Revue Roumaine de Chimie, **2008**, *53*(10), 911–919

SYNTHESIS, SPECTROSCOPIC, ANTIBACTERIAL AND ANTIFUNGAL STUDIES ON COPPER(II) COMPLEXES WITH 2-BENZOTHIAZOLYL HYDRAZONES

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Received December 20, 2007

A series of six complex compounds of Cu(II) with 2-hydroxybenzaldehyde 2-benzothiazolyl hydrazone (H_2L^a) and 2-aminobenzaldehyde 2-benzothiazolyl hydrazone (HL^b) have been synthesized and characterized by elemental and thermal analysis, molar conductance determinations, IR, electronic and EPR spectroscopy. According to the IR spectra, the ligands can coordinate in two tautomeric forms through the azomethine and benzothiazole nitrogen atoms and deprotonated hydroxyl group for H_2L^a, or amino group for HL^b. Depending of the pH and the metal salt used, the following complex compounds were obtained: $[Cu(HL^a)Cl(H_2O)]\cdot H_2O$ and $[Cu(HL^a)Br]\cdot 3H_2O$, with monobasic tridentate ligand; $[Cu_2L_2{}^a]\cdot 2H_2O$, with dibasic tridentate ligand; $[Cu(HL^b)Cl(H_2O)]Cl$ and $[Cu(HL^b)Br(H_2O)]Br$ with neutral tridentate ligand and $[CuL_2{}^b]$ where the ligand is monobasic bidentate. The bonding parameters calculated from the EPR spectra proved that the metal-ligand bonds are of high covalency. Investigations on antimicrobial activity show that the complexes are moderately active against various Gram positive and Gram negative bacteria and fungi.

INTRODUCTION

The interest in the study of hydrazones possessing potential donor sites has been intensively increasing because of their coordination capability, their pharmacological activity and their uses in analytical chemistry as metal extracting agents.[1-3] It has recently been shown that the metal complexes are more potent and less toxic in many cases as compared to the parent compound.

Among the numerous types of hydrazones Schiff bases, the heterocyclic hydrazones having sulphur and nitrogen sites and their metal complexes have received considerable attention during the last years, especially for the large number of their applications. Thus, it was found that the thiazole and benzothiazole hydrazones exhibit anticonvulsant, tuberculostatic, antiinflamatory, analgesic, antibacterial and antifungal activities.[4-8]

In continuation of our works on the synthesis of complex compounds of transition metals with 2-benzothiazolyl hydrazones, [9-13] we report here the synthesis, characterization and biological activity of six complexes of Cu(II) with 2-hydroxybenzaldehyde 2-benzothiazolyl hydrazone (H_2L^a) and 2-aminobenzaldehyde 2-benzothiazolyl hydrazone (HL^b).

A series of 2-benzothiazolyl hydrazones, including 2-hydroxybenzaldehyde 2-benzothiazolyl hydrazone were prepared by Katz,[14] by condensing the 2-hydrazinobenzothiazol with the appropriate aldehydes. Gheorghiu and coworkers have prepared thiazole and benzothiazole derivatives as potential antituberculous agents.[15,16] They have reported the synthesis of 2-aminobenzaldehyde 2-benzothiazolyl hydrazone by the condensation of 2-hydrazinobenzothiazole with *o*-aminobenzaldehyde; m.p.=262 ^{0}C.

The literature contains some reports on the synthesis and characterization of complex compounds with 2-benzothiazolyl hydrazones. Thus, five Cu(II) complexes with 2-hydroxybenzaldehyde

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2-benzothiazolyl hydrazone (H_2L^a) have been reported: $[Cu(HL^a)_2]$ (brown),[4] $[CuL^a{}_2]\cdot 2H_2O$, $[Cu(HL^a)(H_2O)]\cdot Cl$,[17] $[CuL^aPy]$ si $[Cu_2L^a{}_2]$[18] (the last four complexes, dark-green, m.p.>280^{0}C), but no detailed spectral investigations have been made.

RESULTS AND DISCUSSION

The formation of the complexes occurs by the reaction of an ethanolic solution of the ligand, 2-hydroxybenzaldehyde 2-benzothiazolyl hydrazone (H_2L^a) or 2-aminobenzaldehyde 2-benzothiazolyl hydrazone (HL^b) with an ethanolic solution of the metal salt: copper(II) chloride for the complexes (**1**) and (**4**), copper(II) acetate for the complexes (**2**) and (**5**) and copper(II) bromide for the compounds (**3**) and (**6**).

The results of elemental analysis, the molar conductance values in DMF and the spectral data are in agreement with the proposed formulas: $[Cu(HL^a)Cl(H_2O)]\cdot H_2O$ (**1**), $[Cu_2L^a{}_2]\cdot 2H_2O$ (**2**), $[Cu(HL^a)Br]\cdot 3H_2O$ (**3**), $[Cu(HL^b)Cl(H_2O)]\cdot Cl$ (**4**), $[CuL^b{}_2]$ (**5**) and $[Cu(HL^b)Br(H_2O)]\cdot Br$ (**6**). Molecular weight determination in chloroform confirms the dimeric formula for the complex (**2**).

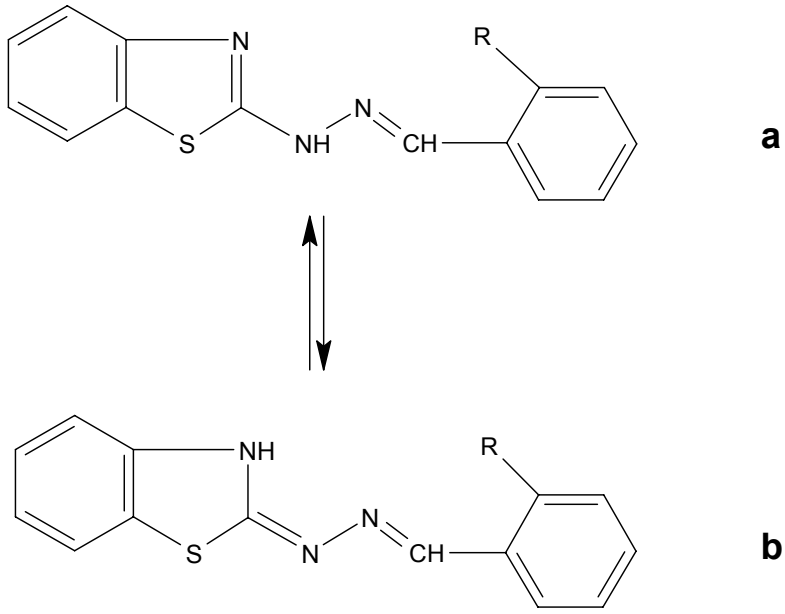
The molar conductance values in DMF, solutions 10^{-4} M, lie in the range of non-electrolytes for the complexes (**1**), (**2**), (**3**) and (**5**) (62, 45, 58 and 55 $\Omega^{-1}cm^2mol^{-1}$, respectively) and 1:1 electrolytes for the complexes (**4**) and (**6**) (72 and 68 $\Omega^{-1}cm^2mol^{-1}$, respectively).

Infrared spectral studies

The important frequencies exhibited by the ligand H_2L^a and its complexes are listed in Table 1 and those for the ligand HL^b and its complexes, in Table 2.

The free ligands show a medium absorption band at 3184-3200 cm^{-1}, assigned to ν(NH) stretching vibration ,[1,19] indicating that they are in the tautomeric form **a** in the solid state (Fig. 1).

This band is also present in the IR spectra of the complexes (**1**), (**3**), (**4**) and (**6**), which is a proof for the coordination of the ligands in the tautomeric form **a**. The IR spectra of the complexes (**2**) and (**5**) do not show band due to ν(NH), suggesting that the ligands pass in the tautomeric form **b** at the formation of these complexes.



R: -OH (H_2L^a) ; R: -NH_2 (HL^b)

Fig. 1 – Tautomeric forms of the ligands.

The very strong band, with two maxima, at 1617, 1610 cm^{-1} (H_2L^a) and 1623, 1610 cm^{-1} (HL^b) may be assigned to the stretching vibration of the hydrazone function, $\nu(C{=}N)_{exocyclic}$ and benzothiazole group, $\nu(C{=}N)_{endocyclic}$, respectively.[20-22] The IR spectra of the complexes (**1**), (**3**), (**4**) and (**6**) show a downward shift of these bands, accompanied by a significant decrease of

intensity, in accordance with the coordination of the ligands through the azomethine and benzothiazole nitrogen atoms, in the tautomeric form **a**. In the IR spectra of the complexes (**2**) and (**5**) the band due to $\nu(C=N)_{exocyclic}$ is also shifted to lower wavenumbers, but a new very strong band, appearing around 1500 cm^{-1}, may be assigned to the skeleton >C=N-N=C< vibration.[1,23] These observations, correlated with the absence of ν(NH) band suggest the deprotonation of the ligands and chelatation through the azomethine and benzothiazole nitrogen atoms in the tautomeric form **b.**[1,23,24] The upward shift of the band due to ν(NN) in the IR spectra of all the complexes is another proof for the coordination of azomethine nitrogen atoms at the metal ion.[19]

The medium absorption band occuring at 2923 cm^{-1} in the IR spectrum of 2-hydroxybenzaldehyde 2-benzothiazolyl hydrazone (H_2L^a) disappears in the spectra of its complexes (Table 1), indicating the deprotonation of the phenolic group and the coordination of the ligand through the phenolic oxygen. This supposition is also supported by the shift to higher wavenumbers of the band due to the stretching vibration of $C\text{-}O_{phenolic}$ when compared to the uncomplexed ligand.[1,19]

The bands assigned to asymmetric and symmetric N-H stretching mode of $-NH_2$ group appearing in the IR spectrum of the ligand HL^b at 3462 cm^{-1} and 3347 cm^{-1}, respectively,[25] are strongly modified in the IR spectra of the complexes (**4**) and (**6**) and are covered by the broad band due to ν(OH) of coordinated water. These observations are in accordance with the coordination of the amine group to the cooper(II) in the complexes (**4**) and (**6**). The IR spectrum of the complex (**5**) do not show any shift of these vibrations, which demonstrates that the $–NH_2$ group is not involved in coordination in this complex.

Except for the complex (**5**), all the complexes show in the IR spectra a broad band at ca. 3400-3460 cm^{-1}, due to ν(OH) absorption of coordinated or crystalline water.[21,24]

Supplementary bands appearing in the IR spectra of the complexes at low wavenumbers may be assigned to the vibrations metal-donor atom: ν(M-O) (610-658 cm^{-1} in the complexes with the ligand H_2L^a) and ν(M-N) at ca. 500 cm^{-1} for all the complexes.[26,27]

On the basis of the IR spectra we can conclude that the ligand H_2L^a coordinates to the metal ion through the azomethine and benzothiazole nitrogen atoms and phenolic oxygen atom, as monobasic tridentate donor in the complexes (**1**) and (**3**) and dibasic tridentate donor in the complex (**2**). The ligand HL^b acts as neutral tridentate NNN donor in the complexes (**4**) and (**6**), coordinating through the azomethine and benzothiazole nitrogen atoms and amine nitrogen atom. In the complex (**5**), the ligand HL^b coordinates as monobasic bidentate donor, through the azomethine and benzothiazole nitrogen atoms.

Table 1

Characteristic bands in the IR spectra of the ligand H_2L^a and its copper(II) complexes (ν_{max}, cm^{-1})

Assignments	H_2L^a	(**1**)	(**2**)	(**3**)
$\nu(OH)_{water}$	-	3423 m	3403 m	3423 s
$\nu(OH)_{phenolic}$	2923 m	-	-	-
ν(NH)	3200 m	3140 m	-	3098 m
$\nu(C=N)_{exo}$	1617 vs	1610 vs	1602 s	1601 vs
$\nu(C=N)_{endo}$	1610 vs	1559 s	-	1545 s
ν(>C=N-N=C<)	-	-	1500 vs	-
$\nu(C_{arom}\text{- N})$	1360 w	1386 m	1366 m	1378 m
ν(C-O phen)	1269 m	1302 s	1305 m	1293 s
ν(NN)	946 m	962 m	968 m	962 m
ν(M-O)	-	611 w	658 w	610 w
ν(M-N)	-	535 w	545 w	525 w

Table 2

Characteristic bands in the IR spectra of the ligand HL[b] and its copper(II) complexes (ν_{max}, cm^{-1})

Assignments	HL[b]	(**4**)	(**5**)	(**6**)
$\nu_{asym}(NH)\ NH_2$	3462 m	-	3462 m	-
$\nu_{sym}(NH)\ NH_2$	3347 m	-	3345 m	-
$\nu(OH)$	-	3436 m	-	3436 m
$\nu(NH)$	3184 m	3184 m	-	3197 m
$\nu(C=N)_{exo}$	1623 vs	1602 m	1612 s	1601 m
$\nu(C=N)_{endo}$	1610 vs	1556 s	-	1551 s
$\nu(>C=N-N=C<)$	-	-	1493 vs	-
$\nu(C_{arom}- N)$	1368 m	1379 s	1372 m	1376 s
$\nu_{as}(C_{arom}–N_{amin})$	1157 m	1137 m	1159 m	1134 m
$\nu(NN)$	936 m	960 m	943 m	955 m
$\nu(M-N)$	-	505 w	500 w	500 w

Thermogravimetric analysis

The TG curves of the compounds (**1**) and (**3**) show an endothermic peak at 130 ^{0}C and 140^{0}C, respectively, due to the loss of crystalline water.[28] The endothermic peaks observed at 220 ^{0}C for the complex (**1**), 175 ^{0}C for the complex (**4**) and 180 ^{0}C for the complex (**6**) correspond to the loss of coordinated water, all these observations being in agreement with the results obtained from the IR spectra. The removal of anionic chloride or bromide of the complexes (**1**) and (**3**) takes place in an endothermic process with maximum at 375 ^{0}C and 300 ^{0}C, respectively.[28] For the compounds (**4**) and (**6**), the anionic and coordinated chloride and bromide are lost around 280-250 ^{0}C.[28] All the complexes lose the organic ligand in a large exothermic process, in the range of 400-650 ^{0}C.[29]

The analytical and thermogravimetrical data, correlated with the observations from IR spectra permitted to conclude that the metal ion is five-coordinated in the complexes (**1**), (**4**) and (**6**) and four-coordinated in the complexes (**2**), (**3**) and (**5**), but the symmetry of coordination polyhedron was established by means of the electronic and EPR spectral studies.

Electronic and EPR spectra

The EPR spectra of the complexes (**1**), (**2**), (**4**) and (**6**), recorded on powdered samples, in K band, show axial symmetry, with $g_{\parallel} > g_{\perp}$ (Figs. 2 and 3). This trend in the values of the experimental EPR parameters (Table 3) suggests a distorted square-pyramidal geometry for the complexes penta-coordinated: (**1**), (**4**) and (**6**) and a planar square geometry for the complex (**2**).[30] In this assumption, the unpaired electron resides in the $d_{x^2-y^2}$ orbital and the observed bands in the UV-VIS spectra may be assigned to the transitions listen in Table 4.[31]

The EPR spectra of the compounds (**3**) and (**5**) gives an isotropic signal (Figs. 2 and 3), so we can interpret the electronic transitions in terms of a pseudo-tetrahedral symmetry (Table 4).

The character of the metal-ligand bond was established on the basis of molecular orbital theory, by correlating the EPR spectral data with the observed transitions in the electronic spectra. The following relations permit the calculation of the covalency parameters α^2, β^2 and β_1^2: [32-34]

$$g_{\parallel} = 2 - \frac{8\lambda_0}{\Delta E_{xy}}\alpha^2\beta_1^2 \quad (1)$$

$$g_{\perp} = 2 - \frac{2\lambda_0}{\Delta E_{xz,yz}}\alpha^2\beta^2 \quad (2)$$

$$A_{\parallel} = P[-\frac{4}{7}\alpha^2 - k + (g_{\parallel} - 2) + \frac{3}{7}(g_{\perp} - 2)] \quad (3)$$

where λ_0 is the spin-orbit coupling constant for the free Cu^{2+} ion (-828 cm^{-1}), k is the Fermi contact term and characterizes the isotropic (s-electron) contribution to the hyperfine interaction;

P= $2\gamma\beta\beta_N\langle r^{-3}\rangle$ = 0,036 cm^{-1};

$\Delta E_{xy} = \Delta(E_{x^2-y^2} - E_{xy})$;

$\Delta E_{xz,yz} = \Delta(E_{x^2-y^2} - E_{xz,yz})$.

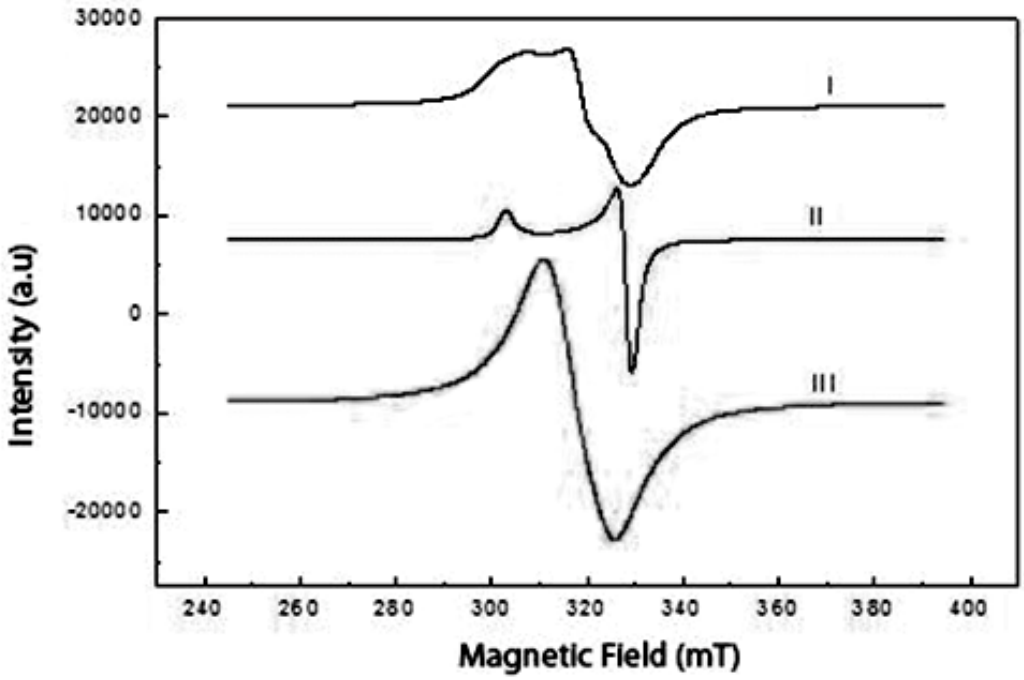


Fig. 2 – K-band EPR spectra of the complexes **1-3** at room temperature.

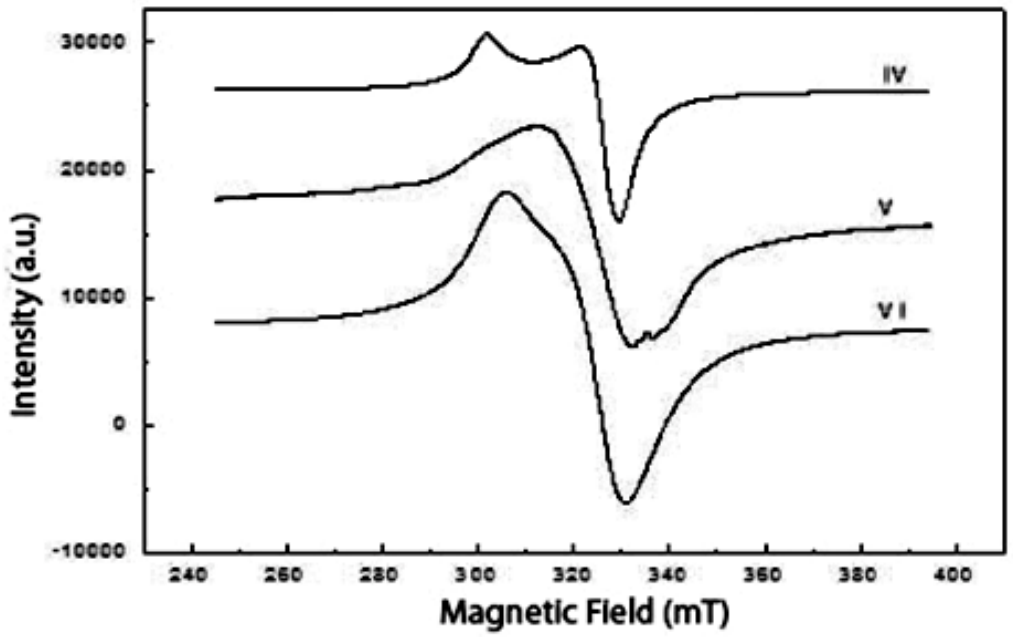


Fig. 3 – K-band EPR spectra of the complexes **4-6** at room temperature.

Table 3

EPR parameters for the copper(II) complexes

Complex	$g_{\parallel}$	$g_{\perp}$	g_0
$[Cu(HL^a)Cl(H_2O)]\cdot H_2O$ (**1**)	2.195	2.051	
$[Cu_2L^a_2]\cdot 2H_2O$ (**2**)	2.221	2.047	
$[Cu(HL^a)Br]\cdot 3H_2O$ (**3**)	-	-	2.125
$[Cu(HL^b)Cl(H_2O)]\cdot Cl$ (**4**)	2.237	2.058	
$[CuL^b_2]$ (**5**)	-	-	2.084
$[Cu(HL^b)Br(H_2O)]\cdot Br$ (**6**)	2.210	2.060	

Table 4

Electronic transitions in the visible region for Cu(II) complexes

Complex	Observed bands (ν_{max}, cm^{-1})	Assignments	Symmetry
$[Cu(HL^a)Cl(H_2O)]\cdot H_2O$ (**1**)	11200 13600 15200	$^2B_1 \rightarrow {}^2A_1$ $^2B_1 \rightarrow {}^2B_2$ $^2B_1 \rightarrow {}^2E$	C_{4v}
$[Cu_2L^a{}_2]\cdot 2H_2O$ (**2**)	14285 15384 16600	$^2B_{1g} \rightarrow {}^2B_{2g}$ $^2B_{1g} \rightarrow {}^2E_g$ $^2B_{1g} \rightarrow {}^2A_{1g}$	D_{4h}
$[Cu(HL^a)Br]\cdot 3H_2O$ (**3**)	10750 13510 15150	$^2B_2 \rightarrow {}^2E$ $^2B_2 \rightarrow {}^2B_1$ $^2B_2 \rightarrow {}^2A_1$	D_{2d}
$[Cu(HL^b)Cl(H_2O)]\cdot Cl$ (**4**)	9090 13900 15625	$^2B_1 \rightarrow {}^2A_1$ $^2B_1 \rightarrow {}^2B_2$ $^2B_1 \rightarrow {}^2E$	C_{4v}
$[CuL^b{}_2]$ (**5**)	11627 13600 15900	$^2B_2 \rightarrow {}^2E$ $^2B_2 \rightarrow {}^2B_1$ $^2B_2 \rightarrow {}^2A_1$	D_{2d}
$[Cu(HL^b)Br(H_2O)]\cdot Br$ (**6**)	10120 12000 14050	$^2B_1 \rightarrow {}^2A_1$ $^2B_1 \rightarrow {}^2B_2$ $^2B_1 \rightarrow {}^2E$	C_{4v}

The coefficients α^2, $\beta_1{}^2$ and β^2 characterize the in-plane σ-bonding, in-plane π bonding and out-of-plane π bonding of Cu^{2+}, respectively. α^2 can take the values between 0.5 and 1, corresponding to pure covalent and pure ionic metal-ligand bond, respectively.

Using the approximation: (4/7 + k) = 1 in the equation (3), we can calculate α^2 which is then utilized for the calculation of β^2 and $\beta_1{}^2$, using the relations (1) and (2).

In the absence of hyperfine interaction, so we can see for the complexes in discussion, we cannot separately calculate the parameters α^2, β^2 and $\beta_1{}^2$, but we can determinate, for the complexes with axial symmetry, the orbital parameters $K_{\parallel} = \alpha^2\beta_1{}^2$ and $K_{\perp} = \alpha^2\beta^2$ from the relations (1) and (2). These parameters are a guide of the metal-ligand bonding nature:[30,35] $K_{\parallel} \approx K_{\perp}$ for the pure σ bonding, $K_{\parallel} < K_{\perp}$ for strong in-plane π bonding and $K_{\parallel} > K_{\perp}$ for strong out-of-plane π bonding.

The values of the bonding parameters calculated for the complexes (**1**), (**2**), (**4**) and (**6**) are presented in Table 5.

The $K_{\parallel}$ and $K_{\perp}$ values are reduced from unit, indicating an important covalent character for the metal-ligand bonds. The values of these parameters are very close for the complex (**2**) and only a little different for the complexes (**1**) and (**4**), in accordance with strong in-plane σ bonding.[30] For the complex (**6**), $K_{\parallel} < K_{\perp}$, indicating strong in-plane π bonding.[30]

$G = (g_{\parallel} - 2)/(g_{\perp} - 2)$ is smaller than 4 for the complexes (**1**) and (**6**), suggesting the existence of spin-spin interactions between the copper centers.

According to the determinations presented above, the following structures have been proposed for the complexes (Fig. 4).

Table 5

Bonding parameters of Cu(II) complexes with axial symmetry

Complex	$K_{\parallel}$	$K_{\perp}$	G
$[Cu(HL^a)Cl(H_2O)]\cdot H_2O$ (**1**)	0.40	0.46	3.2
$[Cu_2L^a{}_2]\cdot 2H_2O$ (**2**)	0.47	0.44	4.70
$[Cu(HL^b)Cl(H_2O)]\cdot Cl$ (**4**)	0.49	0.54	4.08
$[Cu(HL^b)Br(H_2O)]\cdot Br$ (**6**)	0.38	0.50	3.50

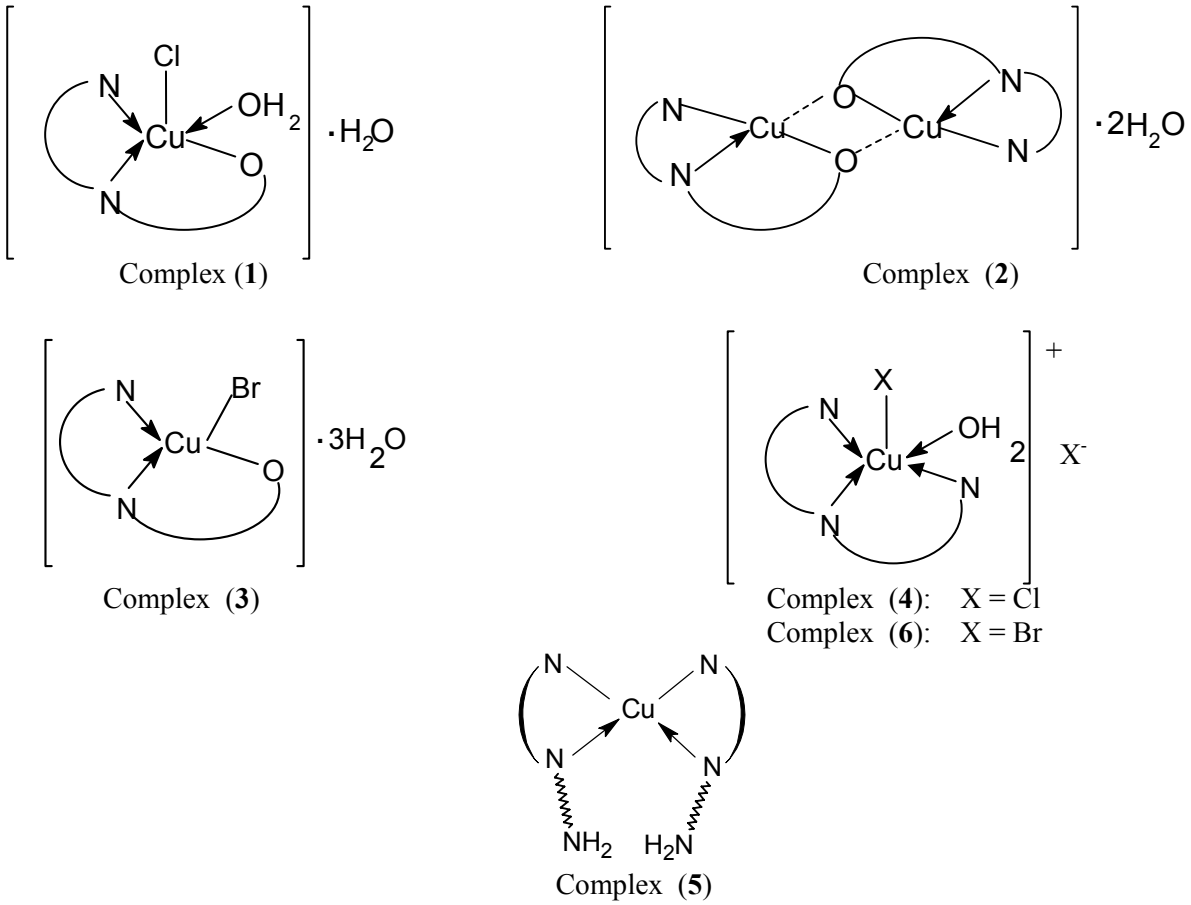


Fig. 4 – Proposed structures for the Cu(II) complexes.

Biological activity

Antibacterial and antifungal activity was determined following the cup-plate agar diffusion technique, against bacillius Gram negative (E. coli, Pseudomonas aeruginosa serotip IV, Proteus), bacillius Gram positive (Staphyloccocus coagulase positive, Streptoccocus β-haemolytic type A and type B) and fungi (Candida albicans, Penicillium). A solution 10^{-4}M of each compound in acetone was used. After incubation for 72 h at 37 ^{0}C the zone of inhibition was measured. The results are presented in Table 6.

Table 6

Biological activity for the ligand and its Cu(II) complexes

Microbial agent		Microbial culture inhibition diameter Ø, [mm]							
		H_2L^a	HL^b	(1)	(2)	(3)	(4)	(5)	(6)
Gram negative bacteria	*Escherichia coli*	0	0	1	0.5	1	1	0	1
	Pseudomonas aeruginosa serotip VI	2	0	2	2	3	1	1	1
	Proteus	0	0	2	1	2	1	1	2
Gram positive bacteria	*Staphylococcus coagulase positive*	2	0	3	3	4	3	2	3
	Streptococcus β-haemolytic type A	3	0	3	3	4.5	3	2	3
	Streptococcus β-haemolytique type B	3	0	3	3	4.5	3	2	3
	Staphylococcus aureus	2	0	3	3	4	3	2	3
Fungi	*Candida albicans*	0	0	1	1	3	1	1	1
	Penicillium	0	0	1	1	1	1	1	1

While the ligand H_2L^a are moderately active against Gram positive bacteria, the ligand HL^b is completely inactive against the microbial agents used. All the copper(II) complexes are biologically more active than the ligand, especially against the Gram positive bacteria. This increase in the antimicrobial activity is more intensive for the complexes (**3**), (**4**) and (**6**), containing chlorine and bromide and is probably due to faster diffusion of the metal complexes through the cell membrane.

EXPERIMENTAL

All the chemical used were reagent grade.

Preparation of hydrazones

2-hydrazinobenzothiazole was prepared according to the literature data, by the condensation reaction of 2-mercaptobenzothiazole (0.01 mol) with hydrazine hydrate (0.01 mol), in ethanol. The mixture was placed in a round-bottomed flask and boiled under reflux for 10 h, until H_2S evolution had ceased. The white crystalline solid formed was filtered off, air dried and recrystallized from ethanol; m.p.=199.5 ^{0}C.[36]

The hydrazone ligands were prepared by refluxing an equimolecular mixture of 2-hydrazinobenzothiazole and the corresponding aldehyde, in the following way:

0.75ml (0.01 mol, ρ = 1.69g/cm^3) salicylaldehyde were mixed with a solution of 2-hydrazinobenzothiazole (1.7278 g, 0.01 mol) and refluxed on a water bath for 2 h. The separated yellow crystalline solid was filtered, washed several times with ethanol and finally with ether; m.p.(HL^b) = 250 ^{0}C.

An amount of 2-aminobenzaldehyde (4.7975 g, 0.029 mol) was dissolved in 10 ml of ethanol. This solution was added to an ethanolic solution of 2-hydrazinobenzthiazole (3.552 g, 0.029 mol). The mixture was refluxed on a water bath for 2h and then allowed to cool at room temperature. The resulting brick precipitate was filtered, washed several times with ethanol and ether; m.p.(HL^c) = 251^{0}C.

Preparation of the complexes

The Cu(II) complexes were prepared by refluxing for 1-2 h the ethanolic solution of the ligand with the respective metal salt in ethanol, as follows:

$[Cu(HL^a)Cl(H_2O)]\cdot H_2O$ (**1**): aquachloro(2-hydroxybenzaldehyde 2-benzothiazolyl hydrazone)copper(II) monohydrate; $[Cu_2L^a_2]\cdot 2H_2O$ (**2**): di-μ-oxo-bis[(2-hydroxybenzaldehyde 2-benzothiazolyl hydrazonato)copper(II)] dihydrate, $[Cu(HL^a)Br]\cdot 3H_2O$ (**3**): bromo[(2-hydroxybenzaldehyde 2-benzothiazolyl hydrazone)copper(II)] trihydrate: a quantity of 0.269 g (1 mmol) 2-hydroxybenzaldehyde 2-benzothiazolyl hydrazone was dissolved in 25 mL ethanol, with heating. To this solution was added the suitable metal salt: 0.171 g (1 mmol) of $CuCl_2\cdot 2H_2O$ for the complex (**1**), 0.199 g (1 mmol) of $Cu(CH_3COO)_2\cdot H_2O$ for the complex (**2**) and 0.224 g (1 mmol) of $CuBr_2$ for the complex (**3**). The complexes so obtained were filtered, washed with ethanol and dried at air.

Analytical data: $[Cu(HL^a)Cl(H_2O)]\cdot H_2O$ (**1**), green-grey: exp.%: C: 41.92; H: 3.51; N: 10.05; Cu: 15.53; calc.%: C: 41.35; H: 3,46; N: 10.38; Cu: 15.86.

$[Cu_2L^a_2]\cdot 2H_2O$ (**2**): light-green: exp.%: C: 48.45; H: 3.22; N: 12.47; Cu: 18.25; calc.%: C: 48.00; H: 3.15; N: 12.03; Cu: 18.33.

$[Cu(HL^a)Br]\cdot 3H_2O$ (**3**): yellow-greenish: exp.%: C: 35.71; H: 3.22; N: 8.72; Cu: 13.35; calc.%: C: 36.05; H: 3.43; N: 9.01; Cu: 13.73.

$[Cu(HL^b)Cl(H_2O)]\cdot Cl$ (**4**): aquachloro(2-aminobenzaldehyde 2-benzothiazolyl hydrazone)copper(II) chloride, $[CuL^b_2]$ (**5**): bis(2-aminobenzaldehyde 2-benzothiazolyl hydrazonato) copper(II) and $[Cu(HL^b)Br(H_2O)]\cdot Br$ (**6**): aquabromo(2-aminobenzaldehyde 2-benzothiazolyl hydrazone)copper(II) bromide were prepared in the same way, using 0.268 g (1 mmol) of ligand mixed in 25 mL ethanol and the following quantities of suitable metal salt: 0.171 g (1 mmol) of $CuCl_2\cdot 2H_2O$ for the complex (**4**), 0.0995 g (0.5 mmol) of $Cu(CH_3COO)_2\cdot H_2O$ for the complex (**5**) and 0.224 g (1 mmol) of $CuBr_2$ for the complex (**6**).

Analytical data: $[Cu(HL^b)Cl(H_2O)]\cdot Cl$ (**4**): dark-green: exp.%: C: 40.35; H: 3.37; N: 13.20; Cu: 15.53; calc.%: C: 39.90; H: 3.32; N: 13.30; Cu: 15.20.

$[CuL^b_2]$ (**5**): brown: exp.%: C: 55.85; H: 3.53; N: 18.60; Cu: 10.23; calc.%: C: 56.18; H: 3.67; N: 18.72; Cu: 10.70.

$[Cu(HL^b)Br(H_2O)]\cdot Br$ (**6**): green: exp.%: C: 33.35; H: 2.63; N: 10.62; Cu: 12.33; calc.%: C: 32.94: H: 2.74; N: 10.98; Cu: 12.55.

Analyses and physical measurements

The purity of the hydrazone Schiff base and its complexes was confirmed by C, H and N analyses, using a Carlo Erba 1180 analyzer. The metal content was determined volumetrically by standard procedures.

Thermogravimetric analysis was carried out in static air atmosphere, at a heating rate of 10 ^{0}C/min, using a MOM Q-1500 derivatograph. Molar conductance measurements were made on a Consort C-533 conductometer. Infrared spectra (in KBr pellets) were recorded on a Perkin Elmer FT-IR spectrophotometer, in the range 4000-400 cm^{-1}. UV-VIS diffuse reflectance spectra were measured on a UV-VIS Jasco 570 spectrophotometer, in the range 200-900 nm. The EPR spectra were recorded on an ART-6-IFIN spectrophotometer, on powdered samples, in K band.

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