Synthesis, Structure, and Antimicrobial Activity of Copper(II) Chelates Containing Imidazole and Condensation Products of α-Amino Acids with Salicylaldehyde and Its Derivatives

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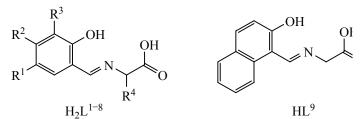[d] University Claude Bernard Lyon 1, France

Abstract—Salicylaldehyde, 5-bromo- and 5-nitrosalicylaldehydes, 2-hydroxynaphthalene-1-carbaldehyde, and 2,3-, 2,4-, and 2,5-dihydroxybenzaldehydes reacted with glycine, alanine, and phenylalanine in ethanol in the presence of imidazole (Im) and copper(II) acetate hydrate to give copper(II) chelates with the composition $Cu(Im)(L) \cdot nH_2O$ (H_2L is the condensation product of the above aldehydes with α-amino acids; $n = 0–2$). The structure of the complex $Cu(Im)(L^1)$ [$H_2L^1 = $ 2-(2-hydroxybenzylideneamino)acetic acid] was determined by X-ray analysis. The crystalline structure of [2-(2-hydroxybenzylideneamino)acetato](imidazole)copper is formed by polymeric chains of the $Cu(Im)(L^1)$ molecules linked through bridging oxygen atoms in the carboxy groups of the Schiff base ligand. The coordination unit has a distorted tetragonal pyramid configuration, where the pyramid base is composed of the phenol and carboxy oxygen atoms, CH=N nitrogen atom in the ligand H_2L^1 and imidazole nitrogen atom. The oxygen atom in the carboxy group in the neighboring molecule occupies the apical position of the coordination pyramid. The other coordination compounds also have polynuclear structure with the Schiff base H_2L acting as doubly deprotonated tridentate O,N,O-ligand and bridging carboxy groups. Thermal decomposition of the complexes includes their dehydration (70–95°C), while complete thermal decomposition occurs at 360–530°C. The synthesized complexes showed selective antimicrobial activity in the concentration range from 75 to 300 μg/ml against a number of standard strains of *Staphylococcus aureus* and *Escherichia coli*.

Amino acid derivatives possess a number of donor atoms and are therefore capable of forming various coordination compounds with metal ions [1–5]. The structure and physicochemical properties of these compounds are determined by the nature of the central atom and its inner-sphere environment. Taking into account that salicylaldehyde and glycine were often used as starting compounds, it was interesting to elucidate how introduction of different substituents into their molecules may affect the composition, structure, and properties of the resulting complexes.

The goal of the present work was to find conditions of synthesis, determined the structure, and examine the properties of copper(II) chelates with imidazole (Im) and Schiff bases $H_2L^{1–9}$ derived from glycine, alanine, and phenylalanine, on the one hand, and salicylaldehyde (H_2L^1, H_2L^7, H_2L^8), 5-bromo- (H_2L^2) and 5-nitrosalicylaldehydes (H_2L^3), 2-hydroxynaphthalene-1-carbaldehyde (HL^9), and 2,5- (HL^4), 2,4- (HL^5), and 2,3-dihydroxybenzaldehydes (HL^6).

We have found that glycine, alanine, and phenylalanine in hot (50–55°C) ethanolic solution reacted with equimolar amounts of salicylaldehyde or its derivatives, imidazole, and copper(II) acetate hydrate to produce finely crystalline compounds **I–IX**. On the basis of the elemental analysis data (Table 1),

H_2L^{1-8} $\qquad$ HL^9

H_2L^1: $R^1 = R^2 = R^3 = R^4 = H$; H_2L^2: $R^1 = Br$, $R^2 = R^3 = R^4 = H$; H_2L^3: $R^1 = NO_2$, $R^2 = R^3 = R^4 = H$; H_2L^4: $R^1 = OH$, $R^2 = R^3 = R^4 = H$; H_2L^5: $R^1 = R^3 = R^4 = H$; $R^2 = OH$; H_2L^6: $R^1 = R^2 = R^4 = H$, $R^3 = OH$; H_2L^7: $R^1 = R^2 = R^3 = H$, $R^4 = CH_3$; H_2L^8: $R^1 = R^2 = R^3 = H$, $R^4 = CH_2C_6H_5$.

the products were assigned the composition $Cu(Im)(L^{1-9})\cdot nH_2O$ (**I**, **VI**, $n = 0$; **II**, **III**, **V**, **VIII**, $n = 1$; **IV**, **VII**, **IX**, $n = 2$). Coordination compounds **I–IX** are insoluble in diethyl ether, poorly soluble in water and alcohols, and readily soluble in dimethyl-formamide (DMF), dimethyl sulfoxide, and aceto-nitrile. Their yields, elemental analyses, and physical properties are given in Table 1.

By analogy with the data of [1, 2], we presumed that copper template condensation of α-amino acids with salicylaldehyde and its derivatives gives Schiff bases H_2L^{1-9} which react with copper acetate in the presence of imidazole to afford copper chelates **I–IX**.

By recrystallization from ethanol we succeeded in isolating single crystals of complex **I**, and its structure was determined by X-ray analysis. Compound **I** crystallizes in monoclinic crystal system (Tables 2, 3). Molecules **I** in crystal form polymeric chains along the [001] axis through the *c* glide plane (Fig. 1). These chains are linked to each other by the hydrogen bonds $N^3–H\cdots O^3$ ($-x$, $-y$, $1 - z$) with the following param-eters: $H\cdots A$ 1.90, $D\cdots A$ 2.757 Å, ÐDHA 176° (Fig. 2). The copper coordination polyhedron in complex **I** is a distorted tetragonal pyramid; this is confirmed by the calculation of the trigonality index τ proposed in [6]: $\tau = (\beta - \alpha)/60$, where α and β are the largest bond angles formed by the central atom. If $\tau = 0$, the coordination entity is an ideal tetragonal pyramid, and $\tau = 1$ corresponds to an ideal trigonal bipyramid. The τ value for compounds **I** is equal to 0.02. The tetragonal pyramid base is formed by the phenol and carboxy oxygen atoms O^1 and O^2, azomethine nitrogen atom N^1 and imidazole nitrogen atom N^2. These atoms deviate by –0.013, –0.014, 0.014, and 0.013 Å, respectively, from the mean-square plane defined by them, and the copper atom deviates from that plane by 0.120 Å toward O^{3a} in the neighboring molecule. This O^{3a} atom occupies the apical position in the Cu^1 coordination pyramid, the $Cu^1\cdots O^{3a}$ distance being 2.571(2) Å. The

Table 1. Yields, effective magnetic moments, electrical conductivities, elemental analyses, and complete decomposition temperatures of copper(II) chelates **I–IX**

Comp. no.	Yield, %	μ_{ef},[a] B.M.	$æ$,[a] Ω^{-1} cm^2 mol^{-1}	Found, %		Formula	Calculated, %		Complete decomposition temperature, °C
				Cu	N		Cu	N	
I	65	1.72	3	20.62	13.38	$C_{12}H_{11}CuN_3O_3$	20.58	13.61	350
II	66	1.73	3	15.43	10.18	$C_{12}H_{12}BrCuN_3O_4$	15.66	10.36	330
III	75	1.77	2	16.84	14.90	$C_{12}H_{12}CuN_4O_6$	17.09	15.07	300
IV	65	1.71	4	17.44	11.52	$C_{12}H_{15}CuN_3O_6$	17.61	11.65	340
V	68	1.75	3	18.27	12.01	$C_{12}H_{13}CuN_3O_5$	18.54	12.26	340
VI	63	1.74	3	19.38	12.74	$C_{12}H_{11}CuN_3O_4$	19.57	12.94	330
VII	65	1.71	3	17.47	11.43	$C_{13}H_{17}CuN_3O_5$	17.71	11.71	360
VIII	75	1.74	2	14.97	9.90	$C_{19}H_{19}CuN_3O_4$	15.24	10.08	330
IX	60	1.72	4	15.85	10.37	$C_{16}H_{17}CuN_3O_5$	16.09	10.64	340

[a] At 294 K.

Table 2. Crystallographic data for complex **I** and parameters of X-ray diffraction experiment

Parameter	Value
Formula	$C_{12}H_{11}CuN_3O_3$
M	308.78
Crystal system	Monoclinic
Space group	$P2_1/c$
Z	4
a, Å	11.058(5)
b, Å	11.580(5)
c, Å	9.677(5)
β, deg	102.76(1)
V, Å^3	1208(1)
d_{calc}, g/cm^3	1.697
Irradiation, λ, Å	MoK_α; 0.7107
μ, cm^{-1}	1.814
Temperature, K	293(2)
Crystal habit, mm	0.10×0.30×0.35
Scan mode	$\theta/2\theta$
θ_{max}, deg	29.62
Ranges of h, k, l	$-13 \leq h \leq 13$
	$-15 \leq k \leq 14$
	$-13 \leq l \leq 13$
Number of reflections: total/independent (N_1), $R_{int}/I > 2\sigma(I)$, (N_2)	10287/3011, 0.0374/2469
Refinement method	Least squares
Weight scheme[a]	K_1 0.055, K_2 0.42
Number of variables	172
R_1/wR_2 (N_1)	0.0356/0.0992
R_1/wR_2 (N_2)	0.0443/0.1032
Goodness of fit S	1.143
$\Delta\rho_{(max)}$, $\Delta\rho_{(min)}$, e/A^3	0.405, −0.466

^{a} $w = 1/[\Sigma^2(F_0^2) + (K_1P)^2 + K_2P]$, where $P = [\max (F_0^2, 0) + 2F_c^2]/3$.

lengths of the other bonds formed by the copper atom with those in the pyramid base are Cu^1-O^1 1.922(1), Cu^1-O^2 1.989(2), Cu^1-N^1 1.942(2), and Cu^1-N^2 1.970(2) Å (Table 3). The angles formed by the apical Cu^1-O^{3a} bond with the other bonds at the copper atom range from 90.0 to 98.1°. The volume of the Cu^1 coordination pyramid is 6.831 Å^3.

The six-membered chelate ring $Cg^1(Cu^1O^1N^1C^1C^2C^3)$ is slightly folded along the $O^1\cdots N^1$ line so that the

dihedral angle between the $Cu^1O^1N^1$ and $O^1C^1C^2C^3N^1$ planes is 4.7°. It should be noted that the corresponding dihedral angle in structurally related complexes, di(μ-O$_{phenoxy}$)-bis{nitrato-2-[2-(hydroxyethyl-imino)methyl]phenolato(imidazole)copper(II)} [7], nitrato-2-[2-(hydroxyethylimino)methyl]phenolato(3-methylpyridine)copper(II) [8], and (3-hydroxypropyl-salicylaldiminato)copper [9], is 20.6°, 14.9°, and 22.7°, respectively and that no such folding was observed in the crystalline structures of nitrato{2-[2-(hydroxy-ethylimino)methyl]phenolato}copper [10], nitrato-2-[2-(hydroxyethylimino)methyl]phenolato(4-methyl-pyridine)copper [11], and {2-[2-(hydroxyethylimino)-methyl]phenolato}copper [12]. The five-membered metallacycle $Cg^2(Cu^1O^2N^1C^8C^9)$ in complex **I** has a skewed conformation; the N^1, C^8, and C^9 atoms deviate from the mean-square plane by −0.022, 0.028, and −0.020 Å, respectively, and the Cu^1 and O^2 atoms, by 0.009 and 0.006 Å, respectively. The imidazole ring $Cg^3(N^2N^3C^{10}C^{11}C^{12})$ is turned through a dihedral angle of 31.7° with respect to the base of the coordination polyhedron.

According to [13] (CgI$\cdots$CgJ < 6.0 Å, β < 60.0°, where β is the angle formed by the CgI$\cdots$CgJ vector and normal to the CgI aromatic ring), π–π stacking exists between the Cg^1 and Cg^1 rings ($1 - x, -y, 1 - z$), as well as between Cg^2 and $Cg^4(C^2C^3C^4C^5C^6C^7)$ ($1 - x, -y, 1 - z$). The distances between the centroids of the above fragments are 3.373 and 3.486 Å, and the angles β are 2.5 and 7.5°, respectively. Apart from the π–π stacking, the interactions metal$\cdots$Cg and X–H$\cdots$Cg (π-ring) are also observed (the distance metal$\cdots$Cg is shorter than 4.0 Å, the distance H$\cdots$Cg is shorter than 3.0 Å, and the angle γ between the H$\cdots$Cg vector and the normal to the aromatic ring is less than 30.0° [13]). Thus, the distance $Cg^4\cdots Cu^1$ ($1 - x, -y, 1 - z$) is 3.779 Å, the distance between the hydrogen atom and metalla-cycle centroid C^8–H$\cdots Cg^1$ ($x, 1/2 - y, 1/2 + z$) is 2.660 Å, and $\gamma = 8.5°$.

Visual microscopic analysis of the other coordina-tion compounds (**II–IX**) showed phase homogeneity of their powders which consisted of crystallites with various shapes. Insofar as we failed to obtain single crystals of these compounds, their structure was studied by elemental and thermal gravimetric analysis, magnetochemistry, and IR spectroscopy.

Judging by the electrical conductivities (æ) of compounds **I–IX** in DMF (Table 1), all these are nonelectrolytes (æ = 2–4 Ω^{-1} cm^2 mol^{-1}). The effective

Table 3. Selected bond lengths d and bond angles ω in molecule **I**

Bond	d, Å	Angle	ω, deg	Angle	ω, deg
Cu^1–O^1	1.922(1)	$O^1Cu^1N^1$	92.9(1)	$N^2Cu^1O^{3a}$	90.15
Cu^1–O^2	1.989(2)	$O^1Cu^1N^2$	90.4(1)	$N^1Cu^1O^2$	83.2(1)
Cu^1–N^1	1.942(2)	$O^2Cu^1N^1$	83.2(1)	$N^2Cu^1O^2$	92.6(1)
Cu^1–N^2	1.970(2)	$O^2Cu^1N^2$	92.6(1)	$Cu^1O^1C^3$	127(1)
Cu^1–O^{3a}	2.571(2)	$N^1Cu^1N^2$	172.7(1)	$O^1C^3C^2$	125.0(2)
O^1–C^3	1.305(3)	$O^1Cu^1O^2$	171.4(1)	$C^3C^2C^1$	122.9(2)
O^3–C^9	1.242(3)	$O^1Cu^1O^{3a}$	98.08	$C^2C^1N^1$	124.6(2)
C^3–C^2	1.430(3)	$O^2Cu^1O^{3a}$	89.96	$C^1N^1Cu^1$	127.3(2)
C^2–C^1	1.432(3)	$N^1Cu^1N^2$	172.7(1)	$Cu^1N^1C^8$	113.7(1)
C^1–N^1	1.285(3)	$O^1Cu^1O^2$	171.4(1)	$N^1C^8C^9$	110.1(2
N^1–C^8	1.454(3)	$O^1Cu^1O^{3a}$	98.08	$C^8C^9O^2$	117.7(2)
C^8–C^9	1.507(3)	$O^2Cu^1O^{3a}$	89.96	$C^9O^2Cu^1$	116(1)
C^9–O^2	1.273(3)	$N^1Cu^1O^{3a}$	95.82		

magnetic moments of **I**–**IX** at room temperature (294 K, Table 1) were 1.71–1.77 B.M.; i.e., they are close to the spin values typical of one unpaired electron.

In order to determine the mode of coordination of ligands H_2L^{1-9} to the central ion we compared the IR spectra of complexes **I**–**IX** with those of the initial α-amino acids and aldehydes, as well as of previously described coordination compounds [1–5] of transition metals with analogous Schiff bases. We found (Table 4)

that Schiff bases H_2L^{1-9} in complexes **I**–**IX** behave as doubly deprotonated tridentate *O*,*N*,*O*-ligands which are coordinated to the metal ion through the phenol and carboxy oxygen atoms and azomethine nitrogen atom to form six- and five-membered chelate rings. This follows from the low-frequency shift of the ν(C=N) and ν(COO⁻) bands by 25–10 cm⁻¹ relative to the corresponding bands of analogous Schiff bases [2, 3]. The IR spectra of all complexes **I**–**IX** contained a number of new absorption bands in the region 530–
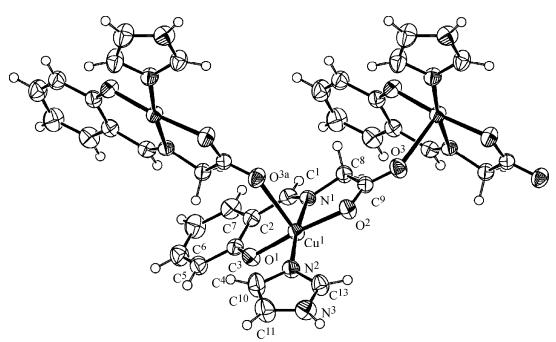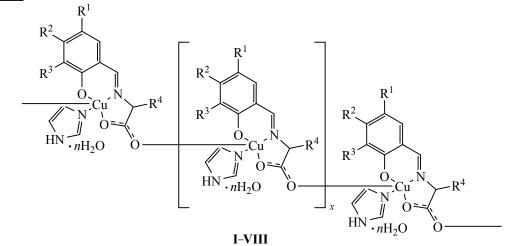

Fig. 1. Polymeric chains in the crystalline structure of compound **I**.

400 cm^{-1} due to ν(Cu–N) (530–510 and 430–405 cm^{-1}) and ν(Cu–O) vibrations (490–450 cm^{-1}). Participation of the other functional groups in Schiff bases H_2L^{1-9} in the coordination can be ruled out, for the position of their characteristic absorption bands was the same as in the spectrum of **I**. According to the IR data, the carboxy group in **I–IX** is a bridging fragment; this is confirmed by the presence of ν_{as}(COO$^-$) and ν_s(COO$^-$) absorption bands at 1609–1605 and 1336–1311 cm^{-1}, respectively. The difference $\Delta = \nu_{as}$(COO$^-$) – ν_s(COO$^-$) is 104–142 cm^{-1}; in keeping with [14], this difference indicates bridging mode of coordination of the carboxy group.

Thermal gravimetric analysis of complexes **I–IX** (Table 1) showed that their thermal decomposition includes dehydration step (70–95°C). Their complete decomposition temperatures (330–530°C) depended on the nature of substituent in the salicylidene fragment of the Schiff base ligand and decreased in the series H > Br > OH > NO$_2$ for complexes with similar compositions.

On the basis of the obtained data we presumed the following structure of linear chains of complexes **I–IX** in crystal.

I–VIII

R^1 = H, Br, NO$_2$, OH; R^2 = H, OH; R^3 = H, OH; R^4 = H, CH$_3$, CH$_2$C$_6$H$_5$; n = 0–2.

As shown in [1, 2, 5] many complexes of biometals with Schiff bases derived from amino acids selectively inhibit the growth and replication of various microorganisms. Coordination compounds **I–IX** were tested for antimicrobial activity *in vitro* (Table 5). The results showed that complexes **I–IX** exhibit both bacteriostatic and bactericidal effects against Gram-positive (*Staphylococcus aureus* ATCC 25923, *Bacillus cereus* GISK 8035) and Gram-negative test cultures (*Escherichia coli* ATCC 25922, *Shigela sonnei*, *Salmonella abony* GISK 03/03) in the concentration range from 75 to 300 μg/ml. The minimum inhibitory (MIC) and minimum bactericidal concentrations (MBC) of complexes **I–IX** are determined mainly by the nature of the R substituent in Schiff base HL$^{1-9}$, and the antibacterial activity of the complexes with similar compositions changes in the series NO$_2$ > H ≥ Br > OH; 3-OH > 4-OH > 5-OH; C$_6$H$_5$CH$_2$ > Me ≈ H. Furthermore, replacement of the benzene ring in the Schiff base by naphthalene reduces the antibacterial activity of the complexes.

EXPERIMENTAL

The X-ray diffraction data for compound **I** were obtained on a Gemini diffractometer (Oxford Diffraction) [15]. The structure was solved by the direct method and was refined by the least-squares procedure in anisotropic approximation for non-hydrogen atoms using SHELX-97 software [16]. The positions of hydrogen atoms were calculated geometrically and were included in the refinement with temperature factors U_H exceeding those of the corresponding carbon and oxygen atoms by a factor of 1.2. The principal crystallographic data for compound **I** and refinement parameters are given in Table 2, and selected bond lengths and bond angles are given in Table 3. The coordinates of atoms were deposited to the Cambridge Crystallographic Data Centre (entry no. CCDC 806259). PLATON program [13] was used to calculate the geometric parameters and plot the structures; only hydrogen atoms involved in hydrogen bonds are shown in the crystal packing of **I** (Fig. 2).

Table 4. IR spectra (ν, cm^{-1}) of copper(II) chelates **I–IX**[a]

Comp. no.	ν(NH)	ν(C=N)	ν$_{as}$(COO$^-$)	ν$_s$(COO$^-$)	Δ[b]	ν(Cu–N), ν(Cu–O)
I	3298, 3253, 3137, 3022, 2960, 2925, 2843, 2794,2694, 2634	1635, 1599	1572	1451	121	535, 468, 458, 413
II	3332, 3136, 3020, 2931, 2768, 2682, 2637, 2600, 2500, 2420	1633, 1603	1570	1452	116	538, 478, 467, 431
III	3143, 3111, 3033, 2930, 2847, 2798, 2702, 2644, 2612, 2512	1631, 1598	1571	1467	104	501, 468, 455, 414
IV	3135, 3035, 2953, 2852, 2850, 2846, 2795, 2707, 2651, 2510	1637, 1595	1586	1447	139	528, 470, 449, 414
V	3320, 3147, 3030, 2951, 2844, 2765, 2700, 2612, 2507, 2430	1634, 1600	1575	1440	135	535, 480, 459, 435
VI	3325, 3142, 3026, 2941, 2837, 2760, 2710, 2605, 2515, 2435	1631, 1604	1580	1438	142	525, 484, 452, 422
VII	3153, 3106, 3028, 2914, 2853, 2796, 2637, 2610, 2507, 2425	1633, 1605	1574	1443	131	533, 478, 458, 414
VIII	3293, 3226, 3125, 3030, 2923, 2848, 2797, 2701, 2636, 2510	1624, 1607	1583	1449	134	516, 477, 459, 418
IX	3339, 3257, 3209, 3131, 2939, 2840, 2785, 2707, 2625, 2508	1626, 1594	1575	1454	121	525, 470, 460, 410

[a] The complexes were preliminarily dried in a drying box at 105°C until constant weight. [b] Δ = ν$_a$(COO$^-$) – ν$_s$(COO$^-$).

The electrical resistivities of solutions of **I–IX** in DMF (20°C, c = 0.001 M) were measured with the aid of an R-38 slide-wire bridge. The IR spectra of **I–IX** (preliminarily dried in a drying box at 105°C until constant weight) dispersed in mineral oil were recorded on a Specord M-80 spectrometer. The effective magnetic moments were determined by the Gouy method. The molar magnetic susceptibilities were calculated with a correction made for diamag-netism from the theoretical magnetic susceptibilities of organic compounds. The thermal stability of complexes **I–IX** was studied on a Paulik–Paulik–Erdey derivatograph in the temperature range from 20 to 1000°C on exposure to air using Al$_2$O$_3$ as reference (corundum crucible).

The antimicrobial activity of complexes **I–IX** was studied *in vitro* by the twofold serial dilution method [17] using a liquid nutrition medium (meat infusion broth, pH 7.0).

[2-(2-Hydroxybenzylideneamino)acetato](imidazole)copper(II) (I). A solution of 10 mmol of salicylaldehyde, 10 mmol of aminoacetic acid (glycine), and 10 mmol of imidazole in 30 ml of ethanol was heated to 50–55°C, 20 ml of a suspension of 10 mmol of
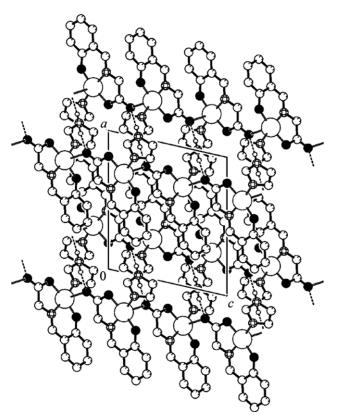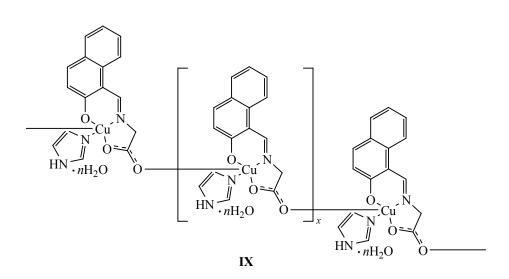

Fig. 2. A fragment of crystal packing of compound **I**.

Table 5. Minimum inhibitory (MIC) and minimum bactericidal (MBC) concentrations (μg/ml) of copper(II) chelates **I–IX** against some test bacterial cultures[a]

Comp. no.	Gram-positive				Gram-negative					
	Staphylococcus aureus, ATCC 25923		*Bacillus cereus* GISK 8035		*Escherichia coli,* ATCC 25922		*Shigela sonnei*		*Salmonella abony* GISK 03/03	
	MIC	MBC	MIC	MBC	MIC	MBC	MIC	MBC	MIC	MBC
I	300	300	150	300	150	300	300	300	300	300
II	>300	>300	150	300	>300	>300	>300	>300	>300	>300
III	150	300	150	300	300	300	150	300	150	300
IV	>300	>300	>300	>300	>300	>300	>300	>300	>300	>300
V	300	>300	300	>300	150	>300	>300	>300	300	>300
VI	150	>300	300	>300	75	>300	300	>300	75	>300
VII	300	>300	>300	>300	>300	>300	>300	>300	300	>300
VIII	75	>300	300	>300	150	>300	>300	>300	300	>300
IX	300	>300	300	>300	300	>300	>300	>300	300	>300

[a] The MIC and MBC values for all initial compounds (imidazole, α-amino acids, and hydroxy aldehydes) exceeded 300 μg/ml.

copper(II) acetate hydrate in alcohol was added, and the mixture was heated for 30–40 min under continuous stirring on a magnetic stirrer. After cooling to room temperature, slow evaporation of the mixture was accompanied by separation of a green solid which was filtered through a glass filter, washed with small amounts of alcohol and diethyl ether, and dried in air until constant weight.

Complexes **II–IX** were synthesized in a similar way using as starting compounds glycine, α-alanine, or α-phenylalanine, 5-bromo- or 5-nitrosalicylaldehyde, 2-hydroxynaphthalene-1-carbaldehyde, or 2,3-, 2,4-, 2,5-dihydroxybenzaldehyde, imidazole, and copper(II) acetate hydrate at a molar ratio of 1:1:1:1. The yields of **I–IX** and their elemental analyses and some physicochemical characteristics are given in Table 1.

IX

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