Copper(II) Complex Compounds with Mixed Hydrazone Ligands

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Three Cu(II) complex compounds with mixed hydrazone ligands have been prepared and characterized in view of their potential biological activity. The complex compounds have the formulas: [Cu(HL^a)(L^c)Br], [CuL^{a}L^c] and [CuL^{b}L^c] . Na, where HL^a = 4-dimethylamino benzaldehyde-2-benzothiazolyl hydrazone, H$_2$L^b = 2-hydroxybenzaldehyde-2-benzothiazolyl hydrazone and HL^c = 2-hydroxy-1-naphthyliden-N,N-dimethyl hydrazone. The complexes have been characterized by elemental and thermogravimetrical analysis, infrared, electronic and EPR spectra. EPR spectral studies of the complexes gave axial symmetry, with $d_{x^2-y^2}$ the ground state. The bonding parameters calculated from the electronic and EPR spectra indicate strong in-plane π-bonding for all the complexes. Investigations on antibacterial and antifungal activities show that the complexes are more active than the free ligands against various Gram positive, Gram negative bacteria and fungi.

Keywords: hydrazones, complexes, copper(II)

The area of metal complexes with hydrazones has been investigated intensively during the last years especially for these compounds pharmacological applications, as tuberculostatic [1-3], antitumor [4-7], antibacterial and antifungal agents [8-11].

The thiazole and benzothiazole hydrazones represent a very interesting class of ligands, due to additional donor sites: nitrogen, sulphur or oxygen atoms, which introduce a wide range in their coordinative and pharmaceutical properties [12-16]. In addition, the thiazole and benzothiazole hydrazones and their metal complexes show an increased biological activity comparatively with simple hydrazones [17,18].

As a continuation of our studies on the chemistry and biological properties of transition metal complexes with 2-benzothiazolyl hydrazones [19-23], we report here the synthesis, characterization and antimicrobial studies on three new Cu(II) complexes with mixed hydrazone ligands. Prior to this publication, we have investigated the coordinative properties of 2-hydroxy-1-naphthyliden-N,N-dimethyl hydrazone and we have synthesized and characterized four complex compounds of Co(II) and Cu(II) with this ligand [24]. These complexes show no significant activity against Gram positive and Gram negative bacteria and fungi, as well as the ligand. On the other hand, 4-dimethylaminobenzaldehyde-2-benzothiazolyl hydrazone and 2-hydroxybenzaldehyde-2-benzothiazolyl hydrazone and their copper(II) complexes are moderately active against various bacteria and fungi [23]. In order to observe how the presence of two different hydrazone ligands influences on the character of the metal-ligand bond and on the biological activity, we have prepared and characterized three new complex compounds of copper(II) with mixed ligands: 2-hydroxy-1-naphthyliden-N,N-dimethyl hydrazone and 4-dimethylamino benzaldehyde-2-benzothiazolyl hydrazone or 2-hydroxybenzaldehyde-2-benzothiazolyl hydrazone.

Experimental part

Preparation of the ligands

All the chemicals used were of A.R. grade. The ligands were synthesized by the procedures reported in previous papers: the condensation reaction of 2-hydrazinobenzothiazole with 4-dimethylaminobenzaldehyde (for the ligand HL^a) [19,20,23] and with 2-hydroxybenzaldehyde (for the ligand H$_2$L^b) [22] and the condensation reaction of N,N-dimethylhydrazine with 2-hydroxy-1-naphthaldehyde (for HL^c) [24], in equimolar quantities; m.p. (HL^a) = 238^{0}C; m.p. (H$_2$L^b) = 250^{0}C; m.p. (HL^c) = 56-57^{0}C.

Preparation of the complexes

[Cu(HL^a)(L^c)Br] (**1**) and [CuL^{a}L^c] (**2**): 0.296 g (1 mmol) of the ligand HL^a and 0.214 g (1 mmol) of the ligand HL^c were dissolved in 30 mL ethanol, with heating. To this solution was added the corresponding metal salt: 0.224 g (1 mmol) of CuBr$_2$ for the complex (**1**) and 0.199 g (1 mmol) of Cu(CH$_3$COO)$_2$. H$_2$O for the complex (**2**). The *p*H was adjusted to ~ 5 with sodium acetate and the resulted solution was refluxed for 2-3 h. The solid products were separated out. These were filtered, washed with ethanol and dried in air.

[CuL^{b}L^c]. Na (**3**) was prepared following the same method, but using 0.269 g of the ligand H$_2$L^b, 0.214 g (1 mmol) of the ligand HL^c and 0.199 g (1 mmol) of Cu(CH$_3$COO)$_2$. H$_2$O.

The purity of the hydrazones and their complexes was confirmed by C, H and N analyses, using a Carlo Erba 1180 analyzer. The copper content was determined by standard procedure.

Elemental analysis

[Cu(HL^a)(L^c)Br] (**1**) brown; found (%): C-53.50; N-12.45; Cu-9.55; calc. (%): C-53.29; N-12.86; Cu-9.80; λ_M(DMF) = 70 Ω^{-1}cm^{2}mol^{-1}; m.p. > 250^{0}C, decomposition.

[CuL^{a}L^c] (**2**), yellow-green; found (%):C-60.45; N-14.35; Cu-10.91; calc. (%): C-60.84; N-14.68; Cu-11.18; λ_M (DMF) = 58 Ω^{-1}cm^{2}mol^{-1}; m.p.> 300^{0}C, decomposition.

[CuL^{b}L^c] . Na (**3**), green; found (%): C-56.70; N-12.64; Cu-11.02; calc. (%): C-57.04; N-12.32; Cu-11.26; λ_M (DMF) = 74 Ω^{-1}cm^{2}mol^{-1}; m.p. > 240^{0}C, decomposition.

Thermogravimetric analysis were carried out in static air atmosphere, at a heating rate of 10 ^{0}C/min, using a MOM Q-1500 derivatograph. Molar conductance measurements

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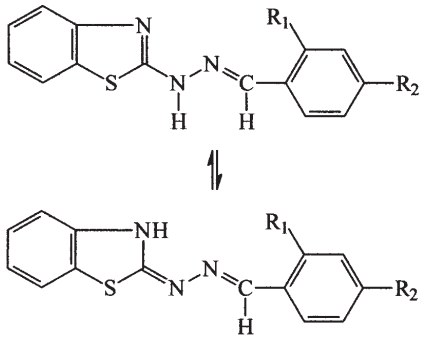
were made on Consort C-533 conductometer. Infrared spectra (in KBr pellets) were recorded on a Perkin Elmer FT-IR spectrophotometer, in the range 4000-400 cm^{-1}. UV-VIS diffuse reflectance spectra were measured on a Specord M-40 spectrophotometer, in the range 200-900 nm. K-band EPR spectra were recorded on an ART-6-IFIN spectrophotometer, at room temperature.

Results and discussion

Infrared spectral studies

The IR spectra of solid 2-benzothiazolyl hydrazones exhibit ν(NH) absorption band around 3200 cm^{-1} [4,25], suggesting that these ligands are in the tautomeric form I in the solid state (fig. 1).



R_1: -H, R_2: $-N(CH_3)_2$ for HL^a and R_1: -OH, R_2: -H for H_2L^b

Fig. 1. Tautometric Forms of 2-benzothiazolyl Hydrazones

This band shifts to higher wavenumbers in the IR spectrum of the complex (**1**), but disappears in the spectrum of the complex (**2**), indicating the participation of the ligand HL^a in the tautomeric form I in the complex (**1**) and the tautomerisation to the form II in the complex (**2**).

The ν(NH) absorption band is also absent in the IR spectrum of the complex (**3**), in accordance with the participation of the ligand H_2L^b in the tautomeric form II at the formation of this complex.

Table 1 gives the most important IR frequencies of the ligands and their chelates to decide the coordination of the hydrazones to the metal ion.

The very strong band, with two maxima, at 1619, 1609 cm^{-1} (HL^a) and 1617, 1610 cm^{-1} (H_2L^b) may be assigned to the stretching vibration of the hydrazone function, $\nu(C=N)_{exocyclic}$ and benzothiazole group, $\nu(C=N)_{endocyclic}$, respectively [25-27]. The IR spectrum of 2-hydroxy-1-naphthyliden-N,N-dimethyl hydrazone (HL^c) shows also a characteristic absorption band at 1619 cm^{-1}, due to ν(C=N) hydrazone function (fig. 2).

The IR spectrum of the complex (**1**) shows a downward shift of ν(C=N) bands, in accordance with the coordination of the ligand HL^a through the hydrazone and benzothiazole

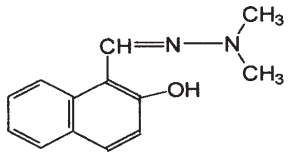


Fig. 2. Structure of 2-hydroxy-1-naphthylides-N,N-dimethyl hydrazone (HL^c)

nitrogen atoms, in the tautomeric form I and the coordination of the ligand HL^c through his hydrazone azomethinic nitrogen. In the IR spectra of the complexes (**2**) and (**3**) only one band is observed at 1606-1603 cm^{-1}, due to $\nu(C=N)_{exocyclic}$ of 2-benzothiazolyl hydrazones and ν(C=N) of the ligand HL^c, in accordance with the participation of these nitrogen atoms in coordination. The new very strong band, appearing in the IR spectra of the same complexes at 1506-1512 cm^{-1}, which may be assigned to the skeleton >C=N-N=C< vibration, indicates the tautomerisation of the 2-benzothiazolyl hydrazones to the form II and the implication of the benzothiazole nitrogen atom in coordination to the metal ion [25,26]. 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 to the metal ion [4].

The medium absorption band occuring at 2923- 2993 cm^{-1} in the IR spectra of the ligands H_2L^b and HL^c, due to the stretching vibration of associated OH group disappears in the spectra of the complexes, indicating the deprotonation of the phenolic group and the coordination of these ligands 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 ligands [4,25].

On the base of the IR spectra we can conclude that the ligand HL^a acts as neutral bidentate NN donor, in tautomeric form I in the complex (**1**) and monobasic bidentate NN donor, in tautomeric form II in the complex (**2**). The ligand H_2L^b acts as dibasic tridentate NNO donor, in tautomeric form II in the complex (**3**). In all the complexes, HL^c coordinates as monobasic bidentate NO donor.

Thermogravimetric analysis

The TG curves of the compounds (**2**) and (**3**) show that they are stable until 300°C. For the complex (**1**), the removal of coordinated bromide takes place in an endothermic process with maximum at 250°C [28]. All the complexes lose the organic ligand in a large exothermic process, in the range of 400-650°C [28].

As result of analytical, thermogravimetrical and IR spectral data we can conclude that the copper(II) is pentacoordinated in the complexes (**1**) and (**3**) and tetracoordinated in the complex (**2**), but the symmetry of

Table 1

SELECTED IR SPECTRAL BANDS OF THE LIGANDS AND THEIR Cu(II) COMPLEXES (ν_{max}, cm^{-1})

Assignments	HL^a	H_2L^b	HL^c	(1)	(2)	(3)
ν_{NHsec}	~3200 m	~ 3200 m	-	3227 m	-	-
$\nu_{OH\ fenolic}$	-	2923 m	2993 m	-	-	-
$\nu_{C=N\ exo}$ $\nu_{C=N\ endo}$	1619 vs 1609 vs	1617 vs 1610 vs	1619 m	1605 vs 1569 s	1606 s	1603 s
$\nu_{>C=N-N=C<}$	-	-	-	-	1506 vs	1512 vs
$\nu_{CO\ fenolic}$	-	1269 m	1271 m	1274 m	1290 m	1276 m
ν_{NN}	942 m	946 m	953 m	944 m	944 w	~ 940 w

vs = very strong ; s = stong ; m = medium ; w = weak.

Table 2
EPR PARAMETERS FOR THE COPPER(II) COMPLEXES

Complex compound	$g_{\|}$	$g_{\perp}$	$A_{\|}$ x 10^4 cm^{-1}
$[Cu(HL^a)(L^c)Br]$ (**1**)	2.200	2.061	185
$[CuL^aL^c]$ (**2**)	2.207	2.060	189
$[CuL^bL^c]Na$ (**3**)	2.200	2.072	179

the complexes and the character of the metal-ligand bonds were appreciated on the base of electronic and EPR spectra.

Electronic and EPR spectral studies

The EPR spectra of the Cu(II) complexes, recorded on powdered samples, in K band, at room temperature are presented in figure 3 and the parameters are listed in table 2.

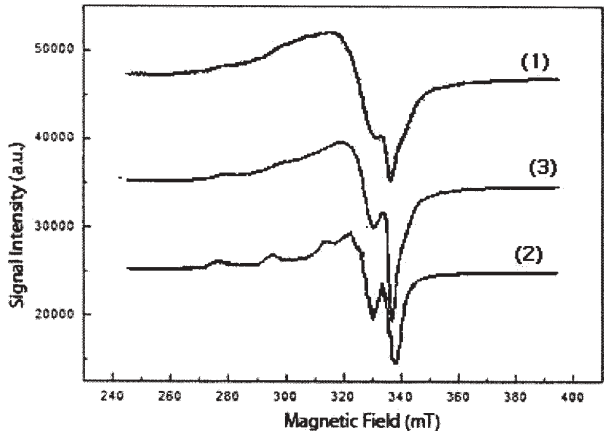


Fig. 3. K-band EPR spectra of the complexes at room temperature

EPR spectra of the three complexes show axial symmetry, with $g_{||} > g_{\perp}$. These results permit to attribute a square-planar symmetry for the complex (**2**) and square-pyramidal symmetry for the complexes (**1**) and (**3**). In this assumption, the significant electronic absorption bands in the diffusion reflectance spectra of complexes, in the visible region, may be attributed to the transitions written in Table 3 [29].

The hyperfine structure is observed for all the complexes, better for the complex (**2**), which also shows a five-line superhyperfine structure (A^N = 14.8 G), consistent with the interaction of Cu(II) with three nitrogen atoms.

The correlation between the EPR spectral data and the observed bands in the electronic spectra allows, on the basis of molecular orbital theory, to calculate the covalency parameters α^2, β^2 and β_1^2 as follows [30-32]:

$$g_{\|} = 2 - \frac{8\lambda_0}{\Delta E_{xy}}\alpha^2\beta_1^2;\ g_{\perp} = 2 - \frac{2\lambda_0}{\Delta E_{xz,yz}}\alpha^2\beta^2;$$

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

where λ_0 is the spin-orbit coupling constant for the free Cu^{2+} ion (-828 cm^{-1}), k is the Fermi contact term which characterizes the isotropic (s-electron) contribution to the hyperfine interaction; $P = 2\gamma\beta\beta_N\langle r^{-3}\rangle$ = 0,036 cm^{-1}; $\Delta E_{xy} = \Delta(E_{x2-y2} - E_{xy})$; $\Delta E_{xz,yz} = \Delta(E_{x2-y2} - E_{xz,yz})$.

Using the approximation: $(4/7 + k) = 1$ in the expression of $A_{||}$, we can calculate α^2 which is then utilized for the calculation of β^2 and β_1^2, using the relations written above. The coefficients α^2, β_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.

Another orbital parameters, $K_{||} = \alpha^2\beta_1^2$ and $K_{\perp} = \alpha^2\beta^2$, are a guide of the metal - ligand bonding nature [33]: $K_{||} \approx K_{\perp}$ for the pure σ bonding, $K_{||} < K_{\perp}$ for strong in-plane π bonding and $K_{||} > K_{\perp}$ for strong out-of-plane π bonding.

The values of the bonding parameters calculated for the three Cu(II) complexes are listed in table 4.

The high values of α^2 indicate a weak overlap of σ-orbitals in xOy plane, that is an important ionic character for these bonds. For all the complexes, the lower values of β_1^2, as well as the ratio $K_{||} < K_{\perp}$ are in accordance with strong in-plane σ bonding. The parameter β^2 has relatively high values, indicating an intermediate character, ionic-covalent, for out-of-plane π bonding.

The parameter $G = (g_{||} - 2)/(g_{\perp} - 2)$ is smaller than 4 for all the complexes, suggesting the strong spin-spin interactions between the copper centers [32].

According to the determinations presented above, we proposed for the complexes the structures presented in figure 4:

Biological activity

All the compounds were evaluated for antibacterial and antifungal activity, following the cup-plate agar diffusion

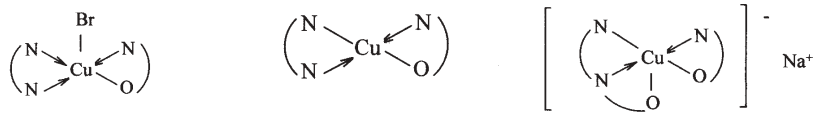
Table 3
ELECTRONIC TRANSITIONS IN THE VISIBLE REGION FOR Cu(II) COMPLEXES

Complex compound	Observed bands ν_{max} (cm^{-1})	Assignments	Symmetry
$[Cu(HL^a)(L^c)Br]$ (**1**)	10634 11363 14285 17094 18690 26315	$^2B_{1g}\rightarrow{}^2A_{1g}$ $^2B_{1g}\rightarrow{}^2B_{2g}$ $^2B_{1g}\rightarrow{}^2E_g$ Charge transfer $n\rightarrow\pi^*$ $\pi\rightarrow\pi^*$	C_{4v}
$[CuL^aL^c]$ (**2**)	11976 13300 16100 19660	$^2B_{1g}\rightarrow{}^2B_{2g}$ $^2B_{1g}\rightarrow{}^2E_g$ $^2B_{1g}\rightarrow{}^2A_{1g}$ Charge transfer	D_{4h}
$[CuL^bL^c]Na$ (**3**)	10900 11400 14200	$^2B_{1g}\rightarrow{}^2A_{1g}$ $^2B_{1g}\rightarrow{}^2B_{2g}$ $^2B_{1g}\rightarrow{}^2E_g$	C_{4v}

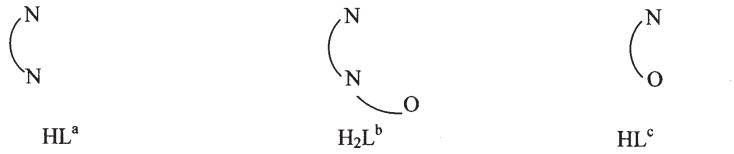
Table 4

BONDING PARAMETERS OF Cu(II) COMPLEXES

Parameter	$[Cu(HL^a)(L^c)Br]$ **(1)**	$[CuL^aL^c]$ **(2)**	$[CuL^bL^c]Na$ **(3)**
α^2	0.77	0.79	0.79
β_1^2	0.44	0.47	0.44
β^2	0.68	0.60	0.66
$K_{\|\|}$	0.34	0.37	0.34
$K_\perp$	0.52	0.48	0.52
G	3.27	3.45	2.77



$[Cu(HL^a)(L^c)Br]$ **(1)** $[CuL^aL^c]$ **(2)** $[CuL^bL^c]Na$ **(3)**



HL^a H_2L^b HL^c

Fig. 4. Proposed Structures of Cu(II) Complexes

Table 5

BIOLOGICAL ACTIVITY FOR THE LIGANDS AND THEIR Cu(II) COMPLEXES

Microbial strain		Microbial culture inhibition diameter Ø [mm]					
		HL^a	H_2L^b	HL^c	Complex **(1)**	Complex **(2)**	Complex **(3)**
Gram negative bacteria	*Escherichia coli*	0	0	0	2	2	2
	Pseudomonas aeruginosa serotip VI	1	2	0	3	3	3
Gram positive bacteria	*Staphyloccocus coagulase positive*	1	2	0	3	4	4
	Streptoccocus β-haemolytic type A	2	3	1	5	4	5
	Streptoccocus β-haemolytic type B	2	3	0	5	4	5
	Staphyloccocus aureus	1	2	1	5	4	5
Fungi	*Candida albicans*	0	0	0	2	2	2

technique, against bacillius Gram negative (E. coli, Pseudomonas aeruginosa serotip IV), bacillius Gram positive (Staphyloccocus coagulase positive, Streptoccocus β-haemolytic type A and type B and Staphyloccocus aureus) and fungi (Candida albicans). A solution 10^{-4}M of each compound in acetone was used. The culture medium and microbial strains were laid in petri plates. The 10μL solution compound impregnated disks were applied to the surface of inoculated plates. After incubation for 72 h at 37°C, the zone of inhibition was measured. The results are presented in the table 5.

The ligand HL^c shows no biological activity against the bacteria and fungi tested, while the ligands HL^a and H_2L^b are weak inhibitors for the same microbial strains. All the copper(II) complexes are moderately biologically active, especially against the bacillus Gram positive. They are also found active against the test fungi used. It is interesting to observe that these complexes are more biologically active than the complexes containing only one type of hydrazone ligands: HL^a, H_2L^b or HL^c [23,24]. This increase in the antimicrobial activity is probably due to the reciprocal influence of two coordinated ligands. The most intensive activity is observed for the anionic complex (**1**) and for the complex (**3**), containing coordinated bromide, probably due to a faster diffusion of these metal complexes through the cell membrane.

Conclusions

We have prepared three new complex compounds of copper(II) with mixed hydrazone ligands: 2-hydroxy-1-naphthyliden-N,N-dimethyl hydrazone and 4-dimethyl-aminobenzaldehyde-2-benzothiazolyl hydrazone or 2-hydroxybenzaldehyde-2-benzothiazolyl hydrazone. The interpretation of the electronic and EPR spectra reveals

strong in-plane π-bonding for all the complexes. All the three complexes are more active than the ligands against various bacteria and fungi.

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