

CZU: 546.73-3:582.232

DOI: 10.46727/c.17-18-05-2024.p31-38

**SINTEZA ȘI STUDIUL PROPRIETĂȚILOR UTILE ALE UNOR COMPUȘI
COORDINATIVI CU LIGANZI CARE CONȚIN ATOMI DONORI DE
ELECTRONI DE AZOT ȘI OXIGEN**

**SYNTHESIS AND STUDY OF THE USEFUL PROPERTIES OF SOME
COORDINATION COMPOUNDS WITH LIGANDS CONTAINING
NITROGEN AND OXYGEN ATOMS AS ELECTRON DONORS**

COROPCEANU Eduard

Institute for Research, Innovation and Technology Transfer, „Ion Creanga” State
Pedagogical University of Chisinau, Republic of Moldova

ORCID: 0009-0008-1525-3808

coropceanu.eduard@upsc.md

Rezumat: A fost realizată sinteza unei serii de compuși coordinațivi cu liganzi ce conțin atomi donori de electroni (N, O) cu structură mono-, di- și polimerică. S-a constatat, că natura ionului metalic generator de complex, a moleculelor utilizate în calitate de agent de coordinare (conținutul atomilor donori de electroni, topologia lor în moleculă, dimensionalitatea moleculei etc.) influențează arhitectura moleculară a noilor complecși și proprietățile manifestate. Pentru o serie de compuși au fost identificate proprietăți utile în domeniul stimulării proceselor biosintetice la microorganisme, sporirea producției la hectar pentru plantele superioare de cultură, manifestarea unor proprietăți utile pentru industrie (luminescență, inhibarea proceselor de coroziune a oțelurilor etc.).

Cuvinte-cheie: compuși coordinațivi, atomi donori de electroni, proprietăți utile, biostimulatori

Abstract: The synthesis of a series of coordination compounds with ligands containing electron-donor atoms (N, O) with mono-, di- and polymeric structure was carried out. It was found that the nature of the complex-generating metal ion, of the molecules used as coordinating agents (the content of electron donor atoms, their topology in the molecule, the dimensionality of the molecule, etc.) influences the molecular architecture of the new complexes and the properties manifested. For a series of compounds, useful properties have been identified in the field of stimulating biosynthetic processes in microorganisms, increasing production per hectare for crop plants, and demonstrating useful properties for industry (luminescence, inhibition of steel corrosion processes, etc.).

Keyword: coordination compounds, electron donor atoms, useful properties, biostimulators

The synthesis of new chemical compounds with useful properties presents a priority direction for research and industry. Coordination compounds represent a class

In addition to oxime coordinating agents, molecules with a pyridine ring were used: pyridine (Py), nicotinamide (PP), sulfanilamide (Sam); with an electron-donor sulfur atom: thiocarbamide (Thio); with a role of bridging ligand containing two pyridine rings: 4,4-bipyridyl (bpy), 1,2-bis-(4-pyridyl)-ethane (bpe), 4,4-trimethylenedipyridine (bpp), 4,4-bipyridyl sulfide (bps); with various electron-donor atoms: (4-pyridylthio)acetic acid (Hpyta) etc. (Fig. 2).

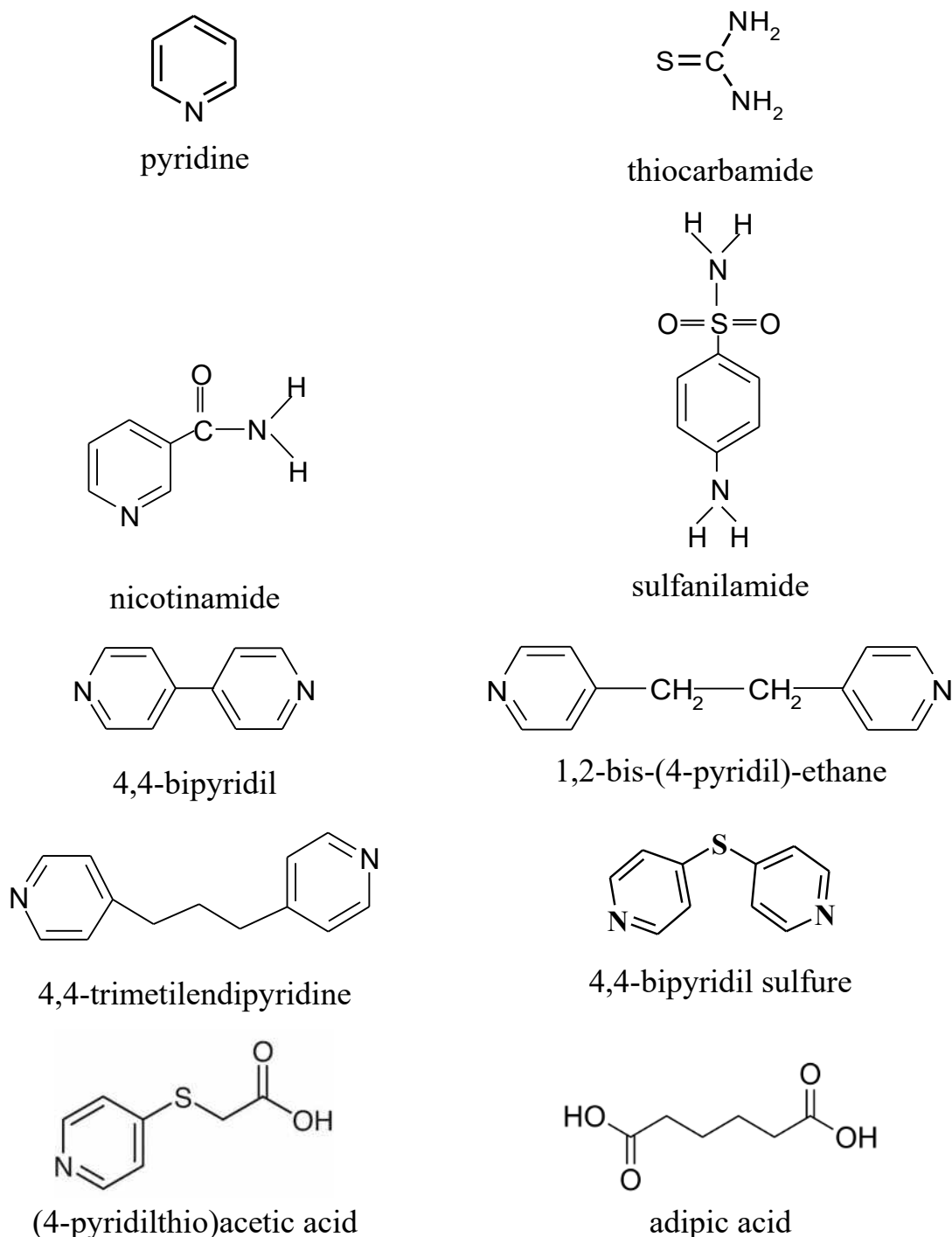


Fig. 2. Some coordinating agents with various functional groups used in the assembly of coordination compounds

A series of mononuclear compounds of cobalt(III), zinc(II), cadmium(II) with mono- or dioximic ligands have been obtained.

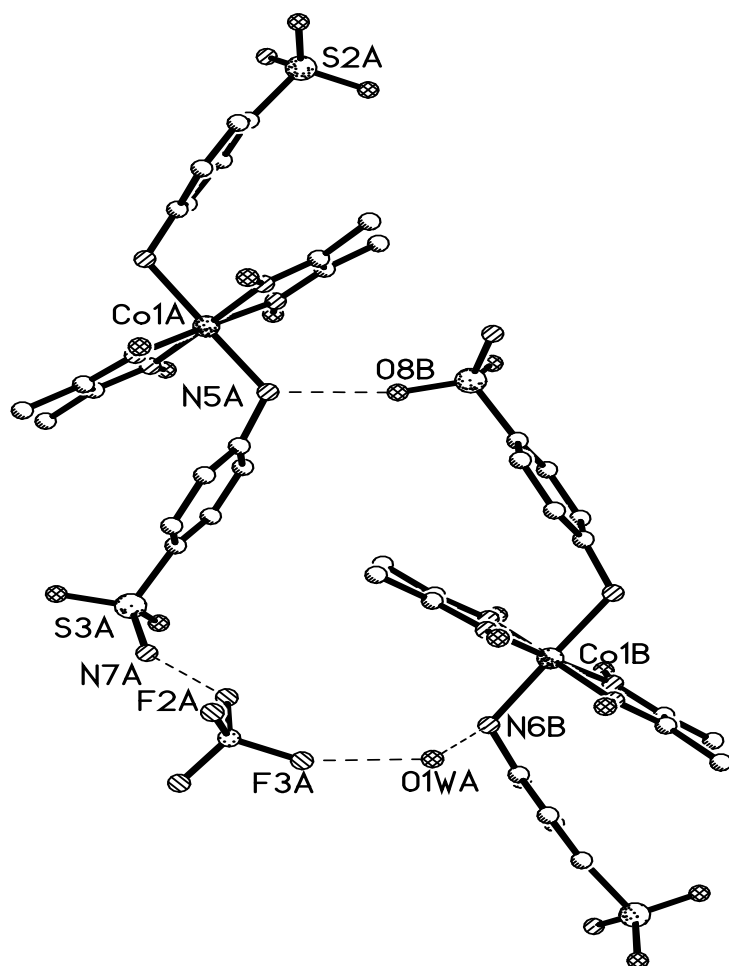


Fig. 3. Formation of cyclic fragments in $[\text{Co}(\text{DH})_2(\text{Sam})_2][\text{BF}_4]\cdot\text{H}_2\text{O}$

Coordination compounds based on dioximes have in the equatorial position of the coordination polyhedron two dioxime residues coordinated to the central ion through nitrogen atoms, and through intramolecular hydrogen bonds between the oxime groups, the molecular architecture of the complex is cemented (Fig. 3). The axial positions of the coordination polyhedron are occupied by ligands that coordinate at the complex-generating atom through electron-donor atoms of nitrogen, sulfur, or phosphorus.

The electrical charge of the complex cation is most often compensated by anions that contribute to the creation of a network of hydrogen bonds,

which gives the crystal lattice distinct characteristics and can influence the properties of new compounds in the solid state. Due to the presence of atoms capable of forming hydrogen bonds (N, O, F) in the crystal lattice of the complexes, different hydrogen bond systems are formed [1].

In the case of using salts of two metals as starting substances in the reaction system, products containing different complex cations of the two metal ions were obtained, in which a different preference is observed in the coordination process of electron donor atoms according to Pearson's theory [5]. In compounds with the general formula $[\text{Co}(\text{DH})_2(\text{Thio})_2][\text{Rh}(\text{Thio})_6][\text{X}]_4$ (in this case, X – monovalent anion) at the cobalt ion coordinates the nitrogen electron donor atoms from dimethylglyoxime and

the sulfur atoms from thiocarbamide, while at the rhodium ion coordinates only the sulfur electron donor atoms from six thiocarbamide molecules.

In order to diversify the composition and structure of cobalt(III) *bis*-dioximate complexes, it was decided to use coordination agents with various electron donor atoms to verify their competitive ability in the bond formation process with the Co^{3+} ion. This process can occur both in reactions using heterofunctional ligands in the initial synthesis system or through their substitution of molecules in the 1,6 positions of the coordination polyhedron of the complex. To carry out the synthesis via the second route, the "building block" $[\text{Co}(\text{DH})_2(\text{H}_2\text{O})\text{Cl}]$ and 3-, 4-pyridinealdoxime, 4-pyridineamidoxime, (4-pyridylthio)acetic acid, etc. were used as heterofunctional ligands (Fig. 4).

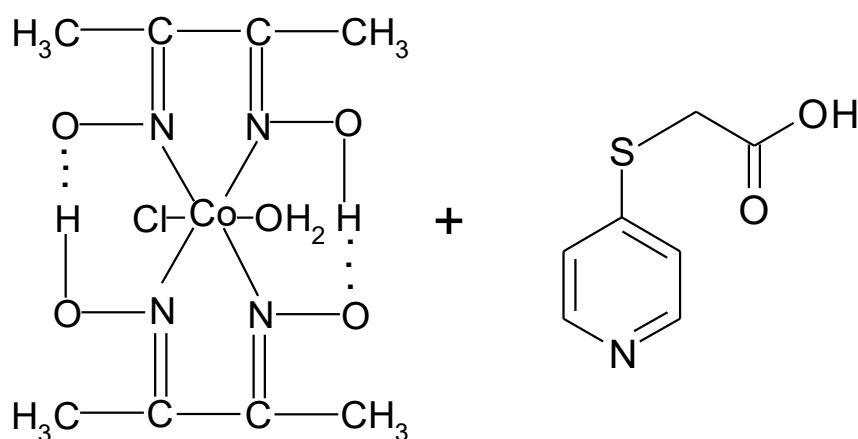


Fig. 4. Scheme of the interaction process of the "building block" $[\text{Co}(\text{DH})_2(\text{H}_2\text{O})\text{Cl}]$ with Hpyta

As a result of the syntheses, a series of products were obtained in which the water molecule from the axial position of the coordination polyhedron is substituted by the nitrogen atom of the pyridine ring. Attempts to use these heterofunctional molecules as bridging ligands were unsuccessful, even though the stoichiometric ratio of "building block":heterofunctional ligand was 2:1.

The use of dipyridine molecules (bpy, bpe) for the assembly of binuclear compounds allowed the production of copper(II), cobalt(III), zinc(II), cadmium(II) compounds. Different stoichiometric ratios between the initial reagents allowed for the obtaining of a series of products, which, due to the spatial configuration that allows the formation of intermolecular cavities, can incorporate different molecules (Fig. 5). This capacity of molecules from the series of bi- and polynuclear compounds allows the

conclusion to be drawn about the possibility of developing porous materials with adsorptive properties [6].

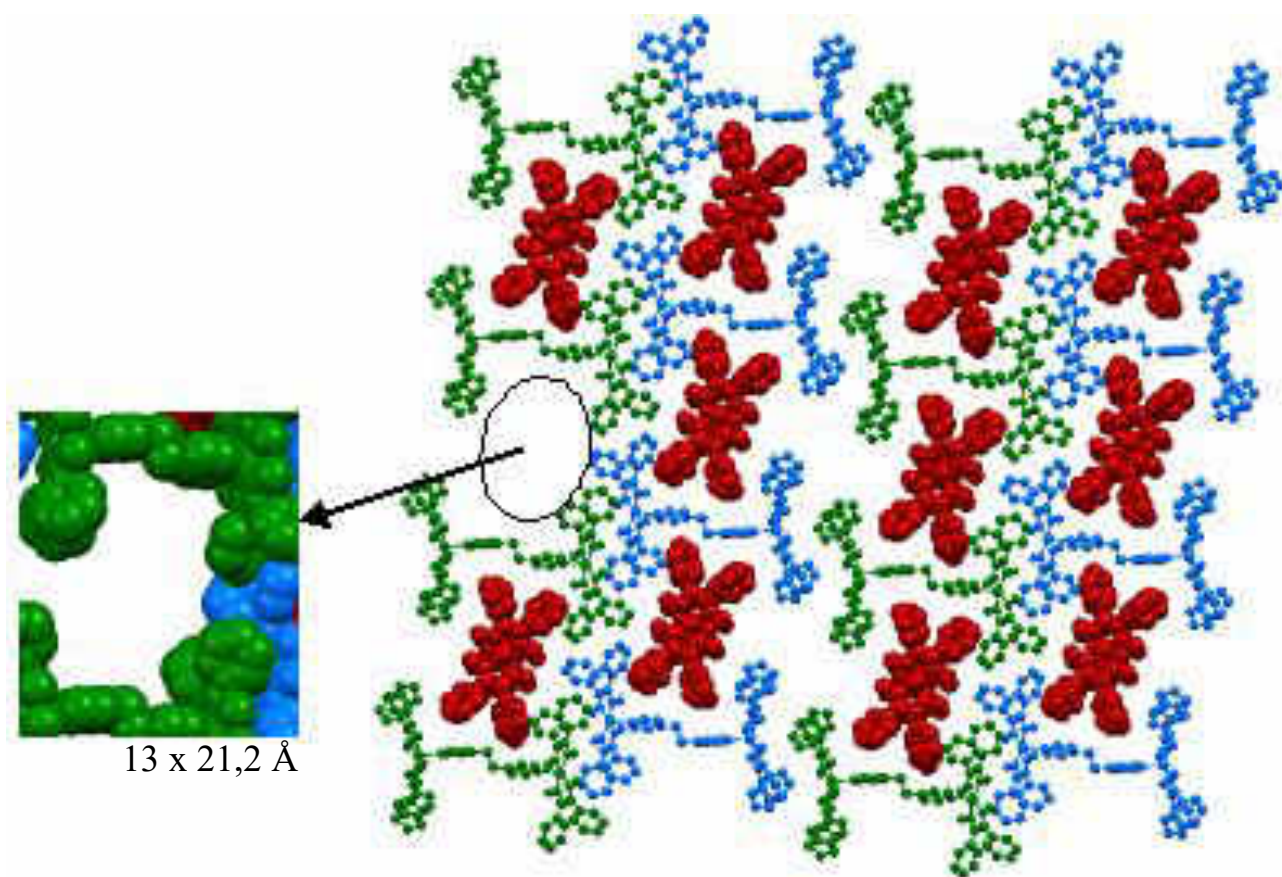


Fig. 5. Formation of intermolecular cavities in $[Cu_2(NioxH)_4bpe]$

To diversify molecular systems, a series of condensations of organic molecules were carried out, which allowed the obtaining of new coordinating agents from the Schiff base class with a geometric configuration that allows their use as a bridging ligand. The presence of more electron-donor atoms in these ligands broadens the coordination possibilities to the metal ion.

Upon the interaction of dichloroglyoxime with various organic molecules (aniline, sulfanilamides, etc.), new dioxime molecules were obtained, which were used for the synthesis of *bis*- and *tris*-dioximates of 3d metals. Some of the representatives of this series exhibit properties that stimulate enzyme synthesis processes in some microorganisms [7].

Particular attention should be paid to the useful properties exhibited by a number of compounds from this series in the field of stimulating physiological processes in microorganisms (increasing biomass accumulation, intensifying enzymogenetic processes, increasing resistance to unfavorable development conditions, shortening the

duration of technological processes, etc.) [1, 2, 8]. Combining biometal ions, ligands with various functional groups, and anions containing some elements with physiological activity in the same complex compound can cause synergistic effects and increase the yield of obtaining useful preparations for the pharmaceutical industries, food, agricultural etc. The use of coordinating compounds of this series for the treatment of crop plants has allowed for increased yield per hectare and resistance to water stress conditions [1].

The coordination polymers obtained exhibit various properties that can be used to solve problems in various branches of the economy [9, 10].

Acknowledgements: The study was carried out within the research subprogram entitled: „Synthesis and study of new materials based on coordination compounds with polyfunctional ligands and with useful properties in medicine, biology and technology” (subprogram code – 010602), funded by the Ministry of Education and Research of the Republic of Moldova.

References

1. COROPCEANU, E., CILOCI, A., ȘTEFÎRȚĂ, A., BULHAC, I. Study of useful properties of some coordination compounds containing oxime ligands. Academica Greifswald, Germany. 2020. 266 p. ISBN 978-3-9402237-24-8
2. BOUROSH P., COROPCEANU E., CILOCI A., CLAPCO S., BOLOGA O., BIVOL C., TIURINA J., BULHAC I. New Co(III) dioximates with hexafluorophosphate ion as stimulators of the proteolytic activity of the micromycete *Fusarium gibbosum* CNMN FD 12. In: Russ. J. Coord. Chem. 2013. V. 39, no. 11, pp. 777-786. <https://doi.org/10.1134/S107032841311002X>
3. COROPCEANU, E., RIJA, A., LOZAN, V., BULHAC, I., DUCA, GH., KRAVTSOV, V., BOUROSH, P. Discrete Binuclear Cobalt(III) Bis-dioximates with Wheel-and-Axle Topology as Building Blocks To Afford Porous Supramolecular Metal-Organic Frameworks. In: Crystal Growth & Design. 2016, 16, pp. 814-820. <https://doi.org/10.1021/acs.cgd.5b01402>
4. COROPCEANU E., CROITOR L., SIMINEL A., CHUMAKOV Y., FONARI M. The luminescence attenuation in the solid state by fluoride anion entrapped in the one-dimensional Zn (II) dioximate and mononuclear Cd (II) dioxime compounds. In: Polyhedron. 2016, 109, pp. 107-114. <https://doi.org/10.1016/j.poly.2016.01.043>
5. BOUROSH, P., COROPCEANU, E., RIJA, A., BOLOGA, O., GDANIEC, M., BULHAC, I., SIMONOV, Yu. Structural evidence of $[\text{Rh}(\text{Thio})_6]^{3+}$ and

- [Rh(Thio)₅Cl]²⁺ cations in three novel ionic systems based on Co(III) dioximates. In: Journal of molecular structure. 2011, 998, pp. 198-205. <https://doi.org/10.1016/j.molstruc.2011.05.033>
6. COROPCEANU, E.B., CROITOR, L., BOTOSHANSKY, M.M., FONARI, M.S. “Wheel-and-axle” binuclear Cu(II) dioximates mediated by 1,2-bis(4-pyridyl)ethane: Synthesis, X-ray study and luminescent properties. In: Polyhedron. 2011, V. 30, pp. 2592-2598. <https://doi.org/10.1016/j.poly.2011.07.007>
 7. COROPCEANU E., URECHE D., RIJA A., CILOCI A., CLAPCO S., DVORNINA E., BULHAC I., COCU M., BOUROSH P. Synthesis and Structures of Nickel(II) Complexes Based on Dianilineglyoxime. Stimulation of the Proteolytic Properties by [Ni(DAnH)₂] · 0.25H₂O. In: Russian Journal of Coordination Chemistry. 2021, V. 47, no. 1, pp. 17-25. <https://doi.org/10.1134/S1070328421010024>
 8. COROPCEANU E., RUDIC V., CEPOI L., RUDI L., LOZAN V., CHIRIAC T., MISCU V., BULHAC I., KRAVTSOV V., BOUROSH P. Synthesis and Crystal Structure of [Co(DmgH)₂(Thio)₂]₂F[PF₆]. The Effect of Fluorine-Containing Co(III) Dioximates on the Physiological Processes of the Microalga *Porphyridium cruentum*. In: Russ. J. Coord. Chem. 2019, vol. 45, nr. 3, pp. 206-213. <https://doi.org/10.1134/S1070328419030059>
 9. CHISCA, D., CROITOR, L., COROPCEANU, E., PETUHOV, O., BACA, S., KRÄMER, K., LIU, S., DECURTINS, S., J. RIVERA-JACQUEZ, H., MASUNOV, A., FONARI, M. From Pink to Blue and Back to Pink Again: Changing the Co(II) Ligation in a Two-Dimensional Coordination Network upon Desolvation. In: CrystEngComm. 2016, 18, pp. 384-389. <https://doi.org/10.1039/c5ce01581b>
 10. CHISCA, D., CROITOR, L., COROPCEANU, E., PETUHOV, O., VOLODINA, G., BACA, S., KRÄMER K., HAUSER, J., DECURTINS, S., LIU, S.-X., FONARI, M. Six Flexible and Rigid Co(II) Coordination Networks with Nicotinamide-Like Ligands: Impact of Non-Covalent Interactions in Retention of Dimethylformamide Solvent. In: Crystal Growth & Design. 2016, 16, pp. 7011-7024. <https://doi.org/10.1021/acs.cgd.6b01226>