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Original scientific paper

## New complexes of Co(II), Ni(II) and Cu(II) with the Schiff base 2,2'-[(3,3'-dimethyl[1,1'-biphenyl]-4,4'-diylbis- (nitrilomethylidene)]bis[6-methoxyphenol]

IONELA ALAN<sup>1\*</sup>, ANGELA KRIZA<sup>1</sup>, OLGUTA DRACEA<sup>2</sup> and NICOLAE STANICA<sup>3</sup>

<sup>1</sup> University of Bucharest, Faculty of Chemistry, Inorganic Chemistry Department, 23 Dumbrova Rosie Street, 020462 Bucharest, Romania, <sup>2</sup> "Cantacuzino" National Institute for Research in Microbiology and Immunology, 103 Spl. Independentei, 050096 Bucharest, Romania and <sup>3</sup> Ilie Murgulescu Institute of Physical Chemistry, Romanian Academy, 202 Spl. Independentei, 77208 Bucharest, Romania

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**Abstract:** The new 2,2'-[(3,3'-dimethyl[1,1'-biphenyl]-4,4'-diylbis(nitrilomethylidene)]bis[6-methoxyphenol] (H<sub>2</sub>L) Schiff base and its complexes with Co(II), Ni(II) and Cu(II) of the type [M(HL)Cl(H<sub>2</sub>O)] (M = Co(II) or Cu(II)), [M<sub>2</sub>L(H<sub>2</sub>O)<sub>4</sub>]X<sub>2</sub> (M = Co(II), X = ClO<sub>4</sub> and M = Cu(II), X = NO<sub>3</sub>) and [M<sub>2</sub>L(CH<sub>3</sub>COO)<sub>2</sub>] (M=Co(II), Ni(II), Cu(II)) were synthesised. The ligand and complexes were characterized by elemental analysis, conductivity measurements, magnetic moments at room temperature, IR, NMR, UV–Vis–NIR, EPR spectra and thermogravimetric analysis. Mole ratios of 1:1 or 1:2 between the ligand and metal were determined from the elemental analysis results. Except for the perchlorate complex that behaved as an electrolyte, the other complexes are non-electrolytes. The spectral data suggested tetrahedral, pseudo-tetrahedral or square-planar stereochemistry, which was confirmed by the magnetic behaviour of complexes. The antimicrobial tests indicated fungicide effects for both the ligand and the complexes.

**Keywords:** Schiff base; *o*-tolidine; *o*-vanillin; EPR spectra; antimicrobial activity.

### INTRODUCTION

Complexes with Schiff bases derived from aromatic diamines and aromatic aldehydes have been intensively studied due to their possible application in various fields.<sup>1–6</sup>

These complexes are also interesting as models for enzymes involved in several biochemical processes.<sup>7,8</sup> Many Schiff bases of this type and their com-

\* Corresponding author. E-mail: ionelaalan@yahoo.com  
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plexes with various metal ions were found to exhibit fungicidal, bactericidal, antimalarial and anticancer properties.<sup>9,10</sup>

Following previous research,<sup>11</sup> in this paper, data is presented concerning the synthesis and characterisation of Co(II), Ni(II), Cu(II) complexes with a new Schiff base obtained through *o*-tolidine (3,3'-dimethylbenzidine) condensation with *o*-vanillin (2-hydroxy-3-methoxybenzaldehyde) (Fig. 1). It is noteworthy that only a few papers with Schiff bases derived from *o*-tolidine are mentioned in the literature.<sup>12,13</sup>

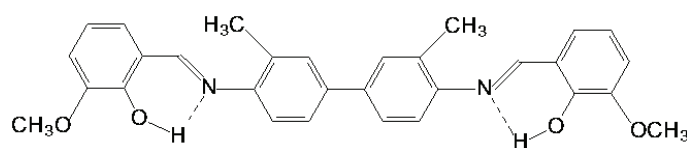


Fig. 1. Structure of the ligand ( $H_2L$ ).

## EXPERIMENTAL

### Materials

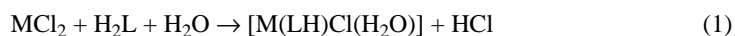
Metal salts (Sigma–Aldrich), *o*-vanillin (Merck), *o*-tolidine (ICN Biomedicals) and triethylamine (Fluka) were used in the syntheses.

### Synthesis of the ligand

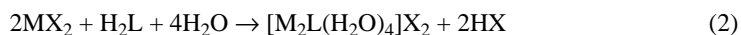
The 2,2'-[(3,3'-dimethyl[1,1'-biphenyl]-4,4'-diylbis(nitrolomethyldiene)]bis[6-methoxyphenol] ( $H_2L$ ) Schiff base was obtained by mixing an ethanolic solution of *o*-tolidine (0.01 mol in 50 mL ethanol) with an ethanolic solution of *o*-vanillin (0.02 mol in 50 mL ethanol), in the presence of acetic acid. The mixture was refluxed for 2 h. After cooling, the obtained precipitate was filtered, washed with and recrystallized from tetrahydrofuran. The yield was 72 %. The reddish–orange crystalline product was stable at room temperature and was non-hygroscopic.

### Synthesis of the complexes

A solution of ligand ( $H_2L$ ) (0.01 mol) in 50 mL tetrahydrofuran was mixed with an equal volume of an ethanolic solution containing 0.01 mol Co(II) or Cu(II) chloride to obtain complexes **1** and **5** according to the reaction:



Complexes **2** and **6** were synthesised using a solution of 0.01 mol ligand in 50 mL tetrahydrofuran and either 50 mL of an ethanolic solution of Co(II) perchlorate (0.02 mol) or of Cu(II) nitrate (0.02 mol), respectively, according to:



The complexes **3**, **4** and **7** were synthesised using 50 mL of a tetrahydrofuran solution of ligand (0.01 mol) and a solution of 0.02 mol of Co(II), Ni(II) or Cu(II) acetate, respectively, in 50 mL of ethanol, according to:



In all cases, the reaction mixture was refluxed at least 4 h and afterwards concentrated to half of the initial volume. The obtained precipitate was filtered, washed, and dried in a

vacuum desiccator over anhydrous  $\text{CaCl}_2$ . The obtained complexes were solid, coloured, stable under atmospheric conditions and non-hygroscopic.

#### Techniques

The contents of the metal were determined volumetrically by complexometric methods for Ni(II) and Co(II) and by an iodometric method for Cu(II). The contents of N, C and H were measured with an ECS-40-10-Costeh microdosimeter, following drying at 105 °C. The melting points were determined using a Stuart Scientific SMP3 apparatus and no correction was applied. The molar conductivities were determined in acetone (**1**, **2** and **4**), ethanol (**3**) or DMF (**5** and **6**) ( $10^{-3}$  M) at room temperature using a Consort C533 conductometer. The IR spectra were recorded in KBr pellets, using a BioRad FTS-135 Fourier transform spectrometer in the range 4000–400  $\text{cm}^{-1}$ . The electronic spectra were recorded on a Jasco V670 spectrophotometer, by the diffuse reflectance technique. The NMR spectra for the ligand were recorded in  $\text{DMSO}-d_6$  on a Varian Gemini 300BB instrument operating at 300 MHz for  $^1\text{H}$  and 75 MHz for  $^{13}\text{C}$ . The magnetic susceptibilities were determined by the Faraday method and were corrected for atomic diamagnetism. The EPR spectra were recorded using a MiniScope MS200 type spectrometer. This was operated in the X-band (9.3 to 9.6 GHz) and it was provided with a rectangular  $\text{TE}_{102}$  resonance cavity. The thermogravimetric analysis was realised using a current Labsys 1200 Setaram derivatograph under a synthetic air flow of  $16.67 \text{ cm}^3 \text{ min}^{-1}$  at a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$ . The microbial strains, isolated from various pathological products, were identified using a VITEK I automatic system. The VITEK cards for identifying and testing the antibiotic sensitivity (GNS-522) were inoculated and incubated according to the directions of the producer. The results were interpreted using the AMS R09.1 program.

#### Antimicrobial activity

The complexes **1–7** were tested to determine their *in vitro* antimicrobial activity using qualitative and quantitative analysis methods.<sup>14</sup> Reference microbial species were used for the tests. These included: the Gram-positive strain *Staphylococcus aureus* 1263, Gram-negative bacteria (*Klebsiella pneumoniae* 1204, *Escherichia coli* IC 13147 and *Pseudomonas aeruginosa* 1246) and the fungal strain *Candida albicans* LS, isolated from various clinical samples. The quality control was performed by the simultaneous testing of the antimicrobial activity on the above-mentioned strains and on the reference strains: *Klebsiella pneumoniae* IC 13420, *E. coli* IC 13529, *S. aureus* IC 13204, *P. aeruginosa* IC 13202 and *C. albicans* IC 249.

The qualitative screening of the action of the synthesized compounds on the bacteria and fungi was realised by two diffusion methods, adapted to the diffusimetric method. The first method consisted of impregnating filter paper disks with a solution a compound in DMSO ( $1000 \mu\text{g mL}^{-1}$ ). The second method consisted of the qualitative determination of the antimicrobial effect of a compound spot distributed on a microbial culture-seeded medium.

The used solvent dimethyl sulphoxide (DMSO) was also tested using the same two methods in order to emphasize the potential antimicrobial activity.

For the quantitative determination of the antimicrobial activity of the ligand and of the complexes, the binary microdilution method in a liquid medium was applied (yeast extract–peptone–glycerol (YPG) medium for the fungi), using 96-well plates, in order to determine the minimal inhibitory concentration (MIC) values. In this manner, binary serial dilutions of stock solutions of the test compounds in DMSO ( $1000 \mu\text{g mL}^{-1}$ ) and of a fluconazole solution (concentration  $128 \mu\text{g mL}^{-1}$ ), as a control solution for the fungi, were obtained.

For the qualitative and quantitative screening, the plates were incubated for 24 h at 37 °C for the bacteria and for 48 h at 28 °C for the fungi. The results were obtained by macroscopic observation.

#### RESULTS AND DISCUSSION

The tetradentate ligand 2,2'-[(3,3'-dimethyl[1,1'-biphenyl]-4,4'-diylbis(nitri-lomethylidene)]bis[6-methoxyphenol] (H<sub>2</sub>L), having a divergent ON–NO donor atom set, was synthesized by 1:2 condensation of *o*-tolidine with *o*-vanillin in ethanol. The analytic and spectral data for H<sub>2</sub>L are presented in the Supplementary material to this paper.

The seven complexes of the prepared ligand with Co, Ni and Cu are given in Table I, together with their solubilities in several organic solvents. The complexes 1–7 were characterised based on chemical and thermal analyses, IR, UV–Vis–NIR and EPR spectral data, as well as magnetic moments at room temperature and molar conductivity.

TABLE I. The prepared complexes 1–7 and their solubility in some organic solvents

Compound	No.	Soluble in
H <sub>2</sub> L		THF, DMSO, CH <sub>2</sub> Cl <sub>2</sub>
[Co(LH)Cl(H <sub>2</sub> O)]	1	Acetone, DMSO, CH <sub>2</sub> Cl <sub>2</sub>
[Co <sub>2</sub> L(H <sub>2</sub> O) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	2	Acetone, DMSO, CH <sub>2</sub> Cl <sub>2</sub>
[Co <sub>2</sub> L(CH <sub>3</sub> COO) <sub>2</sub> ]	3	Acetone, DMSO, EtOH
[Ni <sub>2</sub> L(CH <sub>3</sub> COO) <sub>2</sub> ]	4	Acetone, DMF, DMSO
[Cu(HL)Cl(H <sub>2</sub> O)]	5	DMF, DMSO
[Cu <sub>2</sub> L(H <sub>2</sub> O) <sub>4</sub> ](NO <sub>3</sub> ) <sub>2</sub>	6	DMF, DMSO
[Cu <sub>2</sub> L(CH <sub>3</sub> COO) <sub>2</sub> ]·H <sub>2</sub> O	7	DMSO

The physical, analytical and spectral data of the complexes are given in the Supplementary material to this paper.

#### *NMR spectra of the ligand*

The formation of the Schiff base was confirmed by the <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of the ligand. In the <sup>1</sup>H-NMR spectrum, signals for methylene protons are present at 2.42 (CH<sub>3</sub>) and 3.83 ppm (OCH<sub>3</sub>) and the aromatic protons appear between 7.48 and 7.70 ppm for the fragment derived from the amine. The aromatic protons from the fragment derived from the 3-methoxysalicylaldehyde generate a doublet signal in the range of 6.93 and 7.26 ppm, while the signal of the proton from the azomethine group appears as singlet at 8.96 ppm. In addition, the <sup>13</sup>C-NMR spectrum contains signals which are characteristic for carbon atoms derived from both the amine and the aromatic aldehyde, noting that the characteristic signal for the azomethinic carbon appears at 162.87 ppm. The signals located at 18.03 and 55.91 ppm in the <sup>13</sup>C-NMR spectrum correspond to the carbon atoms from methyl group of the amine and to the methoxy group of the 3-methoxysalicylaldehyde, respectively.

### IR spectra

The most important bands in the IR spectra of the ligand ( $H_2L$ ) and complexes **1–7** are presented in the Supplementary material to this paper. The Schiff base spectrum exhibits two very intense bands, one at  $1615\text{ cm}^{-1}$ , which can be attributed to the stretching vibration of the azomethine group  $\nu(C=N)$ , and another one at  $1253\text{ cm}^{-1}$ , corresponding to the phenolic group  $\nu(C-O)$ .<sup>15</sup> The bands at  $3439$  and  $2780\text{ cm}^{-1}$  may be due to the vibration of intermolecular hydrogen bonds.<sup>15,16</sup>

The stretching frequencies  $\nu(C=N)$  and  $\nu(C-O)$  show significant shifts towards lower values within the IR spectra of complexes **1–7** compared to the corresponding band in the spectrum of  $H_2L$ . This means that both the azomethine nitrogen and the phenolic oxygen atoms are involved in the coordination.<sup>17</sup>

In the spectra of complexes **1** and **5**, the bands corresponding to the azomethine group appear split into two intense bands, one shifted to higher values and one to lower values, as compared to the corresponding band of the ligand, which suggests that the two groups are not identical within the complexes. Moreover, in the spectra of **1** and **5**, a band at about  $2780\text{ cm}^{-1}$ , which is also present in the spectrum of the ligand, appears, which is probably due to the existence of intermolecular hydrogen bonds. However, this band is absent in the spectra of complexes **2–4**, **6** and **7**. These features of the IR spectra of the complexes **1** and **5**, supported by the elemental analysis data, suggest that only one azomethine group is involved in coordination.<sup>12,16</sup>

In the spectrum of complex **2**, a very intense band at  $1102\text{ cm}^{-1}$  ( $\nu_3$ ) and a weak one at  $623\text{ cm}^{-1}$  ( $\nu_4$ ) indicate that the perchlorate ion is present as a free ion.<sup>18</sup> For complexes **3**, **4** and **7**, the  $\Delta\nu = \nu_{\text{asym}}(\text{COO}) - \nu_{\text{sym}}(\text{COO})$  values are  $107$ ,  $113$  and  $101\text{ cm}^{-1}$ , respectively. According to the literature,<sup>15,19</sup> values lower than  $164\text{ cm}^{-1}$  suggest that the acetate group is coordinated in a bidentate form. In the spectrum of complex **6**, a very intense band appears at  $1384\text{ cm}^{-1}$ , which can be assigned to the  $\nu_3$  vibration mode of nitrate present as a free ion.<sup>15,20</sup>

In the spectra of all complexes, the broader bands that appear in the region  $3330\text{--}3450\text{ cm}^{-1}$  can be assigned to  $\nu(\text{OH})$  for water molecules. The presence of some water molecules coordinated in complexes **1**, **2**, **5** and **6** is supported by the presence of a new band in the range of  $700\text{--}900\text{ cm}^{-1}$ , which can be assigned to  $\delta_w(\text{H}_2\text{O})$ .<sup>21</sup> New bands of low intensity in the range  $400\text{--}600\text{ cm}^{-1}$  can be assigned to the stretching vibrations  $\nu(\text{M-O})$  and  $\nu(\text{M-N})$ .<sup>22</sup>

### UV-Vis-NIR spectra and magnetic moments

The UV-Vis-NIR spectral data for the ligand and the complexes are given in the Supplementary material to this paper. The electronic spectrum of the ligand exhibited three bands at  $42,500$ ,  $25,000$  and  $19,800\text{ cm}^{-1}$ , which can be

assigned to  $\pi \rightarrow \pi^*$  intraligand transitions.<sup>23</sup> These bands also appeared in the spectra of the complexes.

The spectrum of complex **1**, in addition to a  $\pi \rightarrow \pi^*$  transition at 25,970  $\text{cm}^{-1}$ , showed bands at 15,380 and at 8,130, 7,220  $\text{cm}^{-1}$ , which can be assigned to d–d transitions  ${}^4A_2 \rightarrow {}^4T_1(\text{P})$  and  ${}^4A_2 \rightarrow {}^4T_1(\text{F})$ , respectively, for Co(II) in a tetrahedral environment. The spectrum of complex **2** also contained a  $\pi \rightarrow \pi^*$  transition at 25,970  $\text{cm}^{-1}$  with further bands at 17,240 and 13,700 and at 8,700 and 7,170  $\text{cm}^{-1}$  resulting from d–d transitions. The corresponding transitions for complex **3** appeared at 20,000, 18,520, 10,580 and 7,200  $\text{cm}^{-1}$ , respectively. It should be mentioned that the bands occurring in the visible and infrared regions, and assigned to the spin-allowed transitions for a  $3d^7$  ion were split into two components. Due to the different nature of donor atoms that generate a distorted tetrahedral stereochemistry, a decrease of the symmetry and an increase in the  ${}^4T$  levels degeneracy occurs. The values of spectral parameters  $10Dq$ ,  $B$  and  $\beta$  for the Co complexes, presented in Table II, are in agreement with a pseudo-tetrahedral stereochemistry. It can be noticed that the values of the spectral parameters for the cobalt complexes are similar. The values of the magnetic moments of Co(II) complexes, presented in Table II, were between 4.11 and 4.84  $\mu_B$ , which are characteristic for Co(II) with a pseudo-tetrahedral geometry.<sup>23,24</sup>

TABLE II. Crystal field parameters and magnetic moments for complexes **1–4**

Compound	Crystal field parameters			$\mu_{\text{eff}} / \mu_B$
	$10Dq / \text{cm}^{-1}$	$B$	$\beta$	
[Co(HL)Cl(H <sub>2</sub> O)] ( <b>1</b> )	4494	734	0.75	4.11
[Co <sub>2</sub> L(H <sub>2</sub> O) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ( <b>2</b> )	4720	722	0.74	4.57
[Co <sub>2</sub> L(CH <sub>3</sub> COO) <sub>2</sub> ] ( <b>3</b> )	4589	853	0.87	4.84
[Ni <sub>2</sub> L(CH <sub>3</sub> COO) <sub>2</sub> ] ( <b>4</b> )	–	–	–	Dia.

For complex **4**, in addition to the  $\pi \rightarrow \pi^*$  intraligand transition at 35,710  $\text{cm}^{-1}$ , the two bands at 19,230 and 15,750  $\text{cm}^{-1}$  can be assigned to the  ${}^1A_{1g} \rightarrow {}^1B_{1g}$  and  ${}^1A_{1g} \rightarrow {}^1B_{2g}$  transitions, respectively. This spectrum suggests the presence of a square-planar stereochemistry for the Ni(II) ion, which was confirmed by the diamagnetic behaviour of this compound.<sup>23,25</sup>

The spectra of the Cu(II) complexes **5–7** showed a  $\pi \rightarrow \pi^*$  transition at 25,640, 25,640 and 25,970  $\text{cm}^{-1}$ , respectively, and in the visible range, a wide and asymmetric band centred at 12,660, 14,285 and 13,245  $\text{cm}^{-1}$ , respectively, corresponding to the  $d_{xy} \rightarrow d_{z^2-x^2-y^2}$  transition. In the case of compounds **6** and **7**, a shoulder appears at lower wavenumbers corresponding to the  $d_{xy} \rightarrow d_{xz,yz}$  transition. The presence of absorption maxima at lower energy indicates a large number of oxygen atoms in the donor atoms set together with nitrogen atoms, for a pseudo-tetrahedral stereochemistry.<sup>26</sup> The magnetic moment values for com-

plexes **5–7** were, respectively, 2.12, 1.97 and 2.03  $\mu_B$ , which are characteristic of metal ions with a  $d^9$  configuration and one unpaired electron.<sup>23,27</sup>

#### EPR spectra

The EPR spectra of the Cu complexes as powders were recorded both at room temperature (293 K) and at liquid nitrogen temperature (77 K). The signals obtained did not show any significant differences at these temperatures; hence, the geometry around the copper ion was not affected by cooling. The EPR signals of these samples measured at room temperature are specific for Cu(II) ions with a tetrahedral or pseudo-tetrahedral geometry.

The signal of sample **5** was wide (about 300 G) and centred at  $g_0 = 2.117$  and on cooling, its width decreased to 270 G and  $g_0 = 2.123$ <sup>28</sup> (Fig. 2).

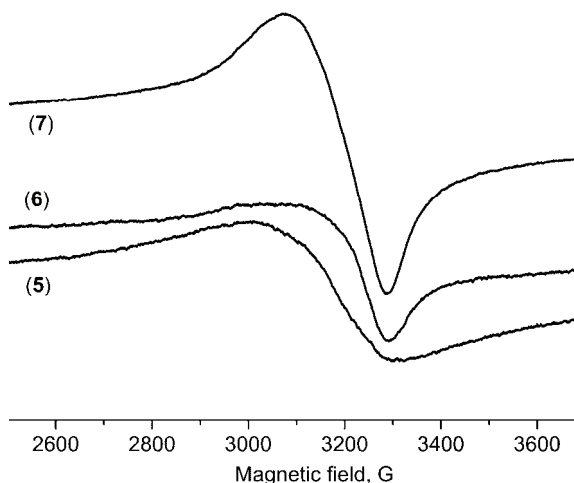


Fig. 2. EPR spectra of complexes **5–7** powders.

Complexes **6** and **7** exhibited an asymmetric signal (Fig. 2), significantly expanded in the lower field area, which indicates axial distortion with a tendency of resolving the hyperfine structure, due to the interaction of the unpaired electron with the nuclear spin of copper.

This tendency, determined by the nuclear electron-spin interaction, was more noticeable in the spectrum of sample **6**, especially at 77 K, when the signal was more intense, but the split value could not be determined (probably  $A_{//} \approx 150$  G). The asymmetry was also well emphasized in the derivative signals ( $d^2$  represents the second derivative of the absorption curve).<sup>29</sup> The  $g_0$  parameter, corresponding to the spectrum intersection with the baseline, had a value ( $2.102 \pm 0.01$ ) for **6** and ( $2.092 \pm 0.001$ ) for **7**, both at room temperature and at 77 K (Fig. 3). The peak widths were within the range 200 to 250 G.<sup>30,31</sup>

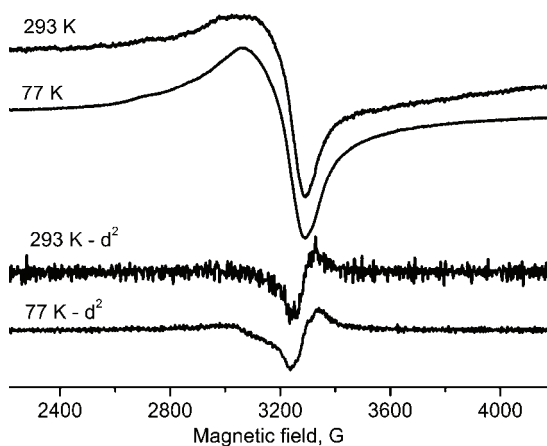


Fig. 3. The EPR spectra of the sample **6** powder registered at 293 K and 77 K with the signal derivative ( $d^2$ ).

#### Thermal analysis

Thermal decomposition the complexes **1** and **7** under air was studied in order to determine the presence and nature of water molecules. The thermogravimetric curves show two major decomposition stages (Table III).

TABLE III. Thermal analysis data for the complexes **1** and **7**

Compound	Temperature range °C	Mass loss, %		Processes
		Exp.	Calcd.	
[Co(HL)Cl(H <sub>2</sub> O)] ( <b>1</b> )	100–180	3.40	3.08	Dehydration
	180–590	86.13	86.15	Oxidative degradation of the ligand
[Cu <sub>2</sub> L(CH <sub>3</sub> COO) <sub>2</sub> ] $\cdot$ H <sub>2</sub> O ( <b>7</b> )	590–800	12.47	12.77	Residue Co <sub>3</sub> O <sub>4</sub>
	50–150	2.65	2.91	Dehydration
	150–490	86.64	85.98	Oxidative degradation of the ligand
	490–800	10.71	11.11	Residue CuO

The first stage corresponds to the elimination of crystallisation water and of coordinated water.

The second stage includes all the processes comprising the detachment of the ligand and of other groups from the metal ion, the removal of chlorine and ligand oxidation, finally resulting in the formation of the metal oxide as a residue.<sup>32</sup>

Based on these data, the water molecule can be considered as coordinated in complex **1** while it is crystallization water in complex **7**.<sup>33</sup>

#### Antimicrobial activity

The results showed that the ligand and the complexes have no antibacterial activity, but they are fungicidal. The ligand and complexes **2**, **3**, **6** and **7** exhibited the best inhibitory activity over the *Candida albicans* species. Therefore, the



quantitative antimicrobial activity ( $MIC$  values in  $\mu\text{g mL}^{-1}$ ) for the most active compounds were determined by measuring the diameters of the inhibition zone generated by the compounds on both the standard and clinically isolated multi-drug resistant fungal strains.<sup>34</sup> The solvent (DMSO) had no antimicrobial activity, this fact representing a great advantage in the testing the complexes and the ligand, which are insoluble in water.<sup>35</sup>

The ligand and complexes **2** and **3** had a pronounced ability to destroy the fungi ( $MIC = 62.5 \mu\text{g mL}^{-1}$ ), while complexes **6** and **7** exhibited poor fungicidal activity ( $MIC > 500 \mu\text{g mL}^{-1}$ ). The  $MIC$  values of the Co(II) complexes were lower than those of the Cu(II) complexes, which suggests an influence of the metal ion on the capacity to inhibit the growth of the fungi.

#### CONCLUSIONS

The 2,2'-[(3,3'-dimethyl[1,1'-biphenyl]-4,4'-diylbis(nitrilomethylidene)]bis-[6-methoxyphenol] ( $H_2L$ ) ligand containing two donor centres was synthesised and characterised by spectral data. The ligand has tetradentate dianionic behaviour ( $N_2O_2$ ) in all the complexes, except for the Co(II) and Cu(II) chloride complexes, where the ligand behaves as a bidentate monoanionic species (NO), according to the IR data. The ligand is able to coordinate the metal ions in a tetrahedral, pseudo-tetrahedral or square planar geometry, as indicated by the electronic, EPR and magnetic data. The antimicrobial activity of the complexes was tested and it was found that the ligand and its complexes have fungicidal activity. The structural formulas suggested for the complexes **1–7** are presented in Figs. 4–6, respectively.<sup>36</sup>

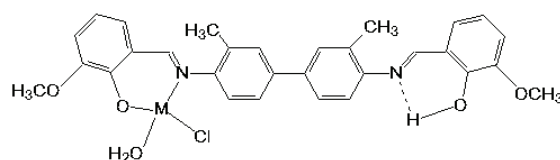


Fig. 4. Structural formulas proposed for the complexes  $[M(HL)Cl(H_2O)]$ , where  $M = \text{Co(II)}$  (**1**) and  $\text{Cu(II)}$  (**5**).

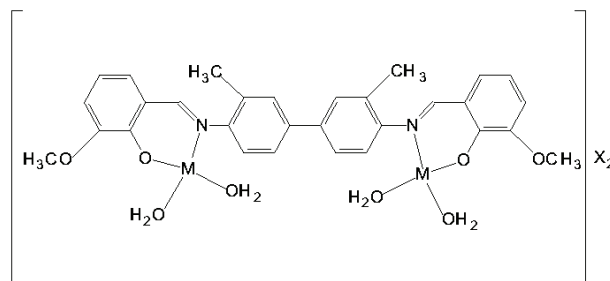


Fig. 5. Structural formulas proposed for the complexes  $[M_2L(H_2O)_4]X_2$ , where  $M = \text{Co(II)}$ ,  $X = \text{ClO}_4$  (**2**) and  $M = \text{Cu(II)}$ ,  $X = \text{NO}_3$  (**6**).

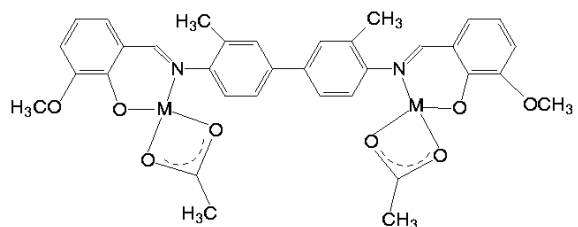


Fig. 6. Structural formulas proposed for the complexes  $[M_2L(CH_3COO)_2]$ , where  $M = Co(II)$  (3),  $Ni(II)$  (4) and  $Cu(II)$  (7).

#### SUPPLEMENTARY MATERIAL

Physical, analytic and spectral data for the ligand and complexes are available electronically from <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

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#### ИЗВОД

#### НОВИ КОМПЛЕКСИ $Co(II)$ , $Ni(II)$ И $Cu(II)$ СА ШИФОВОМ БАЗОМ 2,2'-[(3,3'-ДИМЕТИЛ[1,1'-БИФЕНИЛ]-4,4'-ДИИЛБИС(НИТРИЛОМЕТИЛИДИН)]-БИС[6-МЕТОКСИФЕНОЛ]

IONELA ALAN<sup>1</sup>, ANGELA KRIZA<sup>1</sup>, OLGUTA DRACEA<sup>2</sup> И NICOLAE STANICA<sup>3</sup>

<sup>1</sup>University of Bucharest, Faculty of Chemistry, Inorganic Chemistry Department, 23 Dumbrava Rosie Street, 020462 Bucharest, Romania, <sup>2</sup>"Cantacuzino" National Institute for Research in Microbiology and Immunology, 103 Spl. Independentei, 050096 Bucharest, Romania и <sup>3</sup>Ilie Murgulescu, Institute of Physical Chemistry, Romanian Academy, 202 Spl. Independentei, 77208 Bucharest, Romania

У овом раду, синтетисана је Шифова база, 2,2'-[(3,3'-диметил[1,1'-бифенил]-4,4'-диилбис(нитрилометилидин)]бис[6-метоксифенол] ( $H_2L$ ), као и одговарајући комплекси  $Co(II)$ ,  $Ni(II)$  или  $Cu(II)$  опште формуле  $[M(HL)Cl(H_2O)]$  ( $M = Co(II)$  и  $Cu(II)$ ),  $[M_2L(H_2O)_4]X_2$  ( $M = Co(II)$ ,  $X = ClO_4$  и  $M = Cu(II)$ ,  $X = NO_3$ ) и  $[M_2L(CH_3COO)_2]$  ( $M = Co(II)$ ,  $Ni(II)$  или  $Cu(II)$ ). Поред елементалне микроанализе, мерења проводљивости и магнетног момента на собној температури, за карактеризацију лиганда и комплекса су употребљене IR, NMR, UV-Vis-NIR и EPR спектроскопске методе, као и термогравиметријска анализа. Применом елементалне микроанализе одређен је у испитиваним комплексима 1:1 и 1:2 молски однос између лиганда и јона метала. Комплекс кобалта(II) са перхлоратом као контра-анијоном је електролит, док су остали испитивани комплекси неелектролити. На основу спектроскопских података, претпостављена је тетраедарска, псеудо-тетраедарска и квадратно-планарна геометрија синтетисаних комплекса. Антимикробна испитивања су показала да лиганд и одговарајући комплекси имају фунгицидну активност.

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