

COORDINATION CHEMISTRY IN THE REPUBLIC OF MOLDOVA

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Abstract. This article is dedicated to the history of apparition and development of Coordination chemistry in Moldova. The main scientific centres are characterized, as well as their main research directions. The most valuable results in fundamental and applicative research are described, obtained in the field of coordination chemistry in the republic.

Keywords: organic chemistry, coordination chemistry, coordination compounds, complex combinations, transition metals, template synthesis.

Coordination chemistry is situated between the fields of organic and inorganic chemistry from the point of view of its research objects, and constitutes a logical link between these classical, extremely large scientific domains. Also, coordination chemistry is tangential to several chemistry directions, such as: analytic chemistry, physical, colloidal, quantum chemistry, technological chemistry etc., and to apparently remote fields, such as physics, biology, medicine, agriculture etc., assuring their massive and fast, theoretical and applicative progress, just by its own development.



Alfred Werner

Modern coordination chemistry was founded by the famous Swiss scientist Alfred Werner, laureate of the Nobel Prize. In the Republic of Moldova, coordination chemistry appeared when the young scientist, who later became academician of the ASM, Antonie Ablov arrived in our country. He graduated the Physico-chemical Faculty of the Iasi University (1923-1927), and the Chemical-technological Institute in Iasi (1925-1931) (Romania). Here, A. Ablov attended the courses held by professors Nicolae Costăchescu and Anastasie Obregia, the first one was the direct disciple, and the second – a colleague of the founder of modern coordination chemistry, Alfred Werner. Thus, taught by these two professors, when he arrived in Moldova, A. Ablov brought with him, directly from A. Werner, the most complete coordination theory, which constitutes the basis of modern coordination chemistry.



Antonie Ablov

The entire history of coordination chemistry in Moldova, the former USSR, and in the international scientific community is linked to this famous name - A. Ablov and is fully reflected in the work of dr. hab., prof. D. Batâr.

In 1940 A. Ablov was appointed head of the Chemistry Department of the Agricultural Institute in Chisinau, but this institution was evacuated during the war. Then, A. Ablov headed for a short time the department of Inorganic Chemistry of the Agricultural Institute in Sverdlovsk (Yekaterinburg, today). In 1944, he was recalled at the Agricultural Institute in Chisinau, where he organized a scientific research laboratory and performed a series of works in the field of coordination chemistry. During study years 1944-1947 A. Ablov held the first special course for the students of this institution, entitled „Chemistry of coordination compounds of cobalt with amines”, which may be considered the basis of coordination chemistry in Moldova.

On 1 October 1946, the State University was inaugurated in Chisinau. Prof. A. Ablov became the first dean of the Faculty of Chemistry and the first head of Department of Inorganic chemistry (since 2000 – Department of Inorganic and Physical Chemistry) of this faculty. This department was headed, successively, by: A. Ablov (1946-1958), L. Nazarova (1958-1972), N. Gărbălău (1972-1978), G. Sârţova (1978-1981), N. Samus (1981-1991), A. Gulea (1991-present).

A. Ablov held the following courses for students of higher courses: „Chemistry of coordination compounds”, „Selected chapters of inorganic chemistry”, “Quantum chemistry of inorganic compounds”.

In 1953 A. Ablov publishes the first work performed in Moldova in the field of coordination Chemistry, related to the ammoniates class, criticizing the Biltz theory. In the frameworks of the VIth Unional Conference on chemistry of coordination compounds, A. Ablov discussed the first results regarding cobalt(III) dioximates, class of compounds which later became of central interest in the activity of the Moldovan school in the field of coordination chemistry, founded by A. Ablov.

In 1958, the Presidium of the Academy of Sciences of the former USSR decided to reorganize the chemical sectors of the Moldovan Branch of the AS of USSR. In 1959, on the basis of the three sectors and existent laboratories, the Institute of Chemistry was set up, and prof. A. Ablov became its first director. Therefore, another important centre appears, beside the State University in Chisinau (Moldova), where systematic research in the field of coordination chemistry is accomplished. As the director of the Chemistry Institute, and the head of Department of inorganic chemistry of the SUM until 1958, prof. A. Ablov supervised and directed the development of coordination chemistry in Moldova, especially at the Institute of Chemistry of the ASM and State University in Chisinau (Moldova). A great attention was focused on preparing pedagogical and research staff with scientific titles and degrees. In 1948, the Faculty of Chemistry of the State University of Moldova announced matriculation for PhD studies, and since 1949, including at the specialty „Inorganic chemistry”, which set the basis of preparing highly qualified specialists in Moldova.

Coordination chemistry gave rise to new specific directions in the first years of its development. A. Ablov was one of the first in the former USSR, who began using physical and mathematical methods in coordination compounds research. Thus, the „Laboratory of physical methods of solid body investigations” (1958) appeared, headed by acad. T. Malinovsky, now called „Laboratory of Physical methods of Investigations of Solids”, headed now by the doctor in physical-mathematical sciences Iu. A. Simonov, and remaining a very important centre in research of coordination compounds.

In 1959, in the frames of the laboratory of acad. A. Ablov, a research team of physicians and mathematicians worked on quantum-chemical calculations of coordination compounds, under the direction of PhD in physico-mathematical sciences, today academician, I. Bersuker. This team detached in 1964 into an individual sector – Sector of quantum chemistry in the frames of the Chemistry Institute, in the present – Laboratory of Quantum Chemistry, headed by the dr. hab. in physico-mathematical sciences prof. I. Ogurțov.

Three spectral groups detached themselves out of the inorganic chemistry laboratory: IR and UV/Vis spectroscopy (M. Filipov, Ș. Manole), gamma nuclear resonance spectroscopy, also called Mössbauer spectroscopy (C. Turtă) and mass spectrometry (H. Hariton). The name of the corr. mem. of the ASM, C. Turtă, is also connected to the appearance and development of Mössbauer spectroscopy and magnetochemistry in Moldova.

A. Gulea, presently corr. mem. of the ASM, started his activity at the Institute of Chemistry, and then at the State University of Moldova, after graduating doctoral studies at the Institute of Radium „V.G. Hlopin” in Sankt-Petersburg. Specialist in the field of radiospectroscopy of coordination compounds, he significantly contributed to the development of NMR spectroscopy on various nuclei (^1H , ^{13}C , ^{14}N , ^{19}F , ^{35}Cl , ^{59}Co), being the founder of a scientific school in the area of Stereochemistry and stereodynamics of assembly reactions of coordination compounds.

In 1975, the lab of inorganic chemistry, later renamed to Laboratory of chemistry of coordination compounds, gave rise to another laboratory with a new research direction – Laboratory of bioinorganic chemistry, headed by the dr. hab. in chemistry, prof. D. Bafîr, and since 1988 – by dr. hab. in chemistry C. Turtă.

Recently, the “Centre of Physical Chemistry and Nanocomposites” was created in the frames of the Chemistry Institute, in order to assure the scientific research in the field of chemistry, including coordination chemistry, with modern equipment and highly qualified specialists.

Investigations in the field of Chemistry of coordination compounds significantly extended after the formation, in 1959 of the Institute of Chemistry (director - A. Ablov), which became the main centre of chemistry development in the republic, especially in the frames of the Laboratory of chemistry of coordination compounds, headed by A. Ablov, then by acad. N. Gărbălău, dr. hab., prof. M. Revenco and dr. hab. I. Bulhac. At first, the scientific thematic was oriented towards the realization of syntheses of coordination compounds of transition metals, especial of dioximates of cobalt, copper, nickel, iron, palladium, investigations in the structure and properties of this class of compounds, using the newest physical methods of investigation. Later, the scientific thematic significantly extended, comprising research in the field of template processes, topochemical synthesis, obtaining of mono- and polynuclear coordination compounds. including those with macrocyclic and chelating ligands with programmed properties; synthesis of biologically active coordination compounds of biometals; development of the theory of physical methods of investigation of coordination compounds; development of the theory of electronic and vibronic structure of compounds with mixed valence etc., optimization of quantum-chemical research methods, as well as of methods of molecular design of biologically active systems, with the focus being set on their action mechanism.

One the most important centres in the field of Coordination chemistry – the department of “inorganic chemistry” of the SUM, has carried out investigations according to the scientific thematic “Synthesis, structure, reactivity and properties of coordination combinations of transition metals with organic and inorganic compounds”, since 1947. This scientific direction was founded by acad. A. Ablov and the majority of the research performed by the staff of the department, under his direction and with his direct involvement, was dedicated to the development of chemistry of coordination compounds. Scientific ideas of acad. A. Ablov continue to be implemented at the present day.

At the beginning, investigations were related to transition metals dioximates: on their basis, the coordination polymery of Co(III) dioximates was studied, as well as the *trans* influence in these compounds. Subsequently, the *trans* influence was estimated qualitatively, and sometimes – quantitatively, in the cases of dioximates of cobalt(III) and rhodium(III) (G. Sîrțov, N. Samusi, B. Bavićin, L. Istru, O. Damaskin, T. Luchianet, G. Conunov, G. Șpakov). The kinetics and mechanism of inner sphere substitution reactions of *trans*-dioximates of cobalt(III) and rhodium(III) were studied by the collaborators of the department during several years (G. Sîrțov, L. Istru, T. Bolgari). It was found that the nature of the metal, as well as the nature of the dioxime, influence the values of rate constants and kinetic parameters of the reaction. N. Samusi, O. Damaskin, T. Luchianet, G. Șpakov carried on the research on inner sphere ligands substitution of cobalt(III) *trans*-dioximates in aqueous and non-aqueous solutions, and detailed the obtained results in a monography. The study of reactivity of cobalt(III) dioximates which contain cyanate ions, demonstrated that in acidic medium the ion NCO^- undergoes quantitative transformation into ammonia without the breakage of the cobalt-nitrogen bond (M. Popov).

For the first time, cobalt(III) dimmers were synthesized, in which α -dioxime anions are situated in the *cis* position (A. Ablov, N. Samusi, O. Bologna), which was evidenced by a series of physico-chemical investigations (M. Filipov, A. Gulea, O. Bologna, Iu. Simonov).

A series of research was performed, dedicated to the synthesis, investigation of composition, structure and reactivity of coordination combinations of transition metals with thiosemicarbazones of aldehydes and ketones, initiated by acad. N. Gărbălău and successfully continued to date in the frameworks of the laboratory of Coordination Chemistry of the Chemistry Institute of ASM (N. Gărbălău, M. Revenco, G. Timco, J. Grădinaru, M. Bîrcă, M. Cocu).

Coordination compounds of transition metals with semicarbazones of aldehydes and ketones have been studied for many years at the Department of "Inorganic Chemistry" by N. Samusi, M. Popov, V. Bodiu, V. Țapkov, V. Ciobanu, N. Velișco. Many of these compounds possess antimicrobial activity against a series of pathogenic microbial stems.

During the last years, the scientists of the Department of inorganic and physical chemistry intensively investigated polynuclear coordination compounds of transition metals with chelating or bridge-creating ligands. Methods of synthesis of heteronuclear compounds containing *s*, *p*, *d* and *f* elements with various chelating agents such as (α -dioximes, β -diketones, semicarbazones of aromatic oxyaldehydes) were elaborated, and it was discovered that these compounds possess defined electrical properties, and may be used for obtaining polymetalic oxydic systems which possess certain electrical properties, including supraconductor ones (I. Horoșun, V. Țapkov, S. Iușcenco, S. Tarasevici).

During several years, investigations were performed in the field of coordination compounds of titanium, zirconium and hafnium with organic and inorganic ligands (Ț. Conunov, M. Popov and S. Kudrițki).

During later years, a series of investigations were performed, related to stereochemistry and electronic structure of cobalt coordination compounds with chelating ligands which contain the atoms donating set nitrogen, oxygen and sulfur (A. Gulea, Gh. Novîțchi). In order to accomplish this, the NMR method was widely used: ^1H , ^{13}C , ^{14}N , ^{17}O , ^{19}F , ^{35}Cl , ^{59}Co . For the first time, the NMR ^{59}Co spectral parameters were systemized, in order to be applied in structural studies of cobalt(III) coordination compounds, kinetics and mechanism of reaction of substitution, isotope exchange, as well as of catalytic and spin equilibrium processes. The dynamic NMR method was extended to investigations of paramagnetic cobalt(II) complexes, using the temperature and pressure dependences of spectral parameters. This modality of dynamic NMR investigation favoured stereochemical research of solutions. Thus were determined complex species, geometrical isomers (*cis-trans*-, *fac-mer*-), caused by intramolecular regrouping of stereo-active ligands in the coordination polyhedron of the central atom, intermediate stages were identified, as well as the mechanism of stereochemical transformations of isomers, and the activity of coordinated ligands was evidenced.

Thus, in cobalt(II) carboxylates and diketonates with amines (A. Gulea, D. Batîr, Gh. Novîțchi, E. Iorga), as well as in cobalt(III) dioximates (A. Gulea, O. Bologna, A. Ablov) and polyaminates (A. Gulea, E. Popa, A. Ablov), the *-cis* and *-trans* isomers were identified, as well as the *cis-trans* transformations, as function of the ligands stereoactivity and the reaction medium. In solutions of cobalt(II) pivalate, the *cis*- and *trans*- isomers are likely probable (N. Gărbălău, G. Timco), while in the case of cobalt mono- and dimethyl acetates, conformational isomers appear. In compounds of the type CoL_2A_2 (L – asymmetric diketone, A – aromatic amine), five isomeric forms were evidenced, while in the case of cobalt(III) complexes which contain asymmetric dioximes (methylglyoxime, methyl-carbmetoxy- and ethylcarbmetoxyglyoxime) the *cis-trans* isomerism in the equatorial plan was identified (A. Gulea, G. Sîrțov). In a series of Co(III) dioximates, bond isomers were identified: O,S; N,S; O,N; N,C (A. Gulea, V. Șafranschi, I. Popa). In the cases of complex cations $[\text{Co}(\text{NH}_3)_3\text{dien}]^{3+}$ and $[\text{Co}(\text{OCH}_2\text{CH}_2\text{NH}_2)_3]$, the isomers *mer*- and *fac*-, were identified, respectively, while in solutions – both forms. For the first time, in the case of the *fac*- [cobalt(III) tris (β -aminoethylate)] trihydrate, the polyhedral isomerism *octahedral-trigonal prism* was ascertained (A. Gulea, S. Șova).

Studies were performed regarding formation reactions of polynuclear dioximates of Co(III) - Co(II); Co(III) - Sn(II); Co(II) - Sn(II) which contained fluorine (A. Gulea, Iu. Kokunov). It was demonstrated that fluorine ions stabilize

the *cis*- structure of cobalt(III) in the {bis-[tris(dimethylglyoximato)cobalt(III)]cobalt(II)} octahydrate fluoride, while in the case of cobalt(II) a very unusual type of coordination for α -dioximes occurs (O. Bologa, Iu. Simonov, J. Grădinaru). Synthesis and stereochemistry of Co(II) and Ni(II) carboxylates with aromatic amines, monoethanolamine is evidenced in the work of Gh. Novîţchi, A. Cotovaia and L. Popovschi.

On the basis of fundamental research, applicative works were performed in the field of biotechnology, medicine, agriculture, chemical and nuclear industries (A. Gulea, V. Rudic).

Problems related to environmental protection and radionuclide recovery from contaminated influents, generated by technologies, are solved in collaboration with prof. Al. Cecal (Univ. "Al. I. Cuza", Iasi) and prof. V. Rudic (Institute of Microbiology of the ASM). Very actual is the research regarding the possibility of utilization of coordination compounds in photobiotechnology, as regulators of growth and development of biosynthetic activity of cyanobacteria (A. Gulea, V. Rudic). Original procedures were elaborated, regarding the control of spirulina and dunaliea biosyntheses, and the production of biomass with the necessary chemical composition, which are based on the utilization of coordination compounds of cobalt, iron, and copper. Thus, a series of pharmaceutical preparations were obtained, containing bonded organic fluorine and selenium (A. Gulea, V. Rudic, S. Şova, V. Ciornea) and germanium (Jean Escudie, France).

The technology of preparation of cyanocobalamin (vitamin B₁₂) was optimized in the biomass of cyanobacteria and microscopic algae (A. Gulea, Gh. Novîţchi, V. Rudic, S. Codreanu).

Joint research with chemists from France (Lille University) and USA (Rice University) concern the production of ionic conductors on the basis of heterometallic compounds of bismuth(III), used in radioelectronics (I. Bulimestru, V. Stavila, N. Popa).

Of a great importance are investigations in the field of obtaining inhibitors of cancer cells proliferation, performed in collaboration with prof. Donald Poirier (University Laval, Center of Oncological and Endocrinological Research, Canada), prof. A. Merbach and Helm (University Lausanne, Switzerland) and prof. V. Gudumac (University of Medicine and Pharmacy "N. Testemiţanu"), prof. T. Roşu (University of Bucharest), prof. D. Sofroni (Institute of Oncology).

In 1994 the Laboratory of Coordination Chemistry was founded in the frames of the Department of Inorganic and Physical Chemistry, headed by prof. A. Gulea. Scientific thematic of the laboratory addresses the directed synthesis of coordination compounds of biometals with stereoactive ligands with leukaemia inhibiting activity, stimulators of production of elements containing fluorine, iodine, selenium, vitamin B₁₂. New preparations were synthesized, with potential applications in medicine, biotechnology, apiculture and zootechny. These innovative researches, produced in collaboration with other members of the Department of Inorganic and Physical Chemistry and with researchers from the Institute of Microbiology and Biotechnology, Institute of Zoology, Institute of Applied Physics of the ASM, University of Medicine and Pharmacy "N. Testemiţanu", Laval Agrarian University (Canada), University Paul Sabatier, (Toulouse France), University Lausanne (Switzerland) were highly appreciated at World Saloons at Brussels, Geneva, Pittsburgh, Seoul, Suzhou, Bangkok, Manila, Casablanca, Sofia, Bucharest, Moscow, Sevastopol etc., entitled „Innovations, Research and new Technologies”.

Scientific research performed at the Department was systemized and detailed in 4 monographs, 5 review articles, over 1500 full papers published in specialized journals, and which formed the basis of 14 theses of dr. habilitate and over 100 theses of Ph doctor in chemistry, presented in various geographical areas: Russia, Romania, Ukraine, Germany, France, Bulgaria, Hungary, Syria, Egypt, Algeria, Guinea, Cuba, Vietnam etc.

The main research directions of the work team of the Laboratory Inorganic Chemistry of the Chemistry Institute of the ASM, which was later renamed into Laboratory of Coordination Compounds Chemistry, and now is the Laboratory of Coordination Chemistry, are represented by the synthesis and study of coordination mono-, di- and polynuclear, homo- and heterometallic compounds of transition metals, on the basis of mono-, bi- and polydentate ligands (α -dioximes, carboxylic and aminic acids, β -diketones, polyamines, alcohols, thiosemicarbazides and its derivatives etc.) and template reactions of condensations of thiosemicarbazide with aldehydes and ketones, as well as the study of the composition, structure, physico-chemical and other useful properties.

One of the main classes of coordination compounds, which is always in the centre of attention of researchers, is represented by dioximates and dioximines of several 3d elements: cobalt(III), iron(II), iron(III), rhodium(III), copper(II), etc. A wide class cobalt(III) *trans*-dioximates with thiocarbamide and selenocarbamide was studied, and were evidenced several possibilities of spatial arrangement of axial ligands, with regards to the position and angles towards the equatorial octahedral plan, as well as towards each other. Compounds were synthesized, were the position of axial ligands and the angles formed by their participation represent intermediate values, which confirms the general character of this phenomenon (N. Gărbălău, N. Samusi, Iu. Simonov, E. Coropceanu et al.).

The influence of cobalt(III) dioximates on the kinetics of dyes reduction and on the rate of their fixation on the fabrics, was studied. It was found that including cobalt(III) dioximates into coloring compositions, leads to the decrease of the technological process duration, to the enhancement of quality of fixation of dyes, and to the diminishing of chemical reagents' consumption.

At the interaction of the thiosemicarbazide diacetic acid (H_2L) with $1,6-[Co(DH)_2(H_2O)_2]NO_3 \cdot H_2O$ or $[Co_2(DH)_4OH]NO_3 \cdot 5H_2O$, the diamagnetic complex $[Co(DH)_2(HL)(H_2L)]$ is obtained, where H_2L and HL coordinate in the apical position, through the sulphur atom (N. Gărbălău, V. Lozan). Analogical products were obtained in the cases of α -benzyldioxime, α -furyldioxime and 1,2-cyclohexandiondioxime.

At the interaction of $CoF_2 \cdot 4H_2O$ with dimethylglyoxime in the presence of fluorhydric acid and hydrogen peroxide, crystals of $[Co_2(DH)_4O_2(H_2O)_2] \cdot 2HF \cdot 2/3H_2O$ were obtained with dimeric structure, as well as $[Co_2^{III}Co^{II}(DH)_6]F_2 \cdot 8H_2O$ with trimeric structure. A series of cobalt(III) dioximates were synthesized, containing fluoride ion or its complex anions with the formula $[Co(DioxH)_2L_2][X] \cdot nH_2O$, where $DioxH_2 =$ methyl- (MH_2), dimethyl- (DH_2), diphenylglyoxime ($DfgH_2$) and 1,2-cyclohexandiondioxime ($NioxH_2$), $L =$ Thio, Py, An, γ -pic, NH_3 , PPh_3 , and $X = F$, $[BF_4]$, $[PF_6]$, $[SiF_5]$, $1/2[BeF_4]$, $1/2[SiF_6]$, $1/2[ZrF_6]$, $1/3[AlF_6]$ (N. Gărbălău, E. Coropceanu, O. Bologa et al.).

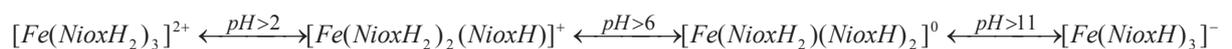
The study of volatile nickel and palladium dioximates with the general formula MeL_2 was realized using mass spectrometry (A. Ablov, H. Hariton, J. Vaisbein). In their mass spectra, the peak of the molecular ion M^+ is observed, whose fragmentation includes, during the initial stage, the formation of the $[Me(L+H)]^+$ ion. This is a consequence of the presence of intramolecular hydrogen bonds. The general flow of the fragmentation demonstrates the equivalence of the four Me-N bonds in the studied dioximates.

For the first time, the possibility of synthesis of iron(III) α -dioximates (D. Batfir, I. Bulhac) and nickel(III) α -dioximates (D. Batfir, L. Chistruga) were demonstrated, by oxidation in crystalline form of $[Fe(DioxH)_2L_2]$ ($L =$ Py or its derivatives) or $[Ni(DioxH)_2]$ in the presence of L with chlorine, bromine or iodine. X-ray investigations of $[Fe(DfgH)_2(3-CH_3-Py)] [I_5]$ ($DfgH =$ monoanion of α -benzyldioxime), demonstrated that during oxidation, the structure of the inner coordination sphere remains intact – octahedral and of *trans* configuration, with the exception of metal oxidation, and the halogen constitutes the external coordination sphere in the form of anion - $[I_5]$. In the case of nickel dioximates, apart from the metal oxidation, the transit of compounds from planar to octahedral structure occurs.

Investigations on dioximates of iron(II) (A. Ablov, C. Turtă et al.) and iron(III) (C. Turtă, I. Bulhac, D. Batfir et al.) with pyridine, and isonitriles using Mössbauer spectroscopy allowed elucidating the electronic structure of these chelates and evidencing of the dependence of Mössbauer spectra parameters on the nature of the coordination node and nature of substituents in the molecules of pyridine, isonitrile and α -dioxime.

Investigations on the interaction of 3d metal cations with α -dioximes in acidic medium allowed the elaboration of a general method of synthesis in acidic medium of several new classes of coordination compounds of transition metals with α -dioximes: tris-dioximines with the general formula $[M(DioxH)_3]X_2$ ($M = Fe^{2+}$, Ni^{2+} , Cu^{2+} ; $DioxH_2 =$ dimethylglyoxime (DH_2) and 1,2-cyclohexandiondioxime ($NioxH_2$); $X = Cl^-$, Br^- , NO_3^- , ClO_4^- , $1/2SO_4^{2-}$, $1/2S_2O_3^{2-}$) and their structural analogues – *cis*-dioximines with general formula $[X_2M(DioxH)_2]$ ($M = Fe^{2+}$, Co^{2+} , Ni^{2+} , Cu^{2+} ; $X = Cl^-$, Br^- , $1/2SO_4^{2-}$, $1/2C_2O_4^{2-}$) (D. Batfir, I. Bulhac, L. Ozol, Iu. Simonov et al.). Utilization of physical methods of investigations enabled the determination of stereochemistry and demonstrated a new structure type in this series of compounds. (C. Turtă, Iu. Simonov, I. Bulhac, A. Gulea et al.).

Investigations using UV spectroscopy demonstrated that in solutions, tris-dioximines of iron(II), nickel(II) and copper(II) behave differently. In compounds of iron(II) with 1,2-cyclohexandiondioxime at pH variations in the range 0 – 14, occurs the consequential and reversible separation of hydrogen atoms from the coordinated hydroxyl and α -dioxime groups:



In the case of tris-dioximines of nickel(II) and copper(II), the decomposition of complexes takes place, with formation of $[Ni(NioxH)_2]$ and $[Cu(NioxH)_2]$, respectively.

The study of tris-dioximines of iron(II) and the products of their deprotonation using Mössbauer spectroscopy, demonstrated that the total electron density „s” around the Mössbauer nucleus, is the same in all investigated compounds, and all contain Fe^{2+} in coupled spin state. In the case of the complex cation tris-(1,2-cyclohexandiondioxime)iron(II) the D_3 symmetry was ascertained with an insignificant distortion along the C_3 axis, for mono- and bisdeprotonated compounds, the symmetry decreases, respectively, to C_{4v} and D_{4h} (C. Turtă, I. Bulhac et al.). The data of Roentgen-electronic spectroscopy show that the factors that have the greatest influence on the metal-ligand bond in nickel(II) dioximes are the geometry of the immediate surroundings of the metal atom, the nature of the atoms of the coordination

node, as well as of atomic groups of the external coordination sphere; in the case of iron(II) compounds, the level of dioxime deprotonation plays the decisive role.

For the first time, a compound of copper(I) with polymer structure was synthesized in the dioximates series (D. Bafîr, L. Ozol, I. Bulhac, Iu. Simonov et al.).

Investigations of electrical properties of *cis*-dichloro-bis-(1,2-cyclohexandiondioxime)cobalt(II), nickel(II), copper(II) and the chain- μ -iodine-(1,2-cyclohexandiondioxime) copper(I), demonstrated that these compounds exhibit significant electrical properties.

One of the most perspective, from the applicative point of view, is the research direction regarding the investigation of catalytical properties of coordination compounds of metals in various chemical processes. As a result of these studies, coordination compounds of transition metals with tridentate thiosemicarbazones were proposed as catalysts and tested at cotton fabrics coloring at „Трехгорная мануфактура”, Russia. Later, it was found that cobalt dioximates may be used as catalysts for cotton fabrics coloring, using methods with one or two stages. These were proposed for implementation at factories from the former USSR (Kalininsk, Iarţev, Ternopol and Tiraspol) (N. Prschina, I. Horoşun et al.). Dioximates of iron(II and III) with pyridine and several its derivatives were proposed as catalysts in polyurethane resins production processes (Perm, Russia) (D. Bafîr, I. Bulhac, M. Fedoseev), as dielectric material (D. Bafîr, L. Ozol, I. Bulhac et al.).

Several dioximates of cobalt(III) with fluorine containing anions (E. Coropceanu, A. Deseatnic, O. Bologa, A. Rija et al.) and of iron(II) (I. Bulhac, A. Deseatnic, O. Ciobănică) with biologically active ligands, exhibit catalyst properties for enzyme biosynthesis in the case of several fungi stems.

In 1961, the laboratory began performing systematic studies regarding the comparative study of metals with thiosemicarbazide, selenosemicarbazide and other ligands obtained on their basis (N. Gărbălău, M. Revenco, N. Beliciuc et al.).

New coordination compounds were synthesized, on the basis of vanadium, chrome, cobalt, nickel, copper, zinc, rhodium with mentioned above ligands, and it was found that the two ligand series have many common features in their behavior. Thus, thio- and selenosemicarbazides, as well as thio- and selenosemicarbazones form complex combinations with 3d metals, which possess analogous structure, composition, physical and chemical properties. Also, the nature of the metal and of functional groups of calcogensemicarbazone determines the character of their interaction and the composition of final products. At the interaction of the salicylic aldehyde of thiosemicarbazone with salicylic aldehyde in alkaline medium with oxovanadium(IV), nickel(II) and copper(II), the template condensation of thiosemicarbazone occurred, at the amidic nitrogen with salicylic aldehyde, giving a new planar tetradentate ligand, which represents the thiosemicarbazide, condensed at both terminal nitrogen atoms with two molecules of salicylic aldehyde (N. Gărbălău, M. Revenco et al.). The selenosemicarbazone of salicylic aldehyde reacts with the salicylic aldehyde in a similar way in the presence of enumerated metals. (N. Gărbălău, M. Revenco).

The template synthesis of iron(III) complexes with tetradentate ligands on the basis of thiosemicarbazide and salicylic acid and its derivatives were also performed (N. Gărbălău, M. Iampolschi, Iu. Simonov et al.).

Chelated compounds of oxovanadium(IV), nickel(II), copper(II) and iron(III) with the mentioned ligand proved to be volatile at vacuum heating, which allowed performing a study using mass spectrometry. Obtained results confirmed the supposition that the ligand is planar and tetradentate on the account of donating atoms O, O, N, N (A. Ablov, N. Gărbălău, C. Indricean et al.).

Syntheses were performed using the template method, of complexes of oxovanadium(IV) and nickel with the tetradentate condensation product on both terminal nitrogen atoms of aminoguanizone with two molecules of salicylic aldehyde, and it was found that this ligand also coordinates to the metal with the set of donating atoms O, O, N, N. It was assumed that the reaction has a general character and may be realized in the case of other analogues of thio – and selenosemicarbazide, as well as of aminoguanidine.

Template reactions have been widely used for a long time in the laboratory, in order to obtain coordination compounds of metals with chelating and macrocyclic ligands (N. Gărbălău, T. Jovmir, N. Beliciuc).

Coordination compounds of iron, cobalt, nickel, copper and rhodium with sulphur containing oximhydrazones were synthesized and their physico- chemical properties and stereochemistry were studied. The laws of formation of mono- and bis- ligand chelates were established (A. Ablov, N. Beliciuc, L. Ciapurin).

Copper(II) coordination compounds with thio- and 4-phenyl-thiosemicarbazones of pyruvic acid were studied, as well as the laws of their formation, chemistry and stereochemistry of coordination compounds of cobalt, nickel and copper with thiosemicarbazones and dithiocarbometoxyhydrazones of amide, anilide and N-diethylamide of pyruvic acid (A. Ablov, N. Beliciuc, L. Nejeleschi et al.).

Cobalt forms exclusively octahedral compounds with two ligand molecules; those monodeprotonated and nondeprotonated form octahedral with coordination node $\text{Co}_2\text{O}_2\text{N}_2\text{S}_2$, and those bis-deprotonated – with coordination

node CoN_4S_2 , i.e. during deprotonation of amidic groups, the ligand changes its coordination mode, as in the case of nickel (A. Ablov, L. Ciapurin).

During several last years, coordination chemistry registered important realizations in the field of synthesis and study of 3d metals compounds with macrocyclic open contour tetradentate ligands, assembled in the basis of the alkylated thiosemicarbazides. These compounds are of interest due to their properties: high chemical stability, solubility in organic solvents, volatility in vacuum at relatively low temperatures, increased thermal stability, intense colors etc. These properties influence the practical aspect: obtaining of extra pure compounds, thermostable colorants, catalysts, biological models, analytical reagents etc.

The template method plays a key role in the synthesis of macrocyclic compounds and their precursors, in which the central metal ion (or another template centre) organizes and directs the process of assembly of the final polydentate ligand, using initial more simple blocks (ligsons). Template assemblies of nickel(II) on the basis of S-alkylisothiosemicarbazides and acetyl acetone were realized (N. Gărbălău, V. Arion, C. Indricean). Some of these products may be qualified as precursors for macrocyclic complexes synthesis at interaction with 1,2-diamines. It was found that nickel(II) ions, as well as oxovanadium(IV) and cobalt(II) ions, can serve as matrices for obtaining of open contour coordination compounds on the basis of S-methylisothiosemicarbazide and acetyl acetone.

As opposed to acetyl acetone, in the case of benzoyl acetone, the mono-S-methylthiosemicarbazone can be obtained relatively easy. The availability of this ligand allows an evident diversification of composition, geometry, structure and properties of formed complexes (J. Grădinaru, Iu. Simonov, V. Arion et al.).

Utilization of the thioamidic group for condensation, served as a supplementary possibility for the diversification of structure, and as a result, of properties displayed by final species. In order to accomplish this, the thiosemicarbazones of acetyl acetone or benzoyl acetone, in combination with 2,6-diformyl-4-methylphenol or oxynaphtaldehyde on nickel, cobalt, oxovanadium or copper matrix. (J. Grădinaru, Iu. Simonov, M. Cocu). Complexes on the basis of oxynaphtaldehyde were tested as pigments for plastic masses coloring. Variation of the colorant concentration and type of polymer led to obtaining pieces of variously intense transparent colors, as well as of non-transparent, variously colored pieces. These investigations are protected by patents (M. Cocu, N. Gărbălău, Ș. Manole et al.).

Coordination compounds of Ni(II) and Cu(II) were obtained, with hexaazamacrocyclic ligands, which contain 14 atoms in the cyclic contour starting from bis-(S-alkylthiosemicarbazones) of nitromalonic dialdehyde, 2,4-pentandione and orthoformic ether, sodium salt of nitromalonic dialdehyde or 1,1,3,3-tetraetoxypropane, which forms malonic dialdehyde on hydrolysis (J. Grădinaru, N. Gărbălău, V. Arion et al.).

A special aspect of isothiosemicarbazones chemistry is the utilization of metal ions with varying oxidation numbers (cobalt and iron) as matrices. Thus, in the case of iron(III), depending on synthesis conditions, three types of compounds may be obtained: two monomers and one dimer (M. Iampolschi, S. Șova, N. Gărbălău). Also, the synthesis of bis-(S-alkylisothiosemicarbazones) of 2,4-pentandione may be realized in the presence of Fe(III) ions, with the formation of coordination compounds in which the central atom has oxidation numbers of +4 and +3.

Using template condensation of bifunctional ligsons, such as alkylated thiosemicarbazide and 1,1,3,3-tetraetoxypropane, macrocyclic compounds were obtained, with *trans*- arrangement of thioalkyl groups (N. Gărbălău, V. Arion, Iu. Simonov).

A major importance is the presence of the template effect in the synthesis of a wide range of binuclear macrocyclic compounds, which contain a set of N and O atoms as donor (N. Gărbălău).

Chelated coordination compounds of tetradentate ligands, with the coordination node $[\text{MN}_3\text{O}]$, were obtained by template condensation on Ni(II) and Cu(II) matrices of mono-S-methylisothiosemicarbazone of acetyl acetone or 1-phenyl-butane-1,3-dione with bifunctional carbonyl compounds – 4-amino-3-penten-2-one or antranilic aldehyde.

As a result of the template condensation of S-alkylisothiosemicarbazides with antranilic aldehyde in the presence of Ni(II) or Cu(II) ions, isomeric coordination compounds were synthesized, and chromatographically separated. Obtained data show that synthesized compounds are chelates of asymmetric and “pseudo symmetric” types. In the latter, the stabilization of the isothiosemicarbazidic block occurs in two different tautomeric forms.

Studies were performed in collaboration with researchers of the Enzymology laboratory of the Institute of Microbiology and Biotechnology of ASM, and the ability of several coordination compounds of Ni(II) and Cu(II) to efficiently stimulate the biosynthesis of enzymes in several mycomycetes was studied and demonstrated.

The interaction of 1,5-bis-thiocarbohydrazone of salicylic aldehyde (H_4L^1) with copper(II) acetate leads to the formation of the complex $[\text{Cu}_8(\text{L}^1)_4(\text{DMF})_8(\text{H}_2\text{O})] \cdot 3.5\text{DMF} \cdot 3\text{H}_2\text{O}$ and $[\text{Cu}_8(\text{L}^1)_4(\text{dmsO})_7] \cdot 6\text{DMSO} \cdot 1.32\text{H}_2\text{O}$ (D. Dragancea, M. Revenco et al.).

A wide class of coordination compounds of transition metals with carboxylic acids was studied (N. Gărbălău, Gh. Popovici, Gr. Timco, C. Indricean et al.). Utilization of methods of X-ray diffraction, magnetochemistry and ESR, allowed ascertaining of binuclearity of copper(II) carboxylates with „fonar” structure and the dependence of the magnetic exchange in these systems on the specifics of their structures, the nature of the radical in the ligand, and the nature of

axial ligands (T. Malinovsky, V. Ivanov et al.) Mass spectrometry studies of metals carboxylates made it possible to establish a high correlation between the structures of these substances in crystalline and vapour form (N. Gărbălău, C. Indricean, Gh. Popovici). A significant number of scientific papers is dedicated to polynuclear or cluster type complexes (M. Iampolschi, B. Cuiavschi, G. Matuzenco et al.).

Various binuclear adducts of copper(II) carboxylates with aromatic amines were synthesized and their structure was determined. It was demonstrated that the character of the acid rest and the nature of the amine in these compounds influence the occurrence of various structural particularities, as well as the possibility of occurrence of an indirect magnetic exchange, involving various types of magnetic centres.

The synthesis and study of paramagnetic molecular compounds became a wide area of intense research, due to the possibility of using these molecules for information storage and realization of quantum computers. In this train of ideas, a class of clusters represents compounds with a cyclic, ring arrangement in the complex architecture, often called “molecular wheels” or “wheels”, in the specialized literature.

The metallocycle $[\text{CrF}(\text{O}_2\text{CC}(\text{CH}_3)_2)_8]$ was synthesized in the laboratory in 1985, and the unusual structure of “molecular wheel” assured obtaining a patent of the former USSR (N. Gărbălău, Gr. Timco et al.).

It should be mentioned that due to its large cavity, this compound can accept small molecules as “guests” inside it. Due to the geometry of the complex $[\text{CrF}(\text{O}_2\text{CC}(\text{CH}_3)_2)_8]$, as well as the negative electrostatic potential of the central cavity of this molecule, the formation of a series of new supramolecular complexes was possible, of the complex $[\text{CrF}(\text{O}_2\text{CC}(\text{CH}_3)_2)_8]$ with various “guest” inclusions: N,N-dimethylformamide, N,N-dimethylacetamide, acetonitril (N. Gărbălău, Gr. Timco et al.). The synthesis of $[\text{CrF}(\text{O}_2\text{CC}(\text{CH}_3)_2)_8]$ in the presence of several secondary amines was performed, subsequently protonated by the pyvalic acid, used for the obtaining of the respective complex. The molecules of resulted compounds contain a large number of N-H...F bonds, which direct the synthesis towards formation of supramolecular dimmers constituted from two hexanuclear “horseshoes” of chrome(III): $[(\text{R}_2\text{NH}_2)_3\{\text{Cr}_6\text{F}_{11}(\text{O}_2\text{CC}(\text{CH}_3)_2)_8\}]_2$, where R= Et, n-Pr, n-pentyl (Gr. Timco et al.).

Obtaining of compounds with “horseshoe” structure allowed to suppose that $[\text{CrF}(\text{O}_2\text{CC}(\text{CH}_3)_2)_8]$ is formed gradually and its precursor, separated in “horseshoe” compounds, or generated *in situ* could be enclosed with another metal cation. The reaction of the mixture constituted of $\text{CrF}_3 \cdot 4\text{H}_2\text{O}$, a secondary amine, pyvalic acid, and a cation of a bivalent metal M^{2+} (where $\text{M}^{2+} = \text{Ni}, \text{Co}, \text{Mn}, \text{Fe}, \text{Cd}$), leads to the formation of octanuclear compounds - $\{[\text{R}_2\text{NH}_2][\text{Cr}_7\text{MF}_8(\text{O}_2\text{CC}(\text{CH}_3)_2)_8]\}$. In the case of utilization of isopropyl- and cyclohexylamine as secondary amines, nonanuclear wheels are obtained, with the general formula $\{[\text{R}_2\text{NH}_2][\text{Cr}_8\text{MF}_9(\text{O}_2\text{CC}(\text{CH}_3)_2)_8]\}$ (Gr. Timco et al.). If M^{2+} is copper(II), an ion which doesn't favour an octahedral geometry, the carcass $\{[\text{R}_2\text{NH}_2][\text{Cr}_{10}\text{Cu}_2\text{F}_{14}(\text{O}_2\text{CC}(\text{CH}_3)_2)_8]\}$ is formed, which contains a dodecanuclear distorted ring with two „horseshoes” each with five centres of chrome(III), linked with Cu^{2+} ions through bridges of F^- and $\text{O}_2\text{CC}(\text{CH}_3)_2$ (Gr. Timco et al.). It should be mentioned that these template syntheses are not limited to those which imply secondary amines as templates. Analogous reactions take place with heterocycles with an active role of template, or even in the case of some mononuclear complexes as templates for the creation of new supramolecular metal cycles (Gr. Timco et al.).

A series of coordination polymers of Cu(II), Co(II), Ni(II) and Zn(II) were synthesized, with chain structures, which contain as bridge ligands the ion o-phthalate and various amines, such as pyridine, imidazole, urotropine and their derivatives, 2,2'-bipyridine, 4,4'-bipyridine and 1,10-phenantroline (N. Gărbălău, S. Baca, I. Filipov et al.). Further, more interesting particularities of this ligand were discovered. For instance, in the quite unusual dimer $[(\text{bpy})_2\text{M}(\text{Pht})\text{H}(\text{Pht})\text{M}(\text{bpy})_2](\text{HPht})(\text{H}_2\text{Pht})\cdot 2\text{H}_2\text{O}$ (where M = Zn(II), Co(II), $\text{Pht}^{2-} =$ dianion of the o-phthalic acid, bpy = 2,2'-bipyridine) $[\text{M}(\text{bpy})_2]$, the metal carcasses are connected through $\text{O}\cdots\text{H}\cdots\text{O}$ bridges, placed between the carboxyl groups of two different phthalate ligands (Iu. Simonov, S. Baca, N. Gărbălău et al.). Data from specialized literature confirm that this complex is the first example of binuclear associate with the $\text{Pht}\cdots\text{H}\cdots\text{Pht}$ unity. As a result of the reaction of cobalt(II) anion with o-phthalic acid and the bidentate ligand – bipyridine, new compounds with nontrivial structure were obtained. As function of the temperature used during the synthesis, coordination compounds with various nuclearity were obtained: mononuclear coordination compounds - $[\text{Co}^{\text{III}}(\text{CO}_3)(\text{bpy})_2](\text{Pht})\cdot 16\text{H}_2\text{O}$ and $[\text{Co}(\text{Pht})(\text{bpy})(\text{H}_2\text{O})_3]\cdot 3\text{H}_2\text{O}$, acyclic dinuclear coordination compounds - $[(\text{bpy})_2\text{Co}(\text{Pht})\text{H}(\text{Pht})\text{Co}(\text{bpy})_2](\text{HPht})(\text{H}_2\text{Pht})\cdot 2\text{H}_2\text{O}$, cyclic dinuclear coordination compounds - $[\text{Co}(\text{Pht})(\text{bpy})(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$, and coordination polymers - $[\text{Co}(\text{Pht})(\text{bpy})(\text{H}_2\text{O})]_n$. The study of magnetic properties as function of temperature, showed the presence of weak antiferromagnetic interactions between Co(II) ions in several compounds, while in others – diamagnetic interactions. Evidencing the specific catalytic properties of these coordination compounds in some oxidation processes extended their practical utilization (S. Baca, I. Filipov, N. Gărbălău et al.).

Polynuclear coordination clusters represent universal construction blocks for the generation of numerous types of periodical and continuous arrangements of molecular-magnetic blocks. Thus, a new linear trinuclear complex compound (S. Baca, Iu. Malaeştean et al.) of Mn(II) was synthesized - $[\text{Mn}_3(\text{O}_2\text{CCHMe}_2)_6(\text{dpa})_2]\cdot 2\text{MeCN}$ ($\text{dpa} =$

=2,2'-dipyridylamine) and the tetranuclear cluster $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CCMe}_3)_6(\text{bpy})_2]$ (bpy = 2,2'-bipyridine) which were linked into coordinative nets with 2,2'-bipyrimidine or hexamethylenetetramine (hmta) as ligands, in order to obtain $\{[\text{Mn}_3(\text{O}_2\text{CCHMe}_2)_6(\text{bpm})]\cdot 2\text{EtOH}\}_n$, $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CCHMe}_2)_6(\text{bpm})(\text{EtOH})_4]_n$ and $\{([\text{Mn}_3\text{O}(\text{O}_2\text{CCHMe}_2)_6(\text{hmta})_2]\cdot \text{EtOH}\}_n$.

A special and universal tridentate ligand proved to be the thiosemicarbazide diacetic acid (H_2Q) – a new complexon, which can form coordination compounds with d and f metals, due to the presence of various functional groups (N. Gărbălău, O. Bologa, J. Vaisbein et al.). In the case of transition metals chelates, this ligand coordinates with oxygen atoms of two carboxylic groups, iminic nitrogen and sulfur. This ligand forms complexes with rare earth metals using the set of donating atoms O, O, N, N, while in the case of alkaline metals – with the oxygen atoms of carboxylic groups.

The composition of Rh(II) and Rh(III) complexes with H_2Q is quite special. Thus, the interaction of alcoholic solutions containing $\text{RhCl}_3\cdot 3\text{H}_2\text{O}$ and H_2Q in the presence of an alkali or organic amine, triphenylphosphine, leads to the formation of products $[\text{RhQClA}]\cdot n\text{H}_2\text{O}$ (A - H_2O , pyridine, α -picoline, PPh_3 , aniline) and $[\text{RhQAACl}]\cdot n\text{H}_2\text{O}$ (AA – α, α' -dipyridyl, o-phenantroline). Electrochemical investigations of solutions demonstrated the irreversible reduction of Rh(III) \rightarrow Rh(I), avoiding the formation of Rh(II) complexes. However, direct interaction of Rh(II) and H_2Q leads to the formation of a special compound with the formula $[\text{Rh}(\text{H}_2\text{Q})_6](\text{OH})_2\cdot 6\text{H}_2\text{O}$ (N. Gărbălău, O. Bologa, V. Lozan et al.), where the polyfunctional, potential tripodic ligand, manifested monodentate capacity, only through the sulphur atom. Monodentate possibilities of H_2Q are also exhibited in the cases of other compounds, for example $[\text{Co}(\text{DH})_2(\text{H}_2\text{Q})]$.

In the case of oxovanadium combination with the formula $[\text{VOQ}(\text{H}_2\text{O})]\cdot \text{H}_2\text{O}$, two isomers were identified (N. Gărbălău, O. Bologa, V. Lozan et al.): *cis*- and *trans*, their geometry being determined by the arrangement of the oxygen atom of the carboxylic groups and of the inner sphere water molecule, towards the atoms of sulphur and oxygen of the thiosemicarbazide fragment. As to combinations with H_2L , only the *trans* configuration occurs. The flexibility of coordinative fragments of the semicarbazid diacetic acid (H_2L) demonstrated another coordination way of the H_2L ligand with Ni(II) - tridentate monodeprotonated with the set of donating atoms O,N,O.

Various combinations of iron(II) and (III), stable in solutions with $\text{pH} \approx 5$ (for Fe(II)) and with more various pH values (for(III)), demonstrated tetradentate functions of ligands, compatibility of organic molecules with the central ion (only in the case of H_2Q) as well as several practically useful properties: assurance of the iron reduction process in metallic anticorrosive coatings (J. Babanov, N. Gărbălău, O. Bologa et al.).

Main research directions of the laboratory of Bioinorganic Chemistry (LBIC) are related to polynuclear carboxylates, as well as to coordination compounds with polymeric structure. The synthesis of a large series of new copper compounds with amino acids was performed: CuA_2 , CuAB , $\text{Cu}_2\text{A}_3\text{B}$, where A, B = amino acid anion (L. Ciapurin, A. Ablov et al.). Their structure is characterized by the coordination of the chelating ligand through N,O atoms of each amino acid anion in the *trans* position of the equatorial plan, forming layers, which form additional Cu-o links with each other, thus forming a distorted octahedral with the coordination node CuN_2O_4 (L. Ciapurin, I. Diacon, S. Donu). Zinc compounds with some amino acids (glycine, alanine, serine) have the property of easily passing through the cell membrane (A. Deseatnic, V. Rudic, C. Turtă et al.). The compound $\text{Cu}(\text{L-Ser})(\text{L-Tre})$ („Setremed[®]”) exhibits significant antitumor properties (B. Kikoti, L. Gatinsky, L. Ciapurin et al.). It successfully passed two clinical trials, and is in the middle of the third, deliberative one. Some compounds of zinc and copper with amino acids stimulate the biomass growth of several microalgae, as well as their content in biologically active substances – polysaccharides, lipids etc. (V. Rudic, V. Bulmaga, L. Ciapurin et al.), which attests the potential of these compounds in the creation of modern biotechnologies.

In the frames of LBIC, the multielectronic theory of polynuclear compounds was elaborated (B. Țucherblat, M. Belinschi). For dimmers with mixed valence d^n-d^{n+1} , it takes into account the crystalline field, degeneration of *nd* orbitals and of multielectronic states. The relation between the parameters of magnetic exchange and of electron transfer in d-metals was elucidated; magnetic moments and heat capacities were also calculated. The theory of double magnetic exchange in tetramers was elaborated (M. Belinschi, V. Gamurar, B. Țucherblat) and it was found that vibronic effects annihilate the double exchange ferromagnetic interaction, which allowed describing the magnetic properties of mixed valence clusters.

The synthesis of $[\text{CuCu}(\text{SalH})_4(\text{H}_2\text{O})_2]\cdot 2\text{DMAA}$, $[\text{CuSr}(\text{SalH})_4(\text{DMAA})_4(\text{H}_2\text{O})]$, $[\text{CuBa}(\text{SalH})_4(\text{DMAA})_4(\text{H}_2\text{O})]$, (DMAA = dimethylacetamide) was performed using salicylic acid (V. Gorincioi, Iu. Simonov, C. Turtă et al.); the copper polyhedron is a tetragonal pyramid, and of the other metal – a cube. The main role during molecules packing into a crystal is played by intermolecular hydrogen bonds with the participation of water and DMAA. These bonds organize dimmers in a chain. The role of the salicylic acid anions is to unify the metal atoms by bridge type carboxylic groups into the *syn-syn* configuration.

Due to their structure and magnetic, catalytic, biological properties, clusters of μ_3 -oxo type on the basis of

carboxylates were always on the list of studied objects in the frames of LBIC. The focus is set on using the mentioned above clusters for modelling active centres of several metalloproteins, as well as for obtaining molecular magnets.

In the frames of LBIC, a wide series of homo- and heterotrinnuclear compounds of iron were studied, with various carboxylic mono- or dibasic acids (acetic, pyromucic, cyanacetic, salicylic), amino acids, halogen acetic acids, aliphatic, pyridine mono- or dicarboxylic acids etc. The obtained results were generalized in 4 Ph doctor theses (S. Bobcova, A. Lăzărescu, V. Mereacre, D. Prodius) and one thesis of doctor habilitate (C. Turtă).

In the class of heterotrinnuclear carboxylates of iron μ_3 -oxo with the fragment $\{Fe_2MO\}$ the localization of the heteroatom in the triangle is difficult. The hypothesis, posted by cor. m. of ASM, C. Turtă, according to which the localization of the heteroatom in the triangle may be solved by introducing into the clusters of monodentate molecules, which posses different affinity towards Fe and M ions, or by realization of intermolecular interactions, which would orient the triangle peaks in well determined columns in the crystal ("stacking") was experimentally confirmed and allowed successful solving of this problem (C. Turtă, V. Mereacre, S. Şova et al.).

It should be mentioned that the issue of localization of the heteroatom in the triangle in the case of various metal surroundings or in the case of a difference between the iron coordination number and that of the heteroatom, remains to be solved.

In the frames of LBIC, Mössbauer spectroscopy and magnetochemistry were successfully applied for investigating a large series of polynuclear homo- and heterometallic clusters on the basis of amino acids (C. Turtă, A. Lăzărescu, Iu. Simonov et al.), aliphatic acids, halogen acetic and cyanacetic acids (S. Şova, I. Cadelnic, F. Jovmir et al.), pyromucic (S. Melnic, D. Prodius, C. Turtă et al.), salicylic acids. On the basis of obtained results, it was ascertained that iron is in a high spin state ($S=5/2$), and anti-ferromagnetic interactions occur between metal ions. The nature of the heterometal and ligands don't influence the total electronic density around the iron atom nucleus, while this one influences the symmetry of the electronic cloud around the Mössbauer nucleus and the values of magnetic exchange interaction.

It was found that some μ_3 -oxotrinnuclear clusters of iron with alpha- or beta amino acids (AMA) $[Fe_3O(AMA)_6(H_2O)_3](NO_3)_7 \cdot nH_2O$ and $[Fe_3O(AMA-H)_6(H_2O)_3]NO_3 \cdot mH_2O$ manifest a positive effect on the biochemical composition and iron accumulation in the biomass of *Spirulina platensis* (V. Rudic, A. Lăzărescu, C. Turtă et al.). The study of the influence of homo- and heterotrinnuclear compounds of iron(III) with amino acids, with the tri- or dichloroacetic acid, pyromucic acid, on the productivity of some microorganisms (cyanobacteria, "Spirulina platensis", and Rhodotorula yeasts stems), demonstrated the possibility of their utilization in creation of new biotechnologies.

A special attention in the LBIC is focused on the research of electronic delocalization in the case of iron clusters with mixed valence of type $[Fe^{III}_2Fe^{II}O]$, as well as in iron carboxylates "polyclusters" with mixed valence, which are obtained at „sewing” iron(III) μ_3 -oxo-acetates with μ_3 -oxo-acetates of iron with mixed valence, research direction initiated and directed by the cor. m. C. Turtă. It was found that in these latter compounds, the "slow" "intermolecular" electron transfer occurs.

Numerous tests of copper and iron carboxylates with physiologically active substances, in collaboration with specialists in the field of plants physiology and microbiology, performed for many years in collaboration with the Institute of Plants physiology and the Institute of Microbiology of ASM, allowed evidencing several compounds which exhibit biological and physiological activity, as compounds with potential application in biotechnology. The preparation "Gajazot" was recommended against chlorosis in vines (S. Toma, S. Velixar, C. Turtă et al.), and „Virinil" is suggested as a regulator and stimulator of roots growing and formation of the calus in the case of industrial-scale production of vine shoots (E. Guţu, N. Ocopnî, L. Ciapurin et al.). Introduction of some iron homo- and heteronuclear μ_3 -oxo carboxylates into the nutrition medium of *Spirulina platensis* leads to biomass increase, as well as to its enrichment in amino acids, peptides, phycobiliproteins and iron accumulation. Administration of the purified *Spirulina* extract - BioR^{Fe} – with an increased iron content, leads to the normalization of main sanguine indices related to anaemia and represent an efficient remedy for the correction of homeostatic deregulations induced by anaemia (C. Turtă, A. Lăzărescu, D. Prodius et al.). The compounds: homo- and heteronuclear μ_3 -oxo-acetates of iron(III) $\{Fe_3O\}$, $\{Fe_2CoO\}$, and $\{Fe_2MnO\}$ with N,N – diethylnicotinamide and other monodentate ligands, exhibit plant growth regulating properties, in the case of such cultured plants as: tomatoes, cucumbers, corn etc. (A. Ştefîrţă, C. Turtă, I. Bulhac et al.). The preparation „Galmet" was proposed for the optimization of growth, productivity and resistance of several cultured plants to suboptimal hydrothermal conditions during vegetation (A. Ştefîrţă, I. Bulhac V. Zubarev et al.).

Another pioneering accomplishment in the class of iron carboxylates was the synthesis and study of tetranuclear iron carboxylates (C. Turtă, S. Bobcova et al.).

Recently, the researchers performed the synthesis and study of μ_3 -dioxo iron heterotetranuclear trichloroacetate, which contain three iron(III) ions, and one Eu(III) ion, $[Fe_3EuO_2(CCl_3COO)_8H_2O(THF)_3] \cdot THF$, with a structure analogical to that of carboxylates of other metals of type "butterfly". Further, were obtained and characterized an entire

set of compounds of this series, where the Eu(III) ions were replaced by La^{III}, Ce^{III}, Pr^{III}, Nd^{III}, Sm^{III}, Gd^{III}, Tb^{III}, Ho^{III}, Er^{III}, Yb^{III} ions (C. Turtă, D. Prodius, V. Mereacre et al.).

In the frames of LBIC, a synthetic method was elaborated, which allowed obtaining a new complex with the composition $[\text{Mn}_{10}\text{Fe}_2\text{O}_{12}(\text{CH}_3\text{COO})_{12}(\text{CHCl}_2\text{COO})_4(\text{H}_2\text{O})_4]\cdot 4\text{H}_2\text{O}$, with a molecular structure. The asymmetric part of the cell unit consists of $[\text{M}_3(\mu_3\text{-O})_3(\text{CHCl}_2\text{COO})(\text{CH}_3\text{COO})_3(\text{H}_2\text{O})]\text{H}_2\text{O}$ and is placed around the axis S_4 , which generates a dodecanuclear complex with three types of metal ions positions. The central part of the neutral molecule of "cuban" type $[\text{Mn}^{\text{IV}}_4\text{O}_4]^{8+}$, surrounded by eight atoms ($x\text{Mn}^{\text{III}}$ and $(8-x)\text{Fe}^{\text{III}}$). All M(III) atoms have octahedral coordination with two different sets of six oxygen atoms, each. The assembly of 12 metal atoms in a cluster occurs through 8 atoms of μ_3 -oxygen and 16 ligands-carboxylates of *syn-syn* type, as a bidentate bridge. The study of magnetic properties of this cluster demonstrated the maintenance of ferromagnetic and molecular magnet properties.

The interaction of trinuclear μ_3 -oxo- acetate cluster or iron(III) with carboxyferrocene lead to the formation of $[\text{Fe}_3^{\text{III}}\text{O}(\text{FcCOO})_6(\text{DMF})_3]\text{ClO}_4$, which was studied using X-ray diffraction, magnetochemistry and voltamperometry (V. Mereacre, C. Turtă et al.).

Researchers synthesized and studied dimeric coordination compounds with the composition $[\text{Ln}_2(\text{CNCH}_2\text{COO})_6(\text{H}_2\text{O})_4]$, ($\text{Ln} = \text{Eu}^{3+}, \text{Nd}^{3+}$) and polymeric, with the composition $\{[\text{Ln}(\text{OOCCH}_2\text{CN})_3(\text{HOOCCH}_2\text{CN})]\cdot 5\text{H}_2\text{O}\}_n$, ($\text{Ln} = \text{Sm}^{3+}$ and Dy^{3+}) (A. Lăzărescu, C. Turtă et al.), $\{\text{FeSr}_2(\text{SalH})_2(\text{Sal})_2\text{NO}_3(\text{DMAA})_4\}_n$, $[\text{FeBa}_2(\text{SalH})_3(\text{Sal})_2(\text{DMAA})_4(\text{H}_2\text{O})]_n$, $\{[\text{Ba}(\text{H}_2\text{O})_4\text{Co}(\text{Pdc})_2(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}\}_n$, ($\text{SalH}_2 = \text{salicylic acid}$, $\text{DMAA} = \text{dimethylacetamide}$, $\text{PDCH}_2 = \text{pyridindicarboxylic acid}$) (A. Lăzărescu, C. Turtă et al.).

Some crown ethers were modified and coordination compounds were obtained on the basis of their modified forms. Synthesized compounds were tested for antihypoxic activity, and it was found that some of them exhibit a more pronounced antihypoxic activity and a more reduced toxicity, as compared to potassium valproate, preparation used in medicine.

The reaction of various benzocrown ethers with calcium salts, CaX_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}, \text{NO}_3, \text{ClO}_4$) gave a set of complexes where the ratio $\text{Ca}:\text{Ligand} = 1:1$. Several compounds of this series were studied using X-ray diffraction and their molecular structure particularities were determined, as function of the nature of the crown ether and anion X (V. Zubarev, I. Bulhac et al.).

Coordination compounds of $\text{Cu}^{2+}, \text{Eu}^{3+}, \text{Nd}^{3+}, \text{Gd}^{3+}, \text{Sm}^{3+}$ with Schiff bases were synthesized, obtained as a result of condensation of 2-hydroxy-3-carboxynaphtaldehydes with various amines (aliphatic, aromatic), sulphonylamides, amino acids, thiosemicarbazide etc. with the following chemical composition: $\{\text{Cu}(\text{Lig})\text{Ln}(\text{NO}_3)(\text{H}_2\text{O})_x\}$, ($\text{Lig} = \text{H}_4\text{L}^1$, $\text{Ln} = \text{Nd}$, $x=6$; Eu , $x=4$; Gd , $x=6$; $\text{Lig} = \text{H}_4\text{L}^2$, $\text{Ln} = \text{Gd}$, $x=3$; Sm , $x=6$) (A. Lăzărescu, T. Popa et al.).

Beside the two main scientific centres of the Republic of Moldova – Institute of Chemistry of ASM and the Faculty of Chemistry of the State University of Moldova, research in the field of coordination chemistry is performed almost at every chemistry faculty in every institution of higher education in the country: the Polytechnic Institute, called today Technical University of Moldova (Ț. Conunov, A. Bircă, V. Bălan, A. Verejan et al.), the Institute, today – Pedagogical State University of Tiraspol (T. Para, E. Melentev, E. Coropceanu, A. Rija et al.), University of Medicine and Pharmacy "N. Testemițanu" (N. Negreață, Gr. Budu, L. Chistruga, S. Bobcov et al.), Agricultural University of Moldova (I. M. Reibel, M. Revenco, A. Sandu et al.).

At present, the list of coordination chemistry specialists is quite voluminous, and the geographical area of their activity is quite vast. The „army” of highly qualified specialists, prepared by the Coordination Chemistry School is represented by 18 doctors habilitate and over 200 Ph doctors in chemistry, specialist in the field of coordination chemistry, which activate in almost all countries of the former USSR, as well as in countries such as Germany, Bulgaria, Vietnam, former Yugoslavia, SUA, Great Britain, France, Israel, Austria, Switzerland etc.

Chisinau remains to date a very important centre in the development of Coordination Chemistry on international scale, proved also by the fact that Chisinau hosted all editions of the Unional scientific Conference with participation of scientists of the international community "Physical and Mathematical methods in Coordination chemistry", beginning with the Ist (1962), except for the IXth edition (1987), which was held in Novosibirsk (Russia). The XVIth edition of the conference will be held in 2009. Since 1985, this conference is entitled "Physical methods in coordination and supramolecular chemistry". The XXIIth International Ciugaev Conference (2005) in the field of Coordination Chemistry, was also held in Chisinau.

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