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FACULTY OF CHEMISTRY
DOCTORAL SCHOOL OF CHEMISTRY

DOCTORAL THESIS SUMMARY

COMPLEXES OF SOME TRANSITION METALS WITH KETONES AND AZOMETHINIC DERIVATIVES OF KETONES

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CHAPTER I. *SCHIFF BASES DERIVED FROM 1-H-INDOLE-2,3-DIONE IN COORDINATION CHEMISTRY*

The Schiff-base organic compounds represent one of the most employed class of ligands in coordination chemistry due to convenient synthetic preparation and high versatility. These aspects influence their ability to form stable complexes with the large majority of transitional-metal ions.

The research area encompassing the coordination compounds with azomethinic ligands as main characters is widely expansive especially due to their potential interest aroused in various interdisciplinary fields such as bioinorganics, catalysis or magnetochemistry [1-4]. Thus, for researchers in bioinorganics, the complexes containing Schiff bases provide structural models of the metal ion coordination sites in metalloproteins or enzymes. The cryomagnetic properties of binuclear complexes originating from Schiff base ligands have permitted the understanding of the mechanism by which the magnetic coupling between the two metallic centres is established, an information that have crucially contributed to the development of this research domain. As for catalysis, the emphasis is mainly placed on the complexes containing chiral Schiff bases, which are efficient in various organic reactions.

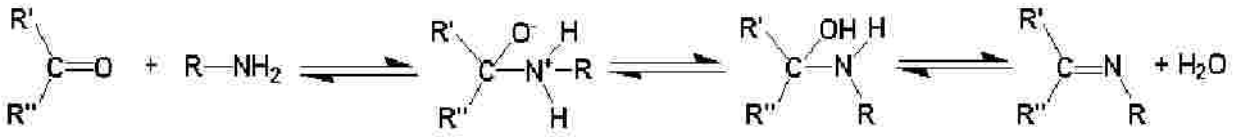


Figure I.1. Schematic representation of the general reaction for obtaining Schiff bases

Schiff bases can display tautomeric isomerism based on the phenol-imine and keto-amine couple, respectively: O–H···N? O···H–N, depending on the nature of intramolecular hydrogen bond [8-9]. The shifting of the tautomeric equilibrium is strongly affected by the chosen solvent. Thus, protic and aprotic solvents governed by high dielectric constants shifts the equilibrium towards the quinonic derivative.

Phenol-imine and keto-amine forms also exist in solid state. Single crystal X-ray diffraction analyses showed a remarkable increase of C=N bond length when phenol-imine form turns into the keto-amine peer. On the other hand, the shrinkage of C–O bond length from 1.279

to 1.263 Å together with the enlargement of C=N bond length from 1.137 to 1.330 Å represent a landmark of the abundance of quinonic form [11].

Tautomerism is frequently encountered for hydrazone, selenosemicarbazone, and tiosemicarbazone derivatives [12-13].

CHAPTER II. *ORIGINAL CONTRIBUTIONS TO THE STUDY OF COMPLEXES CONTAINING AROMATIC LIGANDS*

II.1. Complexes of some transition-metal ions with bidentate Schiff bases derived from 1-H-indole-2,3-dione

As resulted from the dedicated literature, much attention has been granted to the study of the transition-metal complexes containing Schiff bases derived from isatin.

The chemists' interest for this research domain is raised by the versatility of the corresponding Schiff bases when involved in reactions with transition-metal ions [130, 102]. A considerable number of reported studies is dedicated to the medicinal applications of the complexes with Schiff bases originating from isatin [56, 95, 96, 129].

Isatin and the complexes of its Schiff-base type ligands reveal antifungal, antibacterial [131, 132], and antileukemic activities [133].

Following some previously communicated investigations [70, 83, 134], in this subchapter are described the synthesis and characterization of forty-two complexes with aniline-isatin (L^1), o-anisidine-isatin (L^2) si p-anisidine-isatin (L^3). In figure II.1 is depicted the synthetic approach of obtaining Schiff bases via condensation reactions between various amines and isatin using a 1:1 molar ratio [135].

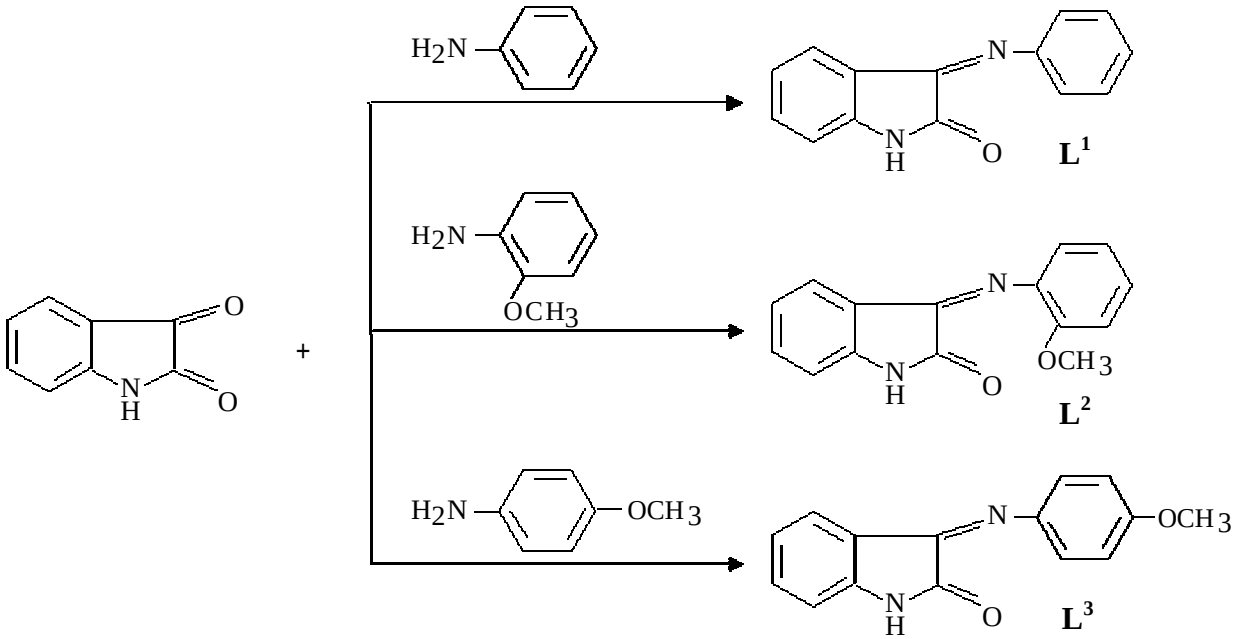


Figure II.1. Condensation reactions for the preparation of the following Schiff-base ligands: aniline-isatin (L^1), o-anisidine-isatin (L^2) and p-anisidine-isatin (L^3)

II.1.1. Synthesis and characterization of Cu(II), Co(II), Ni(II), Zn(II) and Cd(II) complexes with the Schiff base derived from 1-H-indole-2,3-dione and aniline

Spectral analysis

IR spectrum of ligand L^1 was studied in comparison with the IR spectrum of isatin in order to identify the infrared absorption frequencies of the characteristic functional groups.

The IR spectrum of the ligand (figure II.3) showed medium intensity bands at 3176 cm^{-1}, 3064 cm^{-1}, and 1742 cm^{-1}, respectively, which were assigned to the vibrational modes of NH groups belonging to the isatin ring and to the C=O stretching mode, $?_{C=O}$ [136, 137]. Moreover, a new peak could be noticed at 1654 cm^{-1} compared to the IR spectrum of isatin, which represented a proof for the formation of the azomethine group.

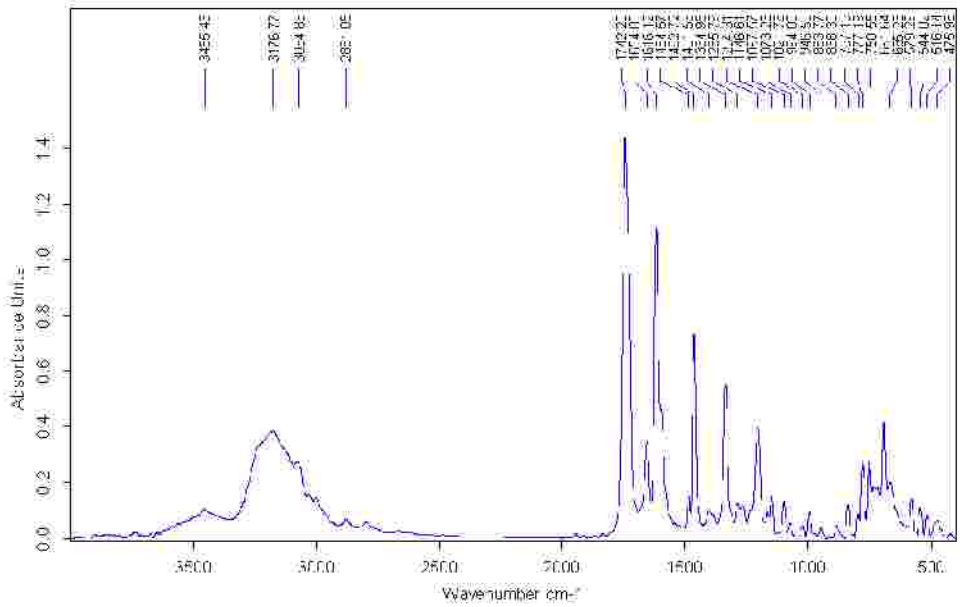


Figure II.3. IR spectrum of aniline-isatin (L^1), a Schiff-base type ligand

^{1}H-NMR spectrum [d^6-DMSO, d(ppm), J(Hz)] of ligand aniline-isatin (figure II.4) was recorded at the room temperature in d^6-DMSO at 300 MHz and consist in the following signals: 11.00 (s, 1H, NH), 7.47 (dd, 7.4, 7.2, 2H, H-11, H-11, H-13); 7.33 (td, 7.7, 1.1, 1H, H-2); 7.25 (tt, 7.4, 1.1, 1H, H-12); 6.97 (dd, 7.2, 1.1, 2H, H-10, H-14); 6.89 (dl, 7.7, 1H, H-1); 6.70 (td, 7.7, 1.1, 1H, H-3); 6.33 (dl, 6.6, 1H, H-4).

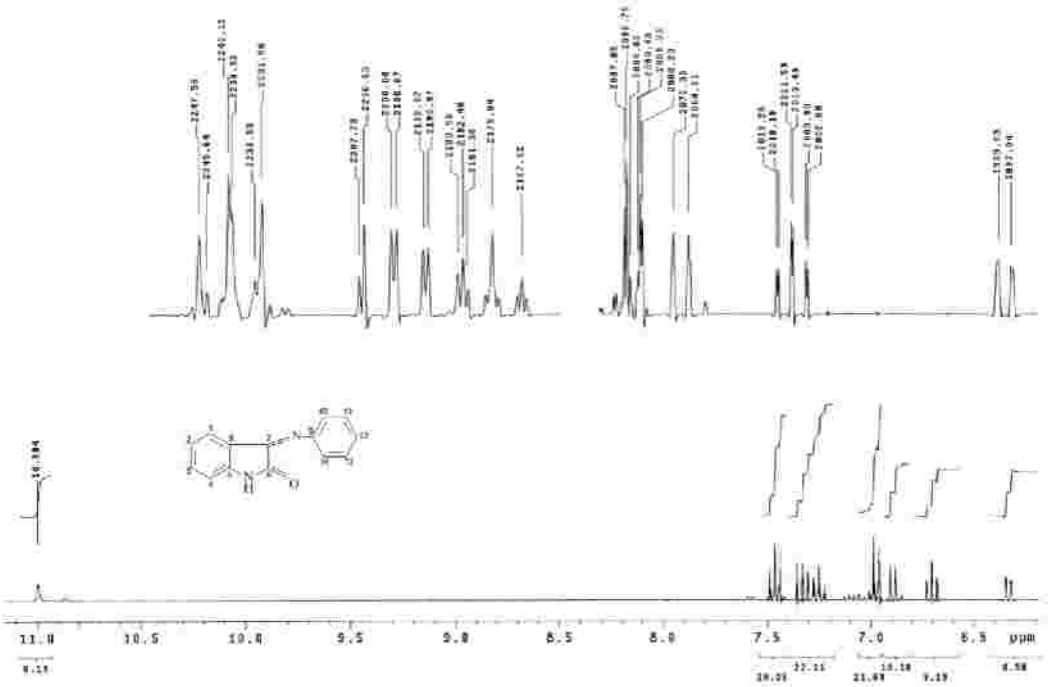


Figure II.4. ^{1}H-NMR spectrum of ligand L^{1}

The obtaining of the Schiff base was also confirmed by the occurrence of the following signals in the ^{13}C-NMR spectrum [d^{6}-DMSO, d(ppm)] (figure II.5): 163.48 (C-8); 154.36 (C-7); 150.55 (C-5); 146.98 (C-9); 134.42 (C-2); 129.59 (C-11, C-13); 125.35 (C-4); 124.92 (C-12); 121.69 (C-3); 117.23 (C-10, C-14); 115.68 (C-6); 111.53 (C-1). The assignments of the chemical shifts of the carbon atoms were established based on the ^{1}H-^{1}H COSY and ^{1}H-^{13}C COSY spectra, which correlate the carbon atoms with the hydrogen atoms (figure II.6).

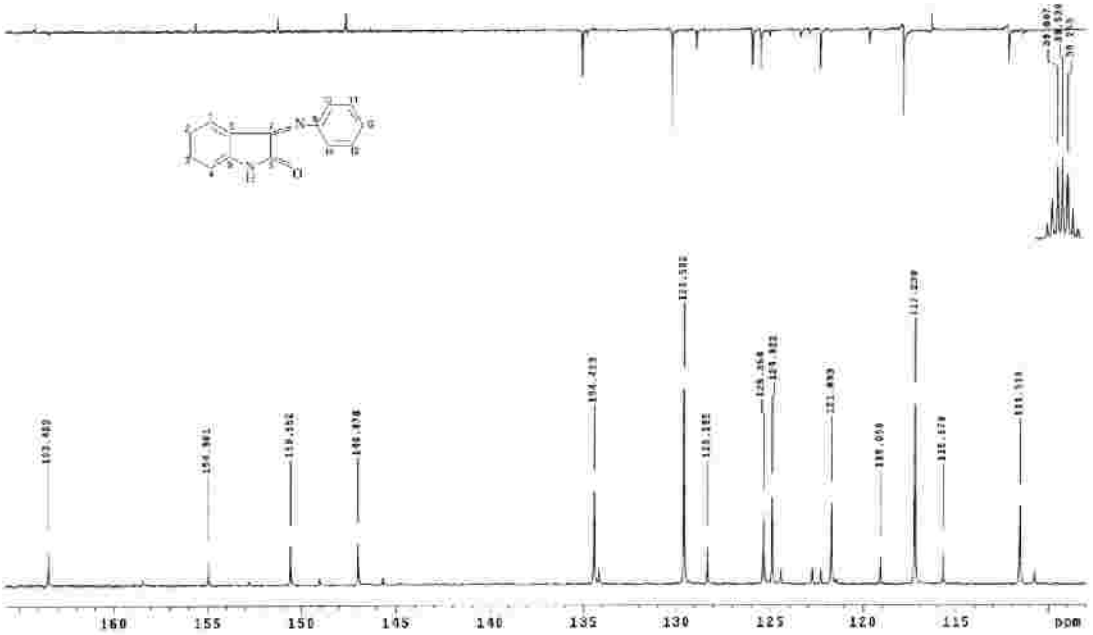


Figure II.5. ^{13}C-NMR spectrum of ligand L^{1}

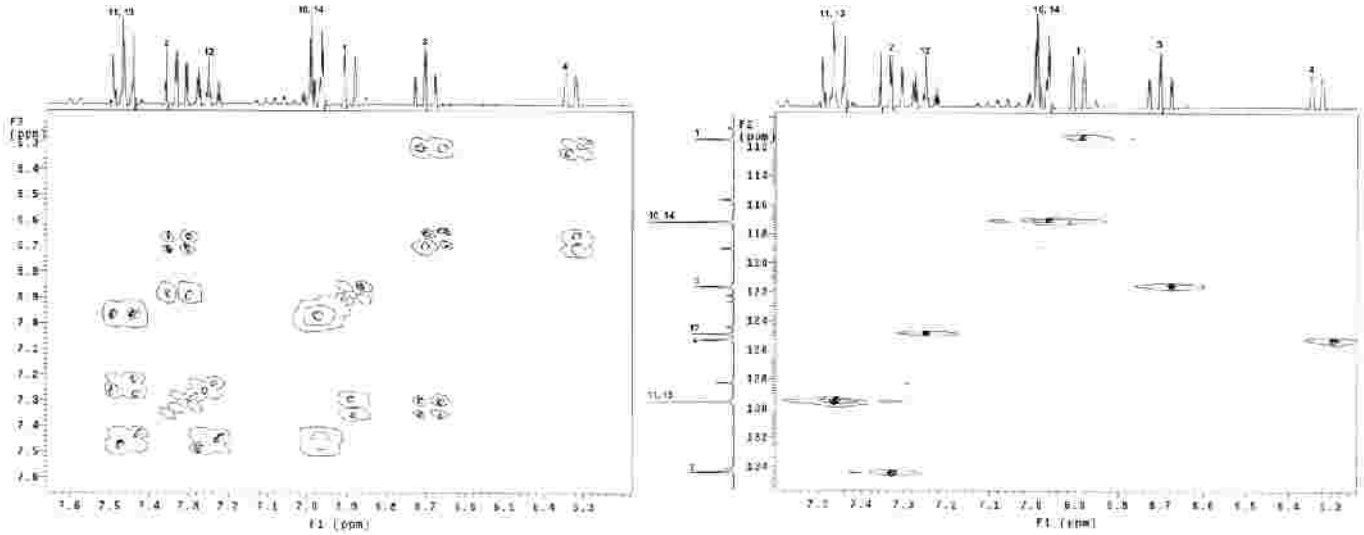


Figure II.6. ^{1}H-^{1}H COSY and ^{1}H-^{13}C COSY spectra of ligand L^{1}

The electronic spectrum of ligand L^{1} (figure II.7) displayed three bands. The band located at 41,666 cm^{-1} (240 nm) and the one at 32,258 cm^{-1} (310 nm) were assigned to p? p*and n? p* transitions originating from the aromatic rings and electronic doublet of the nitrogen atom from the azomethine group [138]. The remaining band located at 25,000 cm^{-1} (400 nm) could be assigned to an intraligand charge transfer [131].

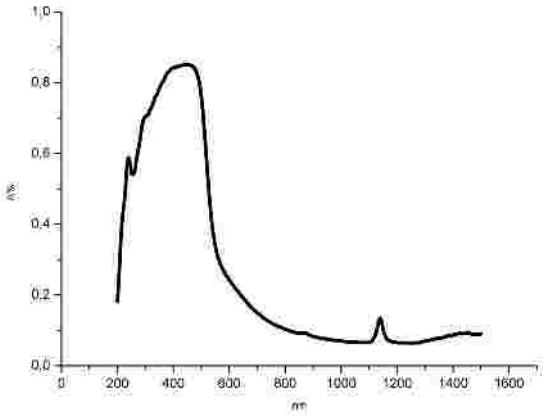


Figure II.7. UV-Vis absorption spectrum of ligand L^{1}

The ligand can adopt either keto or enol tautomeric form in the complexation process, but an acid medium shifts the equilibrium toward the lactime form. The complexes containing the ligand in the enol form can be obtained by adjusting the pH value in such a way the deprotonation is favored.

Complexes containing ligand L^1 were synthesized by mixing the ethanolic solutions of ligand and metallic salts, respectively, in a 1:2 molar ratio. The metallic salts were the corresponding nitrates and perchlorates, and, depending on the reaction conditions, led to the following type of complexes: $[M(HL^1)_2(H_2O)_2](X)_2$, where M = Cu(II), Co(II), Ni(II), Zn(II) and Cd(II), X = NO_3^-, ClO_4^-, and $[M(L^1)_2(H_2O)_2]$, where M = Cu(II), Co(II) and Ni(II), and $[M(L^1)_2]$, where M = Zn(II) and Cd(II).

These coordination compounds were characterized by elemental analysis, IR, UV-Vis-NIR, and EPR (in the case of Cu(II) derivatives) spectroscopies, magnetic susceptibility and molar conductivity measurements, antibacterial activity and thermal analysis. The ligand adopted a bidentate monobasic enol form in the case of $[M(L^1)_2(H_2O)_2]$ and $[M(L^1)_2]$-type complexes, and a bidentate neutral keto form in the case of $[M(HL^1)_2(H_2O)_2](X)_2$-type complexes, where X = NO_3^- and ClO_4^-, respectively.

The molar conductivity values indicated a non-electrolyte nature for $[M(L^1)_2(H_2O)_2]$ and $[M(L^1)_2]$-type complexes, and a 1:2 electrolyte behavior for $[M(HL^1)_2(H_2O)_2](X)_2$-type complexes, where X = NO_3^-, ClO_4^- [139].

IR Spectra

The comparative analysis of IR spectra of the free ligand and newly synthesized corresponding complexes provided information on the coordination fashion of this ligand to the involved metal ions.

The IR spectral data hinted toward a bidentate neutral behaviour of the ligand for the electrolyte-type complexes, with the donor set defined by the azomethine nitrogen atom and the carbonyl oxygen atom. As for the non-electrolyte-type complexes, the ligand revealed a bidentate monobasic behavior, participating to the coordination site with the azomethinic nitrogen atom and the oxygen atom belonging to the deprotonated enolic group.

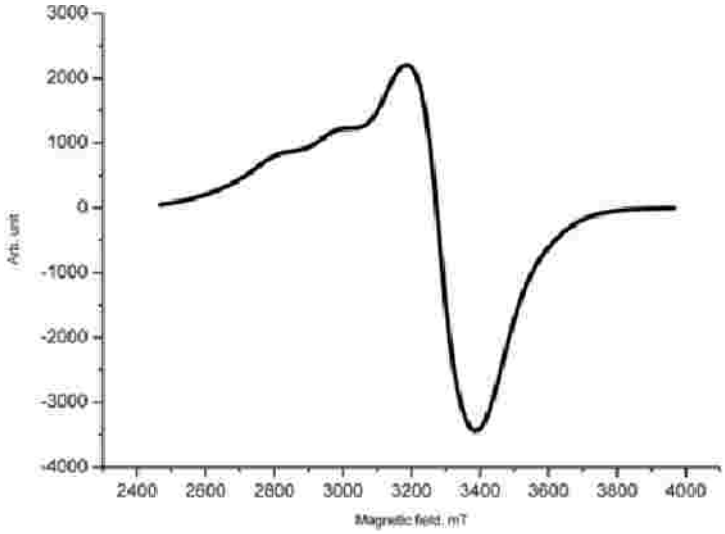
Electronic spectra

Information on the coordination geometry of the metal ions in complexes of general formula $[M(L^1)_2(H_2O)_2]$, $[M(L^1)_2]$ and $[M(HL^1)_2(H_2O)_2](X)_2$, where X = NO_3^-, ClO_4^-, were inferred from the electronic spectra recorded in the 200- 1,500 nm range by diffuse reflectance technique, corroborated with the values of the magnetic moments.

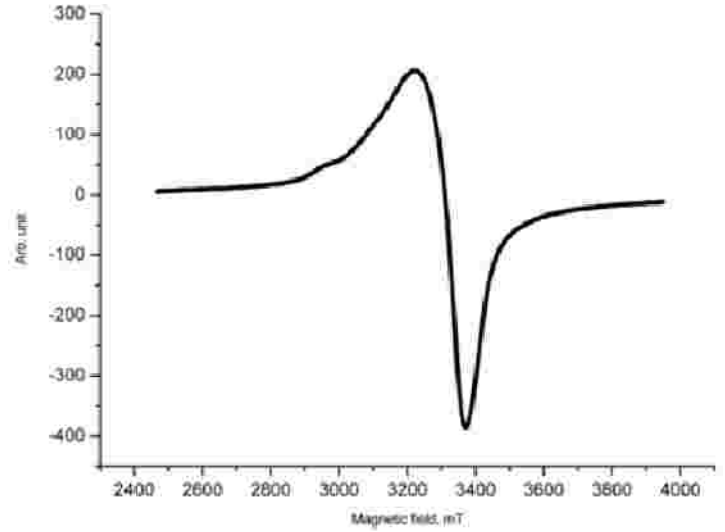
EPR spectra

In the cases of $[Cu(HL^1)_2(H_2O)_2](NO_3)_2$ (**1**) and $[Cu(L^1)_2(H_2O)_2]$ (**3a**) complexes, EPR spectra were recorded at room temperature (figure II.14). For complexes **1** and **3a**, g tensor values were $g_{\parallel}$ =2.257, $g_{\perp}$ =2.0714, and $g_{\parallel}$ =2.259, $g_{\perp}$ =2.130, respectively, which fell within the accepted

data range specific to the complexes with an axially elongated octahedral geometry (D_{4h} symmetry) [148].



$[Cu(HL^1)_2(H_2O)_2](NO_3)_2$



$[Cu(L^1)_2(H_2O)_2]$

Figure II.14. Electron paramagnetic resonance spectra of $[Cu(HL^1)_2(H_2O)_2](NO_3)_2$ (top) and $[Cu(L^1)_2(H_2O)_2]$ (bottom)

Thermal analysis

The presence of water in the composition of the $[M(L^1)_2(H_2O)_2]$-type complexes was evidenced by thermogravimetric analysis (TGA).

TGA and DSC (Differential Scanning Calorimetry) curves recorded for the octahedral complexes **3a**, **6a**, **9a**, **11** and **13** are shown in figures II.15 - II.19.

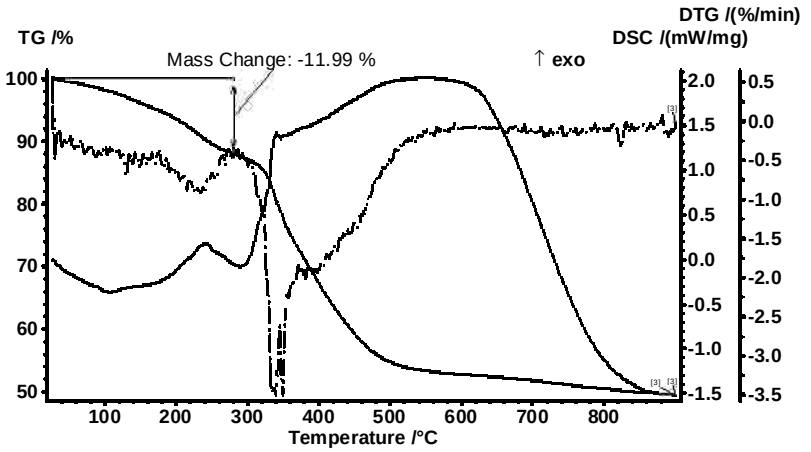


Figure II.15. TGA/DTG/DSC analysis of complex $[Cu(L^1)_2(H_2O)_2]$

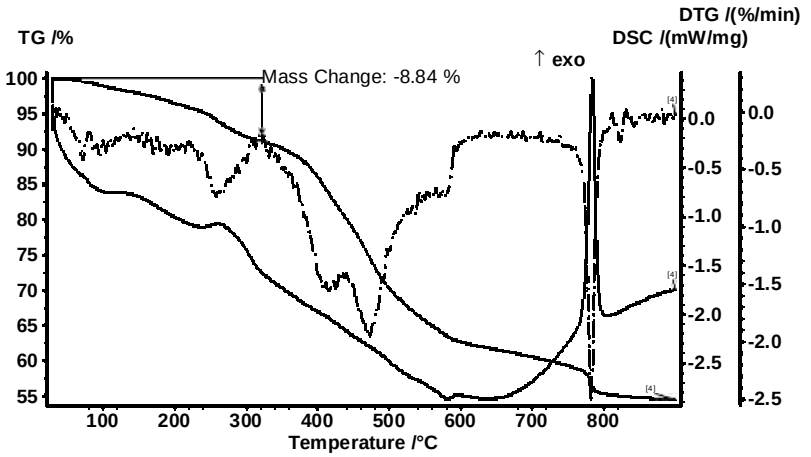


Figure II.16. TGA/DTG/DSC analysis of complex $[Co(L^1)_2(H_2O)_2]$

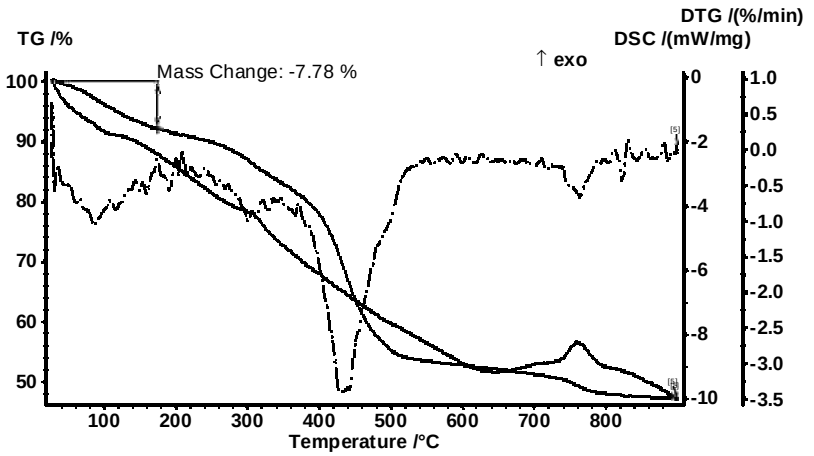


Figure II.17. TGA/DTG/DSC analysis of complex $[Ni(L^1)_2(H_2O)_2]$

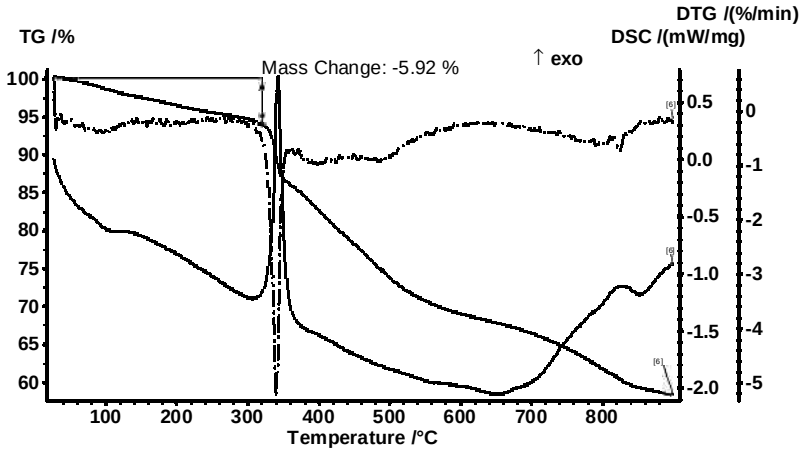


Figure II.18. TGA/DTG/DSC analysis of complex $[Zn(L^1)_2]$

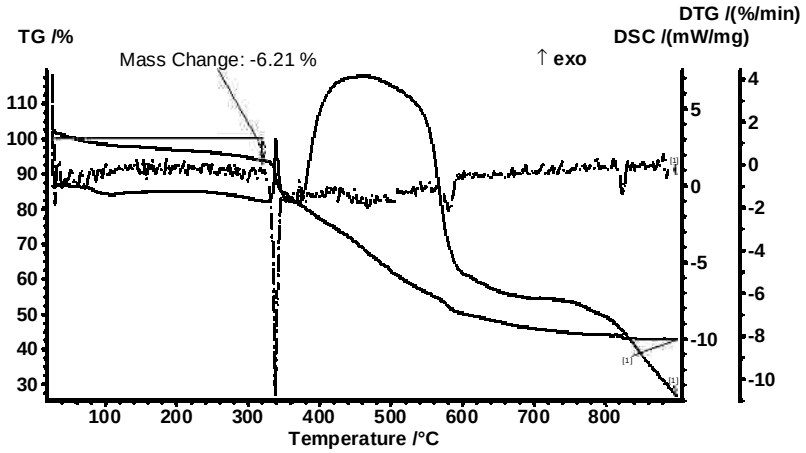
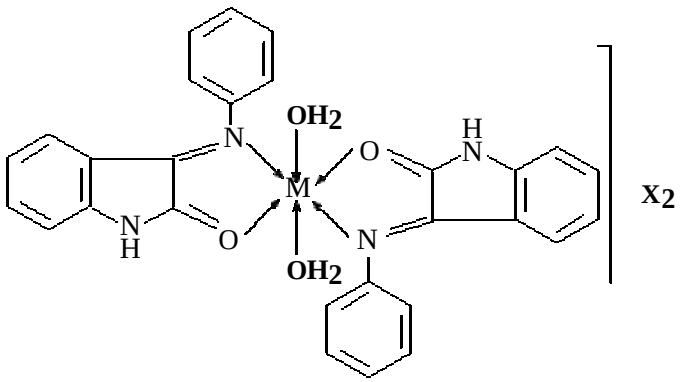
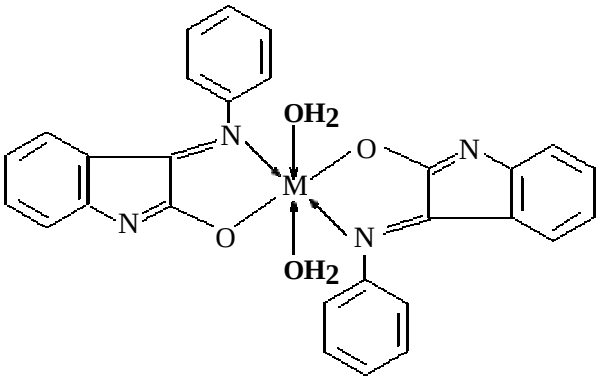


Figure II.19. TGA/DTG/DSC analysis of complex $[Cd(L^1)_2]$

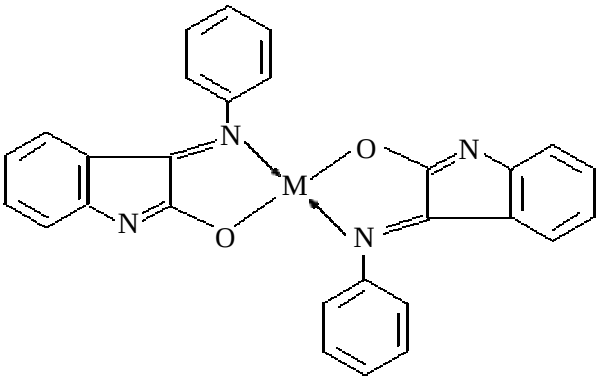
Based on the above-mentioned experimental data, structural formulae (figure II.20) were assumed for the synthesized complexes.



a) $[M(HL^1)_2(H_2O)_2](X)_2$-type complexes, where M = Cu, Co, Ni, Zn, Cd and X = NO_3^- and ClO_4^-



b) $[M(L^1)_2(H_2O)_2]$-type complexes, where M = Cu, Co, Ni, Zn, Cd

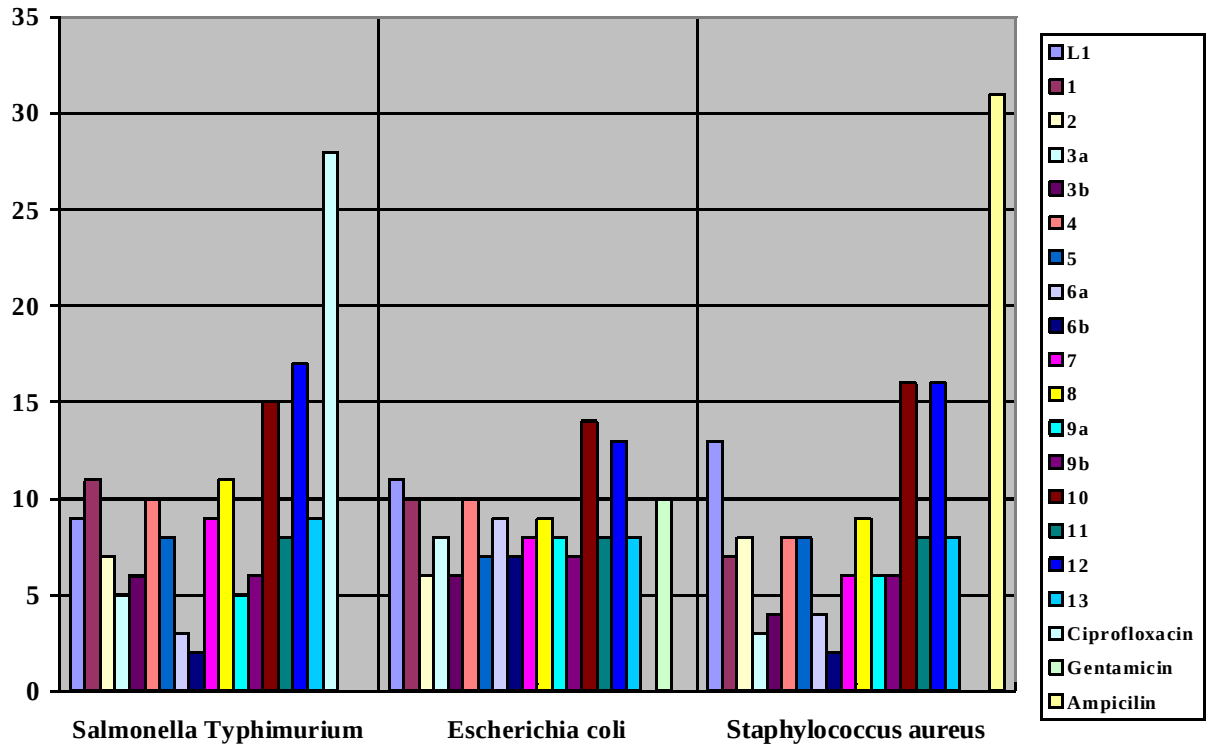


c) $[M(L^1)_2]$-type complexes, where M = Zn, Cd

Figura II.20. Structural formulae assumed for complexes **1 – 19**

Antibacterial activity

Antibacterial activity of ligand L^1 and its complexes was assayed against gram-positive and gram-negative bacteria, *Staphylococcus aureus*, *Escherichia coli* and *Salmonella Typhimurium*, respectively. The experimental data that indicate the inhibition zone diameter (mm) of the assayed compounds are graphically displayed hereunder. Reference antibiotics which are usually employed in the treatment of diseases caused by these bacteria were used for comparison.


35
30
25
20
15
10
5
0
Salmonella Typhimurium
Escherichia coli
Staphylococcus aureus
L1
1
2
3a
3b
4
5
6a
6b
7
8
9a
9b
10
11
12
13
Ciprofloxacin
Gentamicin
Ampicilin

II.2. Complexes of some transition-metal ions with tridentate Schiff bases derived from 1-H-indole-2,3-dione

In this subchapter are discussed the complexes generated by two potentially tridentate ligands, namely the hydrazone resulted from 1-H-indole-2,3-dione and the hydrazide of isonicotinic acid, and the Schiff base derived from the condensation of 1-H-indole-2,3-one with aminobenzyl alcohol.

The reported studies are very rich in data regarding the complexes containing hydrazones formed by isonicotinic acid and a large variety of aldehydes, dialdehydes, or ketones, but there are few publications on hydrazide of isonicotinic hydrazide coupled with 1-H-indole-2,3-dione [124, 162]. Moreover, in the existing publications there could not be found indications regarding complexes of a Schiff base derived from 1-H-indole-2,3-dione and aminobenzyl alcohol.

In figure II.54 are depicted the condensation reactions of obtaining the ligands starting from 1-H-indole-2,3-dione and the hydrazide of isonicotinic acid and aminobenzyl alcohol, respectively.

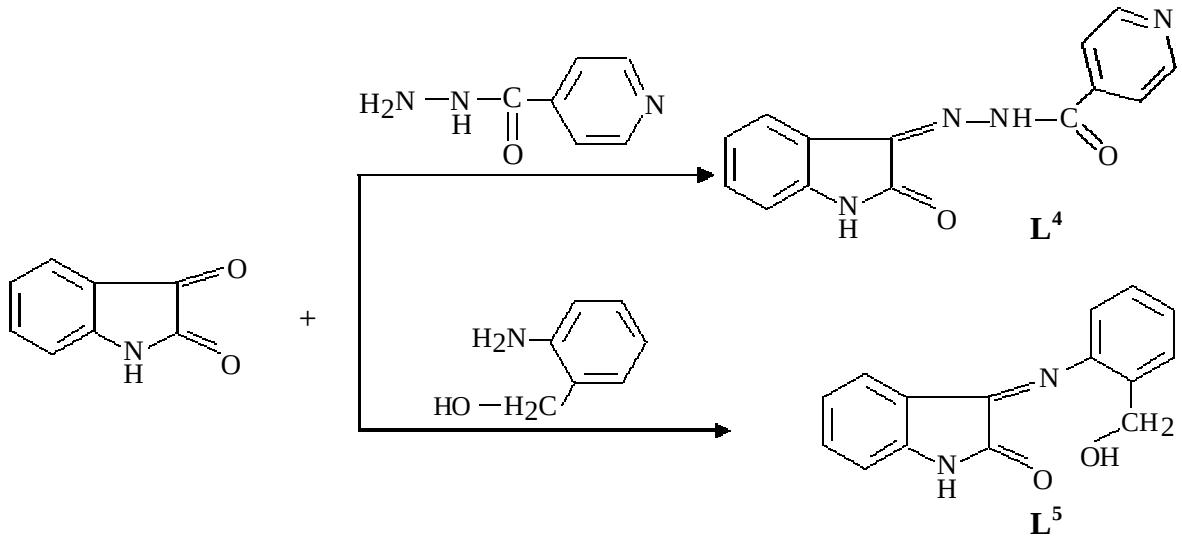


Figure II.54. Condensation reactions for the preparation of the following Schiff-base ligands: L^4 (upper row) and L^5 (lower row)

II.2.1. Synthesis and characterization of Cu(II), Co(II), Ni(II) and Zn(II) complexes with the Schiff base derived from 1-H-indole-2,3-dione and isonicotinic acid hydrazide

Spectral analysis

The IR spectrum of the ligand displayed more or less strong intensity bands in the 4,000 - 400 cm^{-1} range, specifically at 3232, 3165 and 3024 cm^{-1}, which could be assigned to vibrational modes of NH group of hydrazone when compared to the IR spectra of the hydrazide of isonicotinic acid and 1-H-indole-2,3-dione, respectively. Thus, the first mentioned band was related to the vibrational frequency of the NH group from hydrazide [166], and the last two bands to the isatin moiety (figure II.55).

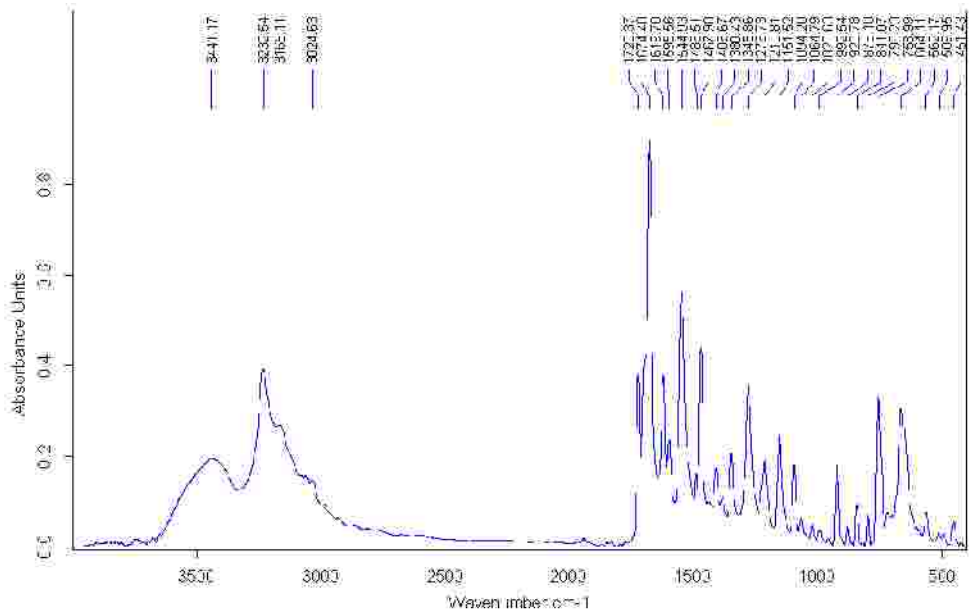


Figure II.55. IR spectrum of the Schiff base isonicotinoyl hidrazon-2 indolinone (L^4)

Strong intensity bands occurred at 1720, 1674, and 1620 cm^{-1} in the range specific to double bonds, a feature that characterizes the stretching frequencies of the carbonyl groups from the isatin moiety and from hydrazide, and of azomethine group, respectively [140].

In the 1,000 - 700 cm^{-1} range medium and medium-to-weak intensity bands were noted at 992, 920, and 753 cm^{-1}, which were assigned to the pulse of pyridine ring, to the N–N bond, and to the $?_{in\text{-}plane}$ vibrational mode of pyridine ring [167].

^{1}H-NMR spectrum [d^6-DMSO, d(ppm), J(Hz)] of the ligand isonicotinoyl hidrazon-2 indolinone (L^4) (figure II.56) was recorded at room temperature in d^6-DMSO at 300 MHz and

showed to following signals: 13.98 (s, 1H, NH); 11.40 (s, 1H, H-5); 8.85 (d, 5.9, 2H, H-15, H-17); 7.76 (d, 5.9, 2H, H-14, H-18); 7.58 (dl, 6.4, 1H, H-1); 7.39 (td, 7.7, 1.1, 1H, H-3); 7.09 (tl, 7.7, 1H, H-2); 6.94 (d, 7.7, 1H, H-4). The first signal at 13.98 ppm assigned to the proton of NH group of hydrazide, and the second one at 11.40 ppm assigned to the proton of NH group of isatin.

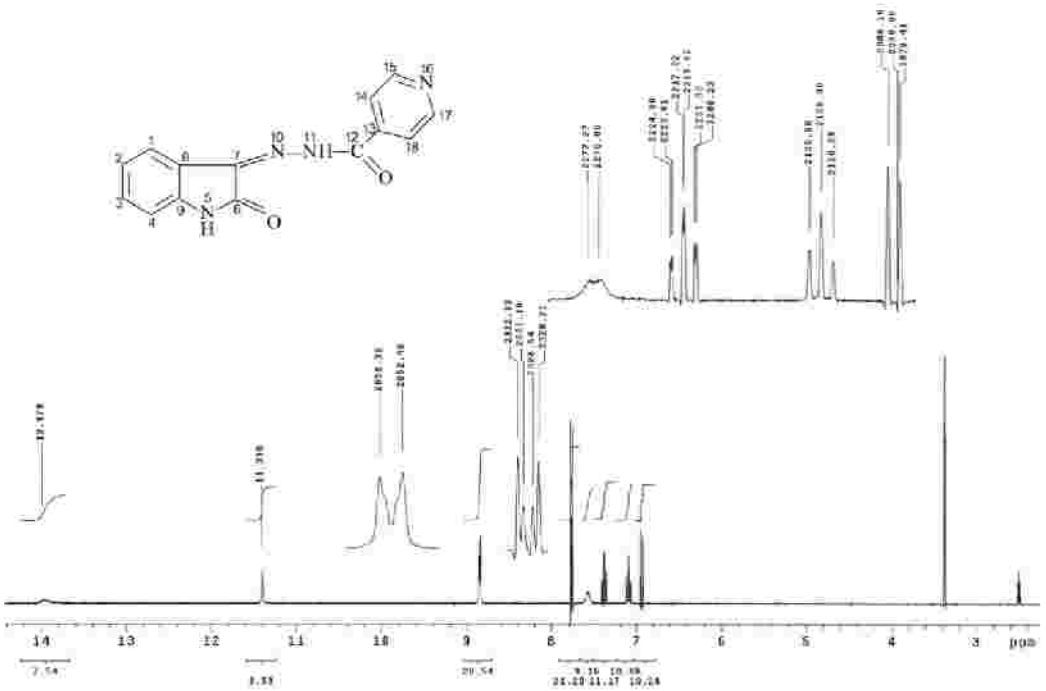


Figure II.56. ^{1}H-NMR spectrum of ligand L^{4}

The structure of the ligand was also sustained by the presence of the following signals in the ^{13}C-NMR [d^{6}-DMSO, d(ppm)]: 162.94 (C-6, C-12); 150.87 (C-15, C-17); 142.73 (C-9); 139.18 (C-13); 132.18 (C-2); 122.83 (C-3); 121.19 (C-14, C-18); 119.55 (C-8); 111.31 (C-4).

The assignments of chemical shifts of the carbon atoms were established based on the ^{1}H-^{1}H COSY and ^{1}H-^{13}C COSY spectra, which correlate the carbon atoms with the hydrogen atoms (figure II.58).

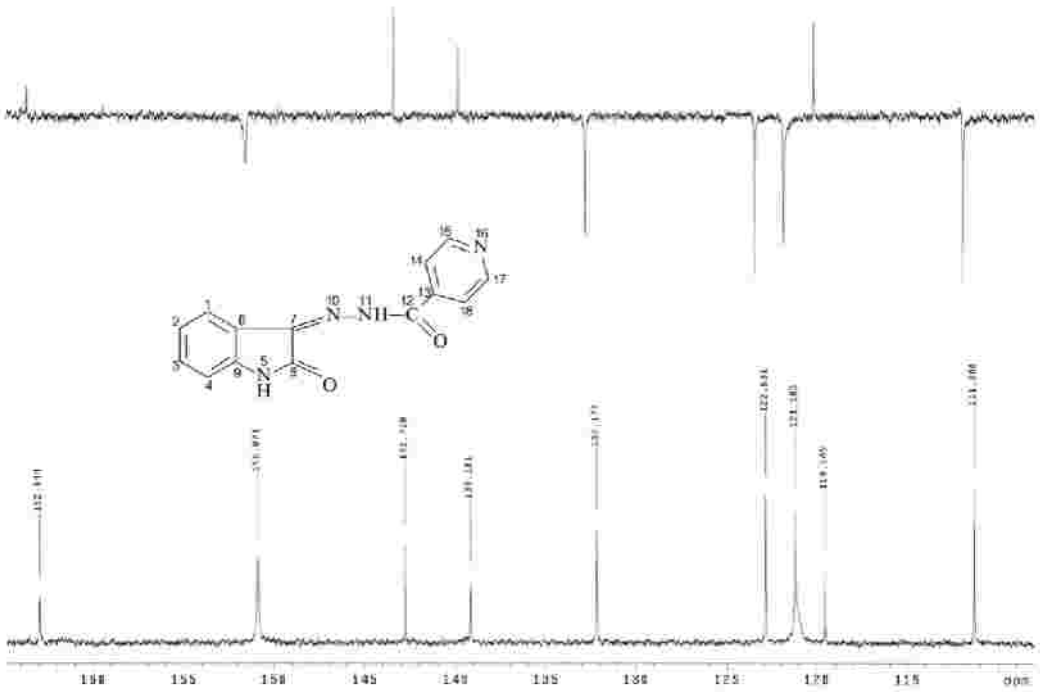


Figure II.57. ^{13}C-NMR spectrum of ligand L^4

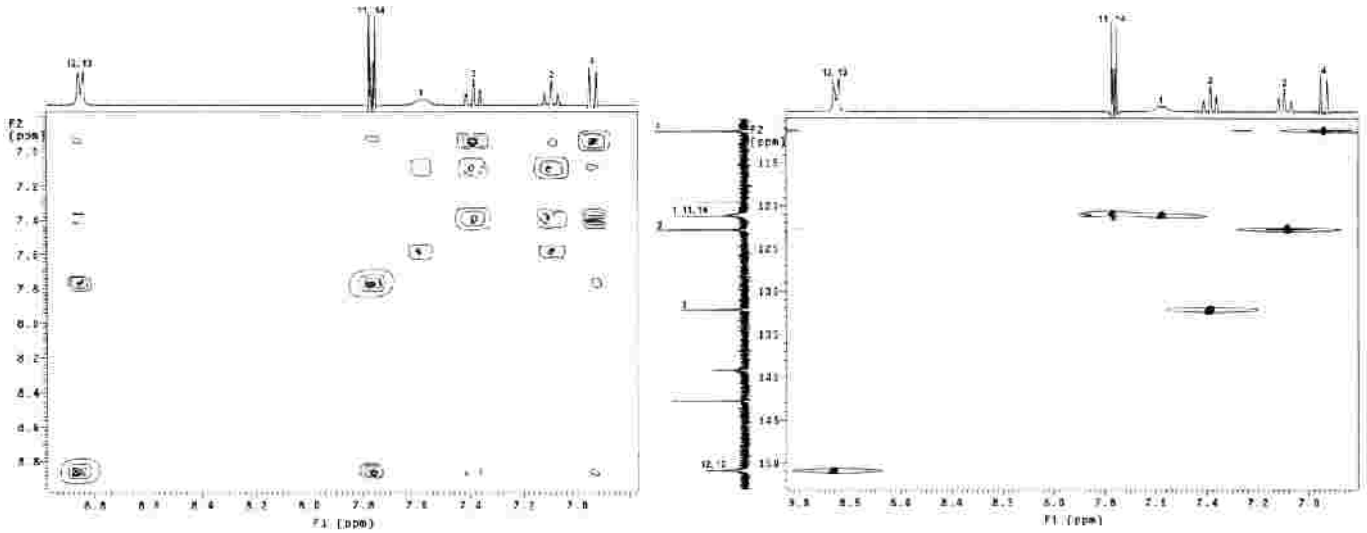


Figure II.58. ^{1}H-^{1}H COSY and ^{1}H-^{13}C COSY spectra of ligand L^4

The electronic spectrum of hydrazone (figure II.59) consisted in three bands assigned to p? p*, n? p* [160], and an intraligand charge-transfer transitions, respectively.

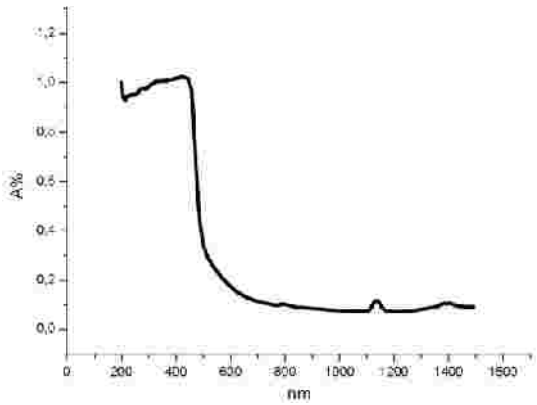


Figure II.59. Electronic spectrum of ligand L^4

$[M(L^4)_2]\cdot xH_2O$-type complexes, where M=Cu(II), x = ½; M=Co(II), x = 2; M=Ni(II), x = 3; M=Zn(II), x = 2, and $[Cu(HL^4)_2](ClO_4)_2\cdot H_2O$ complex were synthesized. These coordination compounds were characterized by elemental analysis (appendix 2, table 4), IR and UV-Vis-NIR spectroscopies, magnetic susceptibility and molar conductivity measurements, antibacterial activity and thermal analysis. Some physical properties of the obtained complexes such as color, melting point, and molar conductivity in DMF (10^{-3} M) are listed in table II.16.

Table II.16. Some physical properties of the obtained complexes

No. cx.	**Complex**	**Color**	**Melting point** (°C)	**? $_m$ [a]** ($O^{-1}cm^2mol^{-1}$)
33	$[Cu(L^4)_2]\cdot ½H_2O$	brown	320*	15,5
34	$[Co(L^4)_2]\cdot 2H_2O$	greenish-brown	301*	13,5
35	$[Ni(L^4)_2]\cdot 3H_2O$	brown	320*	15,8
36	$[Zn(L^4)_2]\cdot 2H_2O$	reddish-brown	318*	16,5
37	$[Cu(HL^4)_2](ClO_4)_2\cdot H_2O$	brown	282*	155

[a] - DMF 10^{-3}M solution

* - decomposition

The molar conductivity values indicated a non-electrolyte nature for all the complexes except for the $[Cu(HL^4)_2](ClO_4)_2\cdot H_2O$ compound, which behaved as a 1:2 electrolyte [139].

IR spectra

Information on the coordination fashion of the ligand L^4 to the metal ions was extracted from the comparative analysis of IR spectra of the free ligand and its corresponding complexes. The most important infrared absorption bands occurred in the spectra of the complexes which offered the essential clues on metal ion coordination site are systematized in table II.17.

Table II.17. Significant infrared absorption frequencies (cm^{-1}) and their assignments for ligand L^4 and its complexes

No. cx.	Complex	?$_{OH}$	?$_{NH}$	?$_{C=O}$*	?$_{C=O}$**	?$_{C=N}$	?$_{C=N}$***	?$_{C-O}$	?$_{pulse\ Py}$	?$_{N-N}$	?$_{Py\ in\ plane}$	?$_{ClO4^-}$
	L^4	-	3232 3165 3024	1720	1674	1620	-	-	992	920	753	-
33	$[Cu(L^4)_2]\cdot½H_2O$	3397	3197	1668	-	1618	1571	1354	990	926	755	-
34	$[Co(L^4)_2]\cdot 2H_2O$	3426	3200	1676	-	1619	1565	1349	987	925	755	-
35	$[Ni(L^4)_2]\cdot 3H_2O$	3400	3180	1673	-	1617	1573	1346	984	926	754	-
36	$[Zn(L^4)_2]\cdot 2H_2O$	3389	3229	1675	-	1630	1575	1357	988	927	755	-
37	$[Cu(HL^4)_2](ClO_4)_2\cdot H_2O$	3443	3215	1681	1621	1580	-	-	-	923	757	1096 626

* group from isatin moiety

** group from hydrazide moiety

*** group from enol form

Electronic spectra

The spectral data together with the values of magnetic moments calculated from the corresponding magnetic susceptibilities for Cu(II), Co(II), Ni(II), and Zn(II) complexes are listed in table II.18.

Table II.18. Electronic spectral data and magnetic moments valid for the ligand L^4 and its complexes

Nr. cx.	Complex	Wavenumber/ wavelength (cm^{-1} / nm)	Assignment	μ_{eff} MB	Geometry
	L^4	41490/240 35460/282 23470/426	n, p? p* CT	-	-
33	$[Cu(L^4)_2]\cdot½H_2O$	29850/335 21739/460 14705/680 10964/912	n, p? p* CT d_{xy}? $d_{x^2-y^2}$ d_{z^2}? $d_{x^2-y^2}$	1,84	Octahedral

Nr. cx.	Complex	Wavenumber/ wavelength (cm^{-1} / nm)	Assignment	μ_{eff} MB	Geometry
34	$[Co(L^4)_2]\cdot 2H_2O$	36363/275 30120/332 22222/450 (?$_3$) 18500/540 (?$_2$) 9090/1100 (?$_1$)	n, p? p* $^4T_{1g}$? $^4T_{1g}$(P) $^4T_{1g}$(F)? $^4A_{2g}$ $^4T_{1g}$(F)? $^4T_{2g}$	4,80	Octahedral
35	$[Ni(L^4)_2]\cdot 3H_2O$	36363/275 30120/332 23200/431 (?$_3$) 15900/629 (?$_2$) 9500/1052 (?$_1$)	n, p? p* $^3A_{2g}$? $^3T_{1g}$(P) $^3A_{2g}$? $^3T_{1g}$ $^3A_{2g}$? $^3T_{2g}$	3,18	Octahedral
36	$[Zn(L^4)_2]\cdot 2H_2O$	3980/250 32753/300 22222/450	n, p? p* CT	dia	Octahedral
37	$[Cu(HL^4)_2](ClO_4)_2\cdot H_2O$	33333/300 23255/430 14773/678 11230/890	n, p? p* d_{xy}? $d_{x^2-y^2}$ d_{z^2}? $d_{x^2-y^2}$	1,93	Octahedral

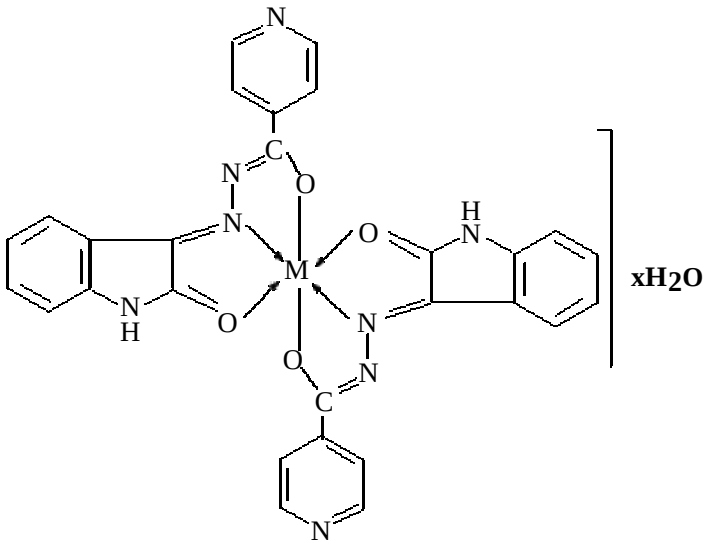
Thermal analysis

Firstly indicated by the IR spectra, the presence of water molecules in the composition of the complexes was reconfirmed by the thermogravimetric analysis (table II.19).

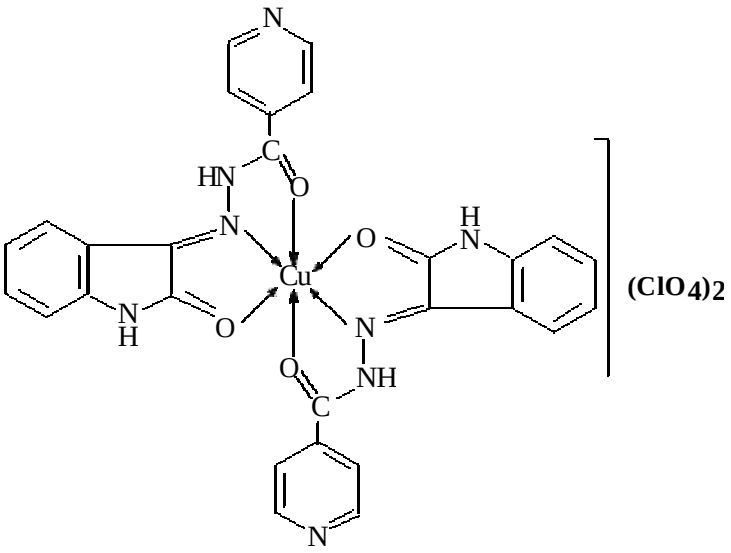
Table II.19. Thermal analysis data valid for $[M(L^4)_2]\cdot xH_2O$-type complexes

Nr. cx.	Complex	Step	Temperature range [oC]	Experimental mass loss [%]	Calculated mass loss [%]	Comments
33	$[Cu(L^4)_2]\cdot ½H_2O$	I	100-125	6.07	5.49	The loss of ½ water molecule of crystallization
		II	125-900	60.22	55.38	Decomposition of the complex
34	$[Co(L^4)_2]\cdot 2H_2O$	I	100-150	6.99	5.76	The loss of 2 water molecules of crystallization
		II	150-900	55.69	53.44	Decomposition of the complex
35	$[Ni(L^4)_2]\cdot 3H_2O$	I	100-160	9.44	8.40	The loss of 3 water molecules of crystallization
		II	160-900	49.95	51.94	Decomposition of the complex
36	$[Zn(L^4)_2]\cdot 2H_2O$	I	100-160	6.40	5.70	The loss of 2 water molecules of crystallization
		II	160-900	55.23	52.93	Decomposition of the complex

In figure II.70 are represented the assumed structural formulae of the complexes of interest based on elemental analysis data, magnetic susceptibility and molar conductivity measurements, thermal analysis and spectral investigations.



a) $[M(L^4)_2]\cdot xH_2O$-type complexes



b) $[Cu(HL^4)_2](ClO_4)_2\cdot H_2O$ complex

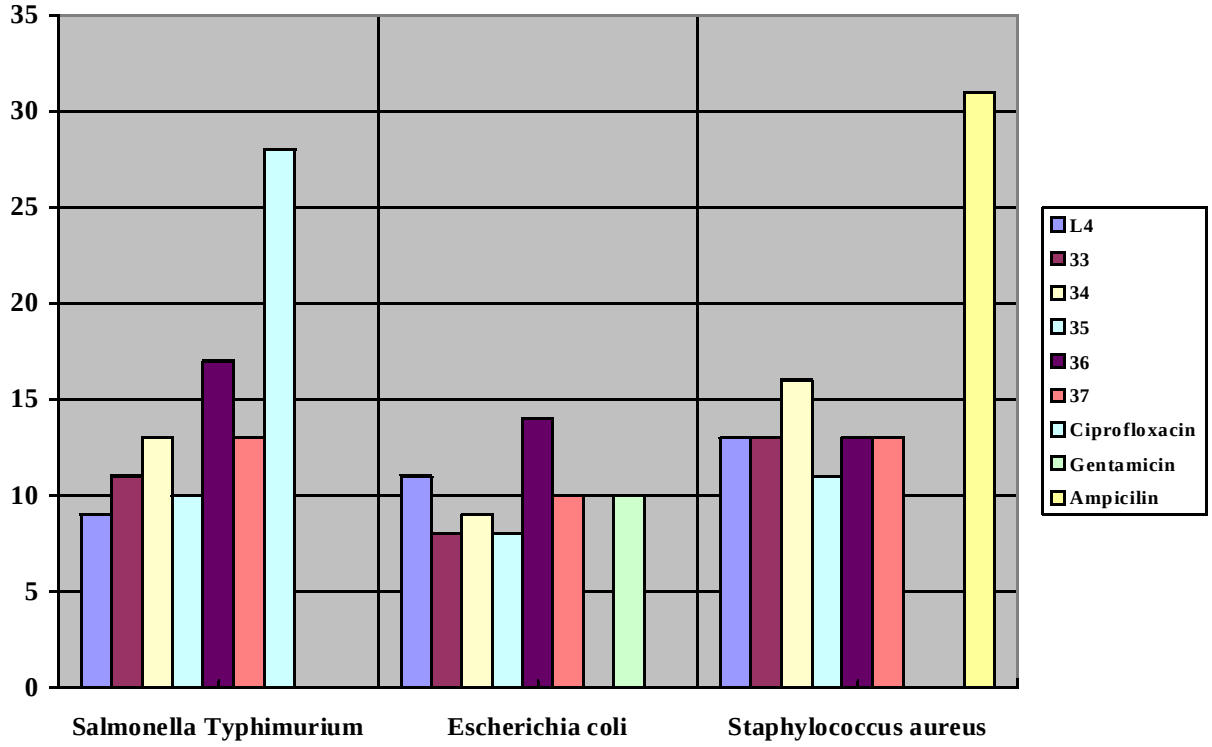
Figure II.70. Structural formulae deduced for complexes **33 – 37**

Antibacterial activity

Antibacterial activity of ligand L^1 and its complexes was assayed against gram-positive and gram-negative bacteria, *Staphylococcus aureus*, *Escherichia coli* and *Salmonella Typhimurium*, respectively. The experimental data that indicate the inhibition zone diameter (mm) of the assayed compounds are listed in table II.20 and graphically displayed hereunder.

Table II.20. Experimental data that provide the inhibition zone diameter (mm) for the ligand and its complexes together with the corresponding graphics

Nr. cx.	*Complex / Reference antibiotic*	Representation of inhibition zone (mm)		
		Salmonella Typhimurium	*Escherichia coli*	*Staphylococcus aureus*
	L^4	9	11	13
33	$[Cu(L^4)_2]\cdot½H_2O$	11	8	13
34	$[Co(L^4)_2]\cdot2H_2O$	13	9	16
35	$[Ni(L^4)_2]\cdot3H_2O$	10	8	11
36	$[Zn(L^4)_2]\cdot2H_2O$	17	14	13
37	$[Cu(HL^4)_2](ClO_4)_2\cdot H_2O$	13	10	13
	Ciprofloxacin	**28**	-	-
	Gentamicin	-	**10**	-
	Ampicilin	-	-	**31**



II.2.2. Synthesis and characterization of Cu(II), Co(II), Ni(II), Zn(II) and Cd(II) complexes with the Schiff base derived from 1-H-indole-2,3-dione and 2-aminobenzyl alcohol

Aiming to obtain a new tridentate Schiff base originating from 2-aminobenzyl alcohol and 1-H-indole-2,3-dione and considering the lack of scientific sources claiming the preparation of at least one complex with such a ligand, we have initiated a research activity regarding the setting of a condensation reaction appropriate for the synthesis of the above-mentioned ligand.

The synthesis parameters were systematically adjusted: ethanol as proper solvent, optimal reaction time, concentration and purification, but the yield of the condensation process did not grow higher than 42%.

The resulting Schiff base is stable in air and relatively soluble in common organic solvents (ethanol, acetone, DMF, and DMSO). This compound was characterized by mean of elemental analysis and IR, NMR and UV-Vis-NIR spectroscopies.

Spectral analysis

A sharp vibrational band located at 3368 cm^{-1} was noticed in the IR spectrum of ligand L^5 which is assignable to OH group belonging to the benzyl alcohol moiety. The Schiff bases containing OH groups could be involved in the formation of synthons through intramolecular hydrogen bonds.

The bands with peak maximum at 3198 and 3042 cm^{-1} were assigned to the NH_{asymm} si NH_{symm} stretching vibrational modes, respectively.

The very-strong and strong intensity bands at 1707 and 1621 cm^{-1} were assigned to the vibrational frequencies of C=O group and newly formed azomethine C=N group, respectively [173].

The C–O bond is quite sensitive to the electronic and symmetry effects which lead to the changing of force constant value and, hence, to a displacement in the position of the infrared absorption bands. The difficulty in assigning the bands is directly influenced by the degree of involvement of the structural elements surrounding the C-O bond and of the variation of the molecular symmetry in the corresponding bond vibrations [174].

The ^{1}H-NMR [d^6-DMSO, d(ppm), J(Hz)] of ligand L^5 (figure II.72) was recorded at room temperature in d^6-DMSO la 300 MHz and showed to following signals: 10.42 (s, 1H, NH); 7.25 – 7.40 (m, 2H, H-2, H-13); 7.02 (m, 2H, H-1, H-3); 6.92 (dl, 7.9, 1H, H-15); 6.86 (dl, 7.5,

1H, H-12); 6.65 (td, 7.3, 1.1, 1H, H-14); 6.62 (dl, 7.9, 1H, H-4), 5.37 (d, 14.7, 1H, H-9); 4.80 (d, 14.7, 1H, H-9).

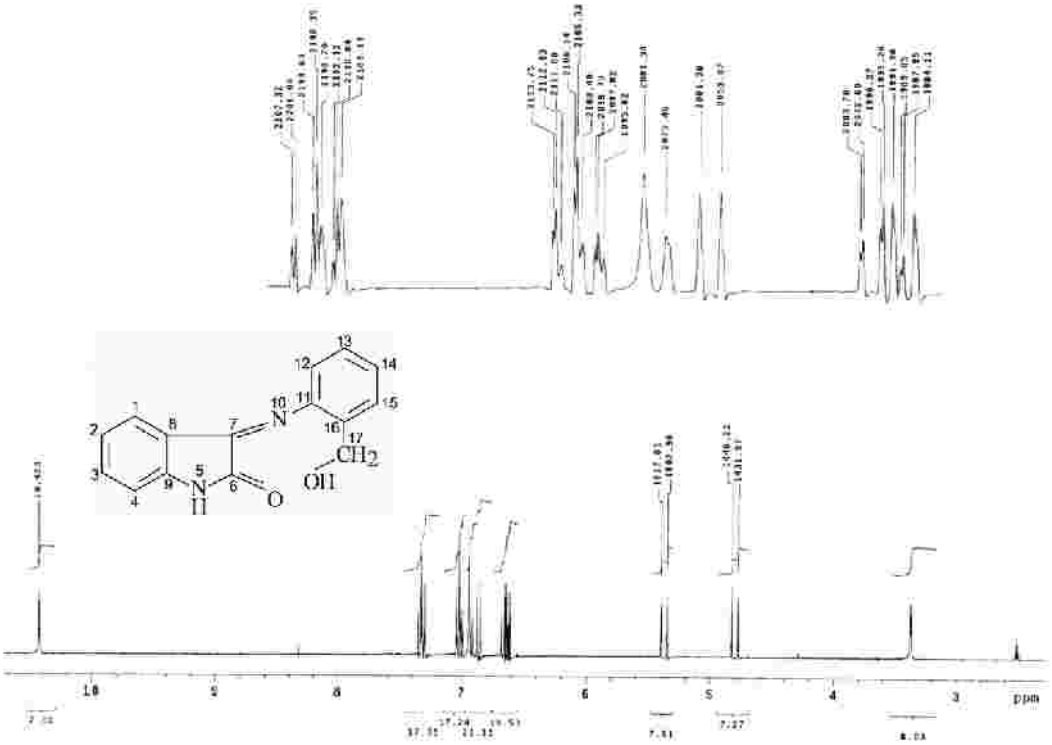


Figure II.72. ^{1}H-NMR spectrum of ligand L^{5}

The obtaining of the Schiff base was supplementary confirmed by the presence of the following signals in the ^{13}C-NMR spectrum [d^{6}-DMSO, d(ppm)] (figure II.73): 174.81 (C-7); 128.05 (C-10); 152.05 (C-8); 142.07 (C-11); 140.22 (C-5); 130.81 (C-2); 128.05 (C-10); 127.07 (C-3); 124.89 (C-13); 124.10 (C-15); 121.95 (C-1); 118.95 (C-6); 117.07 (C-14); 115.02 (C-6); 114.38 (C-4); 109.90 (C-12); 62.17 (C-9).

The assignments of the chemical shifts of the carbon atoms were established based on the ^{1}H-^{1}H COSY and ^{1}H-^{13}C COSY spectra, which correlate the carbon atoms with the hydrogen atoms (figure II.74).

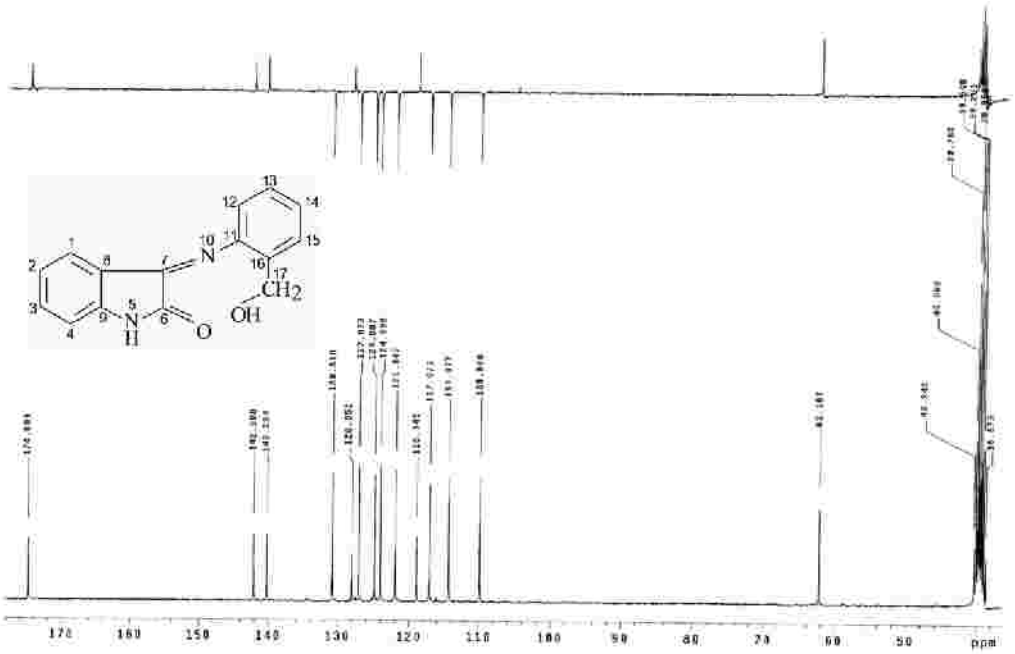


Figure II.73. ^{13}C-NMR spectrum of ligand L^5

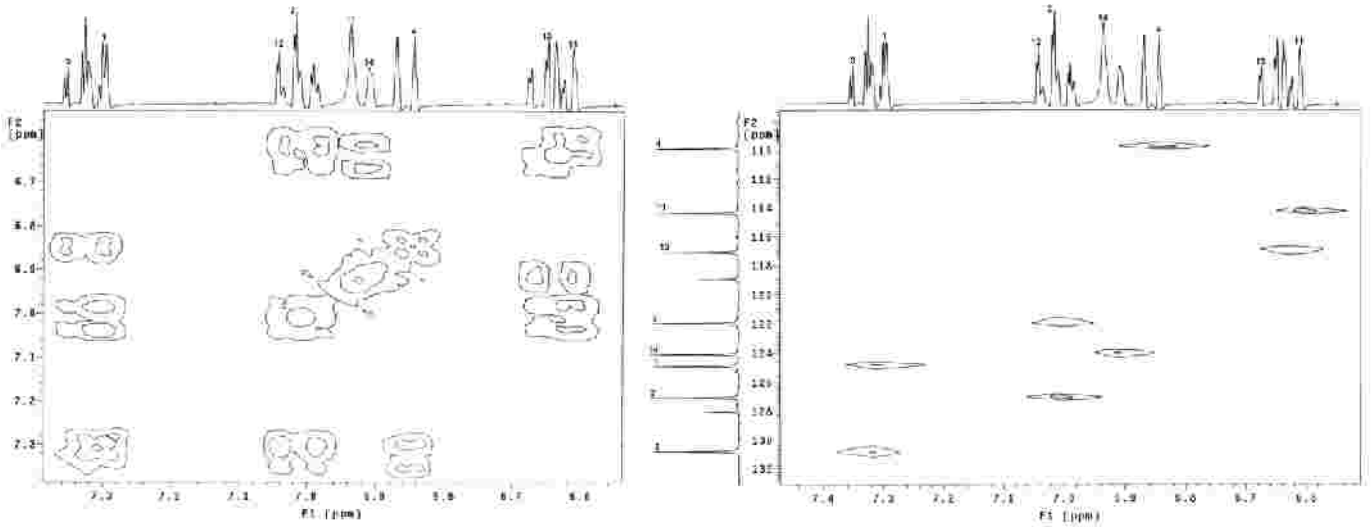


Figure II.74. ^{1}H-^{1}H COSY and ^{1}H-^{13}C COSY spectra of ligand L^5

The electronic spectrum of ligand L^5 contained two absorption bands with the corresponding maxima at 35,714 cm^{-1} (280 nm) and 27,027 cm^{-1} (370 nm) assigned to n, p? p* transitions (figure II.75).

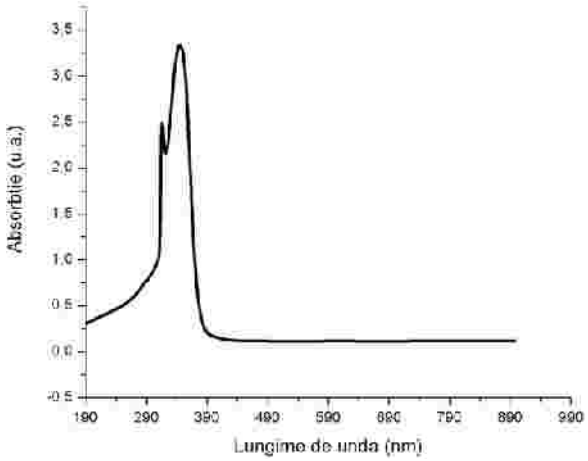


Figure II.75. Electronic spectra of ligand L^5

Three types of complexes, specifically $[M(L^5)_2]\cdot xH_2O$, where M = Cu(II), Co(II), Ni(II), Zn(II), Cd(II), and x = 1, 2, 3, $[Zn(HL^5)_2]Cl_2\cdot 2H_2O$ and $[Cu(L^5)Cl(H_2O)]_2$, were synthesized by mixing the ethanolic solutions of ligand L^5 and corresponding metallic salts in a 1:2 molar ratio with/out triethylamine, except for the last mentioned compound, for which the molar ratio was 1:1 in the absence of a deprotonation agent.

These coordination compounds were characterized by elemental analysis, IR and UV-Vis-NIR spectroscopies, magnetic susceptibility and molar conductivity measurements, antibacterial activity and thermal analysis. Some physical properties of the obtained complexes such as colour, melting point, and molar conductivity in DMF (10^{-3} M) are listed in table II.21.

Table II.21. Some physical properties of the obtained complexes

No. cx.	Complex	Colour	Melting point (°C)	$?_m^*$ ($O^{-1}cm^2mol^{-1}$)
38	$[Cu(L^5)_2]\cdot H_2O$	brown	>320	15
39	$[Cu(L^5)Cl(H_2O)]_2$	brown	298	16
40	$[Co(L^5)_2]\cdot 3H_2O$	brown	>320	16
41	$[Ni(L^5)_2]\cdot 3H_2O$	reddish-brown	>320	19
42	$[Zn(L^5)_2]\cdot 2H_2O$	yellow	280	11
43	$[Zn(HL^5)_2]Cl_2\cdot 2H_2O$	yellow	276	164
44	$[Cd(L^5)_2]\cdot H_2O$	yellow	>320	15

* - 10^{-3}M solution in DMF

** - decomposition

The molar conductivity values indicated a non-electrolyte nature for all the complexes except for the $[Zn(L^5)_2]Cl_2 \cdot 2H_2O$ compound, which behaved as a 1:2 electrolyte [139].

IR spectra

When comparing the IR spectra of the complexes containing the organic chelating agent with the corresponding spectrum of the free ligand, one can notice that, depending on the reaction parameters, the ligand coordinates to a certain metal ion either in a monoanionic tridentate or in a neutral bidentate fashion.

Electronic spectra

The electronic spectra were recorded in the 200 - 1500 nm range by using the diffuse reflectance technique. Indications regarding the geometry of the metallic centre of the synthesized complexes containing the ligand L^5 were obtained by corroborating the UV-Vis spectral data with the values of the magnetic moments.

EPR spectra

In the case of $[Cu(L^5)_2]\cdot H_2O$ and $[Cu(L^5)Cl(H_2O)]_2$ complexes, EPR spectra were recorded on powder solids at both ambient and liquid nitrogen (77 K) temperature. The resulting signals at both temperatures showed no significant difference, a fact that indicated the conservation of the existing coordination polyhedron of the copper(II) ion when being cooled down. Extended EPR spectra (in the 100-4100 G range) were also acquired for both temperature values.

A signal specific to an axial symmetry occurred in the EPR spectrum of complex $[Cu(L^5)_2]\cdot H_2O$ (figure II.81).

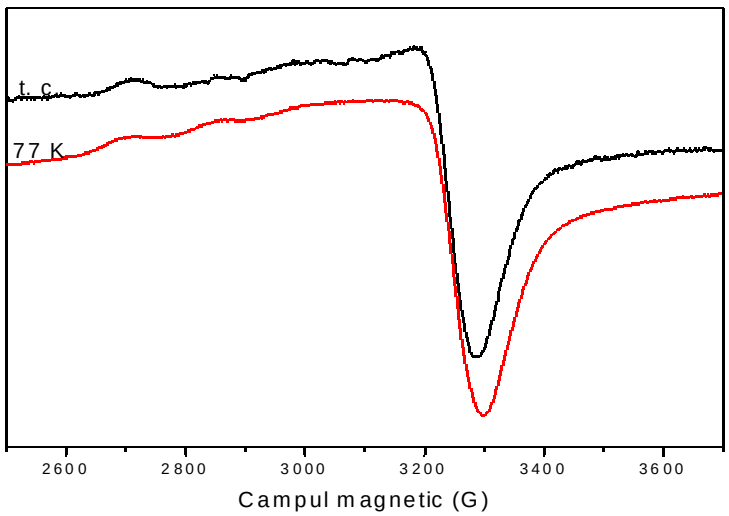


Figure II.81. EPR spectrum of complex $[Cu(L^5)_2]\cdot H_2O$

EPR spectrum of $[Cu(L^5)Cl(H_2O)]_2$ complex recorded at two different temperature values, i.e. ambient and liquid nitrogen temperature, is depicted in figure II.82. In this particular case, an extended spectrum was acquired due to the occurrence of sample signals at low values of the magnetic field, namely half value of the usual applied magnetic field for copper(II) complexes (around 1600 G).

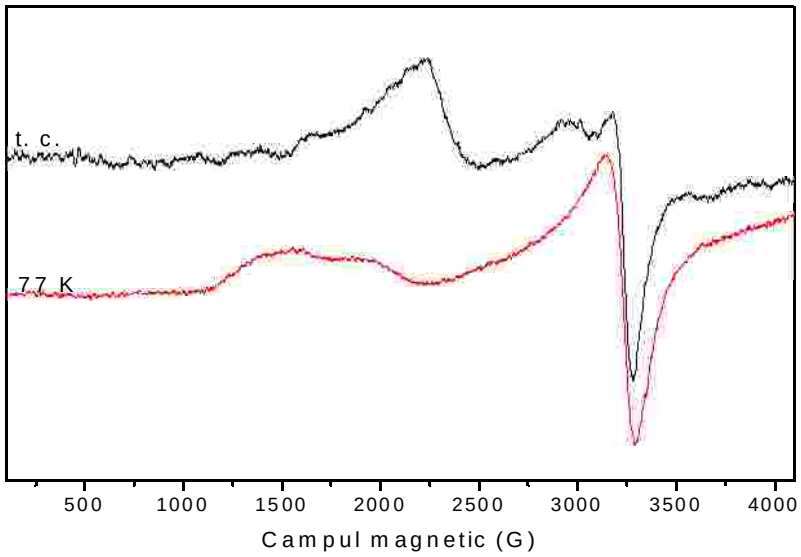


Figure II.82. EPR spectrum of complex $[Cu(L^5)Cl(H_2O)]_2$

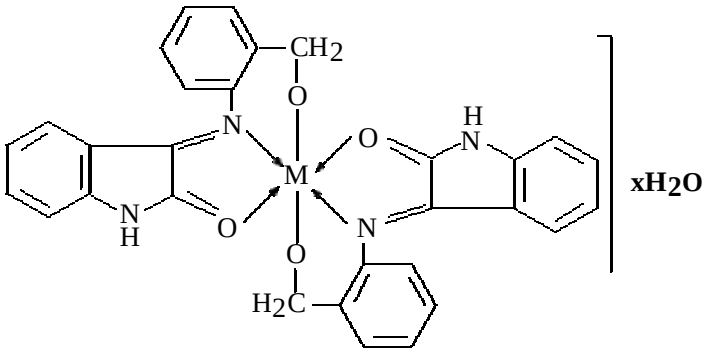
Thermal analysis

Besides the corresponding IR spectra, the existence of water molecules in the composition of the complexes is confirmed by the thermogravimetric analysis data (table II.25).

Table II.25. Thermal analysis data valid for $[M(L^5)_2]\cdot xH_2O$-type complexes

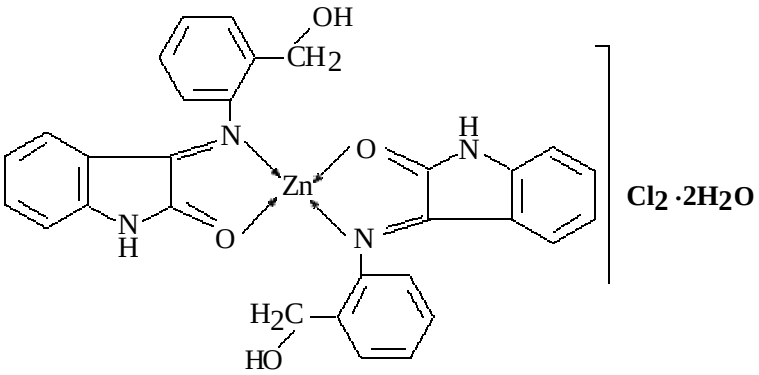
No. cx.	Complex	Step	Temperature range [°C]	Experimental mass loss [%]	Calculated mass loss [%]	Comments
38	$[Cu(L^5)_2]\cdot H_2O$	I	100-145	3.70	3.57	The loss of one water molecule of crystallization
		II	145-570	39.91	37.45	Decomposition of the complex
39	$[Cu(L^5)Cl(H_2O)]_2$	I	120-180	4.52	4.93	The loss of two water molecule of crystallization
		II	180-540	55.36	59.01	Decomposition of the complex
40	$[Co(L^5)_2]\cdot 3H_2O$	I	100-160	9.24	8.77	The loss of three water molecule of crystallization
		II	160-690	37.35	34.16	Decomposition of the complex
41	$[Ni(L^5)_2]\cdot 3H_2O$	I	100-160	8.92	8.77	The loss of three water molecule of crystallization
		II	160-480	43.10	41.94	Decomposition of the complex
42	$[Zn(L^5)_2]\cdot 2H_2O$	I	100-165	6.53	5.96	The loss of two water molecule of crystallization
		II	165-800	37.72	35.93	Decomposition of the complex
43	$[Zn(HL^5)_2]Cl_2\cdot 2H_2O$	I	30-140	4.50	4.84	The loss of two water molecule of crystallization
		II	140-800	55.47	57.82	Decomposition of the complex
44	$[Cd(L^5)_2]\cdot H_2O$	I	100-140	3.50	2.84	The loss of one water molecule of crystallization
		II	140-800	69.27	67.53	Decomposition of the complex

The correlation of the conclusions drawn from these physico-chemical analyses led to the possibility of proposing a sustainable structural model for the complexes (figure II.91).

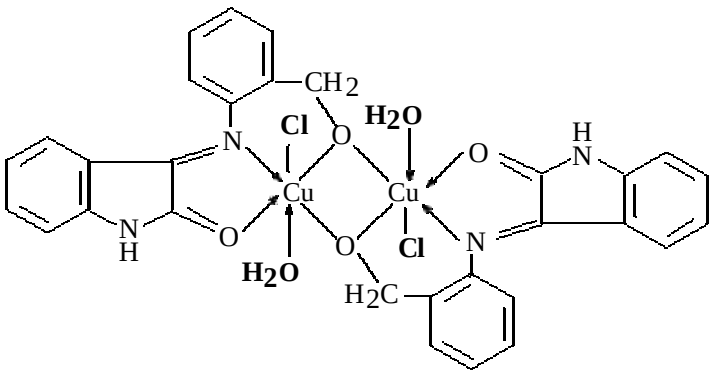


a) $[M(L^5)_2]\cdot xH_2O$-type complexes

(M = Cu(II), Co(II), Ni(II), Zn(II), Cd(II), and x = 1, 2, 3)



b) $[Zn(HL^5)_2]Cl_2\cdot 2H_2O$ complex

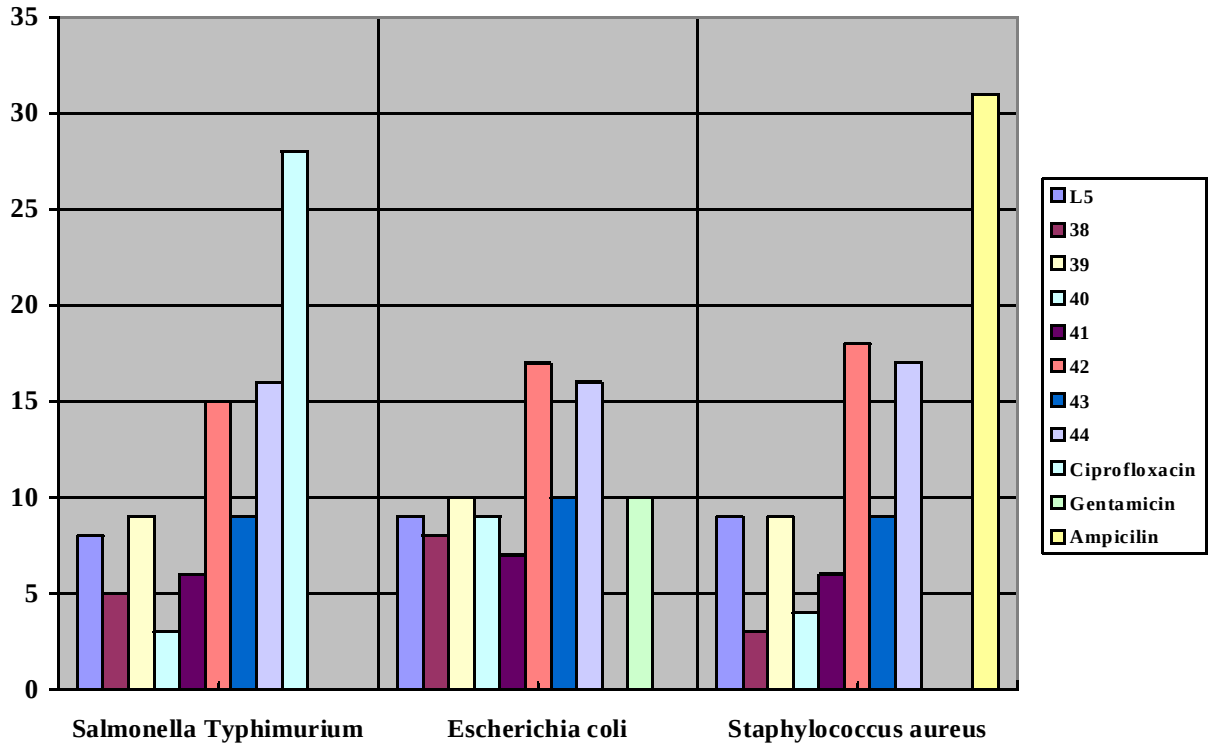


c) $[Cu(L^5)Cl(H_2O)]_2$ complex

Figure II.91. Structural formulae deduced for complexes **38 - 44**

Antibacterial activity

Antibacterial activity of ligand L^5 and its complexes was assayed against gram-positive and gram-negative bacteria, namely *Staphylococcus aureus*, *Escherichia coli* and *Salmonella Typhimurium*, respectively. The experimental data that indicate the inhibition zone diameter (mm) of the assayed compounds are graphically displayed hereunder.



II.4. Complexes of some transition-metal ions with phenyl-2-pyridil ketone and aromatic amines

Following the trend of our laboratory research, eight new complexes containing Schiff bases derived from phenyl-2-pyridil ketone and Cu(II), Co(II), and Ni(II) ions were synthesized.

On the other hand, following the template synthetic approach, a novel coordination compound was obtained starting from nickel(II) perchlorate, phenyl-2-pyridil ketone, and o-anisidine (in a 1:2:2 molar ratio), which was structurally characterized by single crystal X-ray diffraction.

II.4.1. Synthesis and characterization of Cu(II), Co(II) and Ni(II) complexes with Schiff bases derived from phenyl-2-pyridil ketone with aromatic amines

The ligands were prepared according to reported procedures [201] by a condensation reaction between phenyl-2-pyridil ketone and o- and p-anisidine, respectively, in a 1:1 molar ratio. The Schiff bases L^8 and L^9 were isolated from the ethanolic reaction mixtures.

The resulting Schiff bases were separated from solution as yellow crystalline solids, filtered out, washed with ethanol and recrystallized several times from ethanol.

The scheme depicted in figure II.120 illustrates the condensation process between phenyl-2-pyridil ketone and o- and p-anisidine, respectively.

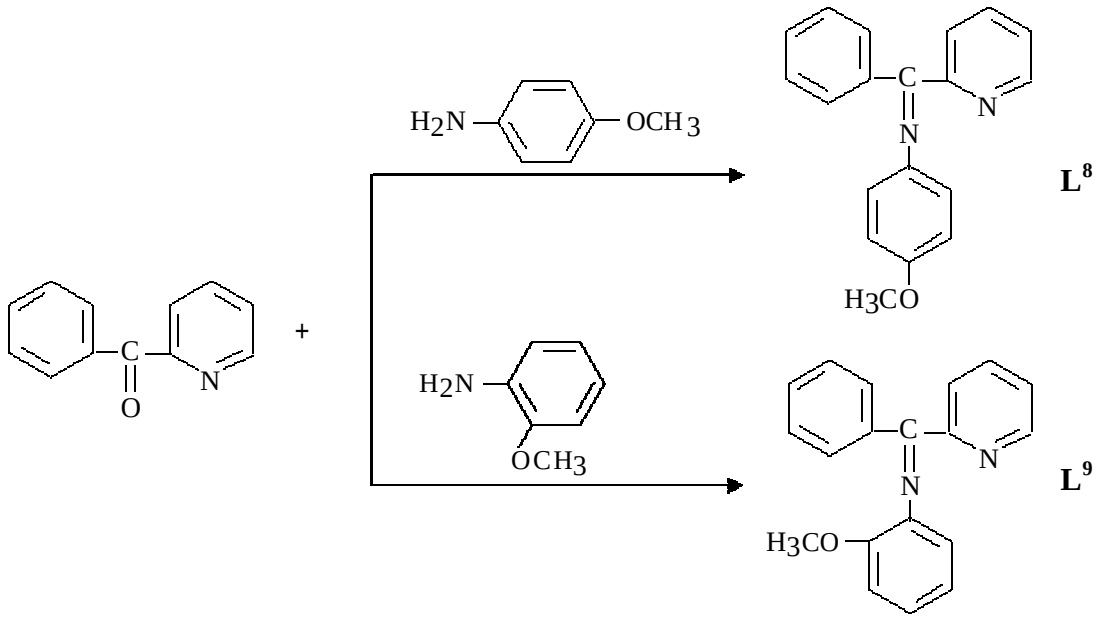


Figure II.120. Condensation reactions for the preparation of the Schiff-base L^8 and L^9

The Schiff bases L^8 and L^9 were stable in air and soluble in common organic solvents such as methanol, ethanol, acetone, DMF, and DMSO. These organic ligands were characterized by elemental analysis, IR and UV-Vis-NIR spectroscopies.

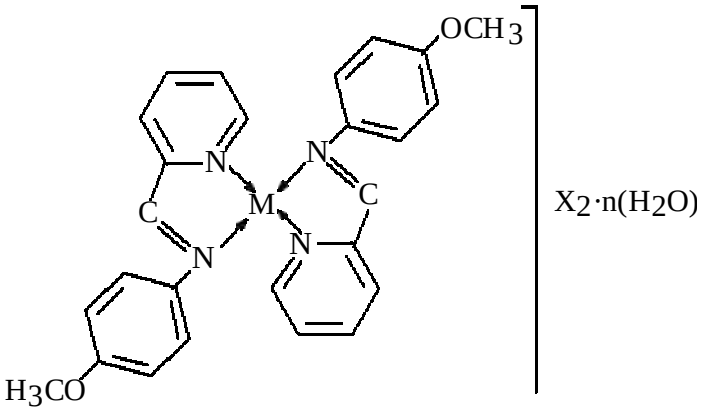
The corresponding complexes were prepared by mixing the ethanolic solutions of ligands L^8 and L^9 and of $M(NO_3)_2$- and $M(ClO_4)_2$-type metallic salts, respectively, in a 1:2 molar ratio. The general formulae of the complexes were:

$[M(L^8)_2](X)_2 \cdot xH_2O$, where M = Cu, Co, Ni; X = NO_3^-, ClO_4^-, x = 0, 1

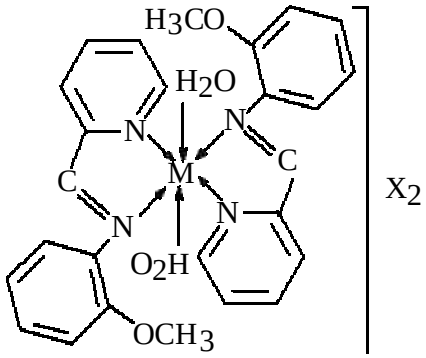
$[M(L^9)_2(H_2O)_2](X)_2$, where M = Cu, Co, Ni; X = NO_3^-, ClO_4^-

The coordination compounds were characterized by elemental analysis, IR, UV-Vis-NIR and EPR (in the case of copper(II)-containing products) spectroscopies, magnetic susceptibility and molar conductivity measurements, and antibacterial activity.

Corroborating the information provided by elemental analysis with the specific features of IR, UV-Vis-NIR, and EPR (where applicable) spectra, it could be inferred the general molecular structures depicted in figure II.131.



a) $[M(L^8)_2]X_2 \cdot nH_2O$-type complexes, where M=Cu, Co, Ni,
$X = ClO_4^-$, NO_3^-, and n = 0, 1



b) $[M(L^9)_2(H_2O)_2]X_2$-type complexes, where M=Cu, Co, Ni,
$X = ClO_4^-$, NO_3^-

Figura II.131. Structural formulae deduced for complexes **59 – 66**

II.4.2. Synthesis and characterization of the Ni(II) complex with phenyl-2-pyridil ketone and o-anisidine

Starting from nickel(II) perchlorate, phenyl-2-pyridil ketone (ppk), and o-anisidine (*o*-MeO-An) in a 1:2:2 molar ratio, a new complex was assembled in methanolic solution *via* template synthetic approach. Following the slow evaporation of the solvent, light brown crystals were grown, which were analyzed by single crystal X-ray diffraction.

The electric conductivity measurements indicated a 1:2 electrolyte behavior for this complex.

The crystal structure of complex $[Ni(ppk)_2(o\text{-MeO-An})_2](ClO_4)_2$ consists of dicationic mononuclear complex units based on nickel(II) ions and the preserved organic compounds accompanied by perchlorate counterions. The crystallographic data and the corresponding refinement parameters are listed in table II.49.

Table II.49. Crystallographic data, details of data collection and structure refinement parameters for compound $[Ni(ppk)_2(o\text{-MeO-An})_2](ClO_4)_2$

Compound	**$[Ni(ppk)_2(o\text{-MeO-An})_2](ClO_4)_2$**
Chemical formula	$C_{38}H_{36}NiN_4O_{12}Cl_2$
M (g mol^{-1})	870.32
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	*Monoclinic*
Space group	$P2_1/a$
a (Å)	15.6445(9)
b (Å)	15.4949(8)
c (Å)	17.5783(10)
a (º)	90.00
ß (º)	113.322(4)
? (º)	90.00
V (Å^3)	3913.0(4)
Z	4
D_c (g cm^{-3})	1.477
µ (mm^{-1})	0.701
F (000)	1800
Goodness-of-fit on F^2	1.025
Final R_1, wR_2 [$I>2\sigma(I)$]	0.0549; 0.1312
R_1, wR_2 (all data)	0.0930; 0.1485
Largest difference in peak and hole (e Å^{-3})	0.597; -0.659

The ligand phenyl-2-pyridil ketone is bound to the metal ion in a bidentate chelating fashion, and two such organic molecules form the basal plane of the nickel(II) polyhedron.

In figure II.132 are illustrated the molecular structures of the two dicationic mononuclear units together with the closest perchlorate counterions that define the crystalline architecture of complex $[Ni(ppk)_2(o\text{-MeO-An})_2](ClO_4)_2$ (most of the hydrogen atoms are omitted for clarity). The two nickel(II) ions, Ni1 and Ni2, are crystallographically independent.

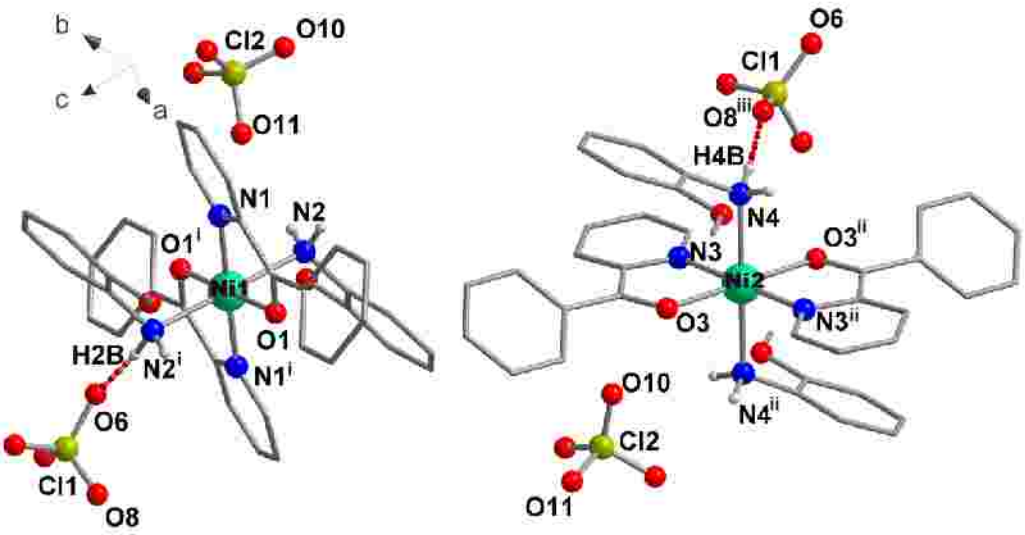


Figure II.132. Molecular structures of the two mononuclear units presented in complex $[Ni(ppk)_2(o\text{-MeO-An})_2](ClO_4)_2$

The coordination geometry of the nickel(II) ions can be described in the terms of a slightly distorted octahedron, specifically an elongation on the N2–Ni1–$N2^i$ and N4–Ni2–$N4^{ii}$ direction, respectively (^{i} = 2-*x*, -*y*, 4-*z*; ^{ii} = 2-*x*, -1-*y*, 3-*z*). Both complex entities correspond to the *trans* isomer resulting from the $[M(AA)_2(B)_2]^{n+}$ general type, i.e. the two unicoordianted ligands are reciprocally opposite.

The packing diagram reveals the formation of rows of mononuclear units containing both Ni1- and Ni2-type ions, parallel to the crystallographic *a* axis. These rows further define layers of discrete complexes parallel to the crystallographic *ab* plane, which are successively separated by similar $Cl(1)O_4^-$ and $Cl(2)O_4^-$-containing planes.

On the other hand, $Cl(1)O_4^-$ anions connect through hydrogen bonds the adjacent complex units containing Ni1- and Ni2-type ions, respectively. Supramolecular zig-zag chains are generated this way, which are reciprocally parallel oriented and propagate in phase (figure II.133).

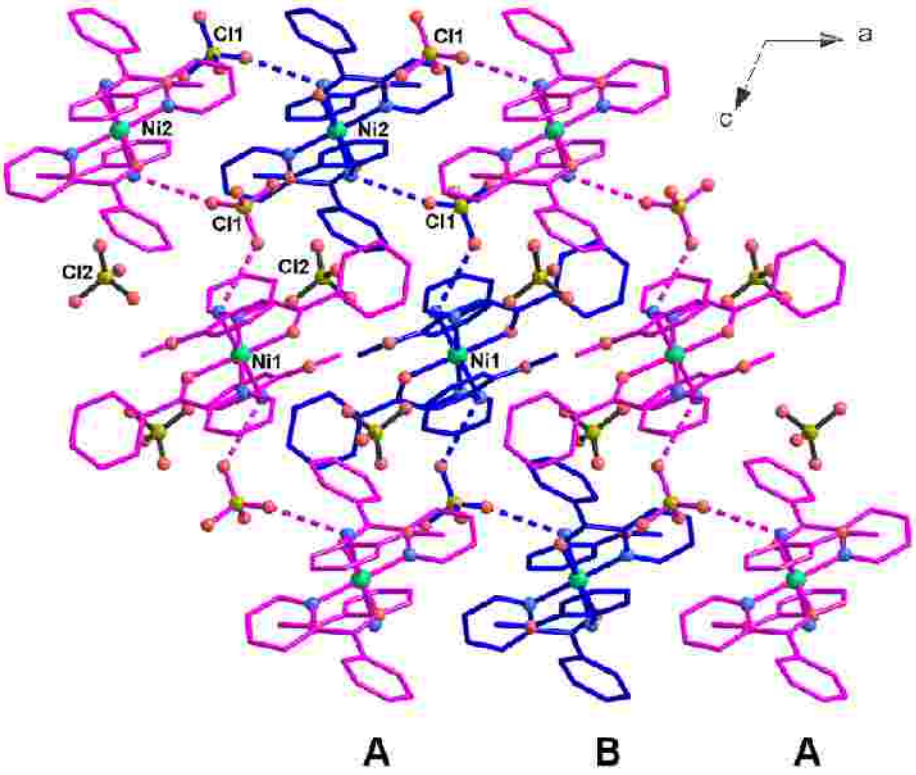


Figure II.133. Packing diagram of complex $[Ni(ppk)_2(o\text{-MeO-An})_2](ClO_4)_2$ - view along the crystallographic *ac* plane (all the hydrogen atoms are omitted for clarity)

CONCLUSIONS

Extensive studies on the ability of azomethine derivatives originating from ketone to form complexes with divalent transition-metal have been tackled within the doctoral research activity.

The results consist in the synthesis of nine azomethine ligands, three of which have not been previously reported. Starting from these ligands, sixty-seven complexes were synthesized, which could be categorized in several general types.

The majority of the resulting complexes contains Schiff bases derived from 1-H-indole-2,3-dione due to the interest aroused by its potential applications in various domains such as biology, biochemistry, medicine, and pharmaceutical industry.

The target ligands were characterized by elemental analysis and IR, NMR and UV-Vis-NIR spectroscopies and the antibacterial activity was evaluated.

Following the synthetic procedures, the isolated coordination compounds derived from these ligands were characterized by elemental analysis, IR, UV-Vis-NIR, and EPR (for Cu(II)-containing complexes) spectroscopies, magnetic susceptibility and molar conductivity measurements, antibacterial activity and thermal analysis.

A new nickel(II) complex derived from phenyl-2-pyridil ketone and 2-methoxy-aniline was prepared according to a template synthetic approach and the growth of single crystals allowed its structural characterization by X-ray diffraction. The crystal structure revealed that phenyl-2-pyridil ketone coordinated in a bidentate chelating fashion and o-anisidine bound in a monodentate mode. Two molecules of ketone derivative defined the basal plane of the metal ion polyhedron, while two o-anisidine molecules occupied the axial position through the sp^3 nitrogen atoms.

The coordination geometry of the nickel(II) ions could be described in the terms of an axially-elongated octahedron. The ionization sphere of the complex was made up of the free perchlorate anions.

Considering that a more increasing number of complexes finds a consistent application in antibacterial therapy, most of the resulting coordination compounds were assayed for their biological activity against gram-positive and gram-negative bacteria, namely *Staphylococcus aureus*, *Escherichia coli* and *Salmonella Typhimurium*, respectively.

In subchapter II.1 there were systematized experimental data regarding the preparation of potentially bidentate Schiff bases by the condensation reaction between 1-H-indole-2,3-dione and

aniline (L^1), o-anisidine (L^2) and p-anisidine (L^3), respectively. Considering the occurrence of tautomerism in azomethine compounds depending on the setting of the synthetic parameters, a new class of complexes containing these ligands coordinated in a monobasic bidentate fashion were successfully prepared. Thus, thirty-two complexes distributed in four different classes were obtained starting from the above-mentioned three ligands that bound in either keto or enol form.

The coordination mode of the ligand was established by corroborating the elemental and thermal analyses data with IR spectra and molar conductivity measurements. The thermogravimetric analysis allowed the estimation of the number of water molecules involved in crystallization and/or coordination in the case of a certain complex. However, the presence of these water molecules was suggested by the identification of characteristic vibrational frequencies in the corresponding IR spectrum.

By corroborating the electronic spectral data with the magnetic susceptibility measurements, it was inferred that the coordination geometry of the metallic center could be described as:

- octahedral for the following types of complexes:

$[M(HL)_2(H_2O)_2](X)_2$, where M = Cu(II), Co(II), Ni(II), Zn(II), Cd(II), and X = NO_3^-, ClO_4^-;

$[M(HL)_2Cl_2]$, where M = Cu(II), Co(II), Ni(II), Zn(II), and Cd(II);

$[M(L)_2(H_2O)_2]$, where M = Cu(II), Co(II), and Ni(II);

- tetrahedral for $[M(L)_2]$-type complexes, where M = Zn(II) and Cd(II).

In the case of complexes $[Cu(HL^1)_2(H_2O)_2](NO_3)_2$ and $[Cu(L^1)_2(H_2O)_2]$, the EPR spectra recorded at room temperature sustained an axially-distorted octahedral geometry of the metal ion, in accordance with the information provided by the corresponding electronic spectra.

The crystal-field parameters which were evaluated from the maxima of the bands occurring in the electronic spectra indicated a weak covalent character of metal-ligand interactions established in the Co(II)- and Ni(II)-containing complexes.

The tetrahedral coordination environment of Zn(II) and Cd(II) ions in the $[M(L)_2]$-type complexes was assumed based on elemental analysis, molar conductivity measurements, the absence of coordinated water molecules, and the monobasic bidentate character of the organic ligand. This assumption was also strengthened by ^{1}H- and ^{13}C-NMR measurements recorded for complex $[Cd(L)_2]$.

The three ligands and their corresponding complexes were assayed against gram-positive and gram-negative bacteria, with promising effects on *Escherichia coli* strains.

The studies on coordination compounds containing one of the two potentially tridentate ligands, i.e. the hydrazone resulted from 1-H-indole-2,3-dione and the hydrazide of isonicotinic acid (L^4) and the Schiff base derived from the condensation of 1-H-indole-2,3-one with aminobenzyl alcohol (L^5) were gathered in subchapter II.2.

The following types of complexes were synthesized starting from ligand L^4 and several transition-metal ions:

$[M(L^4)_2]\cdot xH_2O$, where M=Cu(II), Co(II), Ni(II), Zn(II), x = ½, 2, 3;

$[M(HL^4)_2](ClO_4)_2\cdot H_2O$, where M=Cu(II).

This ligand exhibited a monoanionic tridentate coordination mode through the oxygen atom of the carbonyl group from isatin moiety, the azomethine nitrogen atom, and the oxygen atom of isoniazid moiety - the latter fragment adopting the enol form for $[M(L^4)_2]\cdot xH_2O$-type complexes. The existence of water molecules accommodated in the complexes' lattice was suggested by both IR spectra and thermogravimetric analysis.

The ligand also presented a neutral tridentate coordination behaviour in its keto form, binding to the metal ion through the oxygen atom of the carbonyl group from isatin fragment, the oxygen atom of the carbonyl group from hydrazide fragment, and the nitrogen atom of azomethine group in the case of complex $[Cu(HL^4)_2](ClO_4)_2\cdot H_2O$.

When this ligand and its complexes were assayed against *Escherichia coli* strain, promising results were obtained: the inhibition capacity was higher than *Gentamicin*, i.e. between 8 and 14.

The second tridentate ligand (L^5) was prepared by condensation reaction of 1-H-indole-2,3-dione and 2-aminobenzyl alcohol. The structure of this new ligand was established based on elemental analysis, IR, NMR and UV-Vis-NIR spectroscopies.

Seven new complexes were synthesized starting from ligand L^5 and several transition-metal ions, corresponding to the following general types:

$[M(L^5)_2]\cdot xH_2O$, where M = Cu(II), Co(II), Ni(II), Zn(II), Cd(II), and x = 1, 2, 3;

$[M(HL^5)_2]Cl_2\cdot 2H_2O$, where M = Zn(II);

$[M(L^5)Cl(H_2O)]_2$, where M = Cu(II).

The ensemble of experimental data converged to a monoanionic tridentate coordination mode of the organic ligand controlled by the reaction conditions. The donor set consisted in the azomethine nitrogen atom and the oxygen atoms of amide and phenoxo groups in the case of

$[M(L^5)_2]\cdot xH_2O$- and $[Cu(L^5)Cl(H_2O)]_2$-type complexes. As for the complex $[Zn(HL^5)_2]Cl_2\cdot 2H_2O$, the ligand adopted a neutral bidentate coordination mode through the azomethine nitrogen atom and the oxygen atom of the carbonyl group from isatin moiety, without involving the phenolic group. As various experimental data indicated the lack of coordinated water molecules, in this latter case a tetrahedral environment of the metal ion was suggested.

The oxygen atom of the deprotonated OH group bridged two copper(II) ions in the $[Cu(L)Cl(H_2O)]_2$ dimer. Both ligand molecules bound to the metal ion through the azomethine nitrogen atom and the oxygen atom of the carbonyl group. The coordination sphere of each copper(II) ion is completed by a chloride ion and a water molecule.

An octahedral geometry for the metal centre was assumed for $[M(L)_2]\cdot xH_2O$-type complexes based on the electronic spectra features and magnetic susceptibility measurements; the Schiff base acted as a monobasic tridentate ligand.

EPR spectra were recorded both at ambient and liquid nitrogen temperature for complexes $Cu(L^5)_2]\cdot H_2O$ si $[Cu(L^5)Cl(H_2O)]_2$. Both signals were similar, indicating a conservation of the copper(II) ion coordination geometry in this range of temperature. A signal characteristic to the axial symmetry was recorded for complex $[Cu(L^5)_2]\cdot H_2O$, while an exchange interaction was noticed in the case of complex $[Cu(L^5)Cl(H_2O)]_2$.

The thermogravimetric analysis indicated the presence of a certain number of water molecules in the composition of $[M(L^5)_2]\cdot xH_2O$-type complexes as well as of $[Cu(L^5)Cl(H_2O)]_2$ and $[Zn(HL^5)_2]Cl_2\cdot 2H_2O$, a structural feature also confirmed by the corresponding IR spectra.

Once assayed against the three types of bacteria, the Zn(II) and Cd(II) complexes containing the above-mentioned Schiff bases led to almost two times higher values of the inhibition zone in comparison to the ones determined for ligands L^4 and L^5.

In subchapter II.3 were systematized and analyzed the investigations on condensation reactions of 1-H-indole-2,3-dione and o-phenylenediamine which employed various solvents and different molar ratios.

Depending on the variation of the reaction parameters, different condensation products were obtained and investigated by elemental analysis, IR, NMR, and UV-Vis-NIR spectroscopic techniques.

The synthetic procedure followed in order to obtain ligand L^6, N,N'[-bis-3,3'-indoline-2-2'-one]-1,4-diaminobenzene, consisted in refluxing the solution of the organic reagents in benzene on a water-bath.

Starting from ligand L^6 and the nitrate salts of the corresponding transition-metals, four new complexes were isolated and described as $[M_2(HL^6)(NO_3)_2(H_2O)_4](NO_3)_2$, where M = Cu(II), Co(II), Ni(II), and $[Cd_2(HL^6)(NO_3)_4]$. These formulae were proposed based on various spectral data, molar conductivity and magnetic susceptibility measurements, and thermal analysis. Thus, the ligand seemed to bind in a bis-bidentate fashion, and the resulting complexes possessed the metal ion in an octahedral environment. The calculated values of the crystal-field parameters suggested a weak covalent character of the metal-ligand binding interaction.

The antibacterial activity of the cobalt(II) complex containing the ligand L^6 was significantly higher in comparison with the ligand itself or the other similar metallic derivatives.

The ligand (HL^7), N[-3-indoline-2-one]-1,4-diaminobenzene, was synthesized by refluxing the solution in THF of the two organic starting materials (1:1 molar ratio). Ten new complexes were obtained starting from this ligand and various metallic salts (chlorides, sulphates, nitrates) of Cu(II), Co(II), Ni(II), and Cd(II) in a 1:1 and 1:2 molar ratio, respectively.

The IR spectra of the complexes pointed to a bidentate coordination mode of the ligand L^7 through the azomethine nitrogen atom and carbonyl oxygen atom. The coordination sphere was completed by:

- the chloride ion for $[M(HL^7)Cl_2]\cdot 2H_2O$-type complexes;
- the bidentate sulphate ion and the water molecules for $[M(HL^7)(SO_4)(H_2O)_2]$-type complexes;
- the bidentate nitrate ion and water molecules for $[M(HL^7)(NO_3)(H_2O)_2](NO_3)_2$-type complexes.

It is worth mentioning that the value of the stretching vibrational frequency of the NH_2 group of the ligand, $?_{NH}$, indicated the absence of interaction between its nitrogen donor atom and any of chosen metal ions.

The correlation of the elemental analysis data with the parameters estimated from the EPR (for copper(II)-containing complexes) and electronic spectra as well as with the values of the magnetic moments allowed the assignment of a specific coordination geometry of the metal ion (tetrahedral, square-planar, or octahedral).

When the Shiff base-type ligand and its complexes were assayed against the three targeted bacteria, a low inhibition capacity compared to the reference antibiotics *Ciprofloxacin* and *Ampicilin* was noticed. However, the estimated inhibition capacity of these compounds was closed to antibiotic *Gentamicin*.

Following a solid research trend of our laboratory, eight new complexes containing Cu(II), Co(II), and Ni(II) and Schiff bases derived from phenyl-2-pyridil ketone and p-anisidine (L^8) and o-anisidine (L^9), respectively, were synthesized and structurally characterized by different physico-chemical methods, as detailed in subchapter II.4 of this thesis.

The metallic salts involved in syntheses were nitrates and perchlorates, and the resulting complexes could be described as:

$[M(L^8)_2](X)_2 \cdot xH_2O$, where M = Cu, Co, Ni; X = NO_3^-, ClO_4^-, x = 0, 1;

$[M(L^9)_2(H_2O)_2](X)_2$, where M = Cu, Co, Ni; X = NO_3^-, ClO_4^-.

The IR spectra evidenced both the neutral bidentate coordination mode of the two ligands through the azomethine and pyridine nitrogen donor atoms and the existence of the coordinated water molecules. The d-d transitions evaluated from the electronic spectra allowed the determination of the coordination polyhedron for the metal ion of each complex in accordance with the specific values of magnetic moments.

In the case of copper(II) complexes, EPR spectra were recorded using microcrystalline samples. EPR spectrum of complex $[Cu(L^9)_2(H_2O)_2](ClO_4)_2$ suggested an axially-elongated octahedral geometry.

The EPR spectrum displayed a hyperfine structure on the anisotropic low-field component which allowed the calculation of α^2 parameter. The magnitude of this parameter indicated a mainly covalent character of the metal-ligand bond interactions.

The most probable molecular structures of these complex were formulated based on both the spectral data and the magnetic moments and molar conductivity measurements.

The free ligands and their complexes were assayed for antibacterial activity against pathogenic gram-positive and gram-negative bacteria strains, specifically *Staphylococcus aureus*, *Escherichia coli* and *Salmonella Typhimurium*. The results of the assays indicated a moderate antibacterial activity in comparison to antibiotics *Ciprofloxacin* and *Ampicilin,* but almost similar to antibiotics *Gentamicin*. It is worth mentioning that the biological activity was enhanced by the presence of a four-coordinate metal ion (tetrahedral or square-planar geometry) in the complex of interest. The increase of the coordination number of the metal ion in these complexes diminished the antibacterial activity. Moreover, the nature of the metal ion is crucial: Zn(II), Cd(II) and Co(II) complexes revealed a significantly higher biological activity in comparison to the Cu(II)- and Ni(II)-containing analogues.

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