

1-1-2009

Synthesis, characterization, and antibacterial activity of some transition metals with the Schiff base N-(2-furanylmethylene)-3-aminodibenzofuran

AURORA REISS

STELIAN FLOREA

THEODOR CAPROIU

NICOLAE STANICA

Follow this and additional works at: <https://journals.tubitak.gov.tr/chem>

 Part of the [Chemistry Commons](#)

Recommended Citation

REISS, AURORA; FLOREA, STELIAN; CAPROIU, THEODOR; and STANICA, NICOLAE (2009) "Synthesis, characterization, and antibacterial activity of some transition metals with the Schiff base N-(2-furanylmethylene)-3-aminodibenzofuran," *Turkish Journal of Chemistry*. Vol. 33: No. 6, Article 6. <https://doi.org/10.3906/kim-0807-31>

Available at: <https://journals.tubitak.gov.tr/chem/vol33/iss6/6>

This Article is brought to you for free and open access by TÜBİTAK Academic Journals. It has been accepted for inclusion in Turkish Journal of Chemistry by an authorized editor of TÜBİTAK Academic Journals. For more information, please contact academic.publications@tubitak.gov.tr.

Synthesis, characterization, and antibacterial activity of some transition metals with the Schiff base N-(2-furanylmethylene)-3-aminodibenzofuran

Aurora REISS^{1,*}, Stelian FLOREA¹, Theodor CĂPROIU²,
Nicolae STĂNICĂ³

¹*University of Craiova, Faculty of Chemistry, Department of Inorganic and
Analytical Chemistry, 107I Calea București-ROMANIA
e-mail: reissaurora@yahoo.com*

²*Institute of Organic Chemistry, 202 B Spl. Independentei,
77208, Bucharest-ROMANIA*

³*Institute of Physical Chemistry, Coordination Chemistry Laboratory,
202 Spl. Independentei, 77208 Bucharest-ROMANIA*

Received 31.07.2008

This paper presents the structure and antibacterial properties of some complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) with a new Schiff base N-(2-furanylmethylene)-3-aminodibenzofuran. The structure of each complex was characterized by spectroscopic methods (IR, UV-Vis, ¹H-NMR, and ESR), conductometric and magnetic data, and thermogravimetric and elementary analysis. According to these data, we propose an octahedral geometry for Co(II), Ni(II), and Cu(II) complexes, and a tetrahedral geometry for Zn(II), Cd(II), and Hg(II) complexes. Antibacterial activity of the ligand and its complexes was tested against selected bacteria. The ligand and all the complexes possess antimicrobial activity, and antimicrobial activity of the complexes is higher than that of the free ligand.

Key Words: Schiff base, metal complexes, antibacterial activity.

Introduction

Schiff base complexes have remained an important and popular area of research due to their simple synthesis, versatility, and diverse range of applications.¹ Many potent antibacterial and antifungal compounds synthe-

*Corresponding author

sized by the condensation of aldehydes with various heterocyclic compounds have been reported.²⁻⁴ Some biologically active Schiff base ligands, hydrazine-pyrrole-2-carboxaldehyde, hydrazine-furan-2-carboxaldehyde, and hydrazine-thiophene-2-carboxaldehyde, and their phenyl derivatives, and Co(II), Ni(II), and Cu(II) mixed complexes were synthesized and characterized.⁵ Ligands containing NNO, NSO, and NOO moiety, *o*-(3,5-dichloro-pyridine-2-imino)benzoic acid, *o*-(thiophene-2-aldimino)phenol, and 2-(furan-2-acetylmino) ethane-sulfonic acid, respectively, and their bivalent metal chelates were synthesized and characterized, and the metal chelates were screened against gram-positive and gram-negative bacteria.⁶ Co(II) and Ni(II) complexes with a Schiff base, and N-(2-furanylmethylene)-2-aminothiadiazole,⁷ were prepared and characterized based on their physical, spectral, and analytical data. They possess the composition $[ML_2]X_n$ (where X = NO_3^- , SO_4^{2-} , $C_2O_4^{2-}$, or $CH_3CO_2^-$, and n = 1 or 2). The Schiff base and its complexes were screened for antibacterial activity against such bacterial strains as *Escherichia coli*, *Staphylococcus aureus*, and *Pseudomonas aeruginosa*. The metal ions with different anions had varying antibacterial activity against the bacterial species. The Schiff base derived from 2-furancarboxaldehyde and 2-aminobenzoic acid, and its metal complexes with Fe(III), Co(II), Ni(II), Cu(II), Zn(II), and $UO_2(II)$ ⁸ were reported and characterized using different physicochemical techniques. The ligand and its metal complexes have biological activity against some bacterial species: *Escherichia coli*, *Staphylococcus pyogenes*, and *Pseudomonas aeruginosa*. In addition, all metal complexes inhibit fungi at high concentration (5 mg L^{-1}) to a greater degree than the parent ligand and standards (Traivid and Tavinic).

In some previous communications we reported complexes with a Schiff base derived from 3-aminodibenzofuran and different aldehydes (salicylaldehyde or pyridine aldehyde).⁹⁻¹³ In a continuation of our work we herein present the synthesis and characterization of the complexes obtained by the reaction of the Schiff base derived from the condensation of 3-aminodibenzofuran with 2-furancarboxaldehyde and its Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) metal complexes.

The new Schiff base and its complexes were tested for antibacterial activity against pathogenic bacteria species, such as *Escherichia coli*, *Staphylococcus aureus*, and *Pseudomonas aeruginosa*.

Experimental

Chemicals

$CoCl_2 \cdot 6H_2O$ (Merck, p.a.), $NiCl_2 \cdot 6H_2O$ (Merck, p.a.), $CuCl_2 \cdot 2H_2O$ (BDH England, p.a.), $ZnCl_2$ (Aldrich, p.a.), $CdCl_2$ (Aldrich, p.a.), $HgCl_2$ (Merck, p.a.), and 2-furan carboxaldehyde (Merck, 98%) were used for the synthesis.

IR spectra were recorded in the range of $400-4000 \text{ cm}^{-1}$ on a Perkin Elmer 157 instrument in anhydrous KBr pellets. A Unicam UV2-300 spectrometer was used to obtain electronic spectra in DMF solutions. Molar conductivity was determined using an OK-102 (Hungary) conductivity meter. Magnetic susceptibility was measured with a Faraday balance at room temperature. EPR spectra were registered in powder at room temperature using an Art-5-IFA Bucharest spectrometer operating in the X band; the modulation of the magnetic field was 100 kHz, and Mn^{2+} was used as an internal standard. Metal content was estimated by standard methods.¹⁴ C, H, and N were analyzed using an M.L.W. micro-elementary CHN analyzer. ¹H-NMR

spectra were recorded on a Varian Gemini 300BB. Thermogravimetric analysis was performed with a Du Pont 2000 thermal analyzer.

General procedure: Synthesis of the Schiff base

Ethanolic solutions of 3-aminodibenzofuran and 2-furan carboxaldehyde in 1:1 molar ratio were mixed and refluxed over a water-bath for 3 h. The resulting Schiff base separated out upon cooling, and then the mixture was filtered, washed with ethanol, and air-dried.

General procedure: Synthesis of the complexes

The Schiff base (dissolved in dioxane) and the metal chloride in ethanol were mixed in 1:1 molar ratio and refluxed for 6-8 h. The complexes that separated out after keeping the solution overnight were filtered, and then washed with ethanol and ether, and dried under reduced pressure.

Result

The complexes obtained are variously colored microcrystalline powders; air stable, some of them are hygroscopic solids, insoluble in common organic solvents, but soluble in dimethylformamide (DMF). The results of elemental analysis (C, H, and N), along with molecular formulae and melting points of the Schiff base and its complexes are presented in Table 1. Molar electric conductivities show that all the complexes are non-electrolytes, with $\lambda_M = 10.1\text{-}21.7 \Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ in 10^{-3} DMF solutions at room temperature.

Table 1. Analytical and physical data for the Schiff base and its complexes.

Compound	Color (yield, %)	mp (°C)	Calcd (found)%				λ_M^* ($\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$)	μ_{eff} (BM)
			C	H	N	M		
Schiff base(L)	Yellow (80)	180	78.14 (78.09)	4.23 (4.20)	5.35 (5.30)	-	-	-
[CoLCl ₂ (H ₂ O) ₂]	Brown (68)	235	47.79 (47.59)	3.53 (3.33)	3.27 (3.17)	13.79 (13.69)	10.1	5.2
[NiLCl ₂ (H ₂ O) ₂]	Red brown (73)	220	47.82 (47.79)	3.53 (3.51)	3.27 (3.24)	13.75 (13.73)	17.5	3.12
[CuLCl ₂ (H ₂ O) ₂]	Black (65)	240	47.29 (47.23)	3.49 (3.45)	3.24 (3.20)	14.71 (14.68)	20.3	1.96
[ZnLCl ₂]	Brown (72)	215	51.36 (51.26)	2.78 (2.75)	3.52 (3.51)	16.44 (16.40)	21.7	-
[CdLCl ₂]	Brown (75)	210	45.92 (45.90)	2.49 (2.45)	3.14 (3.13)	25.28 (25.25)	19.5	-
[HgLCl ₂]	Brown (77)	225	38.32 (38.29)	2.07 (2.03)	2.62 (2.61)	37.65 (37.61)	18.7	-

*In 10^{-3} DMF solutions at room temperature.

The structure of the Schiff base, N-(2-furanylmethylene)-3-aminodibenzofuran, and the atom numbering scheme are given in Figure 1.

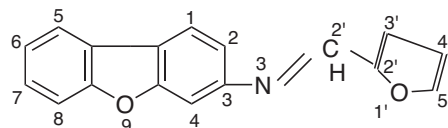


Figure 1. Structure of the Schiff base and the atom numbering scheme.

Infrared spectra

The IR spectra of the Schiff base ligand (L) and its complexes are listed in Table 2. The IR spectra of the complexes were compared with those of the free ligand in order to determine the coordination sites that may be involved in coordination. Upon comparison it was determined that the $\nu_{C=N}$ stretching vibration from the azomethine group is found in the Schiff base at 1635 cm^{-1} . This band is shifted to lower

Table 2. IR data ($4000\text{-}400\text{ cm}^{-1}$) of the Schiff base and its complexes.

Compound	ν_{OH}	$\nu_{C=N}$	ν_{C-O-C} (furan cycle)	δ_{OH}	ν_{M-N}	ν_{M-O}
Schiff base(L)	-	1635	1015	-	-	-
[CoLCl ₂ (H ₂ O) ₂]	3300	1625	1020	840	435	540
[NiLCl ₂ (H ₂ O) ₂]	3400	1620	1020	850	425	535
[CuLCl ₂ (H ₂ O) ₂]	3450	1620	1010	860	425	530
[ZnLCl ₂]	3370	1615	980	845	430	525
[CdLCl ₂]	3350	1625	1010	860	425	525
[HgLCl ₂]	3420	1615	1020	850	435	540

($10\text{-}20\text{ cm}^{-1}$) wavenumbers in the complexes, indicating the participation of azomethine nitrogen in coordination.¹⁵ A band due to ν_{C-O-C} stretching vibration of the furan ring appeared at 1015 cm^{-1} in the Schiff base.¹⁶ This band also shifted to $980\text{-}1020\text{ cm}^{-1}$ in the metal complexes, suggesting the involvement of the oxygen atom O(1') from the furan cycle to the central metallic ion. The oxygen atom O(9) from the dibenzofuranic cycle is too far away to be involved in coordination of the metallic ion.

The new bands at $540\text{-}525$ and $435\text{-}425\text{ cm}^{-1}$ in the spectra of the metal complexes were assigned to ν_{M-O} and ν_{M-N} stretching vibrations.^{15,16}

The presence of coordinated water molecules in the first 3 complexes is determined by the appearance of bands at $3300\text{-}3450\text{ cm}^{-1}$ and a peak at 850 cm^{-1} assignable to the OH stretching and rocking vibrations, respectively.¹⁷

Therefore, it is concluded that the Schiff base behaves as a neutral bidentate ligand in all the complexes and that the coordination takes place in the oxygen atom O(1') from the furan cycle and imino nitrogen of the azomethine link.

Magnetic moment and UV-Vis spectra

Electronic spectra and magnetic measurements were recorded in order to obtain information about the geometry of the complexes.

The μ_{eff} values of the Co(II), Ni(II), and Cu(II) complexes were 5.2, 3.12, and 1.96 B.M., respectively, indicating an octahedral geometry around the metal ions.^{18,19} The Zn(II), Cd(II), and Hg(II) complexes are diamagnetic (Table 1).

The UV-Vis spectrum of the free ligand exhibited 2 bands at 36,630 and 29,673 cm^{-1} assignable to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively.

The electronic spectrum of the Co(II) complex showed bands at 9570, 17,700, and 21,040 cm^{-1} assignable to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$, and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions, respectively, which are characteristic of octahedral configuration.²⁰

The Ni(II) complex exhibited 3 spin-allowed transitions at 10,776, 15,700, and 25,560 cm^{-1} assignable to ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$, and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions, respectively, which suggest an octahedral geometry.²⁰

The Cu(II) complex showed 1 broad band at 15,800 cm^{-1} assignable to ${}^2E_g \rightarrow {}^2T_{2g}$ transition, which is a characteristic of distorted octahedral configuration.²⁰

The electronic spectra of the Zn(II), Cd(II), and Hg(II) complexes presented only 2 peaks in the UV domain due to $L \rightarrow L^*$ transitions. As expected, the electronic spectra of these complexes do not furnish any relevant data towards stereochemistry, but on the basis of analytical, conductance, and infrared spectral data a tetrahedral geometry is proposed for the Zn(II), Cd(II), and Hg(II) complexes.

ESR and ${}^1\text{H-NMR}$ spectra

The EPR spectrum of the Cu(II) complex shows $g_{II} > g_{\perp} > 2.0023$ and a G value within the range of 2.08-4.49, which are consistent with the $d_x^2-y^2$ ground state in an octahedral geometry.²¹

Evidence of the bonding mode of the ligand is also provided by the ${}^1\text{H-NMR}$ spectra of the Schiff base and the diamagnetic Zn(II) complex, which were recorded in CDCl_3 . The signals due to H(2) and H(4) protons (from α positions considering the nitrogen atom of the imino group) from the dibenzofuranic cycle are δ 7.30 ppm and δ 7.48 ppm in the ${}^1\text{H-NMR}$ spectrum of the ligand. These signals are shifted towards the lower field in complex at δ 7.50 ppm and δ 7.68 ppm, respectively. These chemical shift values show the intensification of the diamagnetic effect at the level of the protons from α positions, considering the nitrogen atom of the imino group, and explain the lower values of the shielding constant of the 2 protons.²² Additionally, a decrease in the charge density of iminic nitrogen can be observed, proving its contribution to the covalent bond formed with the metal. This fact confirms again the proposed structure of the complex. The signal due to the H(5') proton of the furan ring is found at δ 8.31 ppm in the ${}^1\text{H-NMR}$ spectrum of the ligand and is shifted to δ 7.77 ppm because of the involvement of the oxygen atom from the furan ring in coordination to the metallic ion.

Thermogravimetric analyses

Thermogravimetric analysis was performed for the Co(II), Ni(II), and Cu(II) complexes. The thermograms of these complexes show nearly the same pattern. In the Cu(II) complex there was no mass loss up to 200 °C, suggesting the absence of lattice water molecules.²³ The first weight loss at ca. 210 °C in a single step is supported by an exothermic peak at the same temperature in the DTA thermogram. The weight loss corresponds to the loss of 2 water molecules (8.17% against and calculated value 8.30%). The high temperature required for water loss indicates that water molecules are strongly bonded to the metal ion, and this type of thermal behavior is characteristic of coordinated water molecules.²⁴ Although the loss of coordinated water molecules is an endothermic process, the existence of an exothermic peak in the DTA curve at the temperature indicates a probable structural change as a result of the decrease in the coordination number from 6 to 4. This explication was confirmed by spectroscopic analysis of the isolated product that lost 2 water molecules.

Above 210 °C the thermogram is horizontal up to 230 °C. Further decomposition proceeds slowly from ca. 240 °C, with a final residue at 780 °C. The second step corresponds to the thermal decomposition of the organic ligand of the complex and a black final residue. Chemical analysis of the black final residue gave no indication that carbon, nitrogen, or hydrogen was present in the composition; it was mainly identified as CuO.

The Ni(II) and Co(II) complexes followed the same trend. From the initial decomposition temperatures the thermal stability of the 3 complexes was deduced in the order Ni(II) > Co(II) > Cu(II).

Discussion

The structures of the complexes of the Schiff base N-(2-furanylmethylene)-3-aminodibenzofuran with Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) were confirmed by elemental analysis, IR, UV-Vis, ¹H-NMR, and ESR, molar conductance, magnetic data, and thermogravimetric analysis. IR spectral data of the compounds showed that the ligand behaves as a neutral bidentate ligand in all the complexes through the azomethine N and furan O(1'). The molar conductance data show that all the complexes are non-electrolytes. The ¹H-NMR spectra of the free Schiff base and the diamagnetic Zn(II) complex indicate the coordination of the ligand through the azomethine N and furan O(1'). On the basis of the above observations, the structure of the complexes may be proposed as follows: an octahedral geometry for the Co(II), Ni(II), and Cu(II) complexes, and a tetrahedral geometry for the Zn(II), Cd(II), and Hg(II) complexes. The metal complex structures are given in Figure 2.

Antibacterial tests

The new Schiff base and its metal complexes were tested for their in vitro antibacterial activity against *Escherichia coli*, *Staphylococcus aureus*, and *Pseudomonas aeruginosa*, using the diffusion method.^{25,26} The diffusion method is simple, yet is routinely used in hospital laboratories; it requires commercial disks, the medium used is Mueller-Hinton agar with 2% of glucose, and the diameter of the zone of inhibition is visually read 24 h after incubation at 37 °C. Antibacterial activity was estimated on the basis of the size of the zone of inhibition formed around the paper disks on the seeded agar plates. Streptomycin was used as a standard. The results are presented in Table 3.

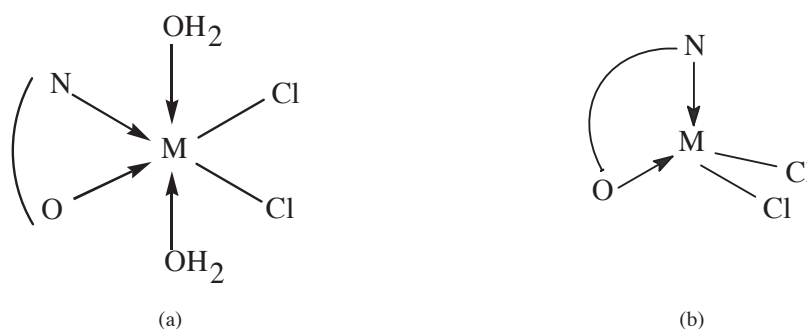


Figure 2. Structural formulae of the metal complexes.

a. $[\text{MLCl}_2(\text{H}_2\text{O})_2]$, where M = Co(II), Ni(II), and Cu(II).

b. $[\text{MLCl}_2]$, where M = Zn(II), Cd(II), and Hg(II).

Table 3. Antibacterial activity of the ligand and complexes.

Compound*	<i>E. coli</i>	<i>St. aureus</i>	<i>P. aeruginosa</i>
Schiff base (L)	++	+	+
$[\text{CoLCl}_2(\text{H}_2\text{O})_2]$	++++	+++	+++
$[\text{NiLCl}_2(\text{H}_2\text{O})_2]$	+++	++	++
$[\text{CuLCl}_2(\text{H}_2\text{O})_2]$	+++	++	++
$[\text{ZnLCl}_2]$	+++	++	++
$[\text{CdLCl}_2]$	++	++	++
$[\text{HgLCl}_2]$	++	++	++
Streptomycin	++++	+++	++++

*C = 5 mg L⁻¹.

Zone of inhibition diameter in mm (% inhibition): +, 6-10 (27%-45%); ++, 10-14 (45%-64%); +++, 14-18 (64%-82%); +++++, 18-22 (82%-100%). Inhibition percentages are relative to the zone of inhibition of the most active compound (22 mm) with 100% inhibition.

Comparing the biological activity of the Schiff base and its metal complexes with the standard the following results were obtained: the biological activity of the Schiff base was less than that of streptomycin; the biological activity of all the metal complexes was higher than that of the free ligand, and the biological activity of the Co(II) complex was equal to that of standard, while the other metal complexes' biological activity was less than that of the standard, streptomycin; the biological activity of the complexes follow the order, Co(II) > Ni(II) = Cu(II) = Zn(II) > Cd(II) = Hg(II). Furthermore, the data in Table 3 show that *E. coli* was inhibited to the greatest degree by the Co(II) complex, followed by the Ni(II), Cu(II), and Zn(II) complexes.

Conclusion

The Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) complexes of the Schiff base derived from 3-aminodibenzofuran and 2-furancarboxaldehyde were prepared and characterized; the study reveals that:

Synthesis, characterization, and antibacterial activity of..., A. REISS, et al.,

- All the complexes are non-ionic in nature and are considered non-electrolytes;
- The Schiff base behaves as a neutral bidentate ligand and is coordinated to the central metallic ion through the azomethine N and furan O(1');
 - The Co(II), Ni(II), and Cu(II) complexes have an octahedral geometry, while the Zn(II), Cd(II), and Hg(II) complexes have a tetrahedral geometry;
 - Thermal decomposition of the first 3 complexes made it possible to establish the number and nature of water molecules, the composition of the complexes, and the intervals of thermal stability;
 - The Schiff base and the complexes inhibited the growth of the tested bacterial species to varying degrees. The values show that the Schiff base became more pronounced when it was coordinated to the metal ions. The biological activity of all the complexes follow the order, Co(II) > Ni(II) = Cu(II) = Zn(II) > Cd(II) = Hg(II). This means that metal chelation significantly affects the antimicrobial behavior of the organic ligand.

In conclusion, the complexes prepared with N-(2-furanylmethylene)-3-aminodibenzofuran could reasonably be used for the treatment of some common diseases caused by *E. coli*.

Acknowledgements

The authors gratefully acknowledge the Filantropia Clinic Hospital, Clinical Laboratory, Craiova, Romania, for performing the antibacterial studies.

References

1. Yamada, S. *Coord. Chem. Rev.* **1999**, *192*, 537-557.
2. Singh R. V., *Synth. React. Inorg. Met-Org. Chem*, **1986**, *16*, 21-27.
3. Mohammad M. A.; El-Enamy M. M.; Basies E. L., *Egypt. J. Pharm. Sci.*, **1981**, *22*, 9-15.
4. Scozzafava, A.; Menabuoni, L.; Mincione, F.; Mincione, G.; Supuran, C. T., *Bioorg. Med. Chem. Lett.*, **2001**, *11*, 575-588.
5. Chohan, Z. H.; S. K. A. Sherazi, *J. Chem. Soc. Pak.*, **1997**, *19*, 196-201.
6. Sharma S.; Sharma A., *Orient. J. Chem.*, **2000**, *16*, 349-353.
7. Chohan, Z. H.; Rauf, A.; Supuran, C. T., *Metal-Based Drugs*, **2002**, *8*, 287-291.
8. Omar, M. M.; Mohamed, G. G.; Hindy, A. M. M., *J. Therm. Anal. Cal.*, **2006**, *86*, 315-325.
9. Kriza, A.; Reiss, A.; Florea, S.; Cproiu, T. *J. Indian. Chem. Soc.*, **2000**, *77*, 207-208.
10. Kriza, A.; Reiss, A.; Florea, S.; Meghea, A. *Polish J. Chem.*, **2000**, *74*, 585-588.
11. Reiss, A.; Kriza, A.; Florea, S.; Cproiu, T.; Stnic, T. *Rev. Roumaine de Chimie*, **2005**, *50(6)*, 445-449.
12. Reiss, A.; Florea, S.; Neamșu, J. *Annals of the University of Craiova, The Chemistry Series*, **2003**, XXXII, 9-12.
13. Reiss, A.; Florea, S.; Gnescu, A.; Clin, El. *Annals of the University of Craiova, The Chemistry Series*, **2004**, XXXIII, 21-23.
14. Macarovic, C. Gh. "Analiza Chimica Cantitativa Anorganica", Ed. Academiei R.S.R., București, 1979.
15. Omar, M. M.; Mohamed, G. G.; Hindy, A. M. M. *J. Therm. Anal. Cal.*, **2006**, *86(2)*, 315-325.

16. Patel, B. K.; Chaudhury, S. C., *J. Indian Chem. Soc.*, **1988**, *LXV*, 661-662.
17. Nakamoto, K. "*Infrared Spectra of Inorganic and Coordination Compounds*", 4th ed., Wiley- Interscience, New York, 1986.
18. Orlin, R. L. *Transition Met. Chem.*, **1976**, *1*, 3-10
19. Figgins, B. P. "*Introduction to Ligand Fields*", J. Wiley, New York, 1976.
20. Lever, B. P. "*Inorganic Electronic Spectra*", Elsevier, New York, 1984.
21. Hathaway, B. J.; Billing, D. E. *Coord. Chem. Rev.*, **1970**, *5*, 143-153.
22. Bratulescu G., "*Introducere în spectroscopia compușilor organici*", Sitech Editure, 2009.
23. Nikolaev, A. V.; Lagvienko, A.; Myachina, L.I. "*Thermal Analyses*", Academic Press, New York, 1969.
24. Pessoa, J. C.; Silva, J. A. J.; Vieira, A. L. ; Vilas-Boas, I. ; Brien, P. O.; Thorton, P. *J. Chem. Soc. Dalton Trans.*, **1992**, 1745-1750.
25. Duca, E.; Duca, M. "*Microbiologie medicală*", Ed. Did. și Ped. Buc., 1979.
26. Zotta, V. "*Chimie farmaceutică*", Ed. Medical, Bucureți, 1985.