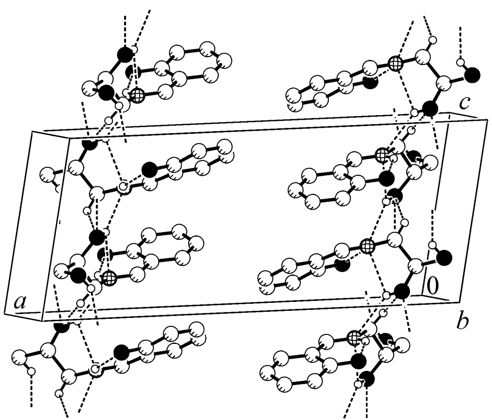


Fig. 4. Fragment of packing of compound HL^1.

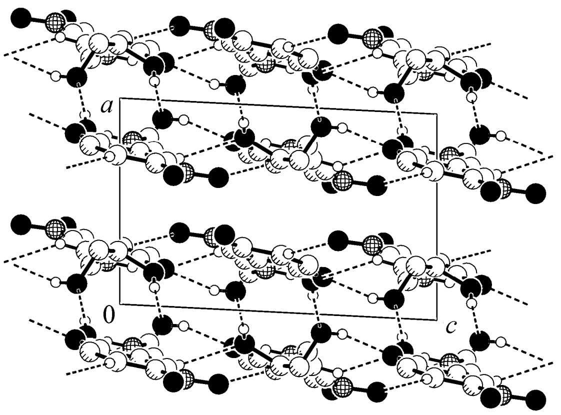
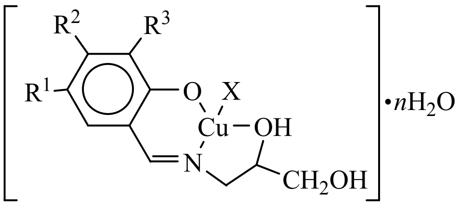


Fig. 5. Fragment of packing of compound HL^4.

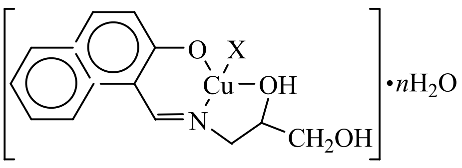
densation products HL^{1-9} could not participate in the coordination with the central ion, as their characteristic absorption bands occurred in the same regions as those in the spectra of initial azomethines. According to the IR spectra, the nitrate ion in the complexes **I**, **IV**, **VI**, **IX**, **XII**, and **XV**–**XVIII** was in the inner coordination sphere; that was confirmed [9] by the presence of the absorption bands at 1295–1285, 1025–1010, 1530–1520 and 800–795 cm^{-1} in the IR spectra.

Thermolysis of the complexes **I**–**XIX** (Table 1) occurred via the dehydration (70–95°C) and complete oxidative degradation of the compounds (330–530°C) steps. The temperature of complete degradation depended on the nature of the substituent R in the salicylidene part of azomethine, and changed in the following order: H > Br > OH > NO_2, the composition of the coordination compound being the same.

Taking into account the obtained physico-chemical data, the distribution of the chemical bonds in the complexes **I**–**XIX** could be represented as shown in the schemes **A** and **B**.



A



B

R^1 = H, Cl, Br, NO_2, OH; R^2 = H, OH; R^3 = H, OH, OCH_3.

EXPERIMENTAL

X-Ray analysis of the condensation products HL^1 and HL^4 was performed with Bruker P4/Smart diffractometer. The structures were solved by direct methods and refined anisotropically by least squares method for non-hydrogen atoms using SHELX-97 software [10]. Hydrogen atoms were included into the refinement in geometrically calculated positions. Their temperature factors U_H were taken by 1.2 times higher than those for the connected carbon and oxygen atoms. The main experimental parameters are given in Table 2, the interatomic distances and angles are collected in Table 3. Coordinates of the basis atoms of those structures were deposited in the Cambridge database (CCDC 877865–877866). Geometrical calculations and figures were performed using PLATON software [8]. The Cambridge database was used for the structures analyzing (version 5.30) [11, 12].

Resistivity of the complexes **I**–**XIX** solutions in DMF (20°C, 0.001 mol l^{-1}) was measured with P-38 slide-wire bridge. IR spectra of the substances were registered with Specord M-80 spectrophotometer (suspension in vaseline oil); the samples were stored in an oven at 105°C to constant mass prior to the measurement. The effective magnetic moments of compounds **I**–**XIX** were determined by the Gouy method. Calculation of the molar magnetic susceptibility corrected for diamagnetism was performed on the basis of the theoretical values of the magnetic susceptibility of organic compounds. Derivatograms of the complexes **I**–**XIX** were recorded with Paulik–Paulik–Erdey derivatograph in the range of 20–1000°C in corundum crucible in air using Al_2O_3 as a reference.

Initial condensation products $HL^{1–5}$ and HL^9 [mp 92–94 (HL^1), 122–124 (HL^2), 140–142 (HL^3), 136–138 (HL^4), 91–93 (HL^5), 167–169°C (HL^9)] were prepared by the procedure described in [13] .

Nitrato-{3-[(2-hydroxyphenyl)methylidene]aminopropane-1,2-diolo}copper(II) (I). 20 ml of an alcohol solution of 10 mmol of copper(II) nitrate trihydrate was added to a hot (50–55°C) solution of 10 mmol of HL^1 in 30 ml of ethanol.. The reaction mixture was heated for 30–40 min under continuous stirring. After cooling to room temperature and slow evaporation, green precipitate was filtered off on a glass filter, washed with a small amount of alcohol, ether and dried in air to constant weight.

The complexes **II**–**XIV**, **XVIII**, **XIX** were prepared similarly from the condensation products $HL^{1–5}$ or HL^9 and hydrates of copper(II) chloride, bromide or nitrate, taken in a molar ratio of 1:1.

Nitrato-{3-[(2,3-dihydroxyphenyl)methylidene]-aminopropane-1,2-diolo}copper(II) dihydrate (XV) was obtained by reacting a hot (50–55°C) solution of 10 mmol of 3-amino-1,2-propanediol with 10 mmol of 2,3-dihydroxybenzaldehyde and 10 mmol of copper(II) nitrate trihydrate in 50 ml of ethanol. The reaction mixture was heated for 25–30 min upon continuous stirring and then slowly evaporated at room temperature during one day.

The complexes **XVI** and **XVII** were prepared similarly from 3-aminopropane-1,2-diol, 2,4- or 2,5-dihydroxybenzaldehyde and copper(II) nitrate trihydrate, taken in a molar ratio of 1:1:1.

Yields of compounds **I**–**XIX** and their physicochemical characteristics are listed in Table 1.

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