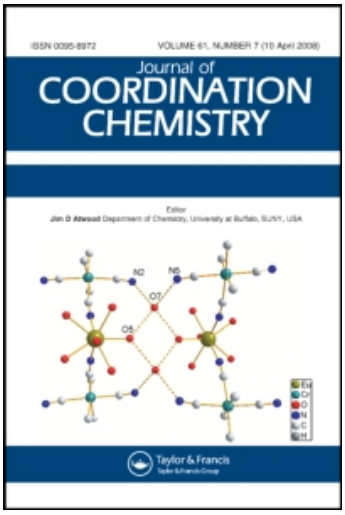


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# *N*-salicylidene-<*span*>*L*</*span*>-glutamatocopper(II) complexes and their antimicrobial effects

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# *N*-SALICYLIDENE-*L*-GLUTAMATOCOPPER(II) COMPLEXES AND THEIR ANTIMICROBIAL EFFECTS

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Reaction of an ethanolic solution of *N*-salicylidene-*L*-glutamatodiaquacopper(II) monohydrate with pyridine, 2-methylpyridine, 4-methylpyridine, 2-aminopyridine, 2,6-diaminopyridine, quinoline, 2-methylquinoline, 4-methylquinoline or 3-methylisoquinoline resulted in solid products containing complexes of the type Cu(sal-*L*-glu)L with distorted square-pyramidal coordination geometry. The products were characterized by elemental analysis, electronic spectroscopy and magnetic susceptibility measurements. Antimicrobial effects were tested on various strains of bacteria, yeasts and filamentous fungi. To compare the influence of individual ligands (neutral as well as anionic) on their biological activity, copper(II) complexes containing water and a Schiff base derived from salicyldehyde and methyl- and ethyl-esters of *L*-glutamic acid [Cu(sal-5-Me-*L*-glu)$(H_2O)_2$ and Cu(sal-5-Et-L-glu)$(H_2O)_2$] were also prepared and studied. Bioactivities of complexes tested were found to decrease in the sequence bacteria > filamentous fungi > yeasts.

*Keywords:* Copper complex; *N*-salicylidene-*L*-glutamate; Spectroscopic and magnetic properties; Antimicrobial agents

## INTRODUCTION

Schiff-base copper(II) complexes derived from salicylaldehyde and various amino acids are of particular interest from a biological activity point of view. They are also bioactive against gram-negative as well as gram-positive bacteria [1,2]. There is further interest in their antiradical [3] and radiodioprotective properties [4]. Most copper(II) Schiff-base complexes have a square pyramidal arrangement around the copper(II) atom. The molecular structure of [Cu(*N*-salicylidene-*L*-glutamato)$(H_2O)_2]\cdot H_2O$ shows [5] that the square pyramidal arrangement is formed (in-plane) by one tridentate *N*-salicylidene-*L*-glutamate(2-) ligand and one water molecule. The apical position is

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TABLE I Analytical data for the copper(II) complexes

| *Complex* | $M_r$ | *% C calc./found* | *% N calc./found* | *% H calc./found* |
|---|---|---|---|---|
| [Cu(sal-L-glu)($H_2O$)$_2$] · $H_2O$ (**1**) | 366.82 | 39.29/39.20 | 3.82/3.90 | 4.67/4.30 |
| Cu(sal-5-Et-L-glu) · 2$H_2O$ (**2**) | 376.87 | 44.62/44.67 | 3.72/3.84 | 5.08/4.90 |
| Cu(sal-5-Met-L-glu) · 2$H_2O$ (**3**) | 362.81 | 43.03/43.71 | 3.86/3.94 | 4.72/4.69 |
| Cu(sal-L-glu)py (**4**) | 395.88 | 51.58/51.53 | 7.08/7.18 | 4.07/4.28 |
| Cu(sal-L-glu)2-Mepy (**5**) | 405.88 | 53.26/53.17 | 6.90/6.91 | 4.47/4.57 |
| Cu(sal-L-glu)4-Mepy (**6**) | 405.88 | 53.26/53.15 | 6.90/6.93 | 4.47/4.50 |
| Cu(sal-L-glu)2-apy (**7**) | 406.88 | 49.75/50.24 | 10.20/10.71 | 4.14/4.29 |
| Cu(sal-L-glu)2-dapy (**8**) | 421.88 | 48.34/49.03 | 13.27/13.30 | 4.26/4.94 |
| Cu(sal-L-glu)qn (**9**) | 441.92 | 57.07/56.76 | 6.34/5.94 | 4.10/4.26 |
| Cu(sal-L-glu)iqn (**10**) | 441.92 | 57.07/56.73 | 6.34/6.04 | 4.10/4.39 |
| Cu(sal-L-glu)2-Meqn (**11**) | 455.94 | 57.96/57.78 | 6.14/6.27 | 4.42/4.54 |
| Cu(sal-L-glu)4-Meqn (**12**) | 455.94 | 57.96/58.10 | 6.14/6.24 | 4.42/4.52 |
| Cu(sal-L-glu)3-Meiqn (**13**) | 455.94 | 57.96/57.79 | 6.14/6.23 | 4.42/4.44 |

occupied by another water molecule. The third water molecule is not directly coordinated to the Cu(II) atom but is connected to the complex by hydrogen bonds.

As part of our investigation of copper(II) ion–drug interactions, in this paper we report the complexation of *N*-salicylidene-L-glutamate (sal-L-glu) in the presence of 2-methylpyridine (2-Mepy), 4-methylpyridine (4-Mepy), 2-aminopyridine (2-apy), 2,6-diaminopyridine (2,6-dapy), quinoline (qn), 2-methylquinoline (2-Meqn), 4-methylquinoline (4-Meqn) and 3-methylisoquinoline (3-Meiqn) (the compounds will be referred to by bold arabic numerals hereafter, see Table I). We determine the stereochemistry and mode of ligand coordination in the solid copper(II) complexes by spectroscopic and magnetic measurements. Moreover, the antimicrobial activity of the products is investigated against various strains of bacteria, yeasts and filamentous fungi. For this reason, we prepared several copper(II) complexes of the general formula Cu(sal-L-glu)L, where L = 2-Mepy, 4-Mepy, 2-apy, 2,6-dipy, qn, iqn, 2-Meqn, 4-Meqn or 3-Meiqn, and Cu(sal-5-Met-L-glu)($H_2O$)$_2$ and Cu(sal-5-Et-L-glu)($H_2O$)$_2$.



## EXPERIMENTAL

Complexes of composition [CuX($H_2O$)$_2$] · ($H_2O$), where X = *N*-salicylidene-L-glutamate (sal-L-glu), and CuX′($H_2O$)$_2$, where X′ = *N*-salicylidene-5-methyl- or -5-ethylester-L-glutamate (sal-5-Me-L-glu or sal-5-Et-L-glu), were prepared as described earlier [6,7]. Complexes of composition $CuXL_2$ (where L = pyridine, 2-Mepy, 4-Mepy, qn, iqn, 2-Meqn, 4-Meqn or 3-Meiqn) were prepared by adding an ethanolic solution of L to a stirred ethanolic solution of [CuX($H_2O$)$_2$] · ($H_2O$) in a mole ratio of 2 : 1. The green products that precipitated were isolated and washed with cold ethanol and dried at ambient temperature [6]. Complexes containing esters of L-glutamic acid were prepared in aqueous media at elevated temperature [7]. Analytical data for the prepared products together with their numbering are given in Table I.

### Spectroscopic studies

Electronic spectra in the region 10 000–28 000 $cm^{-1}$ were measured with a UV–VIS Specord M 40 (Carl Zeiss Jena) spectrophotometer using a Nujol suspension technique. Data are listed in Table II.

TABLE II Electronic spectroscopic and magnetic moment data for the copper(II) complexes

| *Complex* | $\nu_{max}$ $(cm^{-1})$ | $\nu_{max}$ $(cm^{-1})$ | $\mu_{eff}/\mu_B$ |
|---|---|---|---|
| [Cu(sal-*L*-glu)$(H_2O)_2$]·$H_2O$ (**1**) | 15 440 | 26 440 | 1.80 |
| Cu(sal-5-Et-*L*-glu)$(H_2O)_2$ (**2**) | 15 640 | 26 240 | 1.77 |
| Cu(sal-5-Met-*L*-glu)$(H_2O)_2$ (**3**) | 15 720 | 26 240 | |
| Cu(sal-*L*-glu)py (**4**) | 16 920 | 26 680 | |
| Cu(sal-*L*-glu)2-Mepy (**5**) | 17 240 | 26 480 | |
| Cu(sal-*L*-glu)4-Mepy (**6**) | 16 280 | 27 800 | 1.87 |
| Cu(sal-*L*-glu)2-apy (**7**) | 15 260 | 30 000 | |
| Cu(sal-*L*-glu)2,6-dapy (**8**) | 16 600 | 28 680 | |
| Cu(sal-*L*-glu)qn (**9**) | 16 680 | 26 800 | 1.86 |
| Cu(sal-*L*-glu)iqn (**10**) | 17 000 | 26 240 | 1.85 |
| Cu(sal-*L*-glu)2-Meqn (**11**) | 15 800 | 27 960 | |
| Cu(sal-*L*-glu)4-Mequin (**12**) | 15 640 | 27 960 | 1.82 |
| Cu(sal-*L*-glu)3-Meiquin (**13**) | 15 880 | 28 280 | 1.75 |



## Magnetic studies

Magnetic susceptibility measurements were performed at room temperature using an instrument based on the Gouy principle.

## Antimicrobial activities

The antimicrobial activities of the compounds were evaluated by a macrodilution method using the $G^+$ bacteria *Staphylococcus aureus* CCM 3953, the $G^-$ bacteria *Escherichia coli* CCM 3988 and the yeasts *Candida parapsilosis* (purchased from the Laboratory of Medical Mycology, Postgraduate Medical Institute, Bratislava). Cultures of bacteria and yeasts were incubated under vigorous shaking [8]. The effects of the prepared compounds on the filamentous fungi *Rhizopus oryzae*, *Alternaria alternata* (obtained from the Collection of Microorganisms of the Department of Biochemistry and Microbiology, Slovak University of Technology), *Botrytis cinerea* CCM F-16 and *Microsporum gypseum* (from the Laboratory of Medical Mycology, Postgraduate Medical Institute, Bratislava) were tested by a macrodilution technique on a solidified broth medium with static culturing [9]. Chromatographically pure compounds were dissolved in dimethylsulfoxide (DMSO); final concentrations never exceeded 1.0 vol% in either control or treated samples. Concentrations of test compounds ranged from 0.01 to 5.00 mmol $dm^{-3}$ for bacteria, yeasts and filamentous fungi in all experiments.

Antimicrobial activity was characterized by the $IC_{50}$ value (concentration of a compound that in comparison to the control inhibits the growth of microorganisms by 50%) and the MIC value (minimal inhibitory concentration of a compound that inhibits microbial growth by 100%). The $IC_{50}$ and MIC values were read from toxicity curves.

MIC experiments on subculture dishes were used to assess the minimal microbiocidal concentration (MMC). Subcultures were prepared separately in Petri dishes containing competent agar medium and incubated at 30°C for 48 h (bacteria, yeasts) and at 25°C for 96 h (filamentous fungi). The MMC value was taken as the lowest concentration that showed no visible growth of microbial colonies in the subculture dishes.

## RESULTS AND DISCUSSION

On the basis of elemental analyses the copper(II) complexes are of composition CuXL, where X represents the Schiff base derived from salicylaldehyde and L-glutamic acid and L represents the corresponding molecular ligand, and $CuX(H_2O)_2$, when the Schiff base contains an ester of L-glutamic acid. For characterization of the complexes prepared, spectroscopic data and magnetic susceptibility measurements were used.

Electronic spectra (Table II) of the complexes exhibit a broad asymmetrical band with a maximum at about 15 215 $cm^{-1}$ (range 15 440–17 240 $cm^{-1}$) and a shoulder on the low energy side. The band at about 15 215 $cm^{-1}$ is due to d–d transitions and the shoulder at about 27 370 $cm^{-1}$ may be assigned to a charge transfer. These features are typical of five-coordinate copper(II) complexes with an almost square-pyramidal structure [10]. The blue shift of the d–d band, for example from 15 440 $cm^{-1}$ in Compound **1** to 17 240 $cm^{-1}$ in Compound **5** indicates that the extent of square-pyramidal distortion depends on the type of coordinated molecular ligand.

Magnetic properties of seven representative compounds of this group of copper(II) complexes (Table II) show that the complexes can be considered as being magnetically dilute as the values of magnetic moments range from 1.75 to 1.86 BM at ambient temperature. Spectroscopic and magnetic properties are very similar to those found for Cu(*N*-sal-L-glu)$L_2$ (L = pyridine [11] or 4-methylpyridine [12]) as well as for an aqua complex containing the methyl ester of L-glutamic acid [13], for which structural data are available. A square-pyramidal arrangement about each copper(II) atom is created by two O atoms and one N atom of the *N*-salicylidene-L-glutamato ion and an N atom of pyridine or 4-methylpyridine. The apical site is occupied by an N atom of another pyridine or 4-methylpyridine. On the basis of the spectroscopic and magnetic behaviour of the copper(II) complexes under study, we propose a similar arrangement about the copper(II) atom as those found elsewhere [11–13].

Results of the quantitative determination of antimicrobial activity, characterized by $IC_{50}$ and MIC values, are presented in Table III. The compounds tested differ in their bioactivities against bacteria, yeasts and filamentous fungi; the bioactivities decrease in the sequence bacteria > filamentous fungi > yeasts. In general, the antimicrobial activity of copper(II) complexes that contain quinoline as a ligand is higher than the others. The highest inhibition activity against $G^+$ *S. aureus* ($IC_{50} = 0.02\ mmol\ dm^{-3}$, $MIC = 0.08\ mmol\ dm^{-3}$) is for Compound **9**. Its antibacterial activity is about ten times higher than the respective parent compound **1** ($IC_{50} = 0.22\ mmol\ dm^{-3}$, $MIC = 1.25\ mmol\ dm^{-3}$).

However, the effect of the compounds tested on $G^-$ *E. coli* growth was considerably lower. The highest inhibition effect against $G^-$ *E. coli* was recorded for Compound **8** ($IC_{50} = 0.20\ mmol\ dm^{-3}$), about five times higher than the respective basic compound **1** ($IC_{50} = 1.1\ mmol\ dm^{-3}$). Total growth inhibition of $G^-$ *E. coli* was obtained by Compound **8** at a concentration of $2.5\ mmol\ dm^{-3}$ and by Compound **10** at a concentration of $1.25\ mmol\ dm^{-3}$. Growth inhibition data for *S. aureus* and *E. coli* by **9** and **10** are presented in Figs. 1 and 2.

The highest inhibition effect against the yeast *Candida parapsilosis* was observed in the presence of Compound **10** ($IC_{50} = 0.63\ mmol\ dm^{-3}$, $MIC = 2.5\ mmol\ dm^{-3}$). Growth inhibition data for *Candida parapsilosis* by Compound **10** are presented in Fig. 3.

TABLE III Antimicrobial activity of copper(II) complexes characterized by numerical values of $IC_{50}$ and MIC (mmol dm$^{-3}$)

| *Compound* | *Bacteria* | | | | *Yeasts* | | | | *Filamentous fungi* | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *S. aureus* | | *E. coli* | | *C. parapsilosis* | | *R. oryzae* | | *A. alternata* | | *B. cinerea* | | *M. gypseum* | |
| | $IC_{50}$ | *MIC* | $IC_{50}$ | *MIC* | $IC_{50}$ | *MIC* | $IC_{50}$ | *MIC* | $IC_{50}$ | *MIC* | $IC_{50}$ | *MIC* | $IC_{50}$ | *MIC* |
| [Cu(sal-*L*-glu)$(H_2O)_2$]·$H_2O$ (**1**) | 0.22 | 1.25[a] | 1.10 | 5[b] | 1.60 | >5 | 1.50 | 5[b] | 2.50 | >5 | 4.35 | 5[a] | 2.25 | 5[b] |
| Cu(sal-5-Et-*L*-glu)$(H_2O)_2$ (**2**) | 0.58 | 1.25[a] | 4.55 | >5 | 2.70 | >5 | 2.60 | 5[b] | 3.50 | >5 | 2.25 | >5 | >5 | >5 |
| Cu(sal-5-Met-*L*-glu)$(H_2O)_2$ (**3**) | 0.52 | 1.25[a] | 2.56 | >5 | 2.80 | >5 | 1.50 | 5[b] | 3.80 | >5 | > 5 | >5 | 1.00 | >5 |
| Cu(sal-*L*-glu)py (**4**) | 0.22 | 0.31[b] | 1.20 | 2.5[b] | 1.70 | >5 | 1.10 | 2.5[b] | 2.50 | 5[a] | 1.80 | 2.5[b] | 1.80 | 2.5[b] |
| Cu(sal-*L*-glu)2-Mepy (**5**) | 0.22 | 0.31[b] | 3.00 | >5 | 2.50 | >5 | 2.40 | 5[b] | 5.00 | >5 | 4.45 | >5 | >5 | >5 |
| Cu(sal-*L*-glu)4-Mepy (**6**) | 0.22 | 0.31[b] | 0.86 | 2.5[b] | 2.20 | >5 | 0.86 | 2.5[b] | 0.56 | 1.25[b] | 1.25 | 2.5[b] | 0.86 | 2.5[b] |
| Cu(sal-*L*-glu)2-apy (**7**) | 0.31 | 0.63[b] | 1.30 | 5[b] | 1.05 | >5 | 1.60 | 2.5[b] | 2.65 | 5[b] | 3.70 | 5[a] | 1.50 | 5[b] |
| Cu(sal-*L*-glu)2,6-dapy (**8**) | 0.41 | 0.63[b] | 0.20 | 2.5[a] | 0.82 | >5 | 1.50 | 5[b] | 2.50 | >5 | 4.00 | 5[b] | 1.25 | >5 |
| Cu(sal-*L*-glu)qn (**9**) | 0.02 | 0.08[b] | 0.84 | 2.5[b] | 2.00 | >5 | 0.05 | 0.16[b] | 0.10 | 0.31[b] | 2.25 | 5[a] | 1.05 | 5[b] |
| Cu(sal-*L*-glu)iqn (**10**) | 0.12 | 0.16[b] | 0.60 | 1.25[b] | 0.63 | 2.5[b] | 0.34 | 0.63[b] | 0.27 | 0.63[b] | 0.44 | 2.5[b] | 0.45 | 1.25[b] |
| Cu(sal-*L*-glu)2-Meqn (**11**) | 0.21 | 0.63[b] | 1.05 | >5 | 1.10 | >5 | 1.90 | 5[b] | 1.25 | 2.5[b] | 3.10 | 5[a] | 0.57 | 1.25[b] |
| Cu(sal-*L*-glu)4-Meqn (**12**) | 0.46 | 0.63[b] | 1.05 | 2.5[b] | 4.45 | >5 | 0.34 | 0.63[b] | 0.52 | 2.5[b] | 2.40 | 5[a] | 0.98 | 2.5[b] |
| Cu(sal-*L*-glu)3-Meiqn (**13**) | 0.26 | 0.63[b] | 0.92 | 2.5[b] | 0.82 | 5[b] | 0.90 | 2.5[b] | 0.76 | 2.5[b] | 3.00 | 5[a] | 0.50 | 2.5[b] |

[a]Concentration of compound inducing a microbicidal effect (MMC).
[b]Concentration of compound inducing a microbistatical effect (MMS).

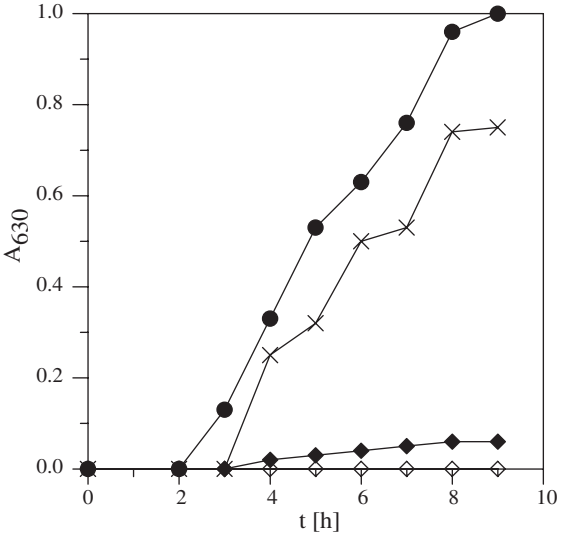


FIGURE 1 Inhibition of growth of *Staphylococcus aureus* by Compound **9**. Final concentrations (mmol dm$^{-3}$): ◇ 0.08, ◆ 0.04, × 0.01, ● 0 (control, 1% DMSO).



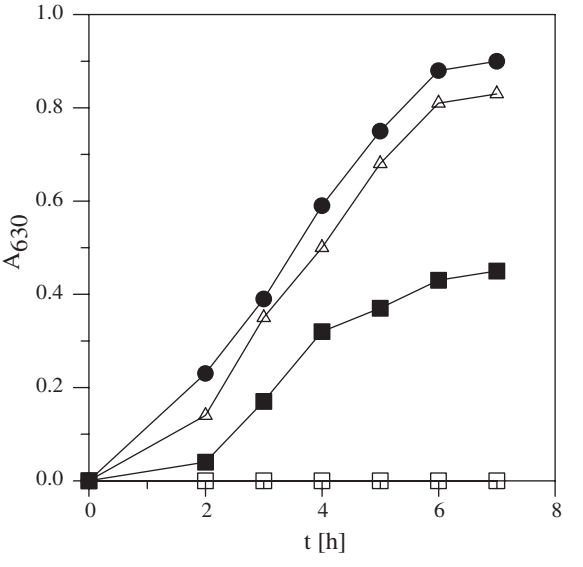


FIGURE 2 Inhibition of growth of *Escherichia coli* by Compound **10**. Final concentrations (mmol dm$^{-3}$): □ 1.25, ■ 0.63, △ 0.31, ● 0 (control, 1% DMSO).

Antifungal efficiency of the compounds tested against filamentous fungi decreases in the order *R. oryzae* > *A. alternata* > *M. gypseum* > *B. cinerea*. The growth of *R. oryzae* was most significantly inhibited by Compound **9** ($IC_{50} = 0.05$ mmol dm$^{-3}$, MIC = 0.16 mmol dm$^{-3}$), which is far more efficient than the parent compound **1** ($IC_{50} = 1.5$ mmol dm$^{-3}$, MIC = 5 mmol dm$^{-3}$). Compound **9** also showed the highest growth inhibition against *A. alternata* ($IC_{50} = 0.10$ mmol dm$^{-3}$,

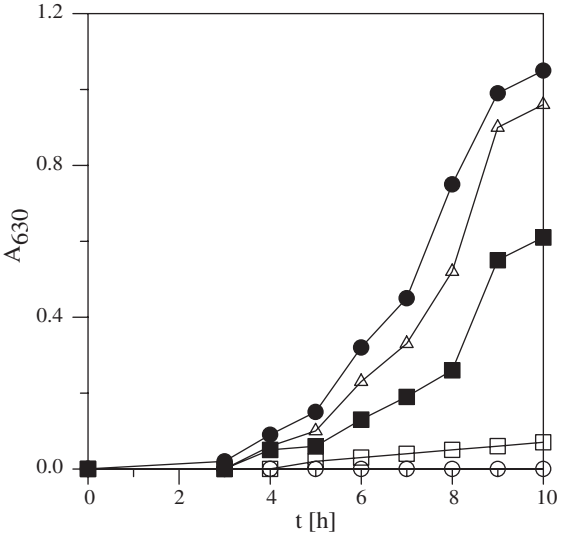


FIGURE 3 Inhibition of growth of *Candida parapsilosis* by Compound **10**. Final concentrations (mmol dm$^{-3}$): ○ 2.5, □ 1.25, ■ 0.63, △ 0.31, ● 0 (control, 1% DMSO).



MIC = 0.31 mmol dm$^{-3}$). The highest inhibition activity against *M. gypseum* and *B. cinerea* was manifested by Compound **10** ($IC_{50}$ = 0.45 and 0.44 mmol dm$^{-3}$, respectively).

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