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**SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL ACTIVITY OF SOME
Cu(II) COMPLEXES WITH *N, N'*-Bis-(PYRIDINE-2-YL-METHYLENE)- 3,3'-
DIMETHYLBENZIDINE SCHIFF BASE**

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Abstract

A new series of complexes with Schiff base (L), was obtained through the condensation of the *o*-tolidine with 2-pyridyl-carbaldehyde, type $Cu_2L_2X_m$, where $m=4$, $X=ClO_4$, Cl, NO_3 , and Cu_2LX_m where $m = 4$, CH_3COO and $m = 2$, $X = SO_4$. The ligand and the complexes were investigated by means of elemental analysis, electrical conductivity, magnetic and spectral measurements. The molar conductivity values show that these compounds are non-electrolytes, except for the perchlorate complex. The analytical data indicate a mole ratio M: L of 1:1 or 2:1. The spectral data and magnetic moments suggest a tetrahedral or octahedral geometry of the complexes. The Schiff base acts as a neutral tetradentate ligand with NN-NN donor system. The compounds were tested for their biological activity.

Keywords: 2-pyridyl-carbaldehyde, antimicrobial activity, EPR spectra, *o*-tolidine

Introduction

The chemistry of complex combinations derived from the Schiff-base has registered lately a spectacular development, due to their catalytic properties in various processes and their usage as structural patterns for the enzymes involved in biochemical processes, but also due to their antimicrobial activity. Thanks to their very good coordination capacity, Schiff bases are used as complexing agents, respectively as reagents in the spectrophotometrical processes of metal ion analysis [1].

The Schiff bases and their complexes are used as catalysts in various chemical and petrochemical industrial processes [2-5]. The metal complexes with Schiff bases favors the development of biochemical processes which are specific to DNA and RNA [6, 7], but they also have an inhibitory effect on other biochemical processes [8].

Following previous research [9], we intended to synthesize and characterize complexes of Cu(II) ions with a new Schiff base obtained through the condensation of *o*-tolidine (3,3'-dimethyl-benzidine) with 2-pyridyl-carbaldehyde (Fig. 1). It must be also mentioned that only a few articles with Schiff bases derived from *o*-tolidine were identified in the specialized literature [10-12].

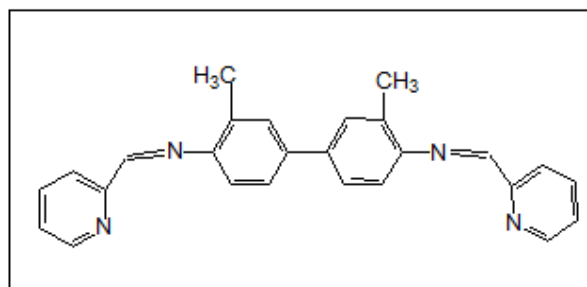


Fig-1: The structure of the ligand (L).

Experimental part

Materials and Methods

In the synthesis metal salts (Sigma-Aldrich) were used, such as 2-pyridyl-carbaldehida (Merck) and 3,3 '-dimethylbenzidine (ICN Biomedicals). In the case of Cu(II), the metal content was volumetrically determined through iodometric methods. The content of N, C and H was determined with a microdosimeter ECS-40-10-Costeh, after drying at 105°C. The melting points were determined with a Stuart Scientific SMP3 apparatus and they are uncorrected. The molar conductivity was determined in DMF, acetone (10^{-3} M) at room temperature, with a Consort C533 conductometer. The IR spectra were recorded in KBr pellet, using a Fourier transform spectrometer BioRad FTS-135 in the region $4000-400\text{ cm}^{-1}$ IR / ATR.

The electronic spectra were recorded by means of a Jasco V 670 spectrophotometer, by the diffuse reflectance technique. The NMR spectrum for the ligand was recorded on a DMSO- d_6 with a Varian Gemini 300 BB apparatus at 300 MHz for ^1H and 75 MHz for ^{13}C . The magnetic susceptibilities were determined through the Faraday method and corrected for the atomic diamagnetism. The EPR spectra were recorded with a MiniScope MS200 type spectrometer, which operates in X-band (9.3 to 9.6 GHz) and wich it is provided with a rectangular

TE₁₀₂ cavity resonance. The microbial strains that were isolated from different pathological products were identified using the VITEK I automatic system. VITEK cards for the identification and testing of the sensitivity to antibiotic (GNS-522) were inoculated and incubated according to the directions of the manufacturer. The results were interpreted by means of the AMS R09.1 aid program.

Synthesis of the ligand

The Schiff base (L) was obtained by mixing an ethanolic solution of *o*-tolidine (0.01 moles in 50 cm³ alcohol) with an ethanolic solution of 2-pyridyl-carbaldehyde (0.02 moles in 50 cm³ alcohol) in the presence of acetic acid. The mixture was refluxed for four hours. After cooling the precipitate obtained was filtered, washed and re-crystallized from methanol. The yield obtained was 68%. The yellow-greenish crystalline solid product is stable at room temperature, soluble in organic solvents except methanol and acetone, the melting point being at 175⁰C. The analytical data are listed in Table 1.

Table-1: The physico-chemical and analytical characteristics for the ligand (L) and of the complexes (1)-(6).

Compound	Color	Elemental analysis % calcd. (exp.)				Solub.*	Melting point (°C)	Λ _M (Ω ⁻¹ cm ² mol ⁻¹)
		M	N	C	H			
(L)	yellow-greenish	-	14.34 (14.89)	79.97 (79.64)	5.67 (5.31)	a, c, d, e	175	-
[Cu ₂ L ₂](ClO ₄) ₄ (1)	black	9.73 (9,32)	8.58 (8,96)	47.82 (47.99)	3.39 (3.75)	a, b, c, d	-	90.9/Ac
[Cu ₂ L ₂ Cl ₄] (2)	reddish-black	12.1 (12,41)	10.67 (10.33)	59.48 (59.23)	4.22 (4.20)	a, c, d	270	13.1/DMF
[Cu ₂ L ₂ (NO ₃) ₄] (3)	brown	10.99 (10.54)	14.53 (14.57)	54.02 (54.23)	3.83 (3.56)	a, c, d	>300	2.9/DMF
[Cu ₂ L(CH ₃ COO) ₄] (4)	brown	16.86 (17.26)	7.43 (7.19)	54.17 (53.77)	4.54 (4.38)	a, b, c, d	299	0/Ac
[Cu ₂ L ₂ (SO ₄) ₂] (5)	brown-greyish	11.55 (11,37)	10.18 (10.35)	56.76 (56.78)	4.03 (4.01)	a, c, d	>300	12.1/DMF
[Cu ₂ L(SO ₄) ₂] (6)	brown	18.75 (17,68)	8.26 (7.87)	46.08 (39.89)	3.27 (3.43)	a, c, d	>300	7.9/DMF

*a-THF, b-Acetonă (Ac), c-DMF, d-DMSO, e-CH₂Cl₂, f-EtOH

Synthesis of the complexes

A quantity of 50 cm³ of ligand solution (0.01 moles) in ethanol was mixed with an equal volume of ethanol solution containing 0.01 moles of metal salt such as perchlorate, chloride, nitrate, and sulphate of Cu(II) or 0.01 moles ligand solution and 0.02 moles ethanolic solution of Cu(II) acetate and respectively sulphate. The obtained

mixtures were refluxed for at least four hours in a water bath and then concentrated at half of its original volume.

The obtained precipitates were filtered, washed and dried in desiccators, on CaCl₂.

Antimicrobial activity

Complexes (1) - (6) were tested to determine the antimicrobial activity, using qualitative and quantitative methods [13]. For the tests, there were used Gram-positive bacterial species (*Staphylococcus aureus* 1263) and Gram negative (*Klebsiella pneumoniae* 1204, *Escherichia coli* IC 13147, *Pseudomonas aeruginosa* 1246), as well as fungal species (*Candida albicans* LS) isolated from different clinical products. The quality control was performed by simultaneous tests of antimicrobial activity and on the reference strains: *Klebsiella pneumoniae* IC 13420, *Escherichia coli* IC 13529, *Staphylococcus aureus* IC 13204, *Pseudomonas aeruginosa* IC 13202, *Candida albicans* IC 249.

The quality screening of the action of synthesized compounds against the bacteria and fungi was determined by two methods of diffusion adapted after the diffusimetric method. The first method consists in impregnating the filter paper disks with the compound solution solubilized in DMSO (1 mg/ml). The second method consists in the qualitative determination of the antimicrobial effect of the compound distributed in the spot, on a medium inoculated with microbial culture. Therefore, on the Petri dishes with a Mueller Hinton medium/respectively an YPG medium, sown "in canvas" with bacterial/fungal inoculums, 10 µl of the test product were dropped in each spot. The used solvent (DMSO) was also tested comparatively, using the two methods, to highlight a potential antimicrobial activity. The reading of the results was performed by measuring the diameters of the inhibition zones generated by various compounds, using a scale ruler.

For the quantitative determination of microbial activity of the ligand and of the complexes, the method of binary microdilution in liquid medium was used (Mueller Hinton for bacteria, respectively liquid YPG for fungi), using plates with 96 wells each, in order to determine the minimum inhibitory concentration (MIC). Binary serial dilutions of stock solutions were made, in DMSO of tested compounds (1 mg/ml) solution, of ceftazidime (concentration 128 µg/ml) as a witness for the bacteria and of fluconazole solution (concentration 128 µg/ml) as a witness for fungi. For each test, we also used a witness of microbial culture (a series of wells containing only an exclusive culture medium inoculated with microbial suspension) and a medium sterility witness, without a microbial culture. Subsequently, 15 ml of microbial suspension with a 0.5 MacFarland density were added in each

well. The plates were incubated at 37⁰C for 24 hours for the bacteria and respectively for 48 hours at 28⁰C for the fungi. The obtained results were analyzed through macroscopic observation [14].

Results and discussions

The obtained complexes are intensely colored, stable at room temperature, non-higrosopic, insoluble in water and with low solubility in common solvents, except DMF and DMSO. The analytical data (Table 1) for the ligand and complexes represented by the proposed structure show that in complexes the metal and the ligand are in mole ratio 1:1 or 1:2. The molar conductivity values of the complexes of 10⁻³ M solutions in DMF indicate their non- electrolytic nature, except for complex (1) [15].

RMN ligand spectra

The obtaining of the Schiff base is confirmed by the existing signals in the spectrum of ¹H NMR and ¹³C NMR ligand (Table 2). This way, in the ¹H NMR spectrum, the multiple signals of aromatic protons is between 7.21 and 7.63 ppm. For the methylene protons, fragment derived from amine, the signals are at 2.41 ppm. In the range between 7.07 and 8.73 ppm, the aromatic protons from the fragment derived from 2-pyridyl-carbaldehyde generate doublet signals, while the signals from the azomethine group protons appear as singlet at 8.56 ppm. The ¹³C NMR spectrum also contains signals specific to carbon atoms, deriving from both the amine and the pyridyl-carbaldehyde, mentioning that the signals specific to the carbon atom from the azomethine group are to be found at 159.57 ppm. The absorption signals located at 132.26 ppm in the ¹³C NMR spectrum correspond to the carbon atoms in the methyl groups of the amine.

Table-2: Spectral data ¹H NMR and ¹³C NMR for ligand (L).

(L)
¹ H RMN(DMSO-d ₆ , δ/ ppm, J, Hz; 60 ⁰ C):
8,73(d;4.7;2H;H-6;6'), 8,56(s;2H;H-7;7'), 8,21(dl;7.9;2H;H-3;3'), 7.07(tl;1.8;7.9;2H;H-4;4'), 7.63(d;2.1;2H;H-11;11'), 7,58(dd;7.9;2.1;2H;H-13;13'), 7,53(ddd;7.9;4.6;1.2;2H;H-5;5'), 7.21(d;7.9;2H;H-14;14'), 2,41(s;6H;CH ₃)
¹³ C RMN(DMSO-d ₆ , δ/ ppm; 60 ⁰ C)
154.10(C-2,2'), 121.08(C-3,3'), 136.83(C-4,4'), 147,97(C-5,5'), 149.46(C-6,6'), 159.57(C-7,7'), 148.47(C-9,9'), 132.26(C-10,10'), 134.26(C-11,11'), 137,64(C-12,12'), 125.34(C-13,13'), 122.75(C-14,14'), 17.42(CH ₃)

IR spectra

Ligand spectrum (Table 3) shows a band at 1625 cm^{-1} , corresponding to the $\nu(\text{C}=\text{N})$ azomethine group. There are also bands at 1582 cm^{-1} , respectively at 776 cm^{-1} , caused by the vibration of the pyridine ring [16]. In the IR spectra of the complexes, considerable shifts toward lower or higher values of these bands can be observed, which indicates the involvement of nitrogen atoms from the azomethine group, respectively from the pyridine ring, in the coordination of the Cu(II) ion. Thus it can be observed that for the complexes, the vibration frequencies values of the azomethine groups are between $1596\text{-}1599\text{ cm}^{-1}$, while for the pyridine ring groups, they are between $1545\text{ to }1572\text{ cm}^{-1}$, along with band displacements to higher values of about $4\text{-}8\text{ cm}^{-1}$ for the vibration of the $\gamma(\text{Py})$ ring [17,18].

Table-3: The values of infrared absorption frequencies (cm^{-1}) and assignments for the ligand and the complexes.

Compound	$\nu(\text{OH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{N})\text{Py}$	$\nu(\text{anion})$	$\nu(\gamma\text{-Py})$	$\nu(\text{M}-\text{N})$
(L)	3433m	1625	1582	-	740	-
$[\text{Cu}_2\text{L}_2](\text{ClO}_4)_4$ (1)	3430	1599	1572	1096 622	746	421s
$[\text{Cu}_2\text{L}_2^4\text{Cl}_4]$ (2)	3366	1597	1564	-	744	422s
$[\text{Cu}_2\text{L}_2^4(\text{NO}_3)_4]$ (3)	3429	1599	1568	1483 1282 1025	744	427
$[\text{Cu}_2\text{L}_2^4(\text{CH}_3\text{COO})_4]$ (4)	-	1599	1545	1575 1389	745	451
$[\text{Cu}_2\text{L}_2^4(\text{SO}_4)_2]$ (5)	3413	1600	1566	1248 1122 1029	746	422
$[\text{Cu}_2\text{L}_2^4(\text{SO}_4)_2]$ (6)	3078	1596	1567	1213 1153 1096	748	423

Vibration bands of very high intensity are to be found in the spectra of complexes, due to the presence of anions in the coordination sphere of the metal or beyond it.

The spectrum of complex (1) shows a very intense band at 1096 cm^{-1} and a weak one at 622 cm^{-1} , which may be ascribed to the vibrations of the perchlorate ion that is present in this compound [19].

Complexes (2) - (6) contain anions in the coordination sphere of the metal ion. Three strong bands are present in the spectrum of complex (3) at 1483 , 1280 and 1025 cm^{-1} respectively; which may be ascribed to the vibration type ν_3 , ν_1 and ν_2 , due to the involvement of the nitrate group in coordination. As the difference between

($\nu_3 - \nu_1$) for the complex is of 203 cm^{-1} , it suggests the presence of the nitrate group as a monodentate in coordination [20], but also an average strength of the bond between the metal ion and the nitrogen atom [21].

The infrared spectrum of complex (4) shows two bands at 1575 and 1389 cm^{-1} , which may be ascribed to $\nu_{\text{asim}}(\text{COO})$, respectively to $\nu_{\text{sim}}(\text{COO})$. The difference value between the two peaks frequencies, $\Delta\nu = \nu_{\text{asim}}(\text{COO}) - \nu_{\text{sim}}(\text{COO})$, is 186 cm^{-1} , indicating that the acetate group, under monodentate form, is participating in the coordination [22].

In their spectra, complexes (5) and (6) show bands that are specific to sulfate groups, coordinated as bidentate forms. Frequencies ν_3 and ν_1 are split into three bands, at 1248 , 1122 and 1029 cm^{-1} for complex (5) and at 1213 , 1153 , and at 1096 cm^{-1} for complex (6). The splitting of these bands suggests a change in the Oh type, respectively of a Td type arrangement with a high symmetry, to a lower symmetry of C_{2v} type [23].

In all the spectra of the complexes, new low intensity bands in the region $421-451 \text{ cm}^{-1}$, which are not to be found in the ligand spectrum, can be attributed to the $\nu(\text{M-N})$ vibrations of the new bonds formed between the metal ion and the ligand [24].

UV-VIS spectra

The information on the geometry of the metal ion can be obtained by analyzing the UV-VIS spectral data recorded at room temperature correlated with the magnetic moments values (Table 4).

Table-4: Electronic spectral data of the synthesized compounds (H_2L) and (1)-(6).

Compound	Absorption band/ cm^{-1}	Assignments	μ/BM
(L)	38460 30300 24100	$\pi \rightarrow \pi^*$	-
$[\text{Cu}_2\text{L}_2](\text{ClO}_4)_4$ (1)	38460 25320 18520 13890 11495	$\pi \rightarrow \pi^*$ TSL \rightarrow M $d_{xy} \rightarrow d_{z^2, x^2-y^2}$ $d_{xy} \rightarrow d_{xz, yz}$	1,68
$[\text{Cu}_2\text{L}_2\text{Cl}_4]$ (2)	37040 25640 14185	$\pi \rightarrow \pi^*$ $d_{xz, yz} \rightarrow d_{x^2-y^2}$	2.12
$[\text{Cu}_2\text{L}_2(\text{NO}_3)_4]$ (3)	25640	$\pi \rightarrow \pi^*$	1,97

	19230	TSL→M	
	13420	$d_{xz,yz} \rightarrow d_{x^2-y^2}$	
	10050	$d_{xy} \rightarrow d_{x^2-y^2}$	
[Cu ₂ L(CH ₃ COO) ₄] (4)	38460	$\pi \rightarrow \pi^*$	1.93
	25000		
	19230	TSL→M	
	14600	$d_{xz,yz} \rightarrow d_{x^2-y^2}$	
	10990	$d_{z^2} \rightarrow d_{x^2-y^2}$	
[Cu ₂ L ⁴ (SO ₄) ₂] (5)	31250	$\pi \rightarrow \pi^*$	2.01
	25640		
	13700	$d_{z^2} \rightarrow d_{x^2-y^2}$	
	12200	$d_{xz,yz} \rightarrow d_{x^2-y^2}$	
[Cu ₂ L ⁴ (SO ₄) ₂] (6)	38460	$\pi \rightarrow \pi^*$	1.73
	24390		
	13420	$d_{xy} \rightarrow d_{z^2,x^2-y^2}$	

The UV spectrum of the ligand (L) has three absorption bands at 38,460,30,300 and 24,100 cm⁻¹ respectively, which may be attributed to the $\pi \rightarrow \pi^*$ transitions. These transitions are to be found in the spectra of the complexes as well, but shifted to lower values, which confirms the Cu(II) ion coordination by the ligand [25].

Besides the band at 18,520 cm⁻¹, corresponding to the transition of the charge transfer, the electronic spectrum of complex (1) also contains bands corresponding to transitions d→d. The two bands have peaks centered at 13,890 and 11,490 cm⁻¹, attributed to the transitions $d_{xy} \rightarrow d_{z^2,x^2-y^2}$ respectively to $d_{xy} \rightarrow d_{xz,yz}$, which correspond to a tetrahedral geometry.

The same transitions occur in the case of complex (4), signalled by the presence of bands at 14,600 cm⁻¹ and respectively at 10,990 cm⁻¹. Similarly, the spectrum of complex (6) contains a broad band centered at 13,420 cm⁻¹, corresponding to a transition of $d_{xy} \rightarrow d_{z^2,x^2-y^2}$ type, which is characteristic to a tetrahedral stereochemistry [26]. Relatively low values of the magnetic moments, determined at room temperature, confirm the tetrahedral stereochemistry [27]. For complexes (2), (3) and (5), it is observed that in their spectra a strong band with peak values each at 14,185,13,420 and respectively at 13,700 cm⁻¹, which suggest an octahedral surrounding of Cu(II) metal ion [28]. The presence of bands at around 19,000 cm⁻¹ in the spectra of complexes (1), (3), and (4), can be explained by the existence of charge transfer transitions. The shoulder-shaped bands appearing in spectra of complexes (1) and (5) may suggest the existence of a distorted rhombic stereochemistry.

The magnetic moments fall in the range between 1.97-2.12 MB, characteristic to a metal ion with d^9 configuration. This suggests the presence of monomer structures and the absence of any metal-to-metal interactions [29].

EPR spectra

For all powder form complexes, the EPR spectra were recorded at room temperature and at liquid nitrogen temperature (77 K). The obtained signals at the two temperatures showed no significant differences; therefore the geometry around the copper ion is not affected by cooling.

Extended signals were recorded as well, but there was no signal at the midpoint of the field, for none of the samples. The EPR signals of these samples taken at room temperature are shown in Fig. 2 and Fig. 3.

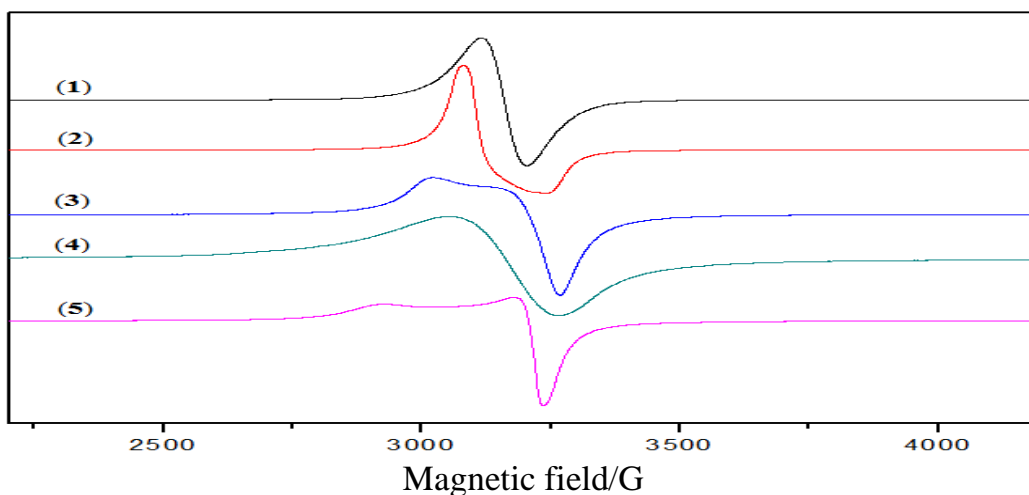


Fig-2:. EPR spectra of the complexes (1) - (5).

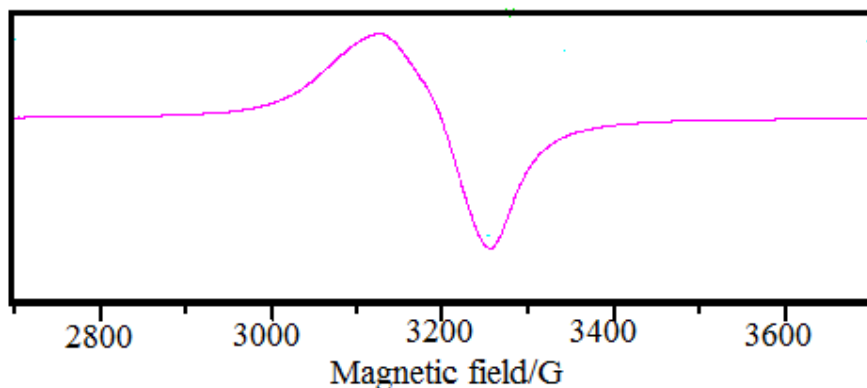


Fig-3: EPR spectra of the complexes (6).

Complex (1) has an EPR signal with cubic symmetry with $g_0 = 2.119$ and peak to peak width $\Delta H = 87$ G. By cooling the sample at 77 K, the line widens slightly ($\Delta H = 93$ G), having a close g factor ($g_0 = 2.116$).

Compound (4) has a similar behavior, but its signal is broader and less asymmetric. At room temperature $g_0 = 2.119 \pm 0.001$ and $\Delta H = 214$ G, and at 77 K, $g_0 = 2.121 \pm 0.001$ and $\Delta H = 219$ G [30].

The signal of the sample (3) has an axial symmetry, having a lorentzian shape line. The line shape changed a little bit when cooled at 77 K. The values of the g tensor, measured after the Kneubuhl method, are $g_{//} = (2.215 \pm 0.001)$, $g_{\perp} = (2.049 \pm 0.001)$ at room temperature, and $g_{//} = (2.208 \pm 0.001)$, $g_{\perp} = (2.049 \pm 0.001)$ at 77 K. For this complex, the geometric parameter calculated by using the formula $g = (g_{//} - 2)/(g_{\perp} - 2)$ is 4.39 and therefore, there is no exchange interactions between the Cu(II) ions. Since $g_{//} > g_{\perp} > 2.0032$, it can be inferred that the unpaired electron is localized in the $d_{x^2 - y^2}$ orbital of the Cu(II) ion [31].

Complex (5) has a similar signal, characteristic to an axial symmetry, but the line shape is Gaussian. The spectral parameters obtained at two temperatures are $g_{//} = (2.285 \pm 0.001)$, $g_{\perp} = (2.068 \pm 0.001)$ at room temperature and $g_{//} = (2.279 \pm 0.001)$, $g_{\perp} = (2.065 \pm 0.001)$ at 77 K.

For this sample as well, the geometric parameter G is higher than 4 (namely 4.19), so that no exchange interactions between copper ions are emphasized. The unpaired electron is located in $d_{x^2 - y^2}$ orbital of the Cu(II) ion. Unlike previous tests, in which the signal change was minor as the sample temperature decreased, in case of this complex, a new low signal appears (Fig. 4), being located at $g_0 \sim 2.15$ [32].

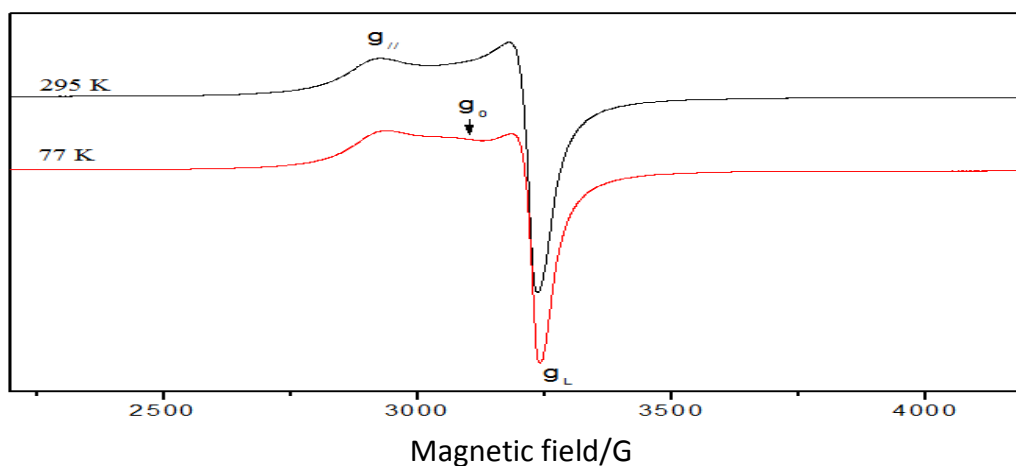


Fig-4: The EPR spectra of the sample (5) powder registered at room temperature (295 K) and 77 K.

Complex (2) has a more special behavior - the main signal has an axial symmetry, but $g_{//} < g_{\perp}$ resulting that the unpaired electron is located in the orbitals d_{z^2} of the Cu(II) ion (Fig. 5). The spectral parameters for this signal are $g_{//} = (2.065 \pm 0.001)$, $g_{\perp} = (2.172 \pm 0.001)$ at room temperature and $g_{//} = (2.056 \pm 0.001)$, $g_{\perp} = (2.172 \pm$

0.001) at 77 K. Similarly, for this complex, there appears an additional signal, better visible at 77 K and also on the derived signals (the derivative of the EPR signal is the second derivative of the microwave energy absorption by the sample and is noted with d2). This additional signal is located at $g_0 = 2.10$ and could be a part of a more complex signal, superimposed on the main signal [33].

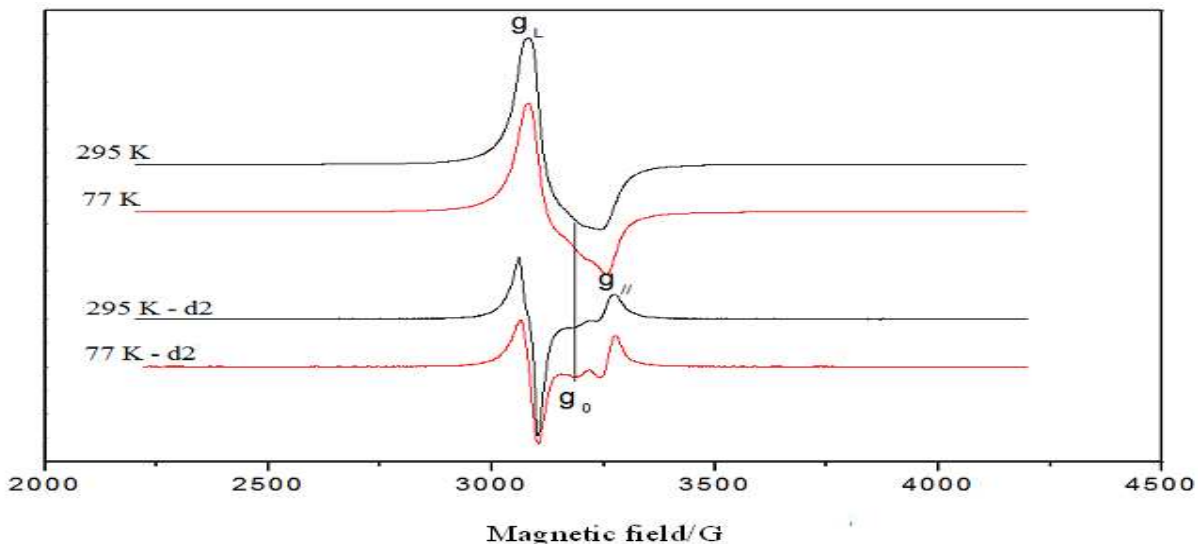


Fig. 5. The EPR spectra of the sample (5) powder registered at room temperature (295 K) and 77 K with the signal derivative (d2)

Complex (6) has a signal with a weak axial deformation in its spectrum, having the g values of its components: $g_{\parallel} = 2.144$ si $g_{\perp} = 2.058$. As the $g_{\parallel} > g_{\perp}$, this means that the unpaired electron is located in the $d_{x^2-y^2}$ orbital of the Cu(II) ion [34].

Antimicrobial activity

After the qualitative test of the antimicrobial activity of the ligand (L) and of complexes (1) - (6), it was determined that they would inhibit the action of bacteria and fungi. It was also found that the solvent used (DMSO) has no antimicrobial activity, which is a great advantage, when testing compounds (1) - (6) and the ligand, which are insoluble in water.

The results (Table 5) obtained from the quantitative testing of the ligand (L) and of complexes (1) - (6) show that they have antimicrobial activity. It results from the literature data fact, if MIC values for tested compounds are between 31.25 and 125 $\mu\text{g/ml}$, this means that the antimicrobial activity is strong, and if the MIC value is greater or equal to 250 $\mu\text{g/ml}$, than the antimicrobial effect is moderate [35, 36].

Table-5: The results of the antimicrobial activity (MIC values in µg/ml) of the ligand (L), complexes (1)-(6), ceftazidim (7) and fluconazol (8).

	(L)	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
<i>S. aureus</i> 1263	125	62.5	125	250	250	62.5	125	64	-
<i>S. aureus</i> IC 13204	250	62.5	125	250	250	62.5	125	64	-
<i>P. aeruginosa</i> 1246	250	62.5	62.5	500	250	62.5	125	64	-
<i>P. aeruginosa</i> IC 13202	250	62.5	62.5	500	125	125	125	64	-
<i>K. pneumoniae</i> 1204	125	62.5	250	125	62.5	62.5	125	8	-
<i>K. pneumoniae</i> IC 13420	125	62.5	250	125	62.5	62.5	125	8	-
<i>E. coli</i> 13147	125	>500	125	250	500	>500	250	16	-
<i>E. coli</i> IC 13529	250	>500	125	250	500	>500	250	16	-
<i>C. albicans</i> LS	125	125	125	>500	>500	250	>500	-	32
<i>C. albicans</i> IC 249	125	125	125	>500	>500	250	>500	-	32

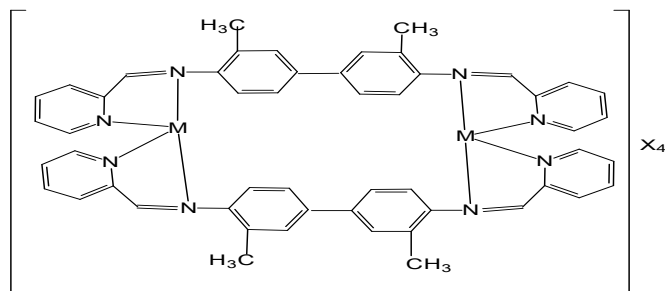
Ligand (L) has a moderate bactericidal activity, but it inhibits pretty well the development of *Candida albicans* type species. Complexes (1), (2), and (5) have the best antimicrobial activity, having MIC values of 62.5 µg/ml to almost all microbial species. However, it should be mentioned that complex (1) inhibits to a lower extent the *Escherichia coli* type strains, while complex (2) has a weaker destructive action on the species *Klebsiella pneumoniae*. A similar behavior has complex (5), but it has a weaker inhibitory action on fungi. The antimicrobial action of complexes (3), (4), and (6) is generally moderate, but it is important to remark the weak fungicidal activity of these compounds. Only complex (4) has a strong inhibitory action on *Klebsiella pneumoniae* strains.

Conclusions

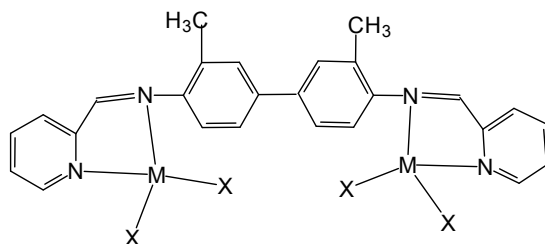
The ligand and its six new complexes with Cu(II) ions were prepared and characterized by physicochemical methods. The RMN spectrum for the ligand shows the existence of two azomethine groups within the ligand. From the elemental analysis of the complexes, a mole ratio M: L of 1:1 or 2:1 was inferred. From the IR spectra, it has been deduced that the ligand is neutral tetradentate and that it coordinates the metal ion through nitrogen atoms, belonging to azomethine groups and pyridine rings. Based on the spectral UV-VIS, EPR

data, and magnetic moments, it was inferred that these complexes have a tetrahedral or octahedral geometry [17].

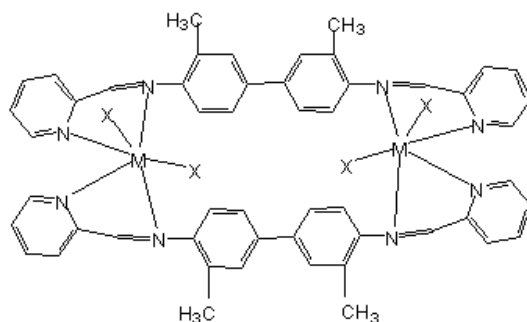
The ligand has a moderate antimicrobial action, but the complexes have a good destructive action against bacteria and, to a lower extent, against fungi. The structural formulas proposed for complexes (1)-(6) are shown in Fig. 6 [37].



$[M_2L_2]X_4$, where $M = Cu(II)$, $X = ClO_4$ (1)



$[M_2LX_m]$, where $M = Cu(II)$, $m = 4$, $X = CH_3COO$ pentru (4); $m = 2$, $X = SO_4$ pentru (6)



$[M_2L_2X_m]$, where $M = Cu(II)$, $m = 4$, $X = Cl$ (2), $X = NO_3$ (3); $m = 2$, $X = SO_4$ (5)

Fig-6. Structural formulas proposed for complexes (1)-(6).

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