

# Synthesis and Characterization of Cu(II), Ni(II) and Co(II) Binuclear Complexes with a new Schiff base (1,3-bis[ortho-(2-carboxy-phenyliminomethyl)-phenoxy]propane)

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A new Schiff base,  $H_2L$  ( $C_{31}H_{26}O_6N_2$ ), was synthesized starting from a dialdehyde [1,3-bis(2'-formylphenyl)-1,3-dioxapropane] and 2-aminobenzoic acid. Corresponding metal complexes with Cu(II), Ni(II) and Co(II) were also prepared. The structure of the Schiff base was characterized using spectroscopic data and by elemental analysis. The complexes of  $[M_2L(OH)_2(H_2O)_4]$  type, where  $M = Cu(II), Ni(II)$  or  $Co(II)$ , were characterized using the data obtained from elemental analyses, molar conductance, IR and electronic spectra, magnetic susceptibility measurements and thermal analysis. These studies support the binuclear formulations of the complexes, of  $M(II) : L$  (2 : 1) type.

**Keywords:** dialdehyde, Schiff base, binuclear complexes

A large number of Schiff bases and their complexes has been studied for their interesting and important properties, e.g. biological activity [1], catalytic activity in hydrogenation of olefins [2] and transfer of an amino group [3], photochromic properties [4], complexing ability towards some toxic metals [5].

Several authors have studied in their papers the biological properties of the Schiff base metal complexes compounds. For example, the Cu(II) complexes with two Schiff bases derived from 4-amino-antipyrine and 2-thiophencarbox-aldehyde and respectively 5-methyl-2-thiophencarbox-aldehyde, were found to be active against the strains of *Staphylococcus aureus* and *Escherichia coli* [1]. The Schiff base, obtained from 2-thiophene carboxaldehyde and 2-aminobenzoic acid and its metal complexes, show antibacterial activity [6]. Salicylidene anthranilic acid possesses antiulcer activity and the complexation with copper shows an increase in antiulcer activity [7].

Thus, the aim of the present study was to synthesize and characterize Cu(II), Ni(II) and Co(II) metal complexes with newly synthesized Schiff base derived from 1,3-bis(2'-formylphenyl)-1,3-dioxapropane (named also 2,2'-(propane-1,3-diylidioxy)dibenzaldehyde) and 2-aminobenzoic acid. The evaluation of the supposed antibacterial activity of these compounds is in progress and antibacterial test results will be presented in future work.

## Experimental part

### Reagents

The dialdehyde, 1,3-bis(2'-formylphenyl)-1,3-dioxapropane, used in the synthesis was prepared according to a procedure described in the literature [8] by the reaction of salicylaldehyde and 1,3-dibromopropane in ethanol and in the presence of a diluted NaOH aqueous solution, by refluxing the reaction mixture for 72 h. All other reagents used were of analytical grade.

### Physico-chemical measurements

The elemental analysis (C, H, N) was carried out with a Costech 2002 analyzer. The metal contents were determined by atomic absorption spectrophotometry using a SOLAAR AA System. The <sup>1</sup>H-NMR spectra were obtained at 400 MHz with INOVA-400 instrument using solutions in DMSO-d<sub>6</sub> and tetramethylsilane as internal standard.

Infrared spectra (in KBr pellets) were recorded on a Bruker Optics FT-IR spectrophotometer in the 4000-400 cm<sup>-1</sup> range. UV-Vis diffuse reflectance spectra were measured on a Thermo UV-Vis Evolution 600 spectrophotometer in the range 200-800 nm. The magnetic measurements on solid samples were performed at the room temperature using the Faraday method with Mohr salt as a standard. The diamagnetic corrections were made by Pascal's constant. Molar conductance measurements were conducted using an inoLab conductometer. Thermal analysis measurements (TG, DTG, DTA and DSC) of the new Schiff base 1,3-bis[ortho-(2-carboxy-phenyliminomethyl)-phenoxy]propane and of metal (II) complexes were carried out in dynamic nitrogen atmosphere (150 mL min<sup>-1</sup>), under non-isothermal linear regimes. A horizontal "Diamond" Differential/Thermogravimetric Analyzer from Perkin Elmer Instruments was used during the measurements. Samples from 0.5 to 1.4 mg contained in alumina crucibles were heated in the temperature range of 20-1000 °C, each time with the heating rate of 4°C min<sup>-1</sup>. For the Schiff base, an additional measurement was performed in dynamic air atmosphere, keeping the same experimental conditions described above. The melting points were measured in glass capillary tubes on Gallenkamp/Sanyo apparatus.

### Preparation of the Schiff base

A solution of 1,3-bis(2'-formylphenyl)-1,3-dioxapropane (1.7 g, 6 mmol) in 20 mL anhydrous benzene was added, dropwise, to a warm solution of 2-aminobenzoic acid

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(1.72 g, 12.55 mmol) in 40 mL anhydrous benzene. The reaction mixture was refluxed for 5 h using Dean-Stark apparatus. The resulting product was filtered off, washed with hot benzene, petroleum ether and dried in air. An amount of 2.88 g pure yellow Schiff base was obtained at a very good yield of 92%.

#### Preparation of the metal complexes

The complexes were prepared using two methods.

According to the first method the Schiff base was prepared "in situ" from the precursors as it follows: a solution of 2-aminobenzoic acid (anthranilic acid) (0.27 g, 2 mmol) in absolute ethanol (5 mL) was added to a solution of dialdehyde [1,3-bis(2'-formylphenyl)-1,3-dioxapropane] (0.28 g, 1 mmol) in absolute ethanol (5 mL). The resulting mixture was refluxed for 2 h and then a methanolic solution 1M of NaOH (2 mL) was added. The reflux and stirring processes were continued for 10-15 min. In the next step the metal salts ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  or  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ) (2 mmol) in absolute ethanol (5 mL) were added to the ligand solution under continuous stirring. The reaction mixture was further stirred under reflux for another 4 h and left standing overnight. The obtained colored product was separated by filtration, washed with distilled water, cooled ethanol (0°C), ethyl ether, dried in air and stored in a desiccator over anhydrous  $\text{CaCl}_2$  under vacuum. A medium yield of ~ 31% was obtained.

According to the second method a solution of NaOH (0.064 g, 1.15 mmol) in absolute ethanol (3 mL) was added (by stirring) to a warm solution (40-60°C) of the Schiff base (0.3 g, 0.574 mmol) in absolute ethanol (25 mL). The mixture was further stirred for another 5-10 min. A warm solution of the metal salts ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  or  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ) (1.15 mmol) in absolute ethanol (10 mL) was added, dropwise, to the ligand solution (by stirring) and the reaction mixture was further stirred under reflux for 2 h. The reaction mixture was left still overnight at the room temperature. The obtained colored product was removed by filtration, washed with warm distilled water, hot methanol, ethyl ether, dried in air and stored in a desiccator over anhydrous  $\text{CaCl}_2$  under vacuum.

Comparing with the first procedure, the second method conducted to a higher value of the medium yield (~ 42%).

#### Results and discussions

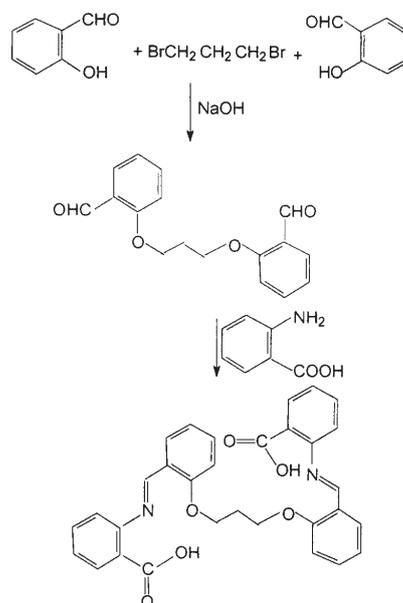
The Schiff base (1,3-bis[*ortho*-(2-carboxy-phenyliminomethyl)-phenoxy]propane) is very unstable in the presence of water and therefore the synthesis was performed from 1,3-bis(2'-formylphenyl)-1,3-dioxapropane and 2-aminobenzoic acid in anhydrous benzene, under reflux. A Dean-Stark apparatus was used for the continuous removal of the water from the reaction mixture. The Schiff base is soluble in warm ethanol, methanol, acetone, chloroform, DMF and DMSO. The dialdehyde used in the synthesis was prepared from salicylaldehyde and 1,3-dibromopropane according to a procedure described in the literature [8].

The reactions are presented in figure 1.

The structure of the new Schiff base was confirmed by the  $^1\text{H-NMR}$  spectroscopy:

$^1\text{H-NMR}$  (DMSO -  $d_6$ ,  $\delta$ , ppm): 2.22 (q, 2H,  $\text{CH}_2$ ), 4.24 (t, 4H,  $\text{CH}_2$ ), 6.93 (dd, 2H, ar), 7.36 (s, 2H, azomethine), 7.02-7.13 (m, 5H, ar), 7.42-7.50 (m, 4H, ar), 7.57-7.80 (m, 5H, ar).

The binuclear complexes of this Schiff base were obtained by two methods. The first method is a template reaction, consisting of refluxing the ethanolic solutions of the precursors of the Schiff base and the metal salts. The



1,3-bis[*ortho*-(2-carboxy-phenyliminomethyl)-phenoxy]propane

Fig. 1. The synthesis of the dialdehyde and the new Schiff bases

second method consists in refluxing of the ethanolic solutions of the isolated Schiff base sodium salt with the metal salts, in a 1 : 2 molar ratio. The compounds are soluble in warm DMF and DMSO and insoluble in water and in most organic solvents, thus suitable crystals for X-ray diffraction studies could not be obtained. All the resulting solid complexes were identified by elemental chemical and physico-chemical analysis. The results are presented in table 1. Elemental analysis results are in good agreement with the proposed composition of the complexes.

#### Molar conductance measurements

The molar conductance values of the complexes in DMF, solutions  $10^{-4}$  M, lie in the range of non-electrolytes [9] as shown in table 1. The three values suggest that no anions are present outside the coordination spheres.

#### Infrared spectra

The data of the IR spectra of the Schiff base ligand ( $\text{H}_2\text{L}$ ) and its complexes (fig. 2) are listed in table 2.

The IR spectra of the complexes are compared with those of the free ligand to determine the coordination sites that could be involved in chelation process. Upon comparison it was found that the  $\nu(\text{C}=\text{N})$  stretching vibration is observed in the free ligand at  $1616\text{ cm}^{-1}$ . This band is shifted to lower wavenumbers in the complexes, indicating the participation of the azomethine nitrogen in coordination (M-N) [10].

The  $\nu(\text{OH})(\text{carbox.})$  and  $\nu(\text{C}=\text{O})$  stretching vibrations are observed at  $3475$  and  $1716\text{ cm}^{-1}$ , respectively, for  $\text{H}_2\text{L}$ . The participation of the carboxylate O atom in the complexes formation was evidenced from the disappearance of  $\nu(\text{OH})(\text{carbox.})$  and  $\nu(\text{C}=\text{O})$  stretching vibrations in the spectra of the complexes. In the same way was justified the appearance of  $\nu_{\text{sym}}(\text{COO}^-)$  and  $\nu_{\text{asym}}(\text{COO}^-)$  vibrations in the spectra of the complexes in the regions  $1383\text{-}1408\text{ cm}^{-1}$  and  $1538\text{-}1554\text{ cm}^{-1}$ , respectively [11]. A medium band, due to  $\nu_{\text{sym}}(\text{Ar-O-C})$  stretching vibration and a weak band, due to  $\nu_{\text{asym}}(\text{Ar-O-C})$  stretching vibration are found at  $1245\text{ cm}^{-1}$  and  $1045\text{ cm}^{-1}$  respectively, in the spectra of  $\text{H}_2\text{L}$  ligand [12]. These bands were shifted to  $1232\text{-}1242\text{ cm}^{-1}$  and to  $1040\text{-}1096\text{ cm}^{-1}$  respectively in the metal complexes. These shifts refer to

Compound	Color	M.p. (°C)	Molecular Weight (g mol <sup>-1</sup> )	Found (calculated)%				$\Lambda_M^*$
				C	H	N	M	
H <sub>2</sub> L	yellow	159	522.2	71.67 (71.23)	5.31 (4.97)	5.50 (5.36)	-	-
[Cu <sub>2</sub> L(OH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]	olive green	>350	753.28	49.98 (49.38)	4.21 (4.51)	3.61 (3.71)	17.7 (16.87)	9.7
[Ni <sub>2</sub> L(OH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]	light green	>350	743.58	49.80 (50.02)	4.27 (4.57)	3.36 (3.76)	16.70 (15.78)	6.7
[Co <sub>2</sub> L(OH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]	pink	>350	744.06	50.59 (49.99)	4.26 (4.56)	3.33 (3.76)	16.80 (15.84)	6.8

\* Molar conductance values in ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>.

**Table 1**  
ANALYTICAL AND PHYSICAL  
DATA FOR THE SCHIFF BASE  
(H<sub>2</sub>L) AND ITS COMPLEXES

**Table 2**  
IMPORTANT INFRARED FREQUENCIES (cm<sup>-1</sup>) of H<sub>2</sub>L AND ITS METAL  
COMPLEXES

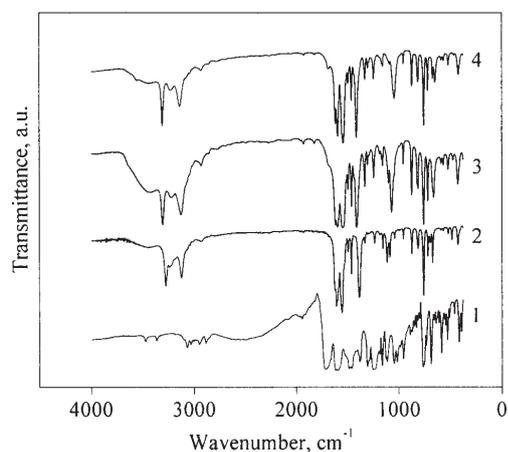


Fig. 2. IR spectra of the complex compounds and Schiff base ligand. 1- Schiff base ligand; 2- complex compound of Cu(II); 3- complex compound of Ni(II); 4- complex compound of Co(II).

H <sub>2</sub> L	[Cu <sub>2</sub> L(OH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]	[Ni <sub>2</sub> L(OH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]	[Co <sub>2</sub> L(OH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]	Assignments
3475 br	disappear	disappear	disappear	$\nu(\text{OH})_{\text{carboxylic}}$
-	3450 br	3440 br	3445 br	$\nu(\text{OH})_{\text{water}}$
-	3276 sh	3305 sh	3308 sh	$\nu(\text{OH})$
1716 m	disappear	disappear	disappear	$\nu(\text{C}=\text{O})_{\text{carboxylic}}$
1616 s	1606 m	1614 m	1614 m	$\nu(\text{C}=\text{N})$
-	1554 vs	1547 vs	1538 vs	$\nu_{\text{asym}}(\text{COO}^-)$
-	1383 m	1408 s	1408 m	$\nu_{\text{sym}}(\text{COO}^-)$
1245 m	1232 w	1241 w	1242 w	$\nu_{\text{asym}}(\text{Ar-O-C})$
1045 w	1084 w	1096 w	1040 w	$\nu_{\text{sym}}(\text{Ar-O-C})$
-	519 w	520 w	517 w	$\nu(\text{M-O})_{\text{carboxylic}}$
-	483 w	471 w	-	$\nu(\text{M-O})_{\text{Ar-O-C}}$
-	424 w	425 w	420 w	$\nu(\text{M-N})$

w = weak, m = medium, s = strong, vs = very strong, br = broad, sh = sharp

the coordination through Ar-O-C etheric O atom. New bands are found in the spectra of the complexes in the regions 471-483 cm<sup>-1</sup> (etheric O) and 515-520 cm<sup>-1</sup> (carboxylate O), which are assigned to  $\nu(\text{M-O})$  stretching vibrations for metal complexes [11,12]. The bands at 416-425 cm<sup>-1</sup> in metal complexes, have been assigned to  $\nu(\text{M-N})$  mode [11,12]. The appearance of  $\nu(\text{M-N})$  and  $\nu(\text{M-O})$  vibrations supports the involvement of nitrogen and oxygen

atoms in complexation with metal ions under investigation.

Therefore, from the IR spectra, it is concluded that H<sub>2</sub>L Schiff base binds to the metal ions through deprotonated carboxylate oxygen atom besides the azomethine nitrogen atom and Ar-O-R etheric oxygen atom.

The broad band, in the range 3440-3450 cm<sup>-1</sup>, is attributed to the existence of coordinated water molecules [13]. The sharp band at 3276-3308 cm<sup>-1</sup> is explained by the

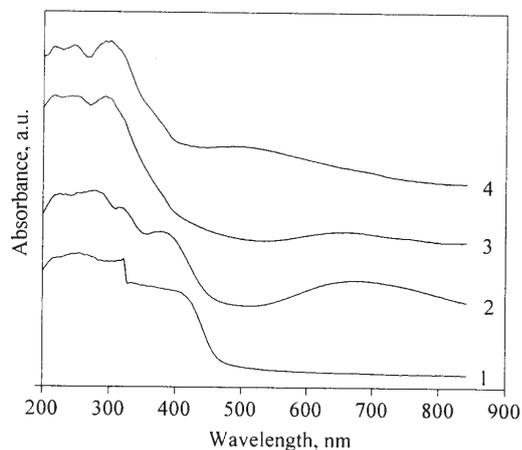


Fig. 3. UV-Vis spectra of the complex compounds and Schiff base ligand. 1-Schiff base ligand; 2- complex compound of Cu(II); 3- complex compound of Ni(II); 4- complex compound of Co(II)

presence of the coordinated OH group, obtained by hydrolysis of one chlorine atom in basic medium [13-15].

#### Magnetic and Electronic Spectral Data

The electronic absorption spectra are often very helpful in the evaluation of the results provided by other methods of structural investigation. The electronic spectral measurements were used to obtain useful information about the stereochemistry of the metal ions in the complexes, based on energies and number of d-d transition peaks.

The electronic absorption UV-Vis spectra of the ligand and its complexes were recorded in the solid state at room temperature, in the 800-200 nm range (fig.3).

The assignments of the spectral bands are given in the table 3 and the magnetic data are presented in the table 4.

The electronic absorption spectrum of the free ligand consists of an intense band, centered at 320 nm ( $31250 \text{ cm}^{-1}$ ) attributed to  $n \rightarrow \pi^*$  transitions of the azomethine group. Another intense band in higher energy region of the spectra ( $260 \text{ nm}$ ,  $38461 \text{ cm}^{-1}$ ) of the free ligand was related to  $\pi \rightarrow \pi^*$  transitions of benzene rings and azomethine ( $\text{-C=N}$ ) groups [16]. These transitions are observed also, in the spectra of the complexes, but they shifted towards higher frequencies, confirming the coordination of the ligand to the metallic ions [17].

The reflectance spectrum of Cu(II) complex exhibits a broad absorption band, centered at  $\sim 660 \text{ nm}$  ( $15151 \text{ cm}^{-1}$ ). Though three transitions are expected in this case ( $d_{xy} \rightarrow d_{x^2-y^2}$ ,  $d_{z^2} \rightarrow d_{x^2-y^2}$  and  $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ ) they are very close in energy and often appear in the form of one broad band envelope [18]. These three transitions are characteristic to  $\text{Cu}^{2+}$  ( $d^9$ ) ion present in a tetragonal

Table 3  
ELECTRONIC TRANSITIONS FOR THE SCHIFF BASE ( $\text{H}_2\text{L}$ ) AND ITS COMPLEXES

Compound	Observed bands ( $\nu_{\text{max}}$ , $\text{cm}^{-1}$ )	Assignments
$\text{H}_2\text{L}$	31250 38461	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$
$[\text{Cu}_2\text{L}(\text{OH})_2(\text{H}_2\text{O})_4]$	15151 26315 31746 35714, 43478	$d_{xy} \rightarrow d_{x^2-y^2}$ $d_{z^2} \rightarrow d_{x^2-y^2}$ $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ LMCT $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$
$[\text{Ni}_2\text{L}(\text{OH})_2(\text{H}_2\text{O})_4]$	15384 33898 40816, 46511	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$
$[\text{Co}_2\text{L}(\text{OH})_2(\text{H}_2\text{O})_4]$	20000 33333 40816, 45454	${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$ $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$

distorted octahedral configuration. The band at  $380$  ( $26315 \text{ cm}^{-1}$ ) is assigned to a charge-transfer process, mainly of the  $\text{L} \rightarrow \text{Cu}$  type. The value of the experimental magnetic moment ( $2.28 \text{ B.M.}$ ) suggests also the existence of a tetragonal distorted octahedral geometry around the two copper (II) ions. The value corresponds to the proposed bimetallic formula for this complex.

The electronic spectrum of Ni(II) complex shows a broad band at  $650 \text{ nm}$  ( $15384 \text{ cm}^{-1}$ ) assigned to  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$  ( $\nu_2$ ) transition, characteristic to  $\text{Ni}^{2+}$  ( $d^8$ ) ion present in a distorted octahedral configuration. Based on the experimental magnetic moment value ( $\mu_{\text{exp.}} = 4.98 \text{ B.M.}$ ) corresponding to a binuclear complex, the same geometry can be attributed to Ni(II) complex.

The reflectance spectrum of the pink Co(II) complex displays an absorption band at  $500 \text{ nm}$  ( $20000 \text{ cm}^{-1}$ ) which can be attributed to the  ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$  ( $\nu_3$ ) transition, characteristic to Co(II) ( $d^7$  high-spin) ion in a distorted octahedral environment [19]. The experimental magnetic moment ( $\mu_{\text{exp.}} = 6.98 \text{ B.M.}$ ) suggests also the existence of

Compound	Temperature (K)	$\chi_g \cdot 10^{-6}$ ( $\text{cm}^3 \text{ g}^{-1}$ )	Molecular Weight ( $\text{g mol}^{-1}$ )	$\mu_{\text{exp.}}$ (B.M.)	$\mu_{\text{calc.}}$ (B.M.)	$\chi_M T$ ( $\text{cm}^3 \text{ K mol}^{-1}$ )
$[\text{Cu}_2\text{L}(\text{OH})_2(\text{H}_2\text{O})_4]$	298	2.4	753.28	2.28	2.45	0.65
$[\text{Ni}_2\text{L}(\text{OH})_2(\text{H}_2\text{O})_4]$	298	13.5	743.58	4.98	4.89	3.10
$[\text{Co}_2\text{L}(\text{OH})_2(\text{H}_2\text{O})_4]$	298	27.0	744.06	6.98	6.90	6.10

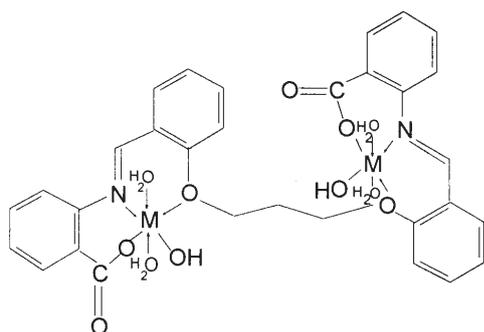
$\chi_g$  = Magnetic susceptibility per gram.  $\chi_M$  = Molar magnetic susceptibility  
exp. = experimental, calc. = calculated

Table 4  
THE MAGNETIC DATA FOR THE METAL COMPLEXES

Compound	Temp. range (°C)	Mass loss (%)	Total mass loss (%)	Lost fragment	Residue exp. (calc.) (%)
		exp. (calc.)			
H <sub>2</sub> L	75-140	6.80 (6.89)		2H <sub>2</sub> O	Unidentified
	140-530	68.71 (70.47)	91.71	2CO <sub>2</sub> , C <sub>17</sub> H <sub>16</sub> O <sub>2</sub> N <sub>2</sub>	7.93
	530-1000	16.20		Unidentified loss	
[Cu <sub>2</sub> L(OH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]	100-330	29.5 (28.94)		4H <sub>2</sub> O, CO <sub>2</sub> , CO, C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	Cu <sub>2</sub> O
	330-370	4.00 (4.51)	80.00 (80.96)	2HO	20.00 (18.98)
	370-500	27.20 (27.34)		2C <sub>7</sub> H <sub>5</sub> N	After 750 °C.
	500-750	19.30 (20.17)		2C <sub>6</sub> H <sub>4</sub>	1.5% nitriding
[Ni <sub>2</sub> L(OH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]	100-250	9.53 (9.68)		4H <sub>2</sub> O	2Ni
	250-400	16.00 (16.40)	83.35 (84.18)	2CO <sub>2</sub> , 2HO	16.41 (15.78)
	400-420	38.99 (37.66)		C <sub>17</sub> H <sub>16</sub> O <sub>2</sub> N <sub>2</sub>	After 600 °C.
	420-600	18.83 (20.44)		2C <sub>6</sub> H <sub>4</sub>	4.40% nitriding
[Co <sub>2</sub> L(OH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]	100-250	9.51 (9.67)		4H <sub>2</sub> O	2Co
	250-380	26.00 (26.34)	84.74 (84.11)	C <sub>3</sub> H <sub>6</sub> O <sub>2</sub> , 2CO <sub>2</sub> , 2HO	15.26 (15.84)
	380-540	28.70 (27.68)		2C <sub>7</sub> H <sub>5</sub> N	After 660 °C.
	540-660	20.53 (20.42)		2C <sub>6</sub> H <sub>4</sub>	4.49% nitriding

Temp. range = Temperature range

**Table 5**  
THERMOGRAVIMETRIC ANALYSIS  
DATA OF THE SCHIFF BASE (H<sub>2</sub>L) AND  
ITS COMPLEXES, IN NITROGEN



Where M = Cu(II), Ni(II) or Co(II)

Fig. 4. The proposed structure for the complexes with new Schiff base

a distorted octahedral geometry and its value corresponds to the proposed bimetallic formula for the Co(II) complex.

### Thermal analysis

Thermal analysis of organic ligands and of metal complexes is used to obtain information about their physical properties and thermal stability, as well as for the nature of the intermediates and final products [20-28].

Table 5 shows the thermogravimetric analysis results of H<sub>2</sub>L Schiff base thermal decomposition and of its metal complexes.

The decomposition of H<sub>2</sub>L Schiff base in nitrogen flow takes place on the entire temperature range RT-1000°C; thus, in the range 75-140 °C two water molecules are lost, producing a weak endothermic effect. At 160°C, the ligand melts with the endothermic effect  $\Delta H = 75.12 \text{ J g}^{-1}$  ( $\Delta H = 36.52 \text{ kJ mol}^{-1}$ ). Between 140 and 530°C the ligand loses two CO<sub>2</sub> molecules and the C<sub>17</sub>H<sub>16</sub>O<sub>2</sub>N<sub>2</sub> group, followed by a constant slow-rate unidentified loss which undergoes even after 1000°C, while in air it takes place up to 595°C.

Cu(II) complex exhibits four decomposition steps. The

first and second stages within the temperature range 100-370 °C could account for the loss of four coordination water molecules, CO<sub>2</sub>, CO molecules, C<sub>3</sub>H<sub>6</sub>O<sub>2</sub> group and two HO. These steps of decomposition are accompanied by two weak endothermic effects. The subsequent steps (370-750°C) involve the loss of two C<sub>7</sub>H<sub>5</sub>N groups and two fragments of benzene rings (2C<sub>6</sub>H<sub>4</sub>), 20.00% residue remaining at the end and corresponding to Cu<sub>2</sub>O (calc. 18.98%).

The TG curve of Ni(II) complex shows four steps of decomposition within the temperature range of 100-600 °C. The first step at 100-250°C corresponds to the loss of four coordination water molecules. The second and third decomposition steps, within the temperature range 250-420°C, corresponds to the loss of two CO<sub>2</sub> molecules, two coordination hydroxyl groups and the C<sub>17</sub>H<sub>16</sub>O<sub>2</sub>N<sub>2</sub> group. A medium endothermic effect is produced together with the thermal decomposition. The loss of two fragments of benzene rings (2C<sub>6</sub>H<sub>4</sub>) takes place within the temperature range 420-600°C, leaving 16.41% nickel metal as residue (calc. 15.78%) which then form the corresponding nitride.

The decomposition curve of Co(II) complex shows also four steps within the temperature range 100-660°C. The first step of the decomposition within the temperature range 100-250°C correspond to the loss of four coordination water molecules with a mass loss of 9.51% (calc. 9.67%). The subsequent steps (250-660°C) correspond to the removal of the organic part of the ligand and of two coordination hydroxyl groups leaving 15.26% cobalt metal as a residue (calc. 15.84%) which then form the corresponding nitride. The overall mass loss amounts to 84.74% (calc. 84.11 %). The second decomposition is a medium heat absorption process.

The results of all the analyses, described previously, indicate the general structure of the complexes presented in figure 4.

## Conclusions

In this study, a new Schiff base ( $H_2L$ ) and its complexes with Cu(II), Ni(II) and Co(II) have been synthesized and characterized by various physico-chemical methods. These studies support the binuclear formulations of the complexes, of  $[M_2L(OH)_2(H_2O)_4]$  type. From the IR spectra, it is concluded that  $H_2L$  Schiff base binds to the metal ions through deprotonated carboxylate oxygen atom besides the azomethine nitrogen atom and Ar-O-R etheric oxygen atom. The distorted octahedral coordination geometries of the metal ions are completed by hydroxyl anions and water molecules. The magnetic data confirm the stereochemistry proposed for these coordination compounds. The molar conductance values of the complexes suggest that no anions are present outside the coordination spheres. Thermogravimetric analysis results are in good agreement with the proposed composition of the complexes.

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