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Crystal structure of the copper(II) ternary complex of *N*-salicylidene-L-serinato with 2,6-diaminopyridine. Toxicity studies against *Drosophila melanogaster*

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Abstract

The ternary [Cu(Sal-(L-Ser))(2,6-diaminopyridine)H_2O] (**1b**) complex has been prepared and the crystal structure determined. The copper(II) cation has a square pyramidal geometry, being coordinated to the tridentate Sal-(L-Ser) Schiff base ligand and the heterocyclic nitrogen atom N(11) of the 2,6-diaminopyridine molecule which occupying the corners of the square base. The coordination sphere about the copper is completed by an axial O(W) atom of a water molecule. Spectroscopic data are discussed. Preliminary toxicity studies [larva-to-adult viability (*V*) and developmental time (in days) (DT)] of several copper(II) compounds including complex **1** and other related previously described complexes [Cu(Sal-(L-Ser))H_2O]·H_2O (**2**) and [Cu(Sal-Ser)(2-aminopyridine)] (**3**) against *Drosophila melanogaster* (*Or-R*) show that these copper(II) complexes display less toxicity than simple copper(II) salts.

Keywords: Copper(II)–Schiff base complexes; *N*-Salicylidene derivative; X-ray structures; Ternary copper(II) complexes; Toxicity of copper(II) complexes; *Drosophila melanogaster*

1. Introduction

The synthesis and characterization of non-enzymatic models for the metal-pyridoxal (vit. B6)-amino acid Schiff base systems [1–3], and the design of new *N*-salicylidene aminoalkanoato complexes with antimicrobial, antiinflammatory, antipiretic and superoxide dismutase-like activities have been the driving forces for the study of new copper(II) *N*-salicylidene-aminoacidato Schiff base complexes [4]. Structural studies on binary [5–16] and ternary [4,17] Schiff base Cu(II) complexes derived from salicylaldehyde and amino acids show structures based on dimeric complex units [5–8], polymeric catena units [9–11] and discrete monomeric complex units [12–16].

On the other hand, it is well known that the presence of excess quantities of an essential metal, such as copper, can be as deleterious as insufficient amounts. Thus, an accidental ingestion of the element can lead to the impossibility of the normal function of the natural biochemical mechanisms of detoxification. For example, Wilson's disease results from a genetically inherited metabolic defect in which copper can no longer be tolerated at normal levels [18]. In this context, we have performed preliminary toxicity studies of several structurally characterized Schiff base copper(II) complexes formed with salicylaldehyde and L-serine against *Drosophila* which is a model organism that has been used for more than 100 years in all genetic fields, from the population genetics to genetics of development. In genetic toxicology, it has been applied in two functions:

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for the use in tests for identifying carcinogens and for studies of the mechanism of mutagenesis by chemicals. A negative response in *Drosophila* provides little evidence for genotoxicity, but a positive response provides good evidence that a chemical is a trans-species mutagen and probably also carcinogenic to mammals [19]. The viability and developmental time are two representative parameters which affects the fitness of an organism [20]. In the present paper, we have prepared a new ternary complex [Cu(Sal-(L-Ser))(2,6-diaminopyridine)H_2O] (**1**) and preliminary toxicity studies of several Cu(II)–Schiff base complexes are performed.

2. Experimental

Salicylaldehyde, L-serine, 2,6-diaminopyridine and copper(II) acetate monohydrate were obtained from Aldrich and used without further purification.

2.1. Synthesis of [Cu(Sal-Ser)(2,6-diaminopyridine)] (*1a*) and [Cu(Sal-Ser)(2,6-diaminopyridine)H_2O] (*1b*)

2,6-Diaminopyridine (4 mmol) was added to a warm solution (60 °C) of 1 mmol of [Cu(Sal-(L-Ser))H_2O]·H_2O in 40 cm^3 of 1:1 v/v EtOH/water mixture. The dark green solution was stirred at this temperature for 2 h. The solution was filtered and left in an open vessel to evaporate at room temperature. Dark green crystals of [Cu(Sal-Ser)(2,6-diaminopyridine)] (**1a**) were obtained (21% yield) after 3 days. *Anal.* Found: C, 47.40; H, 4.31; N, 14.68. Calc. for $C_{15}H_{16}CuN_4O_4$: C, 47.42; H, 4.21; N, 14.75%. IR (cm^{-1}): 269w, 350m, 403w, 735m, 771s, 791s, 1360s, 1449s, 1469m, 1480sh, 1537m, 1568sh, 1599s, 1645s, 3338s and 3430s. UV–Vis (DMSO): λ 663 ($\varepsilon = 185$), 336 (2.5×10^4) and 258 nm (2.3×10^4 dm^3 mol^{-1} cm^{-1}). Λ_M (Ω^{-1} cm^2 mol^{-1}/10^{-3} M) in DMSO, 23 °C = 2.0. A few crystals suitable for X-ray diffraction of composition [Cu(Sal-Ser)(2,6-diaminopyridine)H_2O] (**1b**) were obtained from the mother solution.

2.2. Analysis and physical measurements

Elemental analysis of the complex was carried out using a Carlo-Erba Analyser Model 1106. The IR spectra (KBr pellets) were recorded on a PE 683 with a PE 1600 IR data station and electronic spectra in DMSO solutions on a PE 552 spectrophotometer. Thermogravimetric data in the range from 30 to 700 °C were obtained (heating rate 10 °C min^{-1}) on a PE TGA-2 thermobalance. Magnetic susceptibility measurements (at 298 K) were carried out on polycrystalline samples with a Manics DSM8 pendulum-type magnetometer equipped with a helium continuous-flow cryostat and a Bruker BE15 electromagnet. The magnetic field was approximately 1.5 T. Diamagnetic corrections were estimated from Pascal's constants. The ESR spectra was recorded at X-band frequencies with a Bruker ES200 spectrometer at 298 K.

2.3. Crystallographic studies

X-ray data from a single crystal of [Cu(Sal-(L-Ser))(2,6-diaminopyridine)H_2O] (**1b**) were collected with an Enraf–Nonius CAD4 diffractometer. The cell parameters were determined from a least-squares refinement of 25 reflections randomly searched. The ω–2θ scan method was used for recording the X-ray intensities. The MolEN [21] package was used for applying Lorentz polarization and ψ-scan empirical absorption correction. The structure was solved by direct methods and refined by a full-matrix, least-squares method, using the SHELX-97 [22] package. Hydrogen atoms were positioned in calculated positions and refined using a global isotropic temperature factor. Crystal parameters, data collection details and results of the refinement are summarized in Table 1.

2.4. Biological studies: Larval collection and experiments

The *Drosophila* flies were maintained by serial transfers in 150 ml bottles containing 30 ml of yeast medium

Table 1
Selected crystallographic data for **1b**

	1b
Empirical formula	$C_{15}H_{18}CuN_4O_5$
Formula weight	397.87
Temperature (K)	293(2)
Wavelength (Å)	0.71069
Crystal system	trigonal
Space group	$P32$
Unit cell dimensions	
a (Å)	11.629(3)
b (Å)	
c (Å)	10.805(3)
β (°)	
V (Å^3)	1265.4(6)
Z	3
D_{calc} (g cm^{-3})	1.566
Absorption coefficient (mm^{-1})	1.329
$F(000)$	615
Crystal size (mm)	$0.25 \times 0.27 \times 0.28$
θ Range for data collection (°)	3.50–30.42
Index ranges	$-16 \le h \le 0$, $-14 \le k \le 16$, $-15 \le l \le 0$
Reflections collected	4364
Independent reflections	2681
R_{int}	0.0802
Refinement method	full-matrix least-squares
Data/restraints/parametres	2681/11/246
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0419$, $wR_2 = 0.0668$
R indices (all data)	$R_1 = 0.1747$, $wR_2 = 0.0827$
Goodness-of-fit on F^2	0.931
Largest difference peak and hole (e Å^{-3})	0.437 and −0.875

[water, agar, salt, sugar and inactive yeast, plus a fungicide (methyl-4-hydroxybenzoate) and an antibacterial (propionic acid)] and active yeast powder added on the surface of the medium. The temperature was kept at 25 ± 1 °C; the relative humidity was 65 ± 5% and with day–night cycles. In order to obtain a large number of larvae, the method employed was the following: fly adults were transferred from the serial transfer system to bottles with fresh food for 24 h. When the adults that emerged were 5 days old, they were placed on egg-collecting devices (layers). Each layer consisted of a glass recipient that contains the flies; this recipient is covered by a watch glass containing a mixture of agar, water, AcOH and ethyl alcohol, with a drop of active yeast on it. The eggs are laid onto the surface of this mixture. Every 2 h, the layer glasses were changed, in this way, the eggs of a glass have a similar age, with a maximum difference of ±2 h among them. The watch glasses of the layers were kept at 25 ± 1 °C for at least 22 h in Petri dishes until larvae hatched. These larvae were used in the experiments. The larvae were picked up from the watch glasses one by one with a lancet under a stereoscopic microscope.

Fifty larvae were seeded into 10 × 2 cm vials with 10 ml food. This density prevents the competition among the larvae and so the differences we could find were due to the chemical products added to the medium. The vials were supplemented with a Cu(II) compound at the following concentrations (in ppm): [Cu(Sal-(L-Ser))H_2O]·H_2O (**2**): 0 (control), 50, 100, 500, 750, 1000 and 1500; [Cu(Sal-(L-Ser))(2,6-diaminopyridine)H_2O] (**1a**): 0 (control), 250, 500, 750, 1000 and 1500; [Cu(Sal-(L-Ser))(2-aminopyridine)] (**3**): 0 (control), 500, 750, 1000 and 1500. The number of replications was five for each complex and concentration. Typical Cu(II) salts have been used to study the more direct action of this ion on a live organism: $Cu(SO_4)_2·5H_2O$: 0 (control), 250, 500, 750, 1000 and 1500; and $Cu(acetate)_2·H_2O$: 0 (control), 50, 100, 250, 500, 1000 and 1500.

The number of adult flies which emerged from each vial was counted daily until the exhaustion of the culture. The parameters studied were the larva-to-adult viability (V) and developmental time (in days) (DT). Viability is expressed as: $V = N_A/N_L$, where N_L is the input number of larvae (50 in our case), and N_A, the output number of adults emerging from these N_L larvae. Developmental time is measured in days by the formula $DT = \Sigma N_i d_i / \Sigma N_i$, where N_i is the number of flies emerging on the day d_i after the larvae are placed in the medium. The standard errors of the mean viabilities and developmental times were calculated as $s_y = (s^2/n)^{1/2}$, where s^2 is the variance and n is the number of repetitions [23].

3. Results and discussion

3.1. Crystal structure

The racemic [Cu(Sal-Ser)(2,6-diaminopyridine)(H_2O)] (**1b**) shows a distorted square pyramidal geometry (Fig. 1). Selected bond distances and angles are given in Table 2. The coordination sites are the tridentate N-salicylidene-serinato group [Cu–N(4) = 1.938(4) Å, Cu–O(8) = 1.911(4) Å, Cu–O(1) = 1.961(4) Å] and the heterocyclic N(11) [Cu–N(11) = 2.026(4) Å] of 2,6-diaminopyridine. The coordination sphere about Cu(II) is apically completed by a weakly bonded oxygen atom O(W) of a water molecule [Cu–O(W) = 2.550(4) Å]. An additional H-bond is present between one NH_2 group of 2,6-diaminopyridine and the apical coordinated water of the complex unit [N(16)–H···O(W): distance between heteroatoms 2.941(8) Å; angle 169(6)°] that implies a nearly orthogonal disposition between the Schiff base and the pyridine moieties. The presence of this type of intramolecular H-bond in these ternary complexes at 2.90 ± 0.15 Å seems a general characteristic for these systems {N(heterocyclic ligand)···O(carboxylate of Schiff base) = 2.97 Å in [Cu(Sal-Ser)(2-aminopyridine)] (**3**) [17]; N(heterocyclic ligand)···O(carboxylate of Schiff base) = 2.84 Å in N-salicylideneglycinato–Cu(II)–thiourea [24] and 2.79 Å in N-salicylidenealaninato–Cu(II)–pyrazole [25]; NH_2(heterocyclic ligand)···O(phenolate and carboxylate of Schiff base) = 2.77 and 2.89 Å in [Cu(Sal-Trp)(2-aminopyrimidine)] [4]; N(heterocyclic ligand)···O(carboxylate of Schiff base) = 2.89 Å in [Cu(Sal-Trp)(2-aminopyridine)] (**3**) [4]} and seems to be an important factor in the stabilization of the

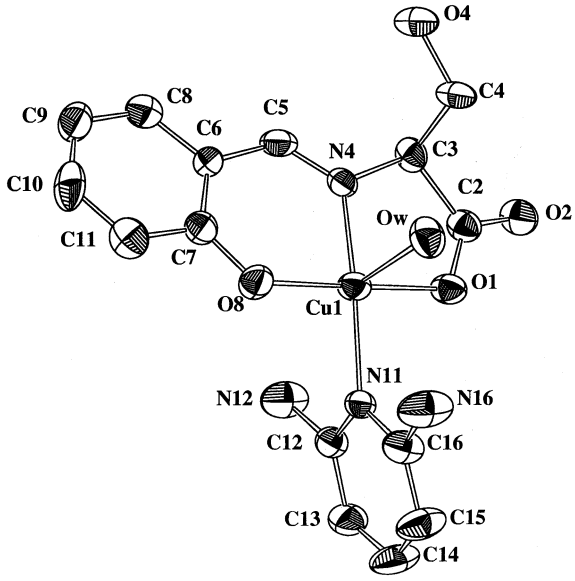

Fig. 1. ORTEP representation of [Cu(Sal-(L-Ser))(2,6-diaminopyridine)H_2O] (**1b**) (hydrogen atoms are omitted for clarity).

Table 2
Selected bond lengths (Å) and angles (°) for **1b**

Bond lengths	
Cu(1)–O(8)	1.911(4)
Cu(1)–N(4)	1.938(4)
Cu(1)–O(1)	1.961(4)
Cu(1)–N(11)	2.026(4)
Cu(1)–OW	2.550(4)
O(1)–C(2)	1.275(6)
C(2)–O(2)	1.229(7)
C(2)–C(3)	1.528(8)
C(3)–N(4)	1.458(7)
N(4)–C(5)	1.279(7)
C(5)–C(6)	1.430(8)
C(6)–C(7)	1.413(8)
C(7)–O(8)	1.335(6)
N(11)–C(12)	1.337(7)
N(11)–C(16)	1.362(7)
C(12)–N(12)	1.375(7)
C(12)–C(13)	1.382(8)
C(13)–C(14)	1.377(9)
C(14)–C(15)	1.348(9)
C(15)–C(16)	1.372(8)
C(16)–N(16)	1.366(8)
Bond angles	
O(8)–Cu(1)–N(4)	93.26(18)
O(8)–Cu(1)–O(1)	173.51(19)
N(4)–Cu(1)–O(1)	83.42(17)
O(8)–Cu(1)–N(11)	92.15(17)
N(4)–Cu(1)–N(11)	162.00(17)
O(1)–Cu(1)–N(11)	89.41(16)
O(8)–Cu(1)–OW	92.18(16)
N(4)–Cu(1)–OW	93.75(16)
O(1)–Cu(1)–OW	93.59(15)
N(11)–Cu(1)–OW	103.19(16)
C(2)–O(1)–Cu(1)	115.4(4)
O(2)–C(2)–O(1)	124.6(5)
O(2)–C(2)–C(3)	117.7(5)
O(1)–C(2)–C(3)	117.6(5)
N(4)–C(3)–C(2)	107.9(4)
C(5)–N(4)–C(3)	119.4(5)
C(5)–N(4)–Cu(1)	126.1(4)
C(3)–N(4)–Cu(1)	113.7(3)
N(4)–C(5)–C(5)	125.1(5)
C(7)–C(6)–C(5)	122.9(5)
C(7)–O(8)–Cu(1)	125.6(3)
C(12)–N(11)–C(16)	117.1(5)
C(12)–N(11)–Cu(1)	112.9(3)
C(16–N(11)–Cu(1)	128.3(4)
N(11)–C(12)–N(12)	116.7(5)
N(11)–C(12)–C(13)	123.8(5)
N(12)–C(12)–C(13)	119.5(5)
C(14)–C(13)–C(12)	117.1(6)
C(15)–C(14)–C(13)	120.4(6)
C(14)–C(15)–C(16)	119.9(6)
N(11)–C(16)–N(16)	116.0(5)
N(11)–C(16)–C(15)	121.5(6)
N(16)–C(16)–C(15)	122.5(5)

complex unit. As in these related complexes, a slight distortion in the basal plane geometry of Cu(II) [observed bond angles vary from 83.42(17)° to 93.75(16)°] and similar bond length values, 1.458(7) Å for the [C(3)–N(4)] bond which is shorter than the usual C–N single bond and 1.279(7) Å for the double bond [C(5)–N(4)], are present. The crystal structure is formed by monomeric units interacting by means of a network of H-bonds [the most important interactions are CO–O*(2)···H–O(4): distance between heteroatoms 2.684(5) Å; angle 163.7° and OW–HW1···O*(8): distance between heteroatoms 2.773(6) Å; angle 178(6)°] as can be observed in Fig. 2. It should be mentioned that treatment of [Cu(Sal-(L-Ser))H_2O]·H_2O (**2**) with 2,6-diaminopyridine, a Lewis base, yields a racemic mixture of **1**. This behaviour is similar to the previously described formation of [Cu(Sal-Ser)(2-aminopyridine)] (**3**) [17] that could be explained by the increment of basicity of Cα–H of the amino acid when the Schiff base is formed.

3.2. IR and electronic absorption

The IR spectra of the ternary compound show two bands at 3430s and 3338s cm^{-1} related to the $\nu_a(NH_2)$ and $\nu_s(NH_2)$. Strong typical bands at 1645 cm^{-1} are related to the νC=N of the Schiff base moiety owing to the imino group [9,26,27]. The ν_{as}(COO) is assigned to the strong band at 1599 cm^{-1} whereas the ν_s(COO) is attributed to the 1360 cm^{-1} peak. The separation between ν_{as}(COO) and ν_s(COO) bands in both cases is consistent with a monodentate coordination of the carboxylate group [26,28]. Other bands, possibly related to the Schiff base moiety, could be tentatively assigned: 1537 cm^{-1} (νPhe ring, νC–H oop); 1449 cm^{-1} (νPhe ring, νC=C). A new medium band appearing at 269 cm^{-1} is assignable to νCu–N(base) [28]. The above mentioned implies the existence of the tridentate bonding scheme of Cu(II) to the Schiff base system and an additional binding between the copper(II) and the amino nitrogen of the base in the ternary complex.

The d–d transition spectra in DMSO of the complex show a broad band centred at 663 nm ($\varepsilon = 185$ dm^3 mol^{-1} cm^{-1}) suggestive of approximate square pyramidal geometry about Cu(II). On the other hand, the band at 258 nm ($\varepsilon = 2.3 \times 10^4$ dm^3 mol^{-1} cm^{-1}) can be assigned to n–π*/π–π* transitions of the salicylidene chromophore. The low value of conductivity ($\Lambda_M = 2.0$ Ω^{-1} cm^2 $mol^{-1}/10^{-3}$ M in DMSO, 23 °C) implies the presence of non-electrolyte-type species [29].

3.3. Magnetic data and ESR spectra

The effective magnetic moment were $\mu_{eff} = 1.80$ BM of complex **1a** is normal for magnetically diluted d^9 systems. The ESR spectrum of **1a** as a polycrystalline powder, recorded at room temperature, shows an axial ESR spectrum with values of $g_{\parallel} = 2.12$ and $g_{\perp} = 2.04$. A simulated spectrum obtained by using the WINEPR program gave good agreement with the experimental g

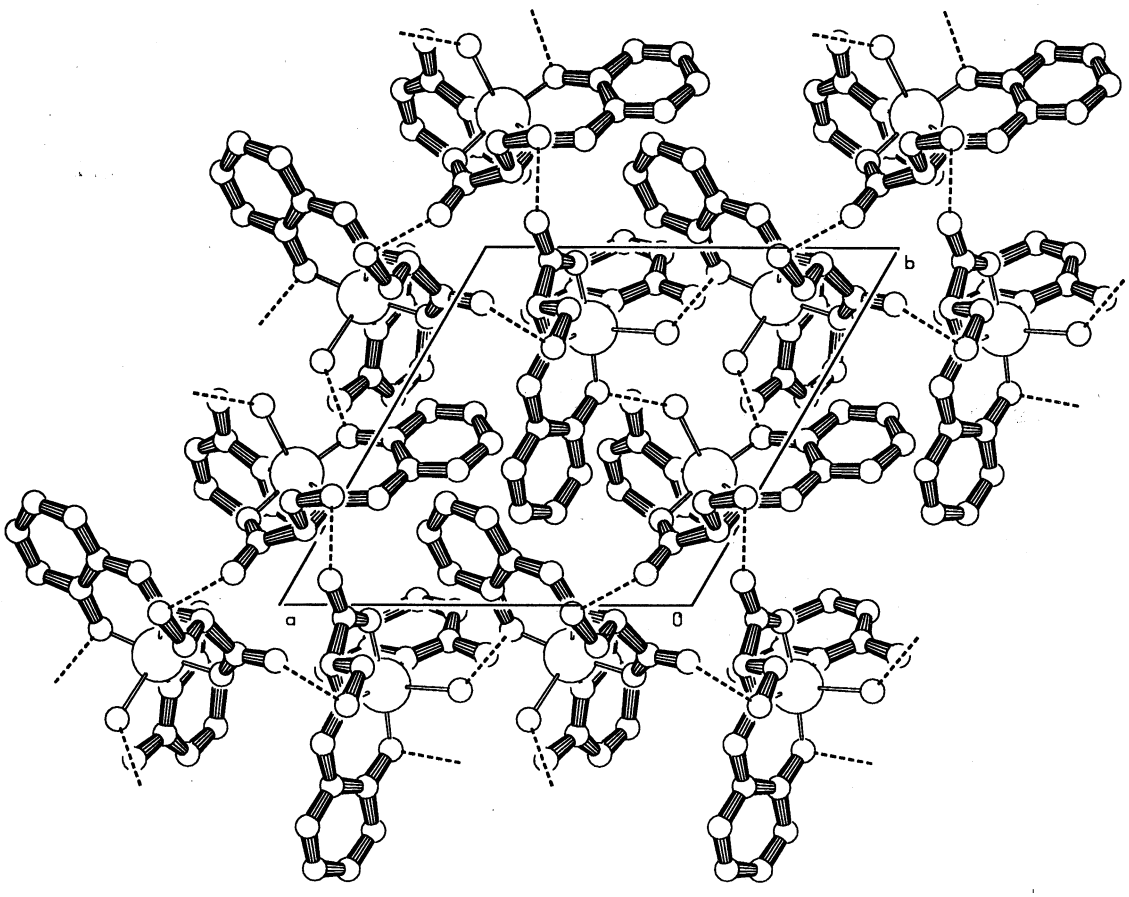

Fig. 2. Network of hydrogen bonds in the crystal structure of **1b**.

values. This spectrum is consistent with a square planar or square pyramidal geometry. The results are in agreement with the symmetry of the Cu(II) derived from the X-ray structure determination.

3.4. Toxicological studies

The results are shown in Table 3. Although this is a preliminary study it is important to point out that Cu(II)–Schiff base complexes **1**–**3** are less toxic than typical inorganic copper(II) salts. Thus LD_{50} values are approximately 900 ppm [185 ppm of Cu(II)] for [Cu(Sal-(L-Ser))H_2O]·H_2O (**2**), 1100 ppm [175 ppm of Cu(II)] for [Cu(Sal-Ser)(2,6-diaminopyridine) (**1a**)] and 840 ppm [145 ppm of Cu(II)] for [Cu(Sal-Ser)(2-aminopyridine)] (**3**) against values of 460 and 350 ppm [approximately 115 ppm of Cu(II)] for typical inorganic salts $CuSO_4$·$5H_2O$ and Cu(acetate)$_2$·H_2O, respectively (Fig. 3). Similar results are obtained for the DT (in days) where high concentrations of inorganic salts yield higher values (increasing this parameter by 1–3 days) than the corresponding Cu(II)-complexes **1**–**3**.

Table 3
Toxicity results of selected copper(II) compounds

ppm	$Cu(SO_4)\cdot 5H_2O$		Cu(acetate)$_2$·H_2O		[Cu(Sal-Ser)(2,6-diampy)] (**1a**)		[Cu(Sal-(L-Ser))·H_2O] (**2**)		[Cu(Sal-Ser)(2-ampy)] (**3**)	
	V	DT	*V*	DT	*V*	DT	*V*	DT	*V*	DT
0	94.8±1.5	12.6±0.1	91.6±1.3	12.1±0.02	94.8±1.5	12.6±0.1	94.0±1.3	11.9±0.1	90.9±3.4	13.1±0.1
50			90.4±3.2	12.0±0.02			94.0±1.1	11.9±0.1		
100			91.2±1.7	12.1±0.1			93.6±1.7	11.9±0.1		
250	92.0±1.5	13.3±0.1	86.0±1.1	12.8±1.0	94.0±1.7	13.5±0.1				
500	42.4±10.7	16.6±0.5	3.6±1.7	18.3±0.8	93.2±1.9	13.6±0.2	92.0±1.8	12.9±0.04	86.4±1.2	13.7±0.2
750	2.8±1.9	19.2±1.0			84.0±6.9	15.1±0.4	87.6±1.8	14.0±0.1	67.6±5.7	15.6±0.2
1000	0		0		59.6±7.8	16.5±0.4	22.0±2.8	16.7±0.2	11.6±2.6	18.6±0.1
1500	0		0		8.4±7.8	19.6±0.8	11.6±3.7	18.1±1.0	0	

V, larva-to-adult viability (in % of emerged adult flies); DT, larva-to-adult developmental time (in days).

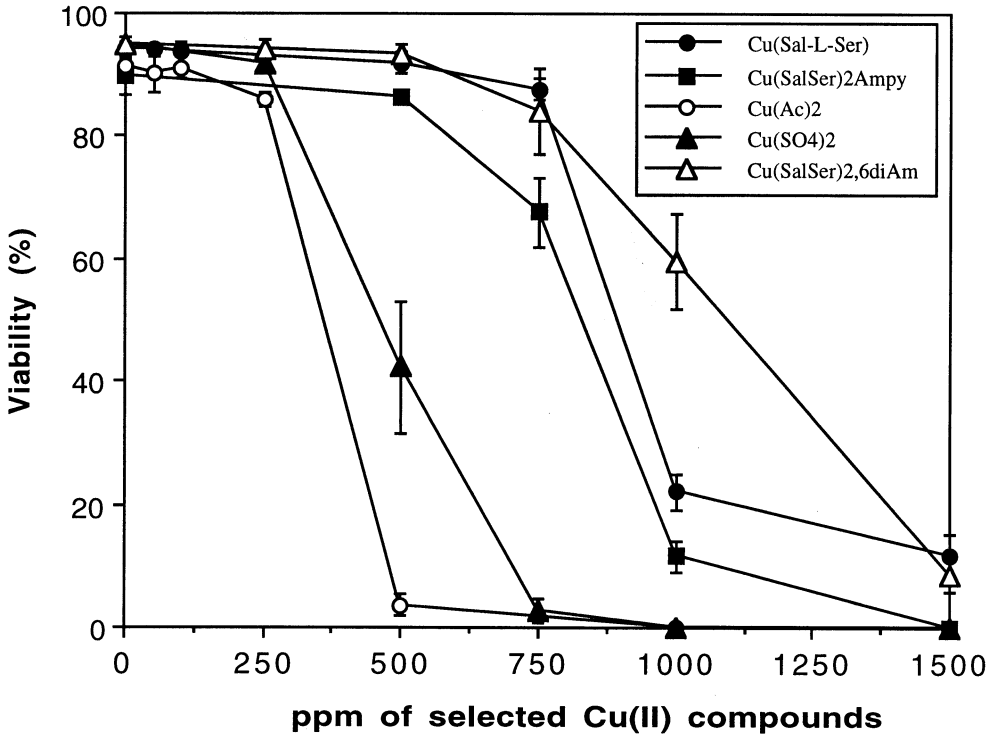

Fig. 3. Toxicity results of selected copper(II) compounds (viability %).

4. Conclusion

As mentioned in Section 1 the presence of excess quantities of an essential metal, like Cu(II), can be toxic, but our results show that the way in which the metal is present can modulate the response of a determinate organism. Thus, simple copper compounds [$CuSO_4 \cdot 5H_2O$ and Cu(acetate)$_2 \cdot H_2O$] in which free Cu(II) is mainly present show a lethal effect against *Drosophila* at low concentrations. Contrarily, the complexation with the tested organic molecules yield a less dangerous system probably based on the stability of the complex Cu(II)–tridentate Schiff base that avoid the presence of large quantities of free Cu(II).

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 190700 for compound **1b**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] J.B. Longenecker, E.E. Snell, J. Am. Chem. Soc. 79 (1956) 142.
[2] E.E. Snell, P.M. Fasella, A. Braunstein, A. Ross-Fanelli, Chemical and Biological Aspects of Pyridoxal Catalysis, McMillan, New York, 1963.
[3] E.E. Snell, A. Braunstein, E.S. Severin, V.M. Torchinsky, Pyridoxal Catalysis: Enzymes and Model Systems, Interscience, New York, 1968.
[4] A. García-Raso, J.J. Fiol, F. Bádenas, E. Lago, E. Molins, Polyhedron 20 (2001) 2877 (and references therein).
[5] P.E. Werner, A. Valent, V. Adelskold, O. Svajlenová, Acta Chem. Scand. A37 (1983) 51.
[6] K. Korhonen, R. Hämäläinen, Acta Chem. Scand. A33 (1979) 569.
[7] K. Korhonen, R. Hämäläinen, U. Turpeinen, Acta Crystallogr., Sect. B 37 (1981) 829.
[8] R. Hämäläinen, U. Turpeinen, M. Ahlgrén, M. Rantala, Acta Chem. Scand. A32 (1978) 549.
[9] M.S. Palacios, E. Medina, F.G. Manrique, M.T. do P. Gambardella, R.H. de A. Santos, M.L. Rodriguez, J.M. Dance, Polyhedron 8 (1989) 2131.
[10] R. Hämäläinen, M. Ahlgrén, U. Turpeinen, M. Rantala, Acta Chem. Scand. A32 (1978) 235.
[11] K. Korhonen, R. Hämäläinen, U. Turpeinen, Acta. Crystallogr., Sect. C 40 (1984) 1175.

[12] J. Krätsmar-Smogrovic, F. Pavelcik, J. Soldánová, J. Sivy, V. Seressová, M. Zemlicka, Z. Naturforsch., Teil b 46 (1991) 1323.
[13] T. Ueki, T. Ashida, V. Sasada, K. Kakudo, Acta Crystallogr., Sect. B 25 (1969) 328.
[14] T. Ueki, T. Ashida, V. Sasada, K. Kakudo, Acta Crystallogr. 22 (1967) 870.
[15] Y. Bkouche-Waksman, J.M. Barbe, A. Kvick, Acta Crystallogr., Sect. B 44 (1988) 595.
[16] A. García-Raso, J.J. Fiol, F. Bádenas, M. Quirós, Polyhedron 15 (1996) 4407.
[17] A. García-Raso, J.J. Fiol, A. López-Zafra, A. Cabrero, I. Mata, E. Molins, Polyhedron 18 (1999) 871.
[18] D.M. Taylor, D.R. Williams, Trace Element Medicine and Chelation Therapy, The Royal Society of Chemistry, Cambridge, 1995, p. 25.
[19] E.W. Vogel, U. Graf, H.J. Frei, M.M. Nivard, Int. Agency Res. Cancer Sci. Publ. 146 (1999) 427.
[20] J.A. Castro, L.M. Botella, J.L. Ménsua, Arch. Insect Biochem. Physiol. 3 (1986) 485.
[21] C.K. Fair, MOLEN, an Interactive Intelligent System for Crystal Structure Analysis, Enraf Nonius, Delft, The Netherlands, 1990.
[22] G.M. Sheldrick, SHELX-97, Programs for Crystal Structure Analysis (Release 97-2), University of Göttingen, Germany, 1997.
[23] R.R. Sokal, F.J. Rohlf, Biometry, 3rd ed, Freeman, New York, 1995, p. 138.
[24] S.A. Warda, P. Dahlke, S. Wocadlo, W. Massa, C. Friebel, Inorg. Chim. Acta 268 (1998) 117.
[25] V. Kettmann, E. Fresová, M. Blohova, J. Krätsmár-Smogrovic, Acta Crystallogr., Sect. C 49 (1993) 1932.
[26] A. Mederos, F.G. Manrique, A. Medina, Anal. Química 77 (1980) 206.
[27] G.O. Carlisle, A. Syamal, K.K. Ganguli, L.J. Theriot, J. Inorg. Nucl. Chem. 34 (1972) 2761.
[28] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York, 1978.
[29] W.J. Geary, Coord. Chem. Rev. 7 (1971) 81.