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**URECHE DUMITRU**

**SYNTHESIS, STUDY OF PROPERTIES AND MOLECULAR**  
**ARCHITECTURE OF “s” AND “d” TYPE METAL**  
**COORDINATION COMPOUNDS WITH POLYFUNCTIONAL**  
**LIGANDS**

**141.01. INORGANIC CHEMISTRY**

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**Doctoral supervisor:**

**BULHAC Ion,** habilitated doctor of chemistry, research associate professor, Institute of chemistry of MSU

**Doctoral co-advisor:**

**BOUROSH Pavlina,** doctor of chemistry, research associate professor, Institute of Applied Physics of MSU

**Composition of the Committee for public defense of the doctoral thesis:**

**GULEA Aurelian,** academician, habilitated doctor of chemistry, university professor, MSU – president;

**BULHAC Ion,** habilitated doctor of chemistry, research associate professor, MSU – doctoral supervisor;

**LOZAN Vasile,** habilitated doctor of chemistry, research associate professor, MSU – reviewer;

**MELNIC Silvia,** doctor of chemistry, associate professor, „Nicolae Testemițeanu”SUMP– reviewer;

**COROPCEANU Eduard,** doctor of chemistry, university professor, ICSPU – reviewer;

**CIOCHINĂ Valentina,** doctor of biology, research associate professor, MSU – secretary of the Doctoral committee.

The defense will take place on october 27, 2023, at 14<sup>00</sup>, during the meeting of the Doctoral committee within the Doctoral School of Biological, Geonomical, Chemical and Technological Sciences, room 349 of the Institute of Chemistry of MSU, 3 Academiei str., Chisinau.

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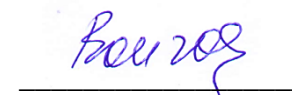
**Doctoral supervisor,**

**BULHAC Ion,** Dr.habil., rsrc. as.prof.



**Doctoral co-advisor,**

**BOUROSH Pavlina,** PhD., rsrc. as.prof.



**Scientific secretary of the Doctoral committee,**

**CIOCHINĂ Valentina,** PhD, rsrc.as.prof.



**Author:**

**URECHE Dumitru**



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## CONCEPTUAL FEMEWORK OF THE RESEARCH

**Actuality and importance of the subject.**  $\alpha$ -Dioximes are compounds obtained by treating some amines and/or their derivatives with dichlorglyoxime. In the literature, symmetrical vic-dioximes are also presented in the form of three geometric isomers: anti-(E, E'), amphi-(E, Z) and syn-(Z, Z') [1, 2]. Structural results available in the CCDC (Cambridge Crystallographic Data Center) confirm that the N,N-chelation mode, which stabilizes the anti-(E, E') form, is most commonly used in dioximes for coordinating these ligands. Dioximes can also coordinate towards metal ion through the oxygen atoms of the oxime groups. The study of compounds based on these complexing agents represents a broad compartment of coordination chemistry. The interest in these compounds is explained not only by their limitless diversity, but also by different variable physico-chemical properties, which make it possible to use these compounds in various areas (in analytical chemistry, catalysis, extraction processes, as semiconductors and models of biological systems).

A special position in the chemistry of new  $\alpha$ -dioxime compounds present cobalt(II) and cobalt(III) compounds, which are characterized by diverse composition and structure; in addition to dioximes of cobalt, the nickel(II), platinum(II), palladium(II), copper(II), zinc(II), cadmium(II), manganese(II), iron(II), iron(III) and nickel(III) dioximes with monomere and/or dimer structure, with coordination geometry that form tetrahedral, square pyramidal and octahedral polyhedra are also known [3-7]. The increased interest in complexes with dioxime ligands is also conditioned by the possibilities of their use as models of physiologically important preparations, as well as in microbiology, medicine or agriculture.

**Aim of the work** consists in synthesis, structure and study of mono- and polynuclear coordination compounds of "s" and "d" metals based on mono- and heterofunctional dioxime ligands with N,N-donor and N,N,O-donor atoms together with heterofunctional ligands of the O,N,O-donor type also involving different inorganic anions.

### **Objectives of the study:**

- synthesis of mono- and heterofunctional dioxime complexing agents using dichloroglyoxime, different aromatic amines and their derivatives as reagents;
- synthesis of coordination compounds with different nuclearity based on "s" and "d" type metals using different reaction conditions;
- studying the obtained compounds by different physico-chemical methods, such as: elemental analysis, IR spectroscopy, NMR and single crystal X-ray diffraction;

- evaluating the comparative antimicrobial activity of the novel proligands and the derivatives from which they were synthesized;
- studying the microbiological properties of the obtained complexes on different strains of micro- and macromycetes as stimulators/inhibitors of microbiological processes.

**The research hypothesis** involves the research synthesis of coordination compounds based on "s" and "d" metal ions by using ligands that comprise di- and tetraoximes, pyridine and its derivatives, including derivatives of pyridinedicarboxylic acid, capable of exhibiting antimicrobial and microbiological properties for practical use.

#### **Synthesis of research methodology and justification of the chosen methods**

Optimum synthesis conditions were applied, following which new di- and tetraoxime complexing agents were synthesized. The study demonstrated that reacting with metal ions these ligands could generate both molecular and ionic complexes with different dimensionality.

Monofunctional dioximes form di- and polynuclear complexes by introducing additional bridging ligands, the dimensionality of the complex being determined especially by the nature of the bridging ligand.

Both proligands and complexes based on them have been studied using modern research methods, which include: elemental analysis (for C, H, N, S and metal), IR spectroscopy, nuclear magnetic resonance ( $^1\text{H}$  and  $^{13}\text{C}$ ), and the structure of the compounds' crystals was established using single crystal X-ray diffraction, as well as for the proligands. For a number of compounds antimicrobial and microbiological properties were investigated. Investigation of the comparative antimicrobial properties of proligands and their particular components demonstrated that in the case of some proligands obtained by condensation, the antimicrobial activity increases.

**Novelty and scientific originality** consists in obtaining 30 new compounds, of which 4 oxime coordination agents, 20 mono- and dinuclear complexes and 6 1D and 2D coordination polymers.

**Theoretical significance:** heterometallic compounds of Ca(II), Sr(II) and Ba(II) and homometallic compounds of Mn(II), Co(II)/Co(III), Ni(II), Cu(II), Zn(II) and Cd(II) with different nuclearity were synthesised.

**Practical importance:** some coordinating agents and some complex compounds exhibit antibacterial and biostimulatory properties in the cultivation of beneficial micro- and macromycetes.

**The obtained results that contribute to the solving of an important scientific problem** in the thesis consist in the development of methods for the synthesis of complexes with different nuclearity and polymer sizes of some „2s”, „3d” and „4d” metals.

**Implementation of the scientific results:** the useful properties of some proligands and coordinative compounds such as antimicrobials and stimulators of enzymogenesis processes when cultivating some strains of micro- and macromycetes have been protected by invention patents from the Republic of Moldova, offering the possibility of their use as plant protection agents.

## CONTENT OF THE THESIS

The work consists of introduction, four chapters, general conclusions and recommendations, reference list of 297 entries. The material of the thesis is presented on 122 pages and contains 71 figures, 11 tables and 3 appendices.

This research includes the synthesis of new oxime proligands, both monofunctional and bifunctional, but also the complexes based on them with different dimensionality. The choice of this class of ligands is motivated by the activity and diverse ways of coordination of oxime groups towards metal ions. Another impetus relates to the manifestation of physico-chemical and biological properties of these compounds, among which we can list potential catalysts of industrial processes [8], antihypoxic preparations [9], preparations with antidote properties [10], antimicrobial activity [11] and sensitive materials for sorption-type gas sensors [12]. As a result, three new dioxime and one tetraoxime proligands were synthesized (Figure 1). Two dioxime complexing agents, di-*p*-aminobenzoylglyoxime (*DpabaH<sub>4</sub>*) N,O – donor and di-*p*-aminotolueneglyoxime (*DpatH<sub>2</sub>*) N – donor, as well as tetraoxime di-*m*-phenylenediaminetetraoxime (*DmFDH<sub>4</sub>*) N,N' – donor were studied by single crystal X-ray diffraction, thus establishing their molecular and crystal structure. For the third dioxime proligand di-*m*-aminobenzoylglyoxime (*DmabaH<sub>4</sub>*) N,O – donor it was not possible to establish the crystal structure, but compared to other three proligands mentioned above it proved to be more favorable for the formation of coordination complexes. The use of these new complexing agents in the syntheses led to obtaining a mononuclear complex and four 1D and 2D coordination polymers. Another known dioxime proligand is dianilineglyoxime (*DAnH<sub>2</sub>*); used in syntheses together with some pyridinic derivatives or dicarboxylic acids it led to synthesis of six mononuclear complexes, four binuclear complexes and a 1D coordination polymer. In addition to oxime proligands, pyridine-2,6-dicarbonyl dichloride compound was also used in the reactions, which being dissolved in various saturated aliphatic alcohols forms esters of pyridinedicarboxylic acid. Based on these esters, seven heterometallic complexes of Co(II) with "2s" metals were synthesized.

The selection of metal ions was not guided by any criteria. The aim was to study the mode of coordination and the behavior of the used ligands towards different metal ions, but also the comparative research of the "ligand-complex" biological activity. This study allowed revealing the influence of the nature of the metal ion on the biological activity of the proligands.

## **1. COORDINATION COMPOUNDS OF "s" AND "d" METALS WITH MONO- AND POLYMERIC STRUCTURE BASED ON POLYFUNCTIONAL LIGANDS**

**Chapter 1** summarizes the specialized literature studied, which includes the classification of different organic ligands, their mode of coordination towards metal ion, the spectroscopic study, the structure and dimensionality of the complex compounds, but also their biological activity. The structure and architecture of different types of coordination complexes of transition metals with different types of ligands, especially with dioximes, are described. Scientific sources also relate about coordination complexes based on pyridinedicarboxylic, pyridine and/or carboxylic acid ligands with alkaline earth and transition metal cations that exhibit biologically active properties.

## **2. METHODS OF SYNTHESIS, ANALYSIS AND RESEARCH**

**Chapter 2** describes the synthesis procedures of new coordination agents, the synthesis of coordination complexes based on "s" and "d" metals with the novel ligands. At the end, the synthesis methods and the devices used for characterizing the compounds are described.

## **3. COORDINATION COMPOUNDS WITH DIFFERENT NUCLEARITY OF "s" AND "d" METALS WITH POLYFUNCTIONAL LIGANDS**

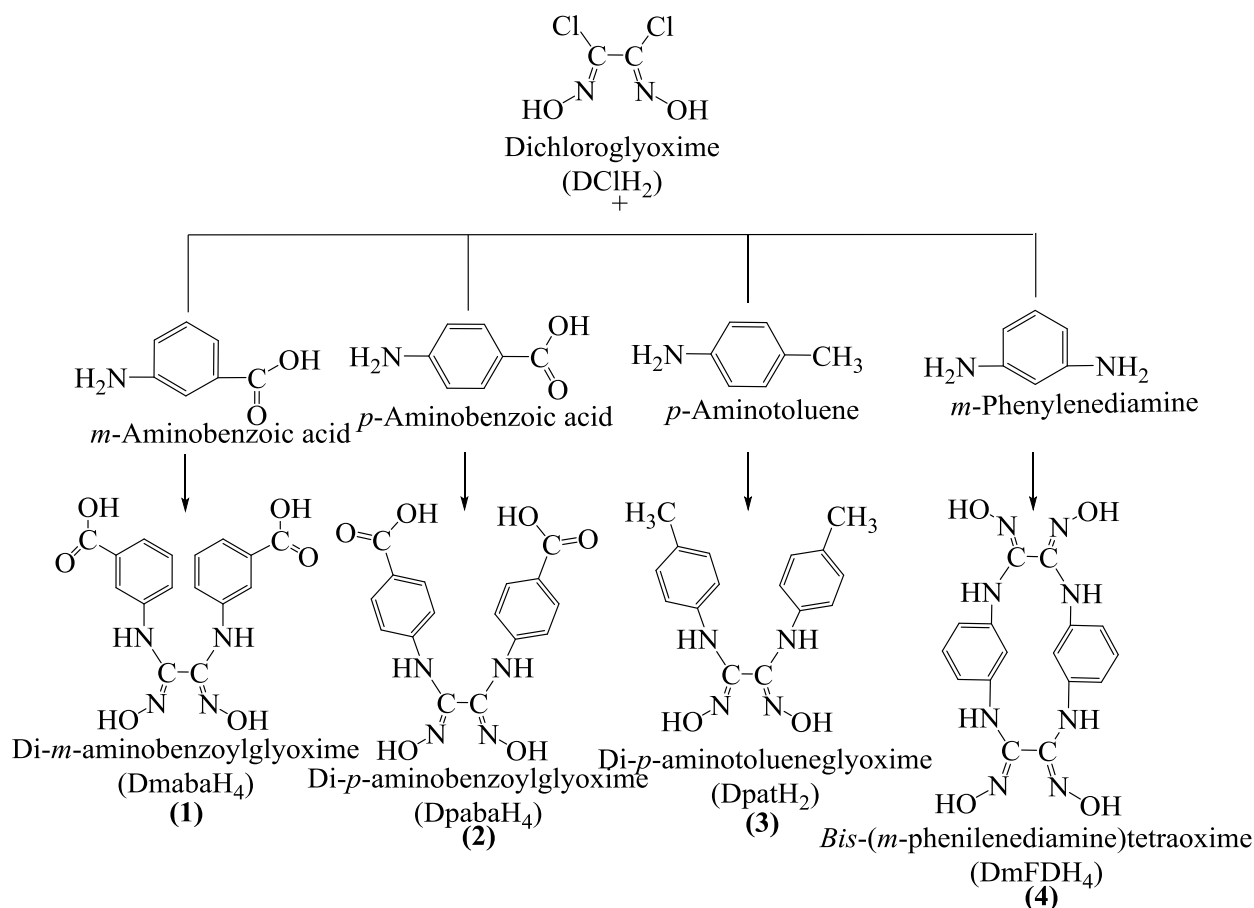
**Chapter 3** describes di- and tetraoxime complexing agents obtained by condensing dichloroglyoxime with aromatic amines and their derivatives, as well as coordination complexes of "s" and "d" metals of different dimensionality based on these ligands and carboxylic, pyridinedicarboxylic and pyridine ligands. The FTIR, NMR spectroscopic analysis and the description of crystal structure of the complexes obtained in single crystal phase are presented.

### **3.1. Synthesis of complexing agents – potential ligands for obtaining coordination compounds**

Using aromatic amines, their derivatives and derivatives of aromatic amino acids in condensation reactions with dichloroglyoxime led to the synthesis of four new oxime

complexing agents (Figure 1), thus completing the class of polyfunctional dioxime proligands. In the IR spectra of compounds **1-4**, the  $\nu(\text{OH})_{\text{oxime}}$  absorption bands characteristic for oxime proligands are present in the 3180-3727  $\text{cm}^{-1}$  region and  $\nu(\text{NH})$  in the 3180-3300  $\text{cm}^{-1}$ . The presence of an  $\nu(\text{NH})$  absorption band and the absence of an intense  $\nu(\text{C-Cl})$  band in the 800-850  $\text{cm}^{-1}$  region proves that condensation has occurred and is not a mixture of substances. Obtaining monocrystals and determining the crystal structure confirmed this fact.

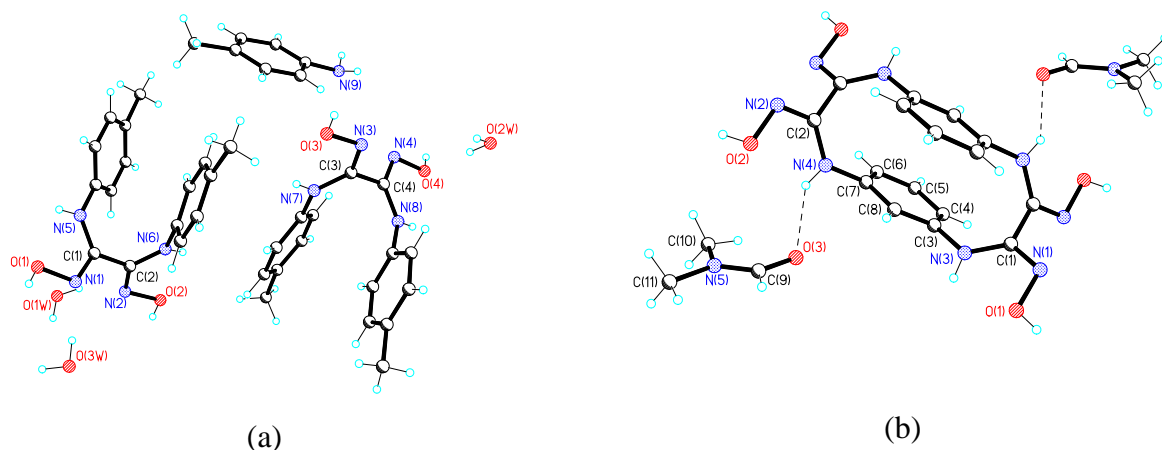
X-ray analysis was possible for compounds **2-4**, as for for compound **1** monocrystals could not be obtained. Compounds **2** and **3** are dioxime proligands containing  $-\text{COOH}$  and  $-\text{CH}_3$  substituents in the *para* positions of the benzene rings. Both compounds crystallize in the centrosymmetric  $C2/c$  (**2**) and non-centrosymmetric  $Pn$  (**3**) monoclinic space groups.



**Fig. 1. Scheme for obtaining new di- and tetraoxime complexing agents.**

Compound **4** is already a tetraoxime that crystallizes in the triclinic space group  $P-1$ . The set of donor atoms of these proligands engaged in the formation of complexes can be  $\text{N}_2\text{O}_2$  in **2**,  $\text{N}_2$  in **3** and  $\text{N}_4$  in **4** (Figure 2).

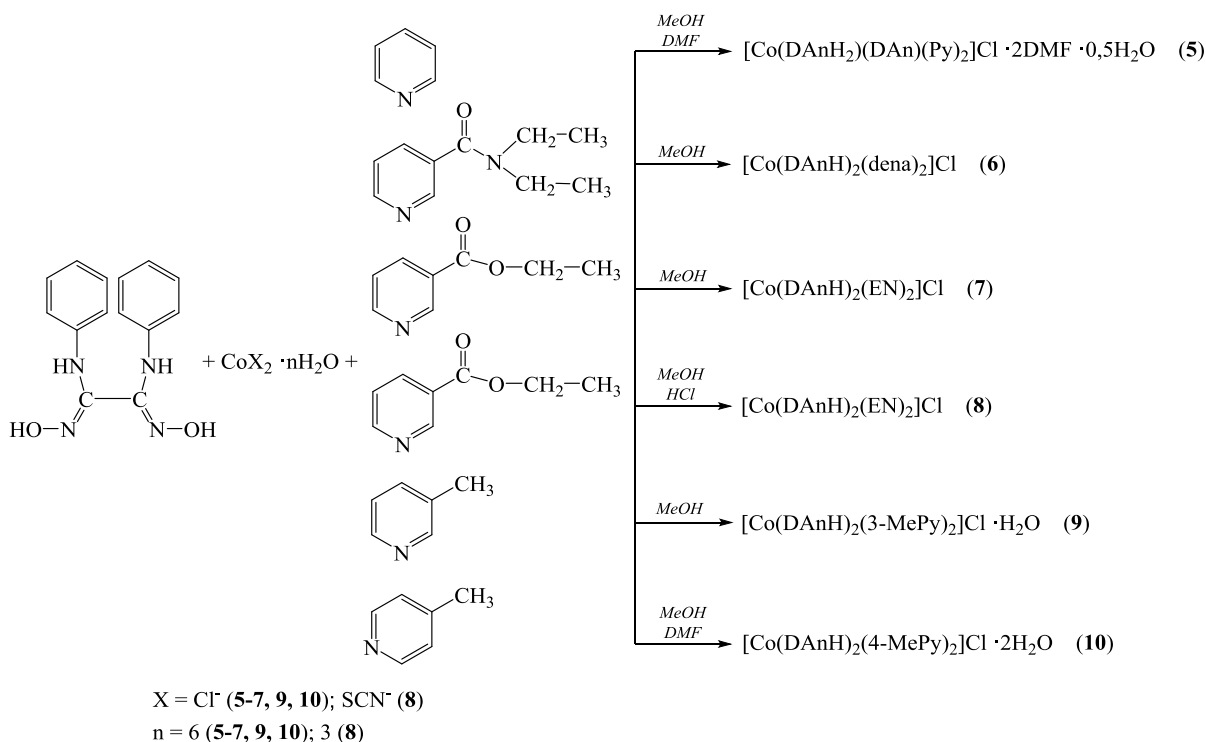




**Fig. 2. Molecular structures of compounds 3 (a) and 4 (b).**

### 3.2. Synthesis of cobalt(III) mononuclear coordination compounds based on $\alpha$ -dioxime and pyridine derivatives

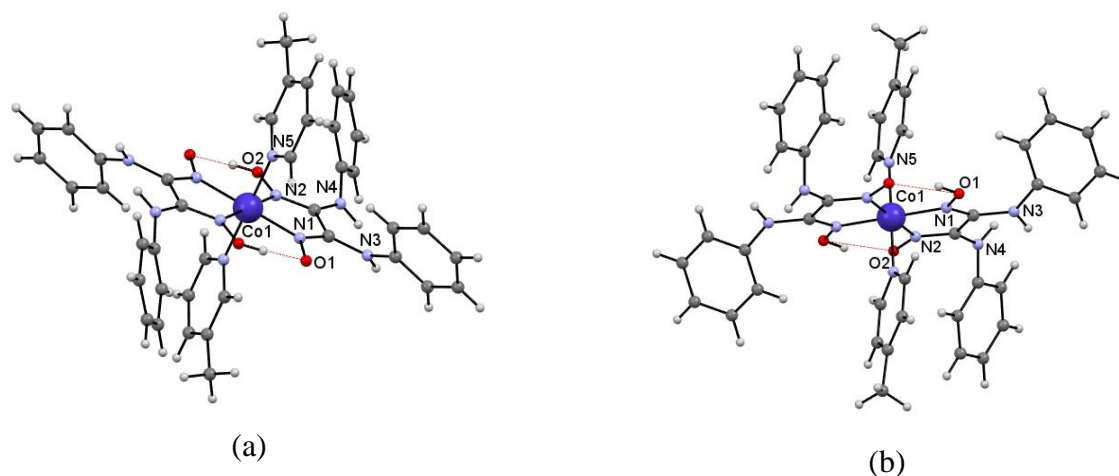
Another proligand used in the syntheses was dianineglyoxime (DAnH<sub>2</sub>), together with different pyridine derivatives, including pyridine were used in the synthesis of compounds **5-10** (Figure 3).



**Fig. 3. Reaction scheme for the synthesis of complexes 5-10.**

Cobalt(III) complexes with dianineglyoxime and different pyridine derivatives obtained represent a set of five new compounds (one of which existing as two polymorphs). All synthesized compounds are ionic, based on complex cations  $[\text{Co}(\text{DAnH}_2)_2\text{L}_2]^+$  (L – pyridine

derivatives) (Figure 4) and  $\text{Cl}^-$  anion. Incorporated molecules were found only in crystals of complex compounds **5**, **9**, and **10**.



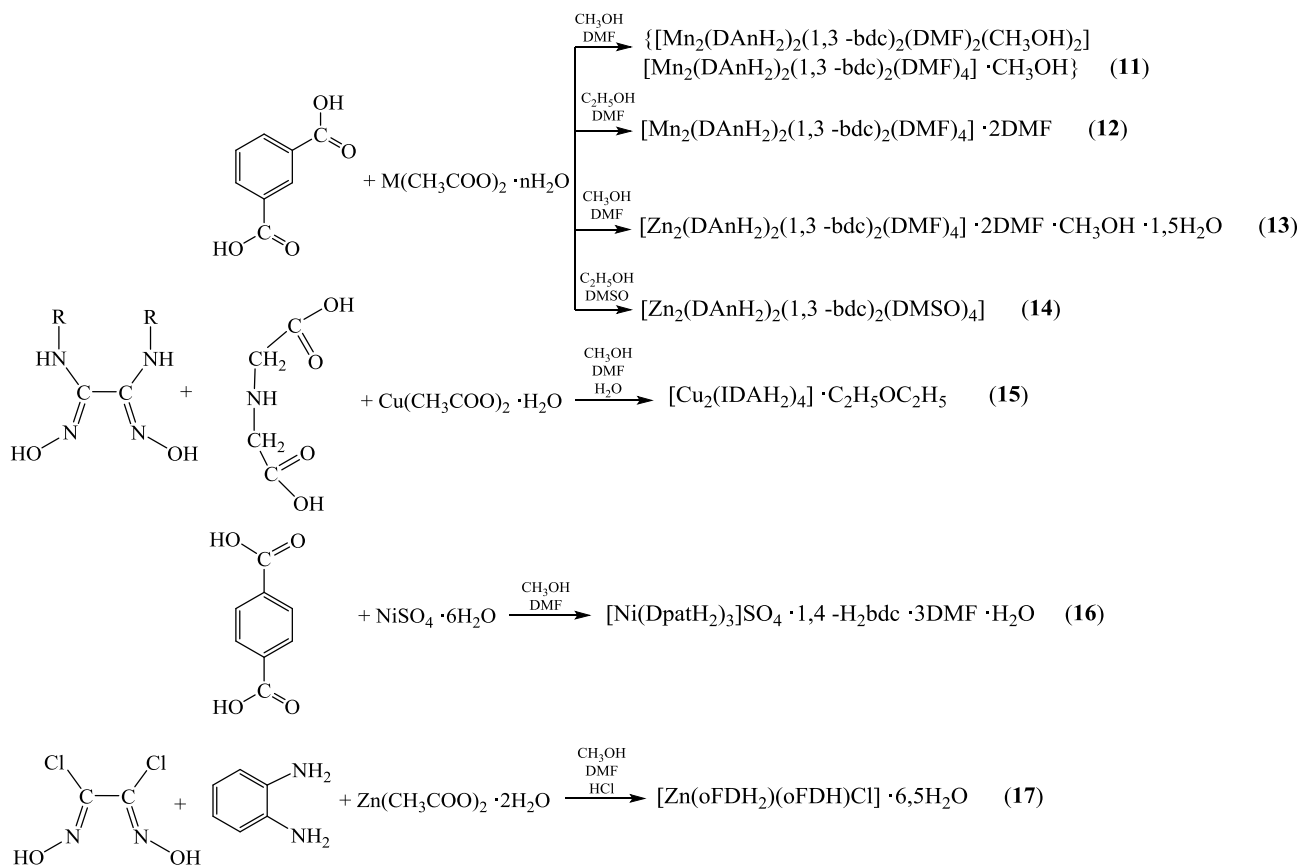
**Fig. 4. Structure of complex cations in compounds 9 (a) and 10 (b), crystallographically independent atoms are labeled.**

$\text{Co}^{3+}$  metal ion in the complex cations is hexacoordinated with the coordination polyhedron in the form of a distorted octahedron, formed by the  $\text{N}_6$  donor atom set in compounds **5-10**. Thus, compounds **5**, **9** and **10** contain inclusion compounds in their outer spheres. The positioning of cations and anions in the crystal lattice reveals cavities in the structure, which are occupied by entrapped molecules of DMF and/or water.

The volume of these cavities constitutes about 28% in **5**, 23.5% in **10** and only 7.2% in **9** of the total volume of elementary cells, and for compounds **6-8**, which do not contain inclusion molecules this volume is less than 6%.

### **3.3. Obtaining the complex combinations of Zn (II), MN (II), with (II) and Ni (II) based on dioxime ligands and/or carboxylic acids**

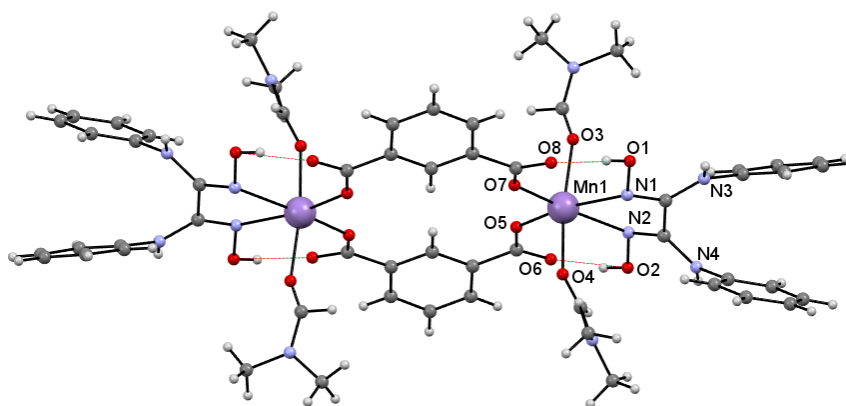
Having the goal of obtaining new compounds of the dioxime type with better nuclearity, only pyridine derivatives have been replaced by dicarboxylic acids, namely by 1,3-, 1,4-benzendicarboxylic, iminodiacetic acids, preserving dianilineglyoxime, and as a result the synthesis of 7 new compounds of zinc(II), manganese(II), copper(II) and nickel(II) succeeded (Figure 5).



R = C<sub>6</sub>H<sub>5</sub> - (11-15), C<sub>7</sub>H<sub>7</sub> - (16); M = Mn(II) și Zn(II); n = 4 or 2.

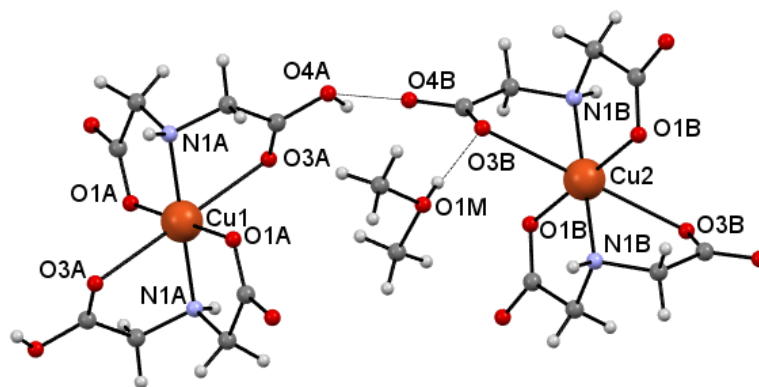
**Fig. 5. Reaction schemes for synthesis of complexes 11-17.**

Structural analysis of complex compounds **11-17** established that compounds **11-14** are binuclear, while **15-17** are mononuclear complexes. The metal atoms are hexacoordinated in compounds **11-14**, and coordination polyhedra of the Mn(II) and Zn(II) are octahedral, formed by N<sub>2</sub>O<sub>4</sub> donor atom set, entrained being three types of ligands (Figure 6).



**Fig. 6. Structure of Mn(II) binuclear centrosymmetric complex in compound 12.**

In case of these complexes the two dicarboxylic acids coordinate in bi-deprotonated form having bridging function, thus linking two metal atoms together. In case of compounds **15** and **16** the way of coordination of the ligands is slightly different. Thereby, in case of compound **15** only the dicarboxylic acid coordinates towards the metal, as a result there are two mononuclear complexes of Cu(II) in the compound: one being a neutral molecular complex, and the other being a complex anion, whose charge is compensated by the protonated cation of dimethyl ether (Figure 7). In case of compound **16**, when dianilineglyoxime was replaced by di-*p*-toluidine-glyoxime (DpatH<sub>2</sub>), an ionic compound is formed, which consists of [Ni(DpatH<sub>2</sub>)<sub>3</sub>]<sup>2+</sup> complex cation, having in the outer sphere the SO<sub>4</sub><sup>2-</sup> anion, a guest molecule of 1,4-H<sub>2</sub>bdc acid, three molecules of DMF and one molecule of water of crystallization.

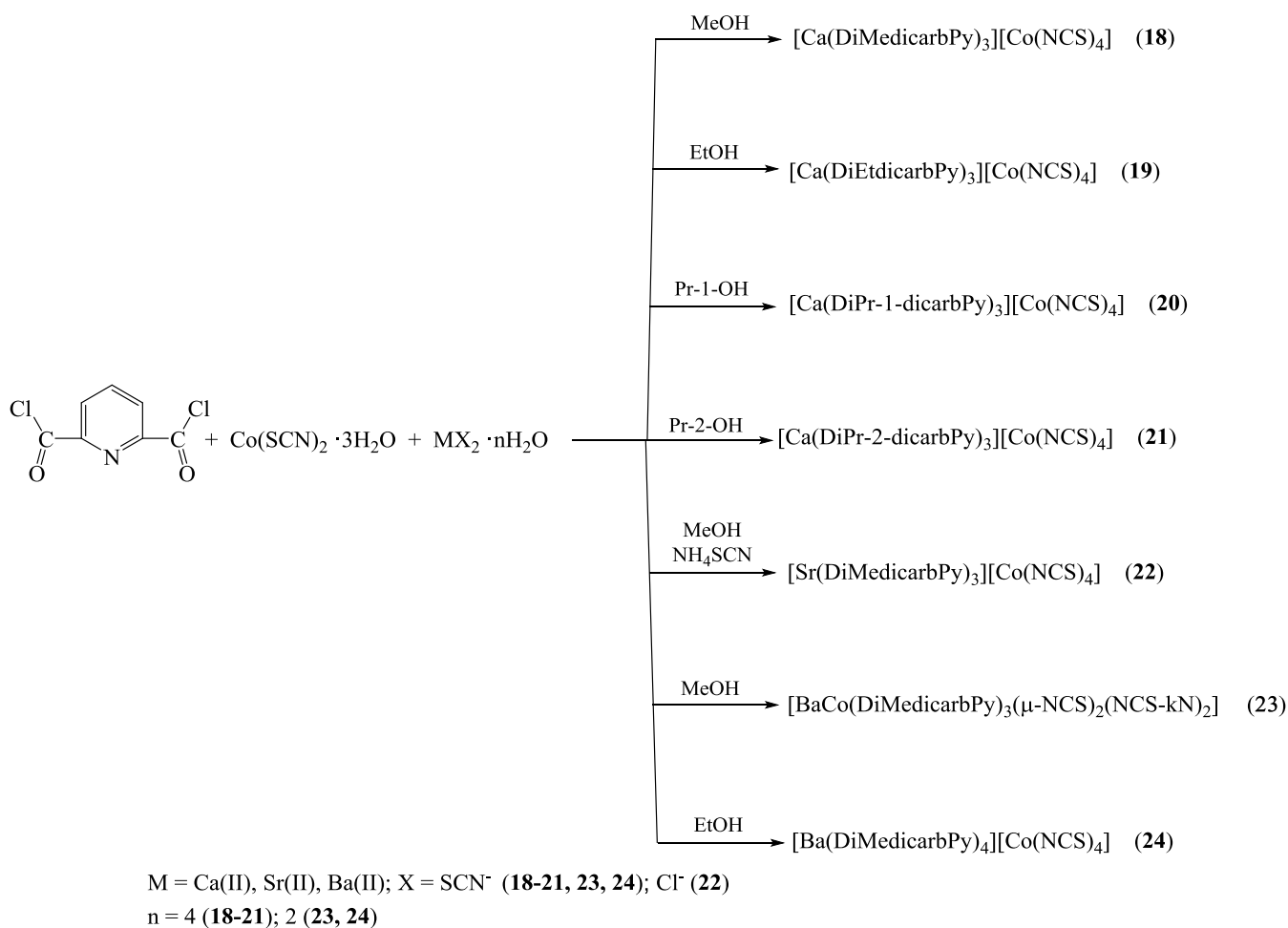


**Fig. 7. Structure of Cu(II) mononuclear complexes of compound 15.**

Dichloroglyoxime and *o*-phenylenediamine were used for the synthesis of compound **17**. Single crystal X-ray diffraction established the molecular structure of the Zn(II) compound, which has the composition [Zn(*o*-FDH<sub>2</sub>)(*o*-FDH)Cl]·6.5H<sub>2</sub>O. The coordination polyhedron of the Zn<sup>2+</sup> ion in this complex represents a tetragonal pyramid formed by four nitrogen atoms that belong to two oxime ligands located at the base of the pyramid, and the top of the pyramid is occupied by the chloride ion, therefore, the coordination node is ZnN<sub>4</sub>Cl, in which the central metal atom is pentacoordinated.

### 3.4. Obtaining bimetallic complexes based on "s" and "d" metals with polydentate ligands

For diversifying the type and nature of the complex compounds, it was further resorted to modifying the class of ligands and entraining in the synthesis of two different types of metal. Therefore, it was possible to obtain seven heterobimetallic compounds based on pyridinedicarboxylic acid esters, Co<sup>2+</sup> ions and "s" type metals (Figure 8).



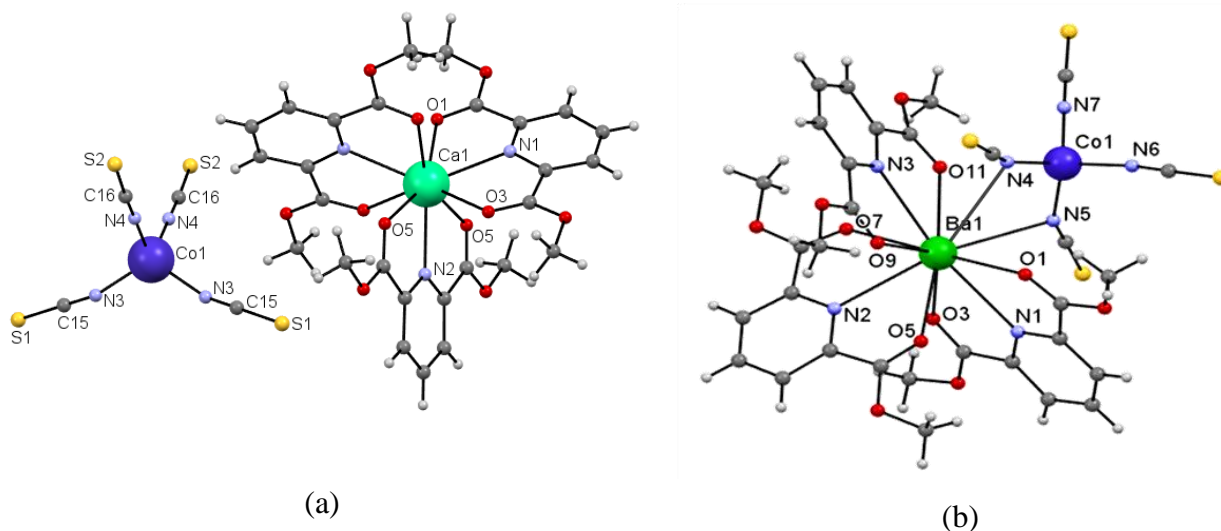
**Fig. 8. Scheme of the equations for the synthesis path of compounds 18-24.**

The 2,6-pyridinedicarbonyl dichloride in various saturated monohydric alcohols was taken as the basis for the synthesis of compounds **18-24**. The analysis of these compounds highlighted the fact that 2,6-pyridinedicarbonyl dichloride forms different esters, depending on the nature of the alcohol used in the synthesis as a solvent. Due to this fact, it was possible to combine two syntheses: one for obtaining the ligand and one for obtaining the heterobimetallic complexes.

The main and most intense absorption bands in the spectra of ligands and compounds **18-24** were the  $\nu(\text{C}\equiv\text{N})$ ,  $\nu(\text{C}=\text{O})$ ,  $\nu_{\text{as}}(\text{C}-\text{O}-\text{C})$  and  $\delta_{\text{nonpl.}}(\text{CH})_{\text{arom.}}$ . The  $\nu(\text{C}\equiv\text{N})$  absorption band appears in the 2032-2062  $\text{cm}^{-1}$  region. In the spectrum of compound **23**, unlike the spectra of the other compounds, two absorption bands  $\nu(\text{C}\equiv\text{N})$  were observed at 2069 and 2032  $\text{cm}^{-1}$  with approximately the same intensity. In this case, the absorption band with higher frequency can be assigned to NCS<sup>-</sup> groups with bridging function.

The X-ray analysis confirmed that refluxing of pyridine-2,6-dicarbonyl dichloride in various aliphatic alcohols results in the formation of pyridine-2,6-dicarboxylic acid esters (L). It

was found that compounds **18-22** and **24** are ionic formed respectively from the complex cations  $[\text{CaL}_3]^{2+}$ ,  $[\text{SrL}_3]^{2+}$  and  $[\text{BaL}_4]^{2+}$  and the complex anion  $[\text{Co}(\text{NCS})_4]^{2-}$  (Figure 9), while compound **23** is a molecular one, in which  $[\text{BaL}_3]^{2+}$  and  $[\text{Co}(\text{NCS})_4]^{2-}$  components are linked via two nitrogen atoms belonging to two  $\text{NCS}^-$  ligands in the latter, as a result of which they serve as bridging ligands.

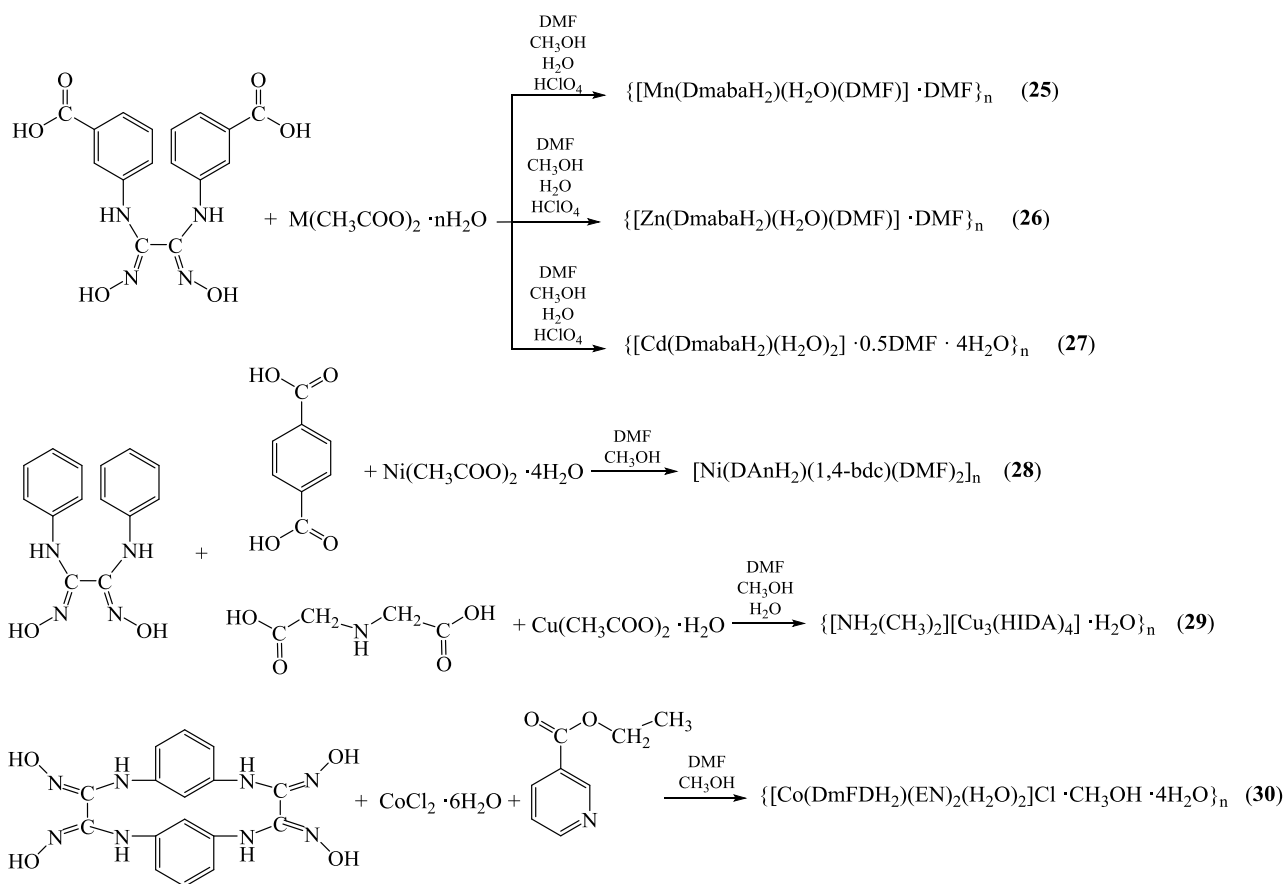


**Fig. 9. Structures of Ca(II) ionic compound in 18 (a) and the molecular compound of Ba(II) in 23 (b).**

The coordination polyhedron of Co(II) in all compounds is a tetrahedron formed by a set of  $\text{N}_4$  donor atoms, which belong to four  $\text{NCS}^-$  anions, while the coordination number of alkaline earth metals is different. Thus, in case of compounds **18-22** the coordination number is **9**, in case of compound **23** it is **11**, and for compound **24** the coordination number is **12**, the coordination polyhedra being formed by the O,N,O donor atoms of the L ligand.

### 3.5. Coordination compounds of Zn(II), Mn(II), Cd(II), Ni(II), Co(III) and Cu(II) with polymeric structure

In reactions between dioximes containing a different number of donor atoms, including those of various origin, six coordination polymers (two 1D and four 2D polymers) were obtained with different salts of Mn(II), Zn(II), Cd(II), Cu(II) and Co(II) (Figure 10). All six polymers have been studied using different methods of physico-chemical analysis, and for five of them the structural formula was established.

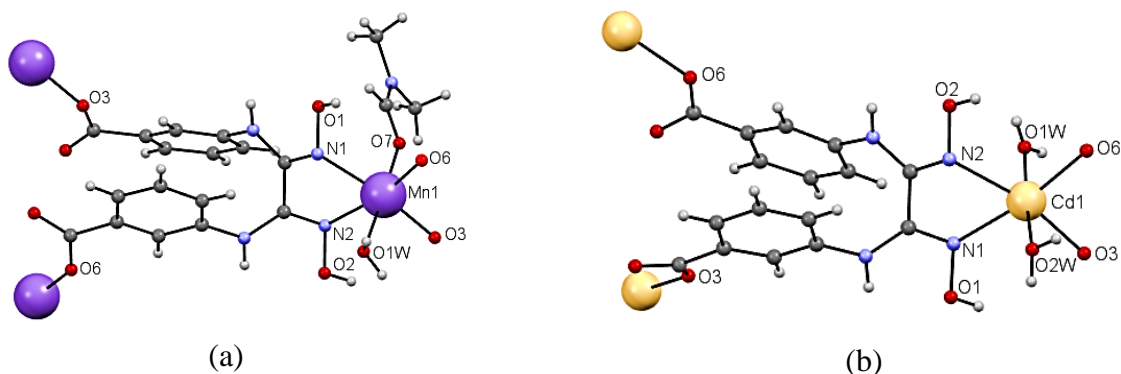


where: M = Mn(II), Zn(II) and Cd(II); n = 2 (26, 27), 4 (25).

**Fig. 10 Synthesis scheme of polymer compounds 25-30.**

The IR spectra of compounds **25-27** contain  $\nu(\text{OH})$  absorption bands of oxime groups at 3374 (**25**), 3449 (**26**) and 3496  $\text{cm}^{-1}$  (**27**), as well as  $\nu(\text{N-H})$  at 3175 (**25**), 3220 (**26**) and 3203  $\text{cm}^{-1}$  (**27**). Intense  $\nu_s(\text{COO}^-)$  absorption bands are observed in the 1377-1388  $\text{cm}^{-1}$  region. The spectrum of compound **28** has a little in common with the spectra of compounds **25-27**. The absorption bands of the  $\nu(\text{OH})$  and  $\nu(\text{NH})$  groups are localized at 3316 and 3045  $\text{cm}^{-1}$  respectively. In the IR spectrum of compound **30**, as well as in the spectra of other dioximes, the absorption bands  $\nu(\text{OH})$  and  $\nu(\text{NH})$  are present at 3353 and 3289  $\text{cm}^{-1}$  respectively. Also present is the band for nicotinic acid ester in the 1287 and 1103  $\text{cm}^{-1}$  region belonging to  $\nu_{\text{as/s}}(\text{C-O-C})$  vibrations.

The X-ray analysis has established that using DmabaH<sub>4</sub> proligand, which contains donor atoms in all terminal fragments, in reactions with salts of Mn(II), Zn(II) and Cd(II) led to the formation of coordination polymers. The asymmetric part of the elementary cells in the crystals of compound **25-27** contains a metal atom and a bi-deprotonated ligand DmabaH<sub>2</sub><sup>2-</sup> in general positions, as well as water and DMF molecules in different ratios. The latter are coordinated to metal atoms (Figure 11) or present in the crystal in the form of incorporated molecules.



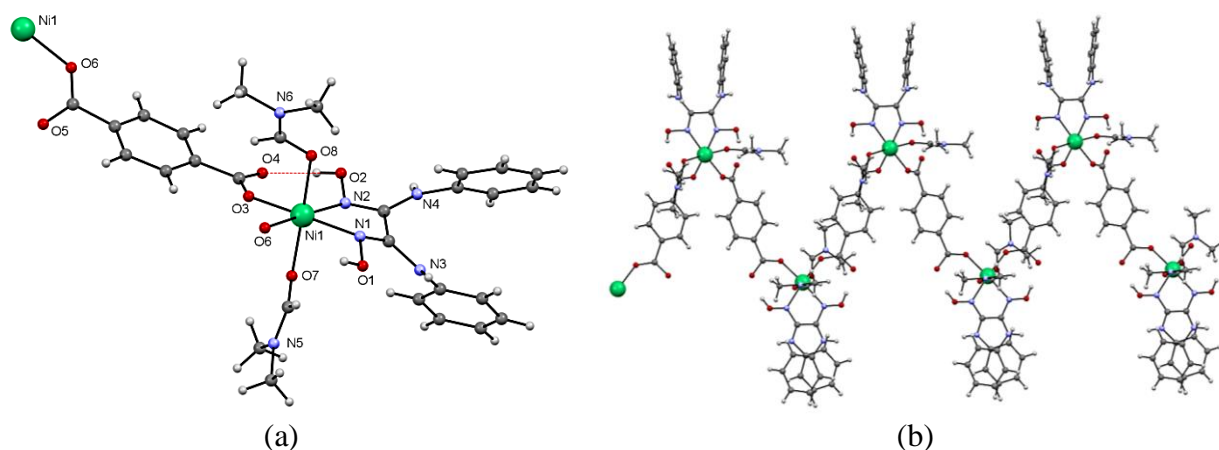
**Fig. 11. Structures of independent crystallographic fragments of coordination polymers of Mn(II) (a), Cd(II) (b) with partial numbering of atoms (compounds 25 and 27).**

The neighbours of each metal atom comprise a  $N_2O_2$  donor set belonging to three different  $DmabaH_2^{2-}$  ligands, and these atoms are located in the equatorial plane of the octahedral coordination polyhedron. The formation of polyhedra of Mn(II), Zn(II) and Cd(II) ions is completed every time with two oxygen atoms belonging to a water and a DMF molecule in compounds **25** and **26**, while in the compound **27** they belong to only two water molecules. As a result, the octahedral coordination polyhedra of metal atoms in compounds **25-27** are made up of the same  $N_2O_4$  donor set.

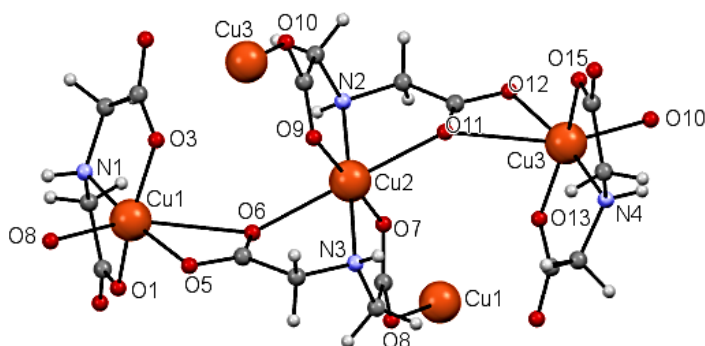
For the synthesis of compound **28** the same reaction conditions were used as in the case of compounds **11-13**, changing only the carboxylic acid. As a result, crystals suitable for single-crystal X-ray analysis were obtained, from which it was established that the novel compound is a polymer. The asymmetric part of the elementary cell contains the metal ion Ni(II), an oxime neutral ligand of  $DanH_2$ , a bi-deprotonated ligand  $(1.4-bdc)^{2-}$  and two neutral ligands (Figure 12). Each  $Ni^{2+}$  ion of this polymer compound (Figure 12) is hexacoordinated and its surroundings have a distorted octahedral geometry, formed by the  $N_2O_4$  donor atom set.

Compound **29** is a little more peculiar compared to the previous ones due to the fact that of the two ligands used in the synthesis ( $DanH_2$  and iminodiacetic acid), only the dicarboxylic acid was engaged in its formation. Iminodiacetic acid in the form of organic salt  $NH(CH_3COO)_2(H_3IDA)$  can serve as a polidentate ligand and coordinate toward metal via the oxygen atoms of the two carboxyl groups and the central nitrogen atom. The interaction of the Cu(II) acetate monohydrate with  $DanH_2$  and  $H_3IDA$  led to a coordination complex with the formula  $\{[NH_2(CH_3)_2]_2[Cu_3(HIDA)_4] \cdot H_2O\}$ , which does not contain dioxime. The asymmetric part of the elementary cell comprises three Cu(II) atoms, four  $HIDA^{2-}$  bi-deprotonated ligands, two dimethylammonium cations and a water molecule (Fig. 13).





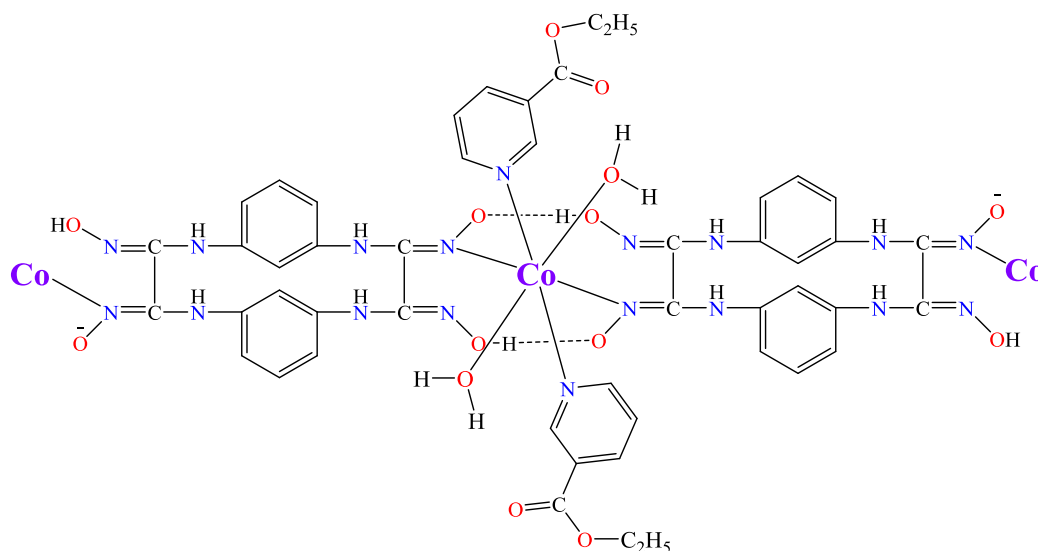
**Fig. 12. Asymmetric part of the coordination polymer 28 with the partial numbering of atoms (a) and fragment of the coordination polymer 1D (b).**



**Fig. 13. Structure of the basic trinuclear fragment of the anionic polymer of compound 29.**

The coordination polyhedron of the central Cu(2) metal atom is formed by the N<sub>2</sub>O<sub>4</sub> atom set, and the other two terminal metal atoms (Cu(1) and Cu(3)) receive the NO<sub>5</sub> in neighborhood.

For compound **30** it was not possible to establish the structural formula because no microcrystals suitable for single-crystal X-ray analysis were obtained. Tetraoxime proligand **4**, ethyl ester of the nicotinic acid and the cobalt salt (II) were used for synthesis of this compound, having air oxygen as oxidant for the transition of Co(II) into Co(III). The product obtained in this synthesis was studied using the assays of elemental analysis and IR spectroscopy. The IR spectrum of complex **30** differs from the tetraoxime spectrum by the emergence of new bands. A wide band at 2722 cm<sup>-1</sup> can be attributed to oscillations of weak hydrogen bond of the O–H···O type, while new bands at 649, 471 and 412 cm<sup>-1</sup> can be attributed to twisting, rocking and M–O<sub>coord.water.</sub> bond vibrations. According to these data it was assumed that compound **30** can be a unidimensional polymer (1D) with the composition {[Co(DmFDH<sub>2</sub>)(EN)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]Cl·CH<sub>3</sub>OH·4H<sub>2</sub>O}<sub>n</sub> (Figure 14).



**Fig. 14. Potential structural formula of the 1D polymer fragment of compound 30.**

The potential structural formula implies that each Co(III) atom is hexacoordinated with a set of  $N_4O_2$  donor atoms, four nitrogen atoms belonging to two bi-deprotonated tetraoxime ligands and two nitrogen atoms – to two neutral EN ligands in axial positions, the charge of the  $Co^{3+}$  cation being compensated by the  $Cl^-$  anion from the external sphere.

#### **4. COMPLEXING AGENTS AND COORDINATION COMPOUNDS WITH BIOLOGICAL ACTIVITY**

Chapter 4 describes the antibacterial and antifungal activities of compounds **1-4** together with the biological activities as stimulators in the cultivation of some strains of micromycetes for compounds **18-20, 22, 23**.

##### **4.1. Antimicrobial activity of newly obtained dioxime coordination agents**

Evaluation of antimicrobial activity of the novel compounds was performed on the following microorganisms: non-pathogenic gram-positive and gram-negative strains of *Bacillus subtilis* NCNM BB-01 (ATCC 33608), *Pseudomonas fluorescens* NCNM PFB-01 (ATCC 25323) and phytopathogenic strains of *Xanthomonas campestris* NCNM BX-01 (ATCC 53196), *Erwinia amylovora* NCNM BE-01 (ATCC 29780), *Erwinia carotovora* NCNM BE-03 (ATCC 15713), as well as strains of fungi *Candida utilis* NCNM Y-22 (ATCC 44638) and *Saccharomyces cerevisiae* NCNM Y-20 (ATCC 4117).

*In vitro* culture inhibition activity of vic-dioxime proligands **1-3** was evaluated both on non-pathogenic gram-positive and gram-negative bacteria as well as on phytopathogenic ones, but also on the fungi listed in table 1. The tests carried out revealed that compound **3** exhibits

average antibacterial and antifungal properties in the 0.007-0.015% concentration range for bacteria and fungi.

**Table 1. *In vitro* antibacterial and antifungal activities of compounds 1–3.**

<b>Compound</b> <b>(conc. 0,5%)</b>	<b>MBC and MFC, %</b>						
	<i>Bacillus subtilis</i>	<i>Pseudomon. fluorescens</i>	<i>Erwinia amylovora</i>	<i>Erwinia carotovora</i>	<i>Xanthom. campestris</i>	<i>Candida utilis</i>	<i>Saccharo. cerevisiae</i>
<b>maba</b>	N/A	N/A	N/A	N/A	N/A	N/A	N/A
<b>paba</b>	N/A	N/A	N/A	N/A	N/A	N/A	N/A
<b>pat</b>	N/A	N/A	N/A	N/A	N/A	N/A	N/A
<b>DAnH<sub>2</sub></b>	N/A	N/A	N/A	N/A	N/A	N/A	N/A
<b>1</b>	N/A	N/A	N/A	N/A	N/A	N/A	N/A
<b>2</b>	N/A	N/A	N/A	N/A	N/A	N/A	N/A
<b>3</b>	0,007	0,015	0,007	0,015	0,015	0,007	0,015
<b>Control (0,5%)</b>	0,06	0,06	0,06	0,06	0,06	0,06	0,06

*MBC* – minimum bactericidal concentration

*MFC* – minimum fungicidal concentration

*N/A* – no activity

According to the data in Table 1, the increase in the antibacterial activity of compound **3** compared to control compound is 4-8 times higher, depending on the tested bacterial and fungal species.

#### **4.2. *Bis-m*-phenylenediaminetetraoxime *bis*-dimethylformamide with antibacterial and antifungal activity**

The structure of compound **4** differs slightly from that of compounds **1–3**, as **4** belongs to the tetraoxime class. Research on tetraoximes is rarely found in the specialized literature. The novel tetraoxime complexing agent **4** was tested on the same bacterial and fungal strains as compounds **1-3**, the results are shown in Table 2.

**Table 2. *In vitro* antibacterial and antifungal activities of compound 4.**

<b>Compound</b> <b>(conc. 0,5%)</b>	<b>MBC and MFC, %</b>						
	<i>Bacillus subtilis</i>	<i>Pseudomon. fluorescens</i>	<i>Erwinia amylovora</i>	<i>Erwinia carotovora</i>	<i>Xanthom. campestris</i>	<i>Candida utilis</i>	<i>Saccharo. cerevisiae</i>
<b>mFD</b>	N/A	N/A	N/A	N/A	N/A	N/A	N/A
<b>4</b>	0,015	0,03	0,015	0,03	0,015	0,015	0,015
<b>Control (0,5%)</b>	0,06	0,06	0,06	0,06	0,06	0,06	0,06

*MBC* – minimum bactericidal concentration

*MFC* – minimum fungicidal concentration

*N/A* – no activity

The data in Table 2 confirm that the increase in the antibacterial activity of compound **4** compared to the control compound is 2-4 times higher, depending on the bacterial species, and antifungal activity is up to 4-times higher. However, at the same time, the activity of this compound is 2-fold lower compared to compound **3**.

### 4.3. Bimetallic coordination compounds – stimulators of cultivation of some strains of micro- and macromycetes

In addition to evaluating antimicrobial activity of compounds **1-4**, microbiological tests of compounds **18-20**, **22** and **23** were also carried out, as well as developing a strategy for application of these compounds in the submerged culture of strains of filamentous fungi *Rhizopus arrhizus* CNMN FD 03, *Aspergillus niger* CNMN FD 06, *Lentinus edodes* CNMN FB 01 and *Fusarium gibbosum* CNMN FD 12.

Data in Tables 3 and 4 reveal that maximum levels of lipolytic activity in the reference group were recorded on the second day of cultivation and constitute 18750 u/mL compared to 17930 and 5625 u/mL marked on the 1<sup>st</sup> and 3<sup>rd</sup> days of cultivation, respectively, for compounds **18**, **22** and **23**. For compounds **19** and **20** these levels were also recorded on the second day of cultivation, but the activity being 30000 u/ mL compared 20708.8 and 22083.3 u/mL recorded on the first and third days of cultivation respectively. Data in Table 3 also show the increased activity for compounds **18**, **22** and **23** on the very first day of cultivation, respective values exceeding the maximum levels of the control by 7.3-98.4% and being 6.7-86.7% higher on the second day compared to control on the respective day.

**Table 3. Influence of coordination complexes 18, 22 and 23 on lipolytic activity of the micromycete *Rhizopus arrhizus* CNMN FD 03**

Coord. complex	Conc., mg/L	1 <sup>st</sup> day		2 <sup>nd</sup> day		3 <sup>rd</sup> day	
		Activity, mg/L	%, of reference*	Activity, mg/L	%, of control	Activity, mg/L	%, of control
<b>18</b>	5	20125	112,2/107,3	22500	120,3	1875	33,3
	10	35583	198,4/189,8	27500	146,7	3750	66,7
	15	26250	146,3/140,0	35000	186,7	3750	66,7
<b>22</b>	5	27562	153,7/147,0	20000	106,7	1875	33,3
	10	21000	117,1/112,0	20000	106,7	1875	33,3
	15	15312	85,4	15000	80,0	1875	33,3
<b>23</b>	5	25667	143,1/137,0	22500	125,4	8125	144,4
	10	20125	112,2/107,3	12500	66,7	4375	77,8
	15	20125	112,2/107,3	12500	66,7	4375	77,8
<b>Control</b>	-	<b>17930</b>	<b>100,0</b>	<b>18750</b>	<b>100,0</b>	<b>5625</b>	<b>100,0</b>

\*198,4/189,8 – of control values on the day/ of maximum control values on the 2<sup>nd</sup> day.

Compounds **19** and **20** also showed a 36.6-98.6% increase in the lipolytic activity compared to the control group right on the first day of cultivation, which was not recorded on the 2<sup>nd</sup> day of cultivation.

The influence of compounds **22** and **23** on amyolytic activity of the micromycete *Aspergillus niger* CNMN FD 06 was tested. The purpose of this study was to establish the optimal conditions for the application of the coordination heterometallic complexes **22** and **23**

containing Ba(II) and Sr(II) in the cultivation technology of the micromycete *Aspergillus niger* CNMN FD 06 as a strategy to increase the biosynthesis of exocellular amylases.

**Table 4. Influence of coordination complexes 19 and 20 on lipolytic activity of the micromycete *Rhizopus arrhizus* CNMN FD 03**

Coord. complex	Conc., mg/L	1 <sup>st</sup> day		2 <sup>nd</sup> day		3 <sup>rd</sup> day	
		Activity, mg/L	%, of reference*	Activity, mg/L	%, of control	Activity, mg/L	%, of control
<b>19</b>	5	41125,0	198,6/137,1	19375,0	64,6	2083,3	9,4
	10	28291,7	136,6/94,3	25000,0	83,3	2083,3	9,4
	15	20125,0	97,2	23750,0	79,2	1250,0	5,7
<b>20</b>	5	23916,7	115,5	31250,0	104,2	2500,0	11,3
	10	23333,3	112,7	20625,0	68,8	1250,0	5,7
	15	28583,3	138,0/95,3	33125,0	110,4	21666,7	98,1
<b>Control</b>	-	<b>20708,3</b>	<b>100,0</b>	<b>30000,0</b>	<b>100,0</b>	<b>22083,3</b>	<b>100,0</b>

\*198,6/137,1 – of control values on the day/ of maximum control values on the 2<sup>nd</sup> day.

Results obtained reveal that compound **23** in concentrations of 1 and 5 mg/L positively influences the accumulation of amylases in the micromycete *Aspergillus niger* on both days of cultivation, the activity varying between 96.68-110.08 u/mL on the 5<sup>th</sup> day and 132.15-143.94 u/mL on day 6 compared to 72.86 and 79.09 u/mL recorded in the control sample on the respective days. The increase in enzyme activity ensured by supplementing the medium with the barium compound varied between 32.7-82.0% (Table 5).

**Table 5. Influence of different concentrations of compounds 22 and 23 on amylolytic activity of the micromycete *Aspergillus niger* CNMN FD 06**

Coordination complexes	Concentration, mg/L	5 <sup>th</sup> day		6 <sup>th</sup> day	
		Activity, mg/L	%, of reference*	Activity, mg/L	%, of control
<b>22</b>	1	69,88	95,9	100,71	127,3
	5	113,06	155,2/142,9	108,57	137,3
	10	74,34	102,0	79,09	100,0
<b>23</b>	1	110,08	151,1/139,2	143,94	182,0
	5	96,68	132,7/122,2	132,15	167,1
	10	72,86	100,0	61,40	77,6
<b>Control</b>	-	<b>72,86</b>	<b>100,0</b>	<b>79,09</b>	<b>100,0</b>

\*% of control values on the day/ of maximum control values on the 6<sup>th</sup> day

Based on the data presented in Table 5, it was decided to expand the research range on the activity of these compounds. Thus, the influence of compound **23** on accumulation of biomass in the micromycete *Lentinus edodes* was monitored. Based on the results obtained, the stimulatory effect of compound **23** on biomass accumulation in the macromycete *Lentinus edodes* was confirmed, the optimal concentration that ensures with small differences the maximum increase in the amount of biomass (22.1-62.5%) being 5.0 and 10.0 mg/L (Table 6).

**Table 6. Influence of different concentrations of compound 23 on biomass accumulation in the micromycete *Lentinus edodes***

Coordination complexes	Conc., mg/L	6 <sup>th</sup> day		7 <sup>th</sup> day		8 <sup>th</sup> day	
		Biomass, g/L	%, of control	Biomass, g/L	%, of control	Biomass, g/L	%, of control
<b>23</b>	1,0	24,77	143,0/121,1*	24,64	133,5/120,4*	23,35	114,0
	2,5	24,27	140,1/118,6*	24,73	133,9/120,9*	23,67	115,7
	5	28,15	162,5/137,6*	26,85	145,4/131,2*	25,23	123,3
	10	27,76	160,3/135,7*	26,13	141,5/127,7*	24,98	122,1
	15	27,13	156,6/132,6*	26,73	144,8/130,6*	24,70	120,7
<b>Control</b>	-	<b>17,32</b>	<b>100,0</b>	<b>18,46</b>	<b>100,0</b>	<b>20,46</b>	<b>100,0</b>

\*%, of control values on the day/ of maximum control values on the 8<sup>th</sup> day

At the same time, the effect of different concentrations of compound 22 on the activity of complex of acidic (pH-3.6), neutral (pH-7.4) and alkaline (pH-9.0) proteases in the above-mentioned micromycete was evaluated. Cultivation was carried out during 4, 5 and 6 days of cultivation - the optimal duration of submerged culture of micromycete that ensures the biosynthesis of proteolytic enzymes at high rates. All data reflecting the influence of complex 22 on the activity of acid, neutral and alkaline proteases are presented in Tables 7, 8 and 9.

**Table 7. The influence of compound 22 on the activity of acid proteases (pH-3.6) in the micromycete *Fusarium gibbosum* CNMN FD 12**

Coordination complex	Conc., mg/L	4 <sup>th</sup> day		5 <sup>th</sup> day		6 <sup>th</sup> day	
		Activity, u/mL	%, of control	Activity, u/mL	%, of control	Activity, u/mL	%, of control
<b>22</b>	1	0,74	88,3	1,33	79,6	1,26	94,0
	5	0,76	90,0	1,05	62,9	1,20	89,9
	10	1,18	140,0	1,44	86,3	1,29	96,1
	15	0,59	70,0	0,92	55,3	0,98	73,1
<b>Control</b>	-	<b>0,84</b>	<b>100,0</b>	<b>1,67</b>	<b>100,0</b>	<b>1,34</b>	<b>100,0</b>

The data in table 7 show that the compound contributes to intensification of the enzyme synthesis in 10 mg/L, so already on the fourth day of cultivation the activity is marked by high values - 1.18 u/mL, exceeding by 40% the control levels on the same day.

**Table 8. Influence of compound 22 on the activity of neutral proteases (pH-7.4) in the micromycete *Fusarium gibbosum* CNMN FD 12**

Coordination complex	Conc., mg/L	4 <sup>th</sup> day		5 <sup>th</sup> day		6 <sup>th</sup> day	
		Activity, u/mL	%, of control	Activity, u/mL	%, of control	Activity, u/mL	%, of control
<b>22</b>	1	0,97	92,0	2,23	99,4	1,85	90,6
	5	1,11	105,3	1,64	73,1	2,58	126,3/115,2*
	10	1,99	189,3	2,14	95,6	2,46	120,8/106,8*
	15	0,85	81,3	1,26	56,3	2,21	108,4
<b>Control</b>	-	<b>1,05</b>	<b>100,0</b>	<b>2,24</b>	<b>100,0</b>	<b>2,04</b>	<b>100,0</b>

\*%, of the maximum control values registered on the 5<sup>th</sup> day.

Based on these data, it can be seen that Sr(II)-containing compound added to the cultivation medium of *Fusarium gibbosum* strain in a concentration of 10 mg/L ensures an 89.3% increase of enzyme activity right from the fourth day of cultivation compared to the maximum values in control group registered on the same day.

**Table 9. Influence of compound 22 on the activity of alkaline proteases (pH-9.0) in the micromycete *Fusarium gibbosum* CNMN FD 12**

Coordination complex	Conc., mg/L	4 <sup>th</sup> day		5 <sup>th</sup> day		6 <sup>th</sup> day	
		Activity u/mL	%, of control	Activity, u/mL	%, of control	Activity, u/mL	%, of control
<b>22</b>	1	0,92	82,5	1,26	96,9	0,98	99,6
	5	1,02	91,3	2,37	182,0	1,54	155,6
	10	1,06	95,0	2,32	178,8	1,67	168,3
	15	1,27	113,8	1,83	141,1	0,92	93,3
<b>Control</b>	-	<b>1,12</b>	<b>100,0</b>	<b>1,30</b>	<b>100,0</b>	<b>0,99</b>	<b>100,0</b>

The data in Table 9 suggest that the Sr(II) compound exerts a positive influence on the biosynthesis of alkaline proteases in a wider range of concentrations. Thereby, on the fifth day - the optimal duration of cultivation of the micromycete that ensures the maximum manifestation of biosynthetic potential of the enzyme of interest, the proteolytic activity of the samples cultivated in the presence of compound **22** varies between 1.26 - 2.37 u/mL, being by 41 ,1 – 82.0% higher compared to the control. Thus, a positive effect exerted all tested concentrations, except for the concentration of 1 mg/L which does not influence the biosynthetic activity. At the concentration of 5 and 10 mg/L the activity is practically identical (the increase being 82% and 78.8%, respectively), maintaining the higher levels even on the sixth day of cultivation.

## GENERAL CONCLUSIONS

1. The scientific literature review, carried out in the thesis, has shown that the subjects submitted for research are insufficiently studied or studied tangentially at international level. This situation demonstrates the need to carry out the proposed research in the thesis to obtain new complexing agents and derived coordination compounds with new physico-chemical, spectral, structural and useful properties.
2. Methods of synthesis were developed, which led to obtaining four novel coordination agents (*bis*-aminobenzoylglyoxime (1), *bis-p*-aminobenzoylglyoxime (2), *bis-p*-aminotolueneglyoxime (3) and *bis-m*-phenylenediametetraoxime (4)), including: monofunctional dioximes (3), heterofunctional dioximes (1 and 2) and a tetraoxime (4); and derived coordination complexes of Mn(II), Co(II, III), Ni(II), Cu(II), Cd(II), Ca(II), Sr(II) and Ba(II).
3. Classic dioxime proligands coordinate toward metal atom as monofunctional ligands in neutral, mono- and bi-deprotonated form via two nitrogen atoms. If the metal atom coordinates two ligand molecules, they can be stabilized predominantly in two forms - neutral and mono-deprotonated.
4. In the crystal lattice of complexes of cobalt (III) molecules are entrapped, which form cavities with dimensions ranging between 7.2–23.5% of the volume of the elementary cell (compounds 9 and 10), while in the crystal lattice of the compounds, which do not contain incorporated molecules this volume is less than 6.0% (6-8).
5. In the synthesis of binuclear Mn(II) and Zn(II) compounds an important role plays the nature of the solvent and its purity. Using DMSO of 99.9% purity leads to transforming the binuclear complex (compound 13) into known coordination polymer, while 98.9% DMSO leads to formation of a dimer compound with DMSO coordination in axial positions of the octahedron (compound 14).
6. Alkaline earth metals (Ca, Sr, Ba) form bimetallic complexes with cobalt(II), in which the structure and composition of depend on the nature of the alkaline earth metal. In case of calcium and strontium, the common formula is  $[Ca/SrL_3][Co(NCS)_4]$ , in case of barium -  $[BaCoL_3(\mu-NCS)_2(NCS-kN)_2]$  and  $[BaL_4][Co(NCS)_4]$ , where L – tridentate ligand, dimethyl/diethylpyridine-2,6-dicarboxylate. Coordination number for the bimetallic complexes also varies; for the first one the CN of calcium and strontium is 9 (compounds 19-22) and 11-12 for the barium complexes (compounds 23 and 24), this fact probably being determined by the radius of the alkaline earth metal atom.



7. Two strategies can be used in synthesis of complex compounds with increased nuclearity, including dioxime-based coordination polymers: a) introducing additional bridging ligands; b) using dioximes that contain substituents with other functional groups.
8. The research on antimicrobial properties of compounds **3** and **4** revealed their essential activity against five species of gram-positive and gram-negative bacteria: *Bacillus subtilis* NCNM bb-01, *Pseudomonas fluorescens* NCNM PFB-01; phytopathogenic: *Xanthomonas campestris* NCNM BX-01, *Erwinia amylovora* NCNM BE-01, *Erwinia carotovora* NCNM BE-03 and two strains of fungi: *Candida utilis* NCNM Y-22 and *Saccharomyces cerevisiae* NCNM Y-20.
9. Bimetallic coordination compounds show biological activity as biocatalysts of enzymogenesis in some micro- and macromycetes: *Rhizopus arrhizus* CNMN FD 03 (**18–23**, 7,3-98,6%); *Aspergillus niger* CNMN FD 06 (**22, 23**, 8,57-82,0%); *Fusarium gibbosum* CNMN FD 12 (**22**, 5,5-89,3%) and *Lentinus edodes* CNMN BD 01 (**23**, 18,6-62,5%).

#### RECOMANDATIONS:

1. The results obtained allow recommending the application of all active compounds as an antimicrobial remedy in agriculture, but also in the biotechnology for cultivating filamentous fungi *Rhizopus*, *Aspergillus*, *Lentinus* and *Fusarium* – producers of valuable bioactive substances, as a strategy for increasing biotechnological performances.
2. Compounds **3** and **4** can be recommended as means for controlling gram-positive and gram-negative bacteria and microbes in agriculture.

The results obtained in the course of completing the thesis can be used in the process of training highly qualified specialists at the following departments: chemistry, agronomy, microbiology.

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3. **URECHE, Dumitru**; BULHAC, Ion; KRAVTSOV, Victor; BOUROSH, Pavlina. A novel copper(II) 2D coordination polymer constructed of iminodiacetic acid. In: *Achievements and perspectives of modern chemistry*. 9-11 octombrie 2019, Chisinau, Republic of Moldova: Publishin house of Academy of Science of Moldova, p. 150. ISBN 978-9975-62-428-2.  
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2. **URECHE, Dumitru**; BULHAC, Ion; VEVERIȚĂ, Anastasia; BOUROȘ, Pavlina; LUPAȘCU, Lucian. *Compusul 2,5,11,14-tetraazatricyclo-[13,3,1,16,10]-icosa-1(19),6,8,10(20),15,17-hexaene-3,4,12,13-tetraontetraoxime bis(N,N dimethylformamide) with antibacterial and antifungal activity*. Patent MD 4745 C1 from 30.09.2021, BOPI 2/2021.
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BULHAC, Ion; **URECHE, Dumitru**; CILOCI, Alexandra; COCU, Maria; CLAPCO, Steliana; LABLIUC, Svetlana. *Tetraisoithiocyanatocobaltate(II) of calcium trisdiethylpyridine-2,6-dicarboxylate with biostimulatory effect on lipolytic activity in fungal strain of Rhizopus arrhizus CNMN FD 03*. Patent application Nr. a 2022 0004 from 2022.02.04.



## ADNOTARE

**URECHE Dumitru, „Sinteza, studiul proprietăților și arhitecturii moleculare ale compușilor coordinativi ai metalelor de tip „s” și „d” cu liganzi polifuncționali”, teză de doctor în științe chimice, Chișinău, 2023.**

**Structura tezei:** teza a fost realizată în cadrul proiectelor: 15.817.02.18A și 20.80009.5007.28 în cadrul Laboratorului Chimia Coordinativă al Institutului de Chimie al USM. Lucrarea este structurată din: introducere, 4 capitole, concluzii generale și recomandări, bibliografie din 297 surse, 3 anexe, 122 de pagini de text de bază, 71 de figuri și 11 tabele. Rezultatele obținute în cadrul tezei au fost publicate în 29 lucrări științifice, inclusiv: 5 articole în reviste cu factor de impact, un articol în revistă națională categoria A, 3 articole în culegeri ale conferințelor, 11 rezumate la conferințele naționale și internaționale, 8 brevete de invenții (3 eliberate, 5 acordate) și o cerere de brevet de invenție.

**Cuvinte-cheie:** compuși coordinativi, liganzi di- și tetraoximici, liganzi heterofuncționali, sinteză, spectroscopie IR, raze X, activitate biologică, micromicete.

**Scopul lucrării** constă în sinteza noilor proliganzi și a compușilor coordinativi mono- și polinucleari, inclusiv polimerici, ai metalelor „s” și „d” cu liganzi homo- și heterofuncționali, caracterizarea lor, precum și studiul activității biologice a acestora.

**Obiectivele cercetării:** sinteza noilor proliganzi di- și tetraoximici și piridindicarboxilici; sinteza complexilor mono- și polinucleari ai metalelor „s” și „d”; caracterizarea compușilor obținuți, utilizând diferite metode de cercetare; studiul proprietăților biologice pentru proliganzii și complexii obținuți.

**Noutatea și originalitatea științifică** constă în obținerea a 30 de compuși noi, dintre care 4 agenți de coordinație oximici, 20 de complecși mono- și dinucleari și 6 polimeri coordinativi 1D și 2D.

**Rezultatele obținute care contribuie la soluționarea unei probleme științifice importantă** în teză constau în elaborarea metodelor de sinteză a complexilor cu diferită nuclearitate și dimensiuni polimerice ale unor metale „2s”, „3d” și „4d”.

**Semnificația teoretică:** au fost sintetizați compuși heterometalici ai Ca(II), Sr(II) și Ba(II) și homometalici ai Mn(II), Co(II)/Co(III), Ni(II), Cu(II), Zn(II) și Cd(II) cu diferită nuclearitate.

**Valoarea aplicativă:** unii agenți de coordinație și compuși complecși manifestă proprietăți antibacteriene și de biostimulatori la cultivarea micro- și macromicetelor utile.

**Implementarea rezultatelor științifice:** proprietățile utile ale unor proliganzi și compuși coordinativi ca cele antimicrobiene și de stimulatori ai proceselor de enzimogeneză la cultivarea unor tulpini de micro- și macromicete au fost protejate prin brevete de invenție din RM, oferind posibilitatea utilizării acestora ca agenți de protecție a plantelor.

## АННОТАЦИЯ

**УРЕКЕ Думитру, „ Синтез, изучение свойств и молекулярной архитектуры координационных соединений металлов типа „s” и „d” с полифункциональными лигандами”, диссертация на соискание учёной степени доктора химических наук, Кишинэу, 2023.**

**Структура диссертации:** диссертация выполнена в рамках проектов: 15.817.02.18А и 20.80009.5007.28 в составе Лаборатории Координационной Химии Института химии МГУ. Работа построена из: введения, 4 главы, общих выводов и рекомендаций, библиографии из 297 источников, 3 приложений, 122 страниц основного текста, 71 рисунка и 11 таблиц. Результаты, полученные в рамках диссертации, опубликованы в 29 научных работах, в том числе: 5 статей в журналах с импакт-фактором, статья в национальном журнале категория А, 3 статьи в материалах конференций, 11 тезисов на национальных и международных конференциях, 8 патентов и одна заявка на патент.

**Ключевые слова:** координационные соединения, ди- и тетраоксимные лиганды, гетерофункциональные лиганды, синтез, ИК-спектроскопия, РСА, биологическая активность, микромицеты.

**Цель работы** состоит в создании новых пролигандов и моно- и полиядерных, в том числе полимерных, координационных соединений «s» и «d» металлов с гомо- и гетерофункциональными лигандами, их характеристика, а также изучение их биологической активности

**Задачи исследований:** синтез новых ди- и тетраоксимных пролигандов, а также пиридиндикарбоксильных; синтез моно- и полиядерных комплексов «s» и «d» металлов; характеристика полученных соединений с использованием различных методов исследования; изучение биологических свойств полученных пролигандов и комплексов.

**Новизна и научная оригинальность** заключается в получении 30 новых соединений, из них 4 оксимных координационных агента, 20 моно- и биядерных комплексов и 6 координационных полимеров с размерностью 1D и 2D.

**Полученные результаты, способствующие решению важной научной задачи в диссертации,** заключаются в разработке методов синтеза комплексов с различной нуклеарностью и размерами полимеров некоторых «2s», «3d» и «4d» металлов.

**Теоретическое значение:** получение новых гетерометаллических соединений Ca(II), Sr(II) и Ba(II), а также гомометаллических соединений Mn(II), Co(II)/Co(III), Ni(II), Cu(II), Zn(II) și Cd(II) с разным количеством атомов металла.

**Прикладное значение:** установлено, что некоторые органические соединения и комплексы проявляют антибактериальные свойства и биостимуляторов при культивировании полезных микро- и макромицетов.

**Внедрение научных результатов:** полезные свойства некоторых пролигандов и координационных соединений, такие как антимикробные и стимуляторы процессов ферментогенеза при культивировании штаммов микро- и макромицетов, защищены патентами на изобретения Республики Молдова, что открывает возможность их использования в качестве средств защиты растений.

## ANNOTATION

**URECHE Dumitru, ,, Synthesis, study of properties and molecular architecture of “s” and “d” type metal coordination compounds with polyfunctional ligands”, PhD thesis in chemistry, Chisinau, 2023.**

**Thesis structure:** the thesis was carried out within the framework of projects: 15.817.02.18A and 20.80009.5007.28 in the Laboratory of Coordination Chemistry of the Institute of Chemistry of MSU. The work comprises: introduction, 4 chapters, general conclusions and recommendations, reference list of 297 entries, 3 appendices, 122 pages of body text, 71 figures and 11 tables. The results obtained in the framework of the thesis were published in 29 scientific works, including: 5 articles in journals with an impact factor, an article in a national journal category A, 3 articles in conference proceedings, 11 abstracts at national and international conferences, 8 invention patents ( 3 released, 5 granted) and a patent application.

**Keywords:** coordination compounds, di- and tetraoxime ligands, heterofunctional ligands, IR spectroscopy, X-ray, biological activity, micromycetes.

**The purpose of the thesis** consists in the creation of new proligands and mono- and polynuclear coordination complexes, including polymers, of "s" and "d" metals with homo- and heterofunctional ligands, their characterization, as well as the study of their biological activity.

**Research objectives:** synthesis of new di- and tetraoxime and pyridinedicarboxylic acid proligands; synthesis of mono- and polynuclear complexes of „s” and „d” metals; characterization of the obtained compounds, using different research methods; the study of biological properties for the obtained proligands and complexes.

**Novelty and scientific originality** consists in obtaining 30 new compounds, of which 4 are oxime coordination agents, 20 are mono- and dinuclear complexes and 6 are 1D and 2D coordination polymers.

**The obtained results that contribute to the solving of an important scientific problem** in the thesis consist in the developing methods for the synthesis of complexes with different nuclearity and polymer sizes of some „2s”, „3d” and „4d” metals.

**Theoretical significance:** heterometallic compounds of Ca(II), Sr(II) and Ba(II) and homometallic compounds of Mn(II), Co(II)/Co(III), Ni(II), Cu(II), Zn(II) and Cd(II) with different nuclearity where synthesised.

**Practical importance:** some complexing agents and some complex compounds exhibit antibacterial and biostimulatory properties in the cultivation of beneficial micro- and macromycetes.

**Implementation of the scientific results:** the useful properties of some proligands and coordination complexes such as antimicrobial activity and stimulation of enzymogenesis for cultivating some strains of micro- and macromycetes received patent protection in the Republic of Moldova, which opens the possibility for their use as plant protection agents.

**URECHE DUMITRU**

**SYNTHESIS, STUDY OF PROPERTIES AND MOLECULAR  
ARCHITECTURE OF “s” AND “d” TYPE METAL  
COORDINATION COMPOUNDS WITH POLYFUNCTIONAL  
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**141.01. INORGANIC CHEMISTRY**

Summary of PhD thesis in chemistry

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Institute of Chemistry of Moldova State University  
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