

## SYNTHESIS, THERMAL BEHAVIOR AND SPECTROSCOPIC INVESTIGATIONS OF METAL COMPLEXES WITH *N*-MODIFIED GLYCINE AS LIGAND

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**ABSTRACT.** The Cu(II), Co(II) and Ni(II) complexes with *N*-modified glycine derived from *p*-nitrophenylserinol were synthesized and characterized by their spectral and thermal properties. The thermal stability of the ligand and synthesized complexes was discussed in the 20-700°C temperature range. The results indicate that the organic compound acts as a bidentate ligand, its coordination involving the carboxylate oxygen and the nitrogen atom belonging to the amino group of the glycine fragment. All complexes correspond to the molar ratio M : L : H<sub>2</sub>O = 1 : 2 : 2. The shape of the ESR spectra at room temperature and the principal values of the g tensor suggest a pseudotetrahedral local symmetry around the metal ions.

**Keywords:** *glycine, metal complexes, thermal behavior, spectroscopic studies*

### INTRODUCTION

Amino acids play a crucial role in intra-cellular process of living organism. A lot of biochemical processes involve metal ions. The metal-amino acid interaction can be treated as a model of metal-protein system. The study of model species such as the simple amino acids can assist in the interpretation of more complex system. Complexes of transition metals with amino acids like glycine, very small biomolecules, have received much attention because they proved biological activity such as antibacterial, antimicrobial or antifungal activities [1-4].

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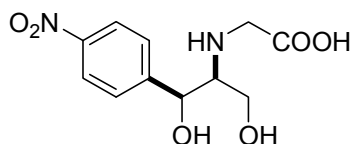
*In-vitro* studies of coordination complexes of Mn(II), Co(II), Ni(II), Cu(II), Cd(II) with glycine and phenylalanine indicated antimicrobial activity for Gram-positive bacteria such as *Bacillus subtilis* and *Staphylococcus aureus*, and Gram-negative such as *E.coli*, *Pseudomonas aeruginosa*, *Proteus vulgaris* and *Candida albicans* [3].

Recently studies of copper (II) complex with glycine report that is a very good antifungal agent for *Phytophthora Capsici*, an important pathogenic species which causes serious disease on plants [5].

Other research indicates that *N*-substituted glycine and their transition metal complexes act as hydrogen buffers in biological reactions [6]. *N*-modified glycines have a lot of applications in biomedicine as analogue of anticonvulsant and antiepileptic agent Milacemide, as *building-units* for *N*-backbone cyclic peptides, even in the detergent industry [7-9].

The ligand **L**=2-[(1*S*,2*S*)-1,3-dihydroxy-1-(4-nitrophenyl)propan-2-yl-amino]acetic acid (Figure 1), was obtained by a literature procedure by treatment of *p*-nitrophenylserinol with the monochloroacetic acid/Na<sub>2</sub>CO<sub>3</sub> system and investigated by spectroscopic methods [10].

Taking into account the important biochemical applications of *N*-modified glycine, we report the synthesis, the spectroscopic and thermogravimetric investigation of the ligand **L** and its transition metal complexes with Cu(II), Co(II) and Ni(II).



**Figure 1.** Structure formula of ligand **L** : 2-[(1*S*,2*S*)-1,3-dihydroxy-1-(4-nitrophenyl)propan-2-yl-amino]acetic acid

## RESULTS AND DISCUSSION

### *The structure of the metal complexes*

The complexation reaction of Cu(II), Co(II) and Ni(II) salts with the ligand solution in each case yields a solid product. All complexes are colored, microcrystalline and stable at room temperature. They are also insoluble in water, non-polar organic solvents (diethyl ether, CHCl<sub>3</sub>, CCl<sub>4</sub>, benzene and toluene) but soluble in methanol or DMSO. Higher melting points of these products as well their different colors when compared to that of the ligand **L**, indicate the formation of metal complexes.

The elemental analysis data (Table 1) and thermal analysis data (Table 2) indicate the molar ratio Metal : Ligand : H<sub>2</sub>O = 1 : 2 : 2., for each complex.

The UV-VIS spectra in CH<sub>3</sub>OH<sub>abs</sub> for the complexes (**1-3**) indicate a slight bathochromic shift by 4-6 nm, but a considerable hyperchromic increase effect of absorbance comparative to the spectrum of the initial ligand (L), like the other similar complexes [4, 11, 12]. The shift of  $n \rightarrow \pi^*$  characteristic band in the UV spectra attributed to the C=O bond (262.4 nm for the ligand; lit. for glycine 270 nm [4] ) is due to the involving of the non-bonding electron pairs of the oxygen in the metal-ligand bond formation. The study shows that the absorption spectra of the obtained complexes are determined by the coordinated organic ligand provides from amino acids what is typical for transitional metal complexes [13-15].

Another proof for the complexation process is the HRMS spectrum for the ligand and its metal complexes (Figure 2a-c). The M+1 peak supports the complexation idea with the transition metal ions, for each of them.

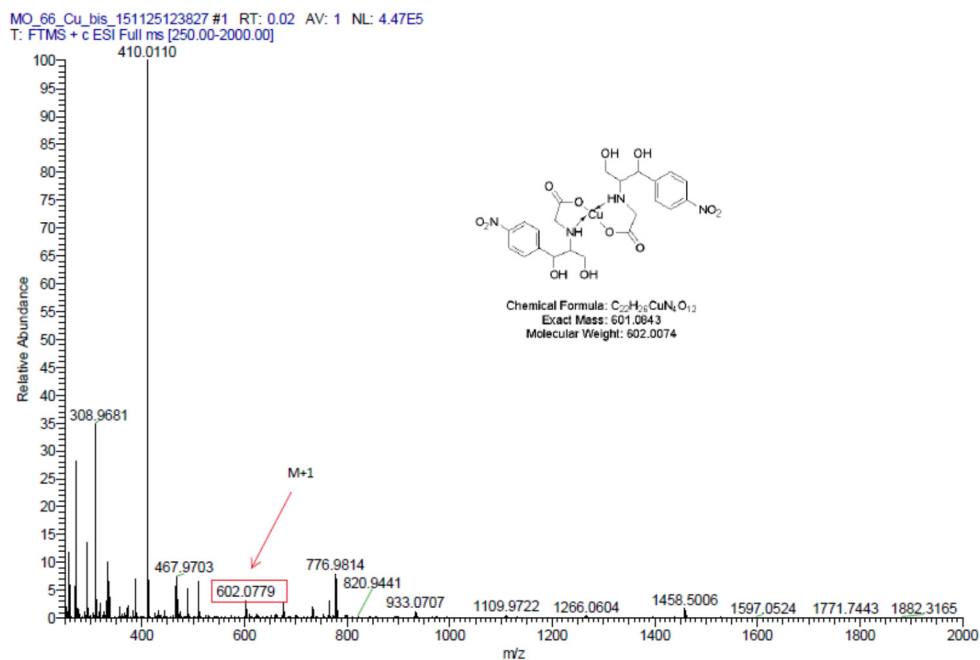


Figure 2a. HRMS spectrum (ESI) of copper complex

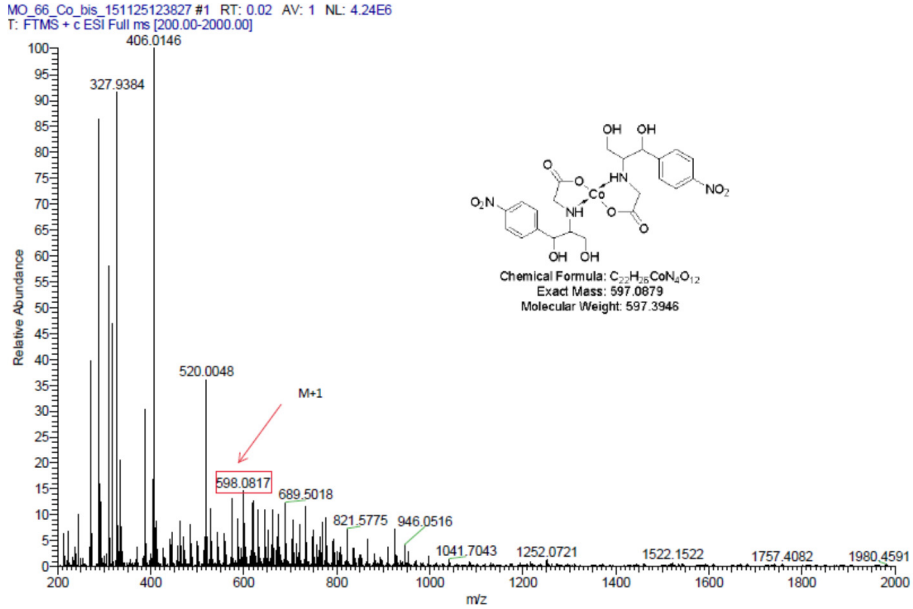


Figure 2b. HRMS spectrum (ESI) of cobalt complex

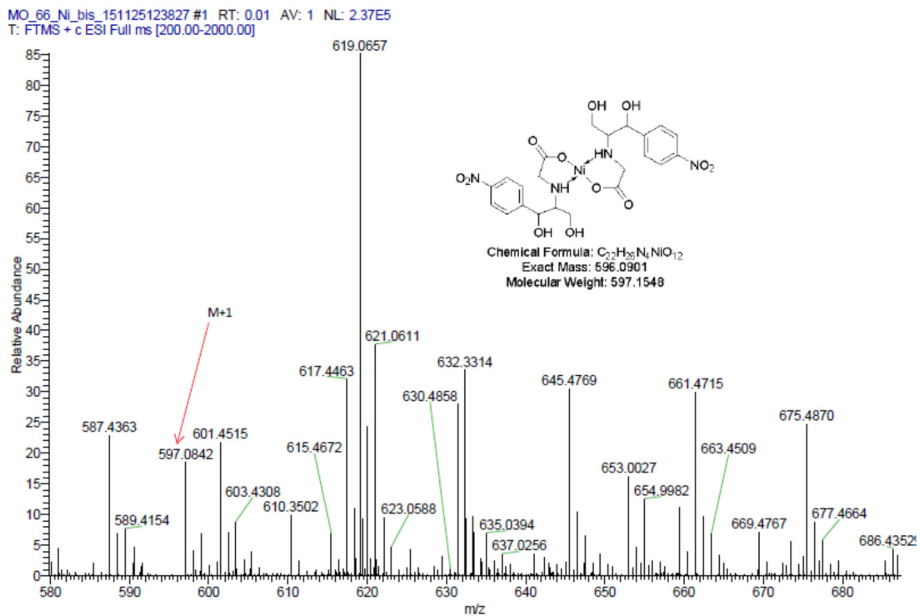


Figure 2c. HRMS spectrum (ESI) of nickel complex

**Table 1.** Physico-chemical and elemental analysis data of the ligand **L** and its metal complexes (**1-3**)

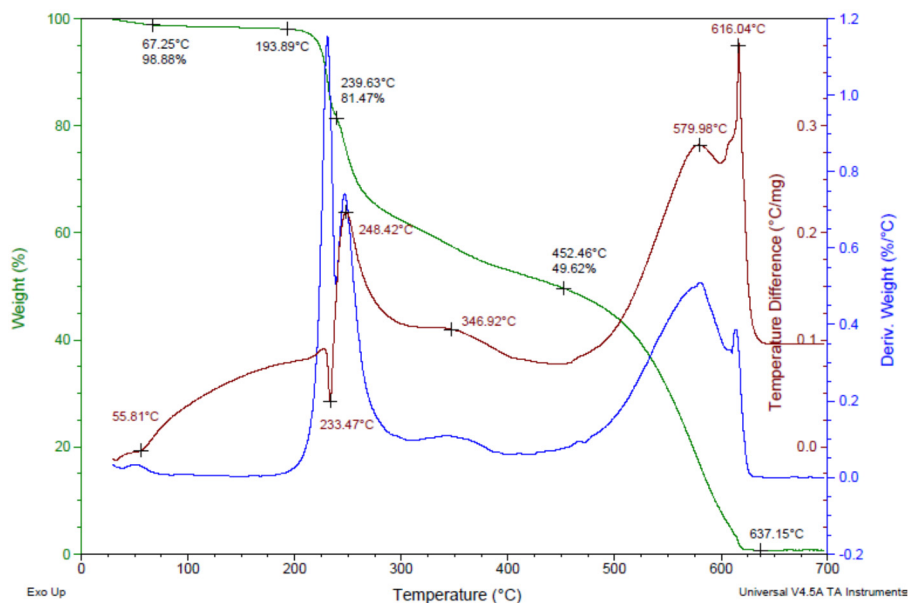
Compound	C <sub>11</sub> H <sub>14</sub> N <sub>2</sub> O <sub>6</sub> ( <b>L</b> )	C <sub>22</sub> H <sub>30</sub> CuN <sub>4</sub> O <sub>14</sub> ( <b>1</b> )	C <sub>22</sub> H <sub>30</sub> CoN <sub>4</sub> O <sub>14</sub> ( <b>2</b> )	C <sub>22</sub> H <sub>30</sub> NiN <sub>4</sub> O <sub>14</sub> ( <b>3</b> )	
Molec.Weight	270.2387	638.0380	633.4252	633.1854	
Yield [%]	58	94	79	40	
Colour	yellow-pale powder	green-turquoise powder	ecru powder	greenish-yellow powder	
[ $\alpha$ ] <sub>546</sub> <sup>25</sup> (c=0.5 CH <sub>3</sub> OH)	+52.42	-53.13	-92.88	-126.51	
Melting point [°C]	213-4	233-4	285-6	254-5	
Visible absorption spectrum data, in CH <sub>3</sub> OH <sub>abs</sub>	$\lambda_{max}$ (nm)	262.4	266.9	268.1	267.5
	$\epsilon$	963	3854	3383	3420
	A	0.499155	1.429968	0.962325	1.088011
Elemental analysis data [%] found. (calcd.)	C	48.57 (48.89)	40.66 (41.41)	40.61 (41.72)	41.67 (41.73)
	H	4.90 (5.22)	4.37 (4.74)	4.32 (4.77)	4.39 (4.78)
	N	10.36 (10.37)	8.77 (8.78)	8.61 (8.85)	8.84 (8.85)

### Thermal investigation

The thermal behaviors of the ligand (**L**) and its metal complexes (**1-3**) are summarized in Table 2 and Figure 3a-d.

The thermogravimetric analysis indicated that the ligand (**L**) is anhydrous and the decomposition involved three steps. In the temperature range 30-194°C a small endothermic peak at 56°C with a mass loss of 1.12% represented the loss of residual water present in the pores. This phenomenon could be explained by the general synthesis of the ligand from aqueous solution [10].

The first decomposition step occurred in the temperature range 194-240°C and it has been accompanied by an endo peak at 233°C. This process could be assigned to the NO<sub>2</sub> group cleavage from the aromatic ring accompanied by the melting, according to the literature data for other nitro-derivatives analogous [10, 16-18]. In the second stage of decomposition of ligand two exothermic peaks at 248°C, respectively at 347°C, indicated the cleavage of glycine rest accompanied by oxidation processes. The last step occurred in the temperature range 452-700°C and it has been accompanied by two strongly exothermic effects at 580°C and at 616°C which indicated the pyrolysis of organic rest. The theoretic weight loss (50.05%) and the experimental one (49.55%) agree with the loss of remaining organic rest. At 637°C the ligand was completely pyrolyzed.

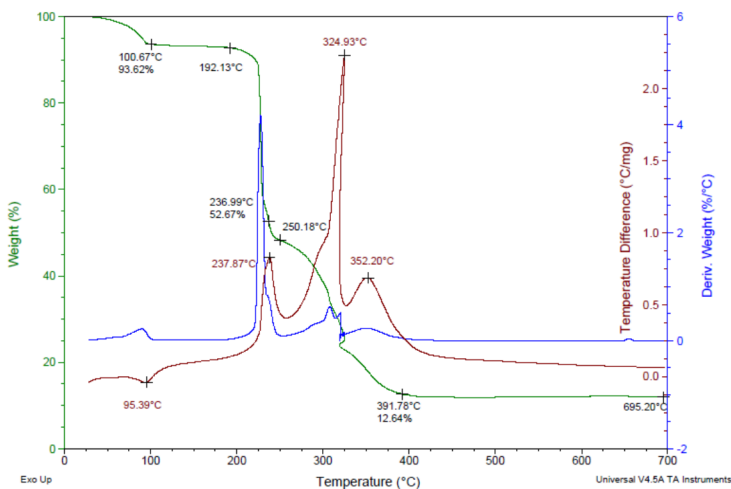


**Figure 3a.** TG-DTG-DTA diagram for the ligand **L**

The aim of the thermal analysis of the metal complexes is to obtain information concerning their thermal stability of these and to decide whether the water molecules are inside or outside the coordination sphere.

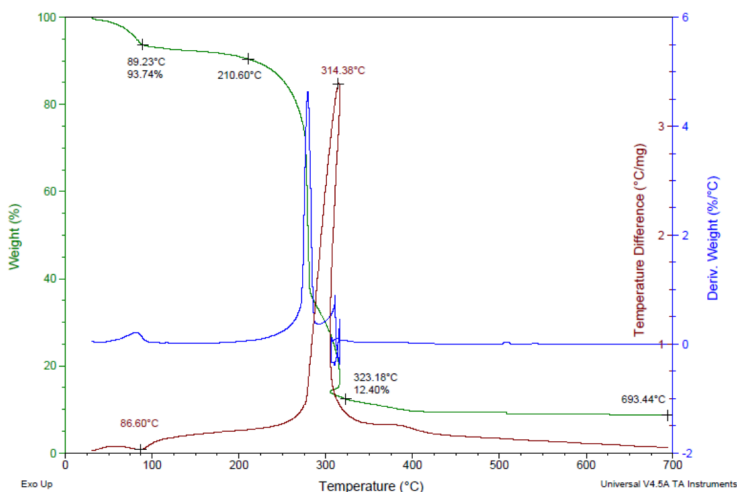
The decomposition of each metal complex occurs in two or three steps. First step corresponds to the loss of water molecules. After that, partial decomposition and then total decomposition of organic ligands takes place. The final products of the pyrolysis are metal oxides.

Thermal decomposition of the copper complex (**1**) was achieved in three stages. These mass losses occur in the temperature range of 30-192<sup>o</sup>C, 192-250<sup>o</sup>C and 250-700<sup>o</sup>C. The first step with an estimated mass loss of 6.40% (calculated 5.64%) could be assigned to loss of 2 moles of hydration water. The second stage of decomposition was observed in the 192-250<sup>o</sup>C with a mass loss of 40.93% (calculated 38.88%) and corresponds to a glycine rest and nitro-groups loss. The third-stage decomposition takes place at 250-700<sup>o</sup>C with two exothermic peaks at 325<sup>o</sup>C, respectively 352<sup>o</sup>C and corresponds to the pyrolysis of organic rest. The final product is CuO residue.

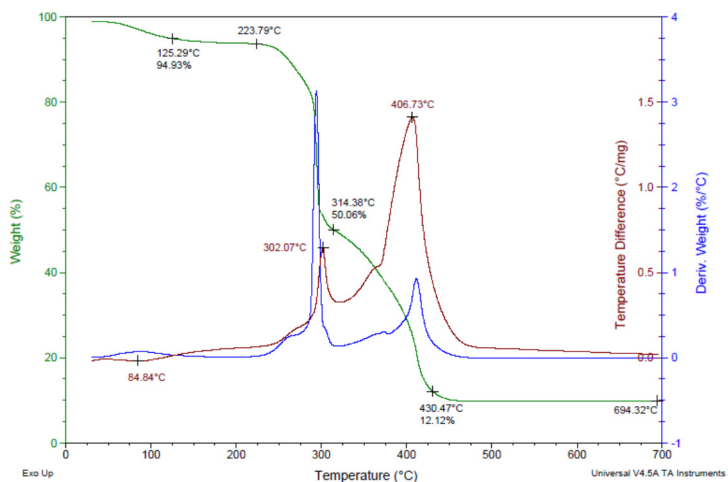


**Figure 3b.** TG-DTG-DTA diagram for copper complex (**1**)

For the cobalt complex (**2**), the first stage decomposition starts in the range 30-211°C, with an endothermic peak at 87°C and a mass loss of 6.26% which correspond to the loss of two moles of hydration water (calculated 5.69%). A strong exothermic effect (see Figure 3c), was assigned to the total pyrolysis of metal complex. The recorded mass loss of 81.34% is in good agreement to the calculated data (81.76%). Finally, the metal oxide remains in the crucible.



**Figure 3c.** TG-DTG-DTA diagram for cobalt complex (**2**)



**Figure 3d.** TG-DTG-DTA diagram for nickel complex (**3**)

**Table 2.** Thermal analysis data of the ligand **L** and its metal complexes (**1-3**) in air atmosphere (10<sup>0</sup>C/min)

Compound	Heat effect on DTA	Temperature (°C)			Mass loss (%)		Assignment
		T <sub>i</sub>	T <sub>max</sub>	T <sub>f</sub>	Calcd.	Exp.	
L	Endo	30	56	194	-	1.12	-residual water present inside pores
	Endo	194	233	240	17.02	17.41	-melting accompanied by NO <sub>2</sub> cleavage group
	Exo	240	248	452	33.03	31.85	-glycine rest (C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> N) and oxidation process
	Exo	452	580	700	50.05	49.55	-pyrolysis of organic rest
	Exo		616				
Cu(L)•2H <sub>2</sub> O ( <b>1</b> )	Endo	30	95	192	5.64	6.40	-2 moles of hydrating water and probably residual water inside pores
	Exo	192	238	250	39.88	40.93	-2 moles of glycine rest and NO <sub>2</sub> groups (2 C <sub>4</sub> H <sub>8</sub> O <sub>8</sub> N <sub>4</sub> )
	Exo	250	325	700	41.27	40.49	-pyrolysis of organic rest
					13.21	12.64	CuO residue
Co(L)•2H <sub>2</sub> O ( <b>2</b> )	Endo	30	87	211	5.69	6.26	-2 moles of hydrating water
	Exo	211	314	323	81.76	81.34	-quickly cleavage and pyrolysis of organic rest
					12.54	12.40	CoO residue
Ni(L)•2H <sub>2</sub> O ( <b>3</b> )	Endo	30	85	224	5.69	5.07	-2 moles of hydrating water
	Exo	234	302	314	41.28	42.76	-2 moles of glycine rest and NO <sub>2</sub> groups (2 C <sub>4</sub> H <sub>8</sub> O <sub>8</sub> N <sub>4</sub> )
	Exo	314	407	430	40.39	38.89	-pyrolysis of organic rest
					12.54	12.12	NiO residue

T<sub>i</sub>=initial temperature, T<sub>max</sub>=maximum temperature, T<sub>f</sub>=final temperature



The TG data showed that the nickel complex starts its decomposition at 85°C. The first decomposition step starts with dehydration and corresponds to loss of two moles of water. Organic ligand molecule is stable until 302°C. The second and third stages correspond to the organic ligand decomposition. The final product is NiO (12.12% exp., calcd. 12.54%).

### ESR spectra

Powder ESR spectra of metallic complexes at room temperature (Figure 4) are typical for pseudotetrahedral monomeric species. The principal values of the  $g$  tensor  $g_{\parallel}=2.560$  and  $g_{\perp}=2.071$  for Cu complex, correspond to a  $\text{CuN}_2\text{O}_2$  chromophore [19]. Similar value for Co complex ( $g_{\parallel}=2.0719$ ,  $g_{\perp}=2.019$ ) and for Ni complex ( $g_{\parallel}=2.065$ ,  $g_{\perp}=2.071$ ) suggest the same local symmetry around the metal ions.

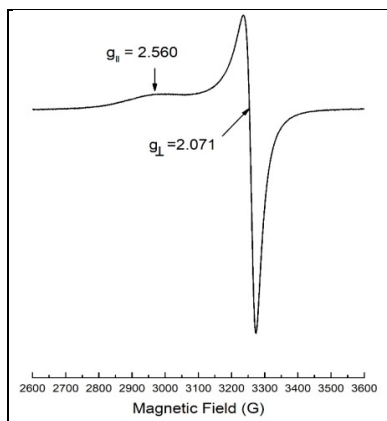


Figure 4. Powder ESR spectrum of copper complex at room temperature

## CONCLUSIONS

Three new transition metal complexes (**1-3**) of an *N*-modified glycine (**L**) as ligand were synthesized and analyzed by elemental, thermogravimetric analysis and spectral studies. The results are in good agreement with the corresponding formulae:  $\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_6$  (**L**),  $[\text{Cu}(\text{C}_{11}\text{H}_{13}\text{N}_2\text{O}_6)_2] \cdot 2\text{H}_2\text{O}$  (**1**),  $[\text{Co}(\text{C}_{11}\text{H}_{13}\text{N}_2\text{O}_6)_2] \cdot 2\text{H}_2\text{O}$  (**2**), respectively  $[\text{Ni}(\text{C}_{11}\text{H}_{13}\text{N}_2\text{O}_6)_2] \cdot 2\text{H}_2\text{O}$  (**3**). The ligand coordinated the metal ions through N and O donor atoms. The ESR spectra at room temperature indicated pseudotetrahedral local symmetry around the metal ions.

During heating in air atmosphere, both the ligand and its metal complexes decompose in multistage. Some stages of pyrolysis are weakly separated one from another. Decomposition of investigated compounds begins with total loss of water, then with gradual destruction of ligand. The final products of pyrolysis are the metal oxides from each of transition metal complexes.

Mass spectra data indicated the M+1 peak corresponding for each of investigated compounds.

## EXPERIMENTAL SECTION

### *Materials and instrumentation*

All reagents and chemicals were purchased from commercial sources and used as received. Elemental analyses were determined on Thermo Scientific Flash EA 1112 Elemental Analyzer. Melting points were measured on an ELECTROTHERMAL<sup>®</sup> instrument and were not corrected. The electronic absorption spectra were performed on CECIL CE 9500 spectrophotometer. Specific rotations were estimated on a Polamat A Karl Zeis Jena photopolarimeter. GC-MS spectra were recorded on a Gas Chromatograph with Mass Spectrometer Shimadzu<sup>®</sup> QP 2010 PLUS. Mass spectra were carried out on a LTQ ORBITRAP<sup>®</sup> XL (Thermo Scientific) instrument which was externally calibrated using the manufacturer's APCI or ESI(+) calibration mix. The samples were introduced into the spectrometer by direct infusion. The EPR measurements were carried out on a Bruker Biospin EMX<sup>micro</sup> spectrometer operating at X-band (9-10 GHz) with continuous wave at X-band ( $\approx$ 9 GHz). The spectra were recorded at room temperature with a microwave frequency of 9.4353 GHz, microwave power of 2 mW, modulation frequency of 100 kHz, modulation amplitude of 2 G. Thermogravimetry and differential thermal analysis (TG/DTA) curves were recorded with a Thermal Analyzer TA Instruments SDT Q600 V20.9 Build 20 on an interval 30-700<sup>o</sup>C, at a heating rate of 10<sup>o</sup>C/min, in alumina crucibles and a dynamic air atmosphere.

### *General synthesis of the metal complexes*

Cu(II), Co(II) and Ni(II) complexes of the ligand L were prepared by following a general method. The metal salt [Cu(NO<sub>3</sub>)<sub>2</sub>•3H<sub>2</sub>O, Co(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O or Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O] (1.24mmol) was dissolved in 10 mL distilled water. To a solution of ligand (L) (2mmol) dissolved in NaOH 1M at pH=12, was added slowly, dropwise, a solution of the metal salt, at room temperature. The mixture was stirred for 2h. By adding a solution of metal ions to a solution of ligand,

immediate color change was observed depending on the metal ion. Also the pH was changed at 5.5-6.00 for the copper complex, 6.50-7.00 for the cobalt complex and 7.00-7.50 for the nickel complex. After standing overnight at room temperature, the resulted precipitates were vacuum filtrated and washed with distilled water and finally dried in air at room temperature.

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