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ACHIEVEMENTS OF THE INSTITUTE OF CHEMISTRY OF THE ACADEMY OF SCIENCES OF MOLDOVA AT 50 YEARS ANNIVERSARY

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Abstract: This communication deals with the appearance and development of the research in the field of chemistry in the Republic of Moldova; at the beginning - in chemistry sections of Moldovan Branch of the USSR Academy of Sciences and then - at the Institute of Chemistry, founded in 1959. The dynamics of changes in the structure and research subjects is traced. Data are presented concerning the research results in the field of the chemistry of coordination compounds, fine organic synthesis, natural products chemistry, physicochemical analysis, quantum chemistry, mineral resources, chemistry of natural water and purification of waste water, the preparation and utilization of active carbons, and ecological chemistry. A detailed account both of basic research and applied investigation is given. The collaboration of our scientists with their colleagues from abroad is considered. Information is presented related to the scientific schools at our institute, its guidance and laboratory′s leaders. The scientific equipment of the institute is mentioned. The relationship of the institute with higher schools, as well as training of young researchers will be presented.

Keywords: Institute of Chemistry, development, research, investigations, collaboration, equipment.

Sustainable development of the society would be impossible without the implementation of the achievements of modern chemical technologies for the needs of industry, agriculture, medicine, for treatment and valorization of wastes and analytical control of pollutants in the environment. All this appears to be especially important for our country that has no mineral resources.

Chemical investigations started in the Republic of Moldova in 1951, in the analytic group attached to the Section of Pedology of the Moldovan Branch of the former USSR Academy of Sciences with the research in the field of chemistry of coordination compounds of cobalt. This research significantly developed after the formation of the Section of Inorganic Chemistry of the Moldovan Branch of the of the former USSR Academy of Sciences in 1956, and even more due to the setting up of the Institute of Chemistry on 15 April 1959, which became, and still remained, the main centre of chemistry science and developments in the republic.

The basis of scientific directions of the Institute was created by famous researchers, members of the Academy, founders of scientific chemistry schools in Moldova: A.V. Ablov (1905-1978) – school of coordination compounds chemistry; G. V. Lazurievski (1906-1987) – school of organic and bioorganic chemistry, Iu. S. Lealicov (1909-1976) – school of polarography, organizer and leader of research related to physical-chemical methods of analysis.

Later, new scientific schools were created: of quantum chemistry – headed by academician I. Bersuker; of bioorganic chemistry, chemistry of natural and physiologically active compounds – headed by academician P. Vlad; of chemistry of coordination, macrocyclic and supramolecular compounds – headed by academician N. Gărbălău; of ecological chemistry – headed by academician Gheorghe Duca and bioinorganic chemistry – headed by the corr. member of the ASM C. Turtă. The chemistry of natural and modified adsorbents, mainly of activated carbon, is being successfully developed by the school of dr. habilitate in chemistry, Professor T. Lupascu.

Scientific studies performed at the Institute of Chemistry are related to such fields as inorganic chemistry (chemistry of coordination compounds), organic chemistry, quantum and physical chemistry, analytical chemistry – branches of chemistry founded and ascertained since the beginning of the Institute’s activity, in particular, and of chemical science in Moldova, in general.

Besides basic research the institute also carries out applied investigations: the obtaining of coordination compounds with useful properties for industry and agriculture (dyes for textile and plastic, ion-selective electrodes, the catalysts for epoxi-resins polimerization, the obtaining of extrapure metals, growth stimulators for plants etc), odorous compounds for perfumery and tobacco industry, production of essential oils, pharmacologically active compounds, development of methods of analysis and purification of natural and waste waters, development of electrochemical methods of metals dosing in environmental objects, and others.

The Institute devotes much attention to the training and education of young researchers. At the institute activate three specialized Scientific Councils for conferring scientific degrees of doctors and doctors habilitate (in inorganic; organic and bioorganic chemistry, and chemistry of natural and physiologically active compounds).

The institute carries out joint research with higher education establishments of our country. Many collaborators are also delivering courses at local universities.

During the years, the institute passed through several structural and research-related reforms.

Now the Institute of Chemistry of the ASM includes the Centre of Physical chemistry and Nanocomposites, created in 2006, and 4 individual laboratories: of Coordination chemistry, Chemistry of terpenoides, Organic synthesis, and Ecological chemistry. The Centre includes 5 laboratories: Bioinorganic chemistry and Nanocomposites, Physico-chemical methods of research, Quantum chemistry and chemical kinetics, Magnetic resonance and Laser spectroscopy, Atomic spectroscopy. The laboratories of the Institute have modern equipment, computers, connected to the internet, a scientific library. During the last 4 years, modern scientific equipment has been purchased, such as: IR, UV/Vis, NMR and Mossbauer spectrometer, elemental analyzer, autosorb, Stopped Flow spectrophotometer, digital Polarimeter and so on.

The scientific potential of the Institute of Chemistry is represented by 103 scientific researchers, including - 3 Full Members, 2 Corresponding Members, 16 Doctors Habilitate and 42 Doctors of Chemistry.

The Institute of Chemistry collaborates with various teams from abroad:

Romania: „Politehnica"University, Bucharest; National Institute of Materials Physics, Bucharest; Institute ECOIND, Bucharest; „C. D. Nenițescu" Institute of Organic Chemistry of the AS of Romania, Bucharest; „G. Murgulescu" Institute of Physical Chemistry of the AS of Romania, Bucharest; "P. Poni" Institute of Macromolecular Chemistry of the AS of Romania, Iasi; „A. I. Cuza" University, Iasi; „Gh. Asachi" University, Iasi;

Russia: Institute of Physical Chemistry and Electrochemistry of the AS of Russia; the Association of science and production „Neorganica" from the city of Electrostali, Moscow region; Institute of Technical Physics, Kazani;

USA: Department of Chemistry and Biochemistry, University of Texas at Austin; Centre for Marine Sciences (CMS), University of North Carolina at Wilmington;

France: Laboratory of synthesis and study of systems of biological interest and Laboratory of molecular and macromolecular photochemistry, University Blaise Pascal, Aubiere Cedex;

Ukraine: Institute of Colloidal Chemistry and Water Chemistry of the NAS of Ukraine;

Poland: Chemistry Faculty of „A. Mickiewicz" University, Poznań; Institute of Physical Chemistry, the AS of Poland; "A. Pawin" Institute of Biochemistry and Biophysics, Polish Academy of Sciences, Warszawa;

Belarus: Institute of Bioorganic Chemistry of the National Academy of Sciences of Minsk;

Holland: Agrarian University from Vageningen;

Spain: Department of Organic Chemistry, Faculty of Pharmacy, University of Valencia, Valencia;

Italy: Institute of Biomolecular Chemistry, CNR, Pozzuoli (Na); Laboratorio di Chimica Bioorgabica Universita degli Studi di Trento;

Germany: University of Leipzig, Institute of Organic Chemistry, Leipzig.

The collaboration of our researchers with scientific teams from abroad is strengthened by scientific conferences with international participation, organized by the institute.

At present, joint scientific research is carried out in the framework of several international projects:

one joint research project – ASM and Russian Foundation for Basis Research; one joint research project – ASM and Belarussian Republican Foundation for Fundamental Research; three joint research project – ASM and the Federal Ministry of Education of Germany (BMBF); two INTAS projects, including one INTAS– Moldova project, and one SCOPES project.

The Institute of Chemistry organized a series of international conferences. The most important are: the Ist to the XVIth International Conferences on ***„Physical methods in coordination and supramolecular chemistry"*** that take place every 3 years, the Ist and the IInd International Conferences of the Chemical Society of Moldova on ***„Realizations and perspectives of modern chemistry"*** held on 6-8 October 2003 and 1-3 October 2007, respectively.

Researchers who took part in those conferences were from 13 European countries: England, Austria, Belgium, Belarus, France, Germany, Greece, Holland, Poland, Romania, Russia, Spain, Ukraine, and the USA.

In 2006 the Institute of Chemistry began publishing the journal **„Chemistry Journal of Moldova"** in English.

The most important results of research

Chemistry of coordination compounds

Investigations in the field of *chemistry of coordination compounds* significantly developed after1956 with the formation in of the Section of Inorganic Chemistry of the Moldavian Branch of the Academy of Sciences of the USSR, named in 1975 the Laboratory of Chemistry of Coordination Compounds. Initially, the scientific theme was oriented towards the synthesis and investigations of coordination compounds of transition metals, especially, of cobalt, copper, nickel, iron, palladium; to investigations of the structure and properties of compounds of this class, using physical methods of investigation and quantum chemistry computation methods. Later, the range of research themes was enlarged significantly, including studies in the field of template processes, topochemical synthesis, in non-aqueous medium and other conditions characteristic to the process of obtaining new mono- and polynuclear coordination compounds, including ones 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 the electronic and vibronic structure of compounds with mixed valence, enhancement of quanto-chemical methods of investigation, and of methods of molecular design of biologically active systems, with a special focus on the mechanisms of their action.

Due to the utilization of the electronic absorption spectra in a series of cobalt(III) transdioximines, the phenomenon of isomerisation was discovered and later confirmed by the separation of crystalline compounds and by detailed investigations of their properties. Research was also performed in the field of chemistry of coordination compounds of transition metals with thiosemicarbasones. It was the first time that metal complexes with selenosemicarbazide and various selenosemicarbazones were obtained and studied. During the investigation of magnetic properties of Fe(III) coordination compounds with thiosemicarbazones using methods based on magnetic susceptibility and the gamma resonance effect, the electron spin isomerism was discovered at several chelates. Systematic research was performed regarding Cu(II) complex compounds with carboxylic, hydroxy carboxylic and amino acids. Complexes of lantanides with organic amines were synthesized and studied. A new direction in magnetochemistry was developed – the theory of magnetic exchange interaction in polynuclear clusters, which allowed describing more adequately the temperature dependence of their magnetic susceptibility and electronic spin resonance spectra.

The synthesis of physiologically active and catalytically active complexes of microelements on the basis of diketones and dioximes with bioligands was carried out. The complexes of cobalt(III) dioximines with sulfamides were synthesized.

After the passing away of academician *Antonie Ablov* (1978), academician *Nicolae Garbalau* became head of the Laboratory of Chemistry of Coordination Compounds, who was the founder of the scientific school in the field of chemistry of coordination compounds, macrocyclic and supramolecular compounds. Research in the field of chemistry of coordination compounds includes the elaboration of modern concepts in coordination and supramolecular chemistry, study of new complexes of 3d-elements with organic polyfunctional ligands. Investigations are related to: directed synthesis using original procedures of new mono- and polynuclear coordination and supramolecular compounds of transition metals with chelating and macrocyclic ligands, determination of their structure and specific properties, including practically useful ones.

Concepts and fundamental laws of template assembly of macrocyclic and supramolecular systems, including highly polynuclear clusters, were elaborated.

In 2006, after the decease of academician *Nicolae Gărbălău*, dr. hab. *Ion Bulhac* was elected head of the laboratory.

Fundamental results are presented in over 620 articles and 4 monographs. On the basis of the conducted research, a number of elaborations were offered and protected by over 40 patents; these could be classified as follows: catalysts, colorants, stimulators of biological processes, new coordination compounds for obtaining extra-pure metals, ion-selective electrodes, and anticorrosion coating agents.

Bioinorganic Chemistry

On 18 June 1975, according to the decision of the State Committee for Sciences and Technology of the Council of Ministries of the former USSR, research in a foremost direction was launched, which allowed the creation of a new Laboratory of Bioinorganic Chemistry, aimed at the study of biologically active coordination compounds. The dr. hab. *Dumitru Batîr* was elected as head of this laboratory (1974 - 1988).

The synthesis and study of coordination compounds of biometals is the basic task of the Bioinorganic Chemistry laboratory, headed at present by the corr. member of the ASM *Constantin Turtă, the founder of the scientific school of bioinorganic chemistry, and of Mossbauer spectroscopy applications in chemistry.* Investigations are related to: coordination compounds of biometals (Fe, Co, Mn, Cu, Zn, Ni) with α- dioximes, Schiff bases and carboxylic acids, including amino acids, and determination of their molecular and crystalline structure. The molecular and crystalline structure of tri- and tetranuclear iron(III) clusters, mono- and dimmers of copper(II) with amino acids and of mononuclear dioximates of iron and cobalt were determined. The electronic structures of iron(II) and (III) dioximates, of homo- and heteronuclear clusters containing iron were determined, allowing a more adequate interpretation of spectra of such compounds. The electron delocalization in iron oxo-carboxylates with mixed valence and the spin isomerism for iron(III) dioximates were determined using Mossbauer spectroscopy and magnetochemistry. The obtained results were published in over 400 scientific papers.

Regarding the applicative area, coordination compounds possessing anticancer, antiviral, antibacterial, anti-coccidal and antidote properties were revealed, as well as several growth regulators for plants and algae.

The preparation “Gajazot” with anti-chlorosis properties and the preparation „Cu-12” were recommended for implementation in viticulture. The elaborations are protected by 16 patents.

Quantum chemistry

Simultaneously with the creation of the institute and broadening the area of chemical investigations, a number of organizational measures were undertaken in order to apply physical methods of research and quantum-chemical computations in chemistry; thus the quantum group was created, and later, in 1962, reorganized into the Laboratory of quantum chemistry, headed by academician *Isaak Bersuker, the founder of the scientific school of quantum chemistry.*

Research in the field of quantum chemistry was quite significant from the very beginning, being highly appreciated at the international level.

Computational studies of the electron-vibrational interactions were carried out – the effect and pseudo Jahn-Teller effect, new methods were elaborated and existing methods were enhanced, of as well as of electronic structure and properties of coordination compounds, and computation software programs were created and upgraded. The study of the influence of the electronic structure on nuclear configurations of polyatomic systems and their dynamics lead to the elaboration of a new concept in the theory of structure and particularities of polyatomic systems – the concept of vibronic interaction, which resulted in a scientific discovery, registered in 1978 in the State Registry of the USSR, no. 202: *„Явление туннельных расщеплений уровней энергии многоатомных систем в состоянии электронного вырождения" („The Phenomenon of Tunneling Splitting of Energy Levels of Polyatomic Systems in Electronic Degenerate States")* (I. Bersuker). On the basis of this scientific discovery, the vibronic theory of segnetoelectricity was developed. Special attention was focused to the catalysis theory, research being directed towards the study of the elementary catalytic act; new regularities in the formation of the crystalline structure were revealed (electronic crystallochemistry). The quanto-chemical interpretation of transinfluence was elaborated. Significant scientific results were achieved in the development of the theory of physical methods of investigation of materials structure and their peculiarities.

At present, the Laboratory of Quantum Chemistry is headed by dr. hab., professor *Ivan Ogurțov*. The following research has been performed: vibronic effects in coordination compounds stereochemistry; localization-delocalization effects in polynuclear coordination compounds and their development in spectroscopy; magnetic properties and the possibility of their utilization in molecular electronics; vibronic effects in crystallochemistry; vibronic effects and the activation of small molecules in catalytic chemical reactions; magnetism in polynuclear coordination compounds; calculation methods, semiempirical and *ab initio* calculations of coordination compounds electronic structure; the study of the structure-activity (chemical, biological etc.) relationship; computer modelling and design of biologically active compounds.

A new concept was postulated and developed in the frames of the theory of molecules and crystals – the theory of vibronic interactions; the polyelectronic quantum chemistry theory of dimer, trimer and tetramer clusters with mixed valence was elaborated.

Chemistry of natural compounds

Along with coordination chemistry, the chemistry of natural compounds and organic synthesis developed. The founder of these investigation was a*cademician Gheorghe Lazurievski.* The Organic Chemistry Section, founded in 1956, was the second structural unit of the Chemistry Institute, later named as the Laboratory of Chemistry of Natural Compounds (1959-1975). In 1975 this laboratory is divided into two: Laboratory of Chemistry of Steroidal Compounds (headed by the dr. in chemistry *Petru Ciobanu)* and the Laboratory of Chemistry of Isoprenoids (headed by the dr. in chemistry *Dumitru Popa).* In 1976, both laboratories were reorganized. The first one became the Laboratory of Chemistry of Ethero-oleaginous Plants (headed by academician *Pavel Vlad)*, and the second one returned to its original line and has been headed ever since by Dumitru Popa, under the name of the Laboratory of Chemistry of Plants growth and development Regulators. In 1991 these two laboratories were unified into a single research unit- the Laboratory of Chemistry of Terpenoides, headed by academician Pavel Vlad.

Initially, research was related to the study of chemical composition of vegetal raw material and of wastes resulting from the industry of production of essential oils. Later, the area of scientific interest included fundamental research into new structural-selective and stereospecific methods of total and partial synthesis of terpenic polyfunctional compounds, first of all, related to the drimanic sesquiterpenoides class, that has a vast range of biological activity, and their multilateral investigation.

In the frameworks of investigations of alkaloid generating plants, detailed study of periwinkle, meadow-rue and buirush were performed, and several indole type alkaloids were extracted, two of which – brevicolin and brevicarin, were new compounds of the β-carbolynic series. Their structure and biogenesis were established, multiple chemical transformations of these compounds, including mutual transformations, were carried out.

Wastes from the essential oils production were used to obtain and study sclareol and 13-episclareol. Methods of their isolation were elaborated and a range of chemical reactions, such as oxidation, hydrocloruration, amination were studied; stereochemistry of diterpenoides from labdanic group was established, the preparation methods of valuable odorous compounds from sclareol were elaborated.

About 40 polyfunctionalized diterpenoids of clerodane structure were extracted and identified. They present taxonomic interest. Research related to the elaboration of plants-growth regulators, chemistry of odour compounds and essential oils were developed. Further, investigations were conducted on triterpenic saponines, as well as steroidal glycosides extracted from various plants.

For three decades, the team of organic and bioorganic chemists has been headed by academician *Pavel Vlad, the founder of the scientific school of bioorganic chemistry, chemistry of natural and physiologically active compounds and fine organic synthesis.*

In the field of *Chemistry of Terpenoides,* under academicean Pavel Vlad'sguidance, the study of terpeniodes was performed. Investigations are related to labdanic and isoagatanic diterpenoides, drimanic sesquiterpenoides, norlabdanic compounds, scalaranic and heilantanic sesterterpenoids. The methods of their synthesis on the basis of the raw materials, isolated from vegetal wastes after the essential oils production, were elaborated.

Regarding fundamental studies, the cleavage products of a number of accessible labdanoids were investigated, the stereochemistry of a range of labdane compounds was revealed, semi-synthetic methods of preparation of a large number of drimanic sesquiterpenoids and norlabdanic derivatives were elaborated. The general, structure selective and stereospecific ways of the biomimetic synthesis of cyclic mono-, sesqui-, di- and sesterterpenoids have been performed by superacidic cyclization of the aliphatic precursors. New general reactions for organic chemistry were elaborated. The results of these investigations were published in over 350 publications.

In the field of applied research, the methods for the reduction of norambreinolide have been elaborated and implemented; new products such as ambrol, chetoxide, sclareoloxide, and ionoxide were prepared. Methods of sclareol isolation as well as of anetol-enriched fennel oil preparation were elaborated. Methods for the ozonolitic preparation of the norambreinolide and sclareoloxide were devised. More than 20 compounds, having strong ambergris odour with norlabdanic and homotrichinanic skeletons, were obtained. On the basis of these compounds, a range of original flavouring compositions suitable for tobacco aromatization were prepared, and several of drimanic compounds with biological activity were synthesized. These elaborations are protected by over 50 patents. Compounds of practical importance have been used in perfumery and tobacco industry. Now investigations are directed towards obtaining biologically active compounds for pharmacology.

Organic chemistry

In 1962, on the initiative of dr. *Alexandr Şamşurin*, the Laboratory of Organic Synthesis was founded. The staff of that laboratory started its activity by obtaining preparations for pests control and of several compounds with attracting properties. During 1972 -1982 the Laboratory of Organic synthesis, named in 1976 as the Laboratory of Chemistry of Preserving compounds, was headed by dr. hab. *Grigore Junghietu*. In 1984 dr. *Miron Krimer* took the lead of the laboratory which was then named the Laboratory of Pesticides Chemistry, and in 1991 named again, the Laboratory of Organic synthesis. After the decease of the dr. *Miron Krimer*, the Laboratory of Organic Synthesis has been headed by dr. hab. *Fliur Macaev.*

Methods of the synthesis of heterocyclic indole derivatives from the respective pirilium salts were elaborated. The condensation reactions of indole and oxindole with ketones and keto-aldehydes were investigated in detail. Significant research was performed in the field of the synthesis of a number of attractants, juvenile hormones and phytoestrogens of cumestan series. A new method of the synthesis of pyrocarbonic acid esters was elaborated, and their several transformations were investigated. The method of the synthesis of 8 – oxyquinolin and its new derivatives was elaborated. Investigations were performed in order to obtain highly effective antibacterial preparations that could be used as food stabilizators. Physico-chemical properties of pectic compounds were studied, as well as the possibility of their use in winemaking.

The syntheses and chemical transformations of heterocyclic compounds are performed under the direction of dr.hab. Fliur Macaev. Investigations are related to aromatic hydrocarbons, heterocyclic compounds, alkaloids, steroids – analogues of vitamin D, monoterpenes – carene, carvone. The methods of preparation of these natural compounds good sintons for obtaining of biologically active compounds were improved.

Regarding fundamental research, a detailed study of alkylation reactions using tosilates of several natural alcohols was carried out, conditions for the acetyl group migration from enol acetates were elucidated and the reactivity of resulted diketones was studied. Two new types of acid and alkaline recyclization of thiocarbamoilate derivatives of chinazolin-4-one were discovered, which allowed the synthesis of several new oxa(tia)diazoles.

In the applied area, methods of obtaining of several important preparations, used in food industry, agriculture and medicine were elaborated. The compounds with psycho- stimulating, anticonvulsant, sedative, tranquilizing, antimycotic and cardiac activity regulation properties were prepared. Also, compounds with a significant tuberculostatic activity were obtained. The methods of the synthesis of several intermediates in obtaining physiologically active compounds, Biotin (vitamin H) and vitamin $D_{3,}$ were optimized.

The results of research are presented in over 200 scientific publications and protected by 30 patents.

Analytical chemistry

The Institute of Chemistry became an important centre of *analytical chemistry – research direction founded by academician Iurie Lealicov*. The Laboratory of Analytical Chemistry was founded in 1957 when Professor Iurie Lealicov laid the foundations of electrochemical methods of analysis.

In the frames of physico-chemical investigations, the theory and practice of polarography were investigated, as well as the kinetics of processes accompanied by the adsorption of metals complexes on the electrode, and the possibility of utilization of the effect of inhibition– acceleration of electrochemical reactions on the analysis of alloys, electrolytes, semiconductors, of waste waters, soil and air at industrial factories, of mineral clays, trace amounts of pesticides, of standard samples of nonferrous metals and alloys. The quanto-chemical computation of the system catalyst – activator – oxidant, was performed for the first time, which allowed a deeper understanding of the catalytic process mechanism. Several methods were proposed for the determination of compounds in various objects and media – soil, water, air, vegetal materials, and foodstuffs. Over 20 methods of determination of Pb, Cd, Fe, Cu, Mo, As, Ti and other elements were devised, applicable to various objects that were widely applied in the national economy.

In 1973, dr. *Ion Vatamanu* was appointed head of the Laboratory of Analytical Chemistry (called the Laboratory of Electrochemical Methods of Investigation for a short period), and in 1991 dr. *Ludmila Chiriac* was elected head of laboratory. Methods and advanced techniques for the increase of selectivity and sensitivity of electrochemical methods of analysis were elaborated and tested under the guidance of dr. hab., professor *Mihail Revenco*. Catalytic currents and adsorption phenomena of species were used in voltammetry and stripping adsorptive polarography; chemical activation and carbon fibres microelectrodes electrochemistry were used for the determination of toxic metals in waters, soil.

Methods of analysis were developed for the determination of main components and of traces in electronic materials. The behaviour of several organic polydentate and polyfunctional reagents such as oxy acids, metalochromic indicators, thiazinic dyes, thiosemicarbazones was studied, in complex forming reactions, and the influence of these interactions on the selectivity and sensitivity of electrochemical methods of analysis of heavy metals was estimated. Efficient methods of the analysis of metals, such as Pb, Cu, Cd, Fe, Ni, Zn and Mo applicable to foodstuffs and environmental objects were elaborated. New technologies of carbon fibre microelectrodes were proposed and tested in order to improve the sensibility and selectivity of toxic metals traces analyses.

Ecological chemistry

Recently, research in the field of ecological chemistry gained a significant importance; in our country this scientific direction was founded by academician *Gheorghe Duca*, the President of our Academy.

The scientific school founded by academician Gheorghe Duca revealed the fundamental mechanisms of homogeneous catalysis, developed the theory of redox phenomenon in the environment, elucidated the oxidation and reduction mechanisms during the formation of oenologic products quality; elaborated the concepts of physico-chemical and biochemical treatment of waste waters, the technologies of wastes valorization, of production of medicinal preparations, cosmetic products, decrease of atmospheric nox, methods of estimation of chemical harm in case of pulmonary and gastro-intestinal cancer, has developed new procedures of obtaining biologically active compounds directly from winery by-products, ecological audit, ecological education, contributed to the creation of the redox concept regarding the action of peroxides on ecological systems etc.

The Laboratory of Ecological Chemistry of the Institute of Chemistry passed through three steps of its development. It was founded as the Laboratory of Chemistry of Mineral Resources, due to the fact that natural, mineral and vegetal resources are the main source of national wealth. The first head of the laboratory was dr. *Nicolai Lobanov*. The dr. *Valeriu Ropot* headed the laboratory, called then the Laboratory of Mineral Resources and Chemistry of Water.

Chemical and physico-chemical investigations were performed on the local bentonites, the chemical composition and adsorptive-structural properties of clays in the Republic Moldova were determined, as well as the conditions of thermal activation of bentonites that are used as natural sorbents for the purification of various liquids.

Investigations in the field of adsorbents and sorption of various toxic compounds, as well as the study of regularities of formation of water quality, resulted in the elaboration of purification technologies for various water categories and methods of their complex analysis, technologies of valorization of wastes obtained during water purification, elaboration on their basis of technologies for cyclic water utilization, preparation of activated carbons for medicinal use.

After the passing away of Dr.Valeriu Ropot, dr. habilitate *Tudor Lupascu* reorganised the Laboratory of Mineral Resources and Water Chemistry into the Laboratory of Ecological Chemistry.

Elaboration of procedures of adsorbents synthesis, determination of their adsorptive capacity and structural parameters, utilization of disperse systems for the protection of waters and human health – these are the main scientific directions in the field of Ecological Chemistry, being worked out under the guidance of dr. habilitate Tudor Lupaşcu. Investigations are related to: local vegetal subproducts, activated carbons obtained from these sources of raw material, mineral adsorbents, sources of natural and waste waters; technologies of water potabilization; medicinal preparations on the basis of activated carbons.

Theoretical and practical bases were elaborated for the synthesis of activated carbons from vegetal regenerable subproducts. The mechanism of adsorption of organic and inorganic pollutants on common and oxidized activated carbons was established. Procedures of natural and waste waters treatment were elaborated. Medicinal preparations on the basis of activated carbons were created and their capacity for human body detoxification was estimated. The processes of modification of mineral adsorbents and the possibility of their utilization for the immobilization of organic compounds and heavy metals from the aquatic medium were investigated. Compositions for covering interior walls of buildings on the basis of disperse systems were elaborated. The procedures of production of activated carbons and compositions for walls covering are protected by 12 patents. The processes and mechanisms of immobilization, migration, transformation of pollutants in the system water-suspensions were studied and ascertained for the waters in the case of the rivers Nistru and Prut.

The results of scientific investigations performed in the frames of the institute are presented in over 4300 scientific papers, including around 80 collective and individual monographs and thematic selections, over 240 author certificates and patents, over 120 technological elaborations have been introduced into the national economy.

Considering the current necessities of our country's development, the National Council of Accreditation certified the following scientific directions of the Institute of Chemistry (Certificate no. 004 Decision 14/AC on 16 February 2006):

1. *Directed synthesis and study of coordination compounds with various useful properties.*
   Original methods of synthesis of mono- and polynuclear ones of transitional metals and biometals with polyfunctional and polydentate ligands will be elaborated and realized, leading to the broadening of fundamental knowledge of modern coordination chemistry and its new compartments – chemistry of macrocyclic and of supramolecular compounds; allowing to obtain new compounds with useful properties for microelectronics, textile industry, agriculture, medicine, veterinary.
2. *Directed synthesis of organic biologically active compounds, including natural compounds.*
   Theoretical bases of fine organic synthesis will be developed, including that of natural compounds, especially drimanic sesquiterpenoides and labdanic diterpenoides and of heterocyclic derivatives which contain oxygen, nitrogen, sulphur. Original structural– and regioselective and stereospecific methods of the synthesis of the compounds mentioned above will be elaborated, using modern synthesis methods. The focus will be set on obtaining biologically active compounds potentially useful for medicine, industry and agriculture.
3. *Investigation of chemical and physico-chemical processes, elaboration of methods for the analytical control of ecosystems and non-polluting technologies.*

Theoretical bases will be elaborated for the elucidation of physico-chemical processes and mechanisms for the obtaining of adsorbents with well-defined properties. The processes and mechanisms of pollutants transformation and immobilization in aquatic systems will be ascertained. New methods and techniques of analytical control of chemicals in various environmental objects will be elaborated.

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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

Antonie Ablov

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.

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. Batîr.

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, Ş. 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 (^{1}H, ^{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. Batîr, 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 thematics 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. Bavîkin, L. Istru, O. Damaskin, T. Luchianeț, G. Conunov, G. Şpakov). 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. Luchianeț, G. Şpakov 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. Bologa), which was evidenced by a series of physico-chemical investigations (M. Filipov, A. Gulea, O. Bologa, 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. Velişco. Many of these compounds posses 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 oxyaldehides) 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. Horoşun, V. Țapkov, S. Iuşcenco, 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. Novițchi). In order to accomplish this, the NMR method was widely used: ^{1}H, ^{13}C, ^{14}N, ^{17}O, ^{19}F, $^{35}C1$, ^{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 intramollecular 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. Novițchi, E. Iorga), as well as in cobalt(III) dioximates (A. Gulea, O. Bologa, 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 (methylglioxime, methyl-carbmetoxy- and ethylcarbmetoxyglioxime) 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. Şafranschi, I. Popa). In the cases of complex cations $[Co(NH_3)_3dien]^{3+}$ and $[Co(OCH_2CH_2NH_2)_3]$, 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. Şova).

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(dimethylglioximato)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. Novițchi, 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 regardin the possibility of utilization of coordination compounds in photobiotechnology, as regulators of growth and development of biosynthetical activity of cyanobacteria (A. Gulea, V. Rudic). Original procedures were elaborated, regarding the control of spirulina and dunaliela 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 B_{12}) was optimized in the biomass of cyanobacteria and microscopic algae (A. Gulea, Gh. Novițchi, 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 heterometalic 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 (Universitaty 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. Testemițanu”), 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 B_{12}. 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. Testemițanu” , 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 Laboraory 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 dimethylglioxime in the presence of fluorhidric 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), diphenylglioxime ($DfgH_2$) 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 intramollecular 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. Batîr, I. Bulhac) and nickel(III) α-dioximates (D. Batîr, 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 $[Fe(DfgH)_2(3\text{-}CH_3\text{-}Py)_2][I_5]$ (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. Batîr 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, izonitrile 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 $[M(DioxH_2)_3]X_2$ (M – Fe^{2+}, Ni^{2+}, Cu^{2+}; $DioxH_2$ – dimethylglioxime (DH_2) and 1,2- cyclohexandiondioxime ($NioxH_2$); X – Cl^-, Br^-, NO_3^-, ClO_4^-, ½SO_4^{2-}, ½$S_2O_3^{2-}$) and their structural analogues – *cis*-dioximines with general formula $[X_2M(DioxH_2)_2]$ (M – Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}; X – Cl^-, Br^-, ½SO_4^{2-}, ½$C_2O_4^{2-}$) (D. Batîr, 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:

$$[Fe(NioxH_2)_3]^{2+} \xleftrightarrow{pH>2} [Fe(NioxH_2)_2(NioxH)]^{+} \xleftrightarrow{pH>6} [Fe(NioxH_2)(NioxH)_2]^{0} \xleftrightarrow{pH>11} [Fe(NioxH)_3]^{-} .$$

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. Batîr, 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, Iarțev, Ternopol andTiraspol) (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. Batîr, I. Bulhac, M. Fedoseev), as dielectric material (D. Batîr, 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. Găbălău, 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 aminguanizone 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 dithiocarbometoxyhidrazones of amide, anilide and N-diethylamide of pyruvic acid (A. Ablov, N. Beliciuc, L. Nejelschi et al.).

Cobalt forms exclusively octahedral compounds with two ligand molecules; those monodeprotonated and nondeprotonated form octahedral with coordination node $Co_2O_2N_2S_2$, 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, axovanadium 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, Ş. 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. Şova, 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 bifuctional 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 $[MN_3O]$, were obtained by template condensation on Ni(II) and Cu(II) matrices of mono-S-methylizothiosemicarbazone of acetyl acetone or 1-phenyl-butane-1,3-dione with bifuctional carbonyl compounds – 4-amino-3-penten-2-one or antranylic aldehyde.

As a result of the template condensation of S-alkylisothiosemicarbazides with antranylic 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 mycromicetes 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 $[Cu_8(L^1)_4(DMF)_8(H_2O)]\cdot3.5DMF\cdot3H_2O$ and $[Cu_8(L^1)_4(dmso)_7]\cdot6DMSO\cdot1.\ 32H_2O$ (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 $[CrF(O_2CC(CH_3)_3)_2]_8$ 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 $[CrF(O_2CC(CH_3)_3)_2]_8$, 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 $[CrF(O_2CC(CH_3)_3)_2]_8$ with various "guest" inclusions: N,N-dimethylformamide, N,N-dimethylacetamide, acetonitril (N. Gărbălău, Gr. Timco et al.). The synthesis of $[CrF(O_2CC(CH_3)_3)_2]_8$ 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): $[(R_2NH_2)_3\{Cr_6F_{11}(O_2CC(CH_3)_3)_{10}\}]_2$, where R= Et, n-Pr, n-pentyl (Gr. Timco et al.).

Obtaining of compounds with "horseshoe" structure allowed to suppose that $[CrF(O_2CC(CH_3)_3)_2]_8$ 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 $CrF_3 \cdot 4H_2O$, a secondary amine, pyvalic acid, and a cation of a bivalent metal M^{2+} (where M^{2+} = Ni, Co, Mn, Fe, Cd), leads to the formation of octanuclear compounds - $\{[R_2NH_2][Cr_7MF_8(O_2CC(CH_3)_3)_{16}\}]$. In the case of utilization of isopropyl- and cyclohexylamine as secondary amines, nonanuclear wheels are obtained, with the general formula $\{[R_2NH_2][Cr_8MF_9(O_2CC(CH_3)_3)_{18}\}]$ (Gr. Timco et al.). If M^{2+} is copper(II), an ion which doesn't favour an octahedral geometry, the carcase $\{[R_2NH_2][Cr_{10}Cu_2F_{14}(O_2CC(CH_3)_3)_{22}]\}$is formed, which contains a dodecanuclear distortioned ring with two „horseshoes" each with five centres of chrome(III), linked with Cu^{2+} ions through bridges of F^- and $O_2CC(CH_3)_3$ (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-phtalate 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 $[(bpy)_2M(Pht)H(Pht)M(bpy)_2)](HPht)(H_2Pht)\cdot 2H_2O$ (where M = Zn(II), Co(II), Pht^{2-} = dianion of the o-phtalic acid, bpy = 2,2'-bipyridine) $[M(bpy)_2]$, the metal carcases are connected through O···H···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 Pht···H···Pht unity. As a result of the reaction of cobalt(II) anion with o-phtalic 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 - $[Co^{III}(CO_3)(bpy)_2]_2(Pht)\cdot 16H_2O$ and $[Co(Pht)(bpy)(H_2O)_3]\cdot 3H_2O$, acyclic dinuclear coordination compounds - $[(bpy)_2Co(Pht)H(Pht)Co(bpy)_2](HPht)\cdot(H_2Pht)\cdot 2H_2O$, cyclic dinuclear coordination compounds - $[Co(Pht)(bpy)(H_2O)]_2\cdot 2H_2O$, and coordination polymers - $[Co(Pht)(bpy)(H_2O)]_n$. 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 - $[Mn_3(O_2CCHMe_2)_6(dpa)_2]\cdot 2MeCN$ (dpa =

=2,2′-dipyridylamine) and the tetranuclear cluster $[Mn_4O_2(O_2CCMe_3)_6(bpy)_2]$ (bpy = 2,2′-bipyridine) which were linked into coordinative nets with 2,2′-bipyrimidine or hexamethylentetramine (hmta) as ligands, in order to obtain $\{[Mn_3(O_2CCHMe_2)_6(bpm)]\cdot 2EtOH\}_n$, $[Mn_4O_2(O_2CCHMe_2)_6(bpm)(EtOH)_4]_n$ and $\{([Mn_3O(O_2CCHMe_2)_6(hmta)_2]\cdot EtOH\}_n$.

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 $RhCl_3\cdot 3H_2O$ and H_2Q in the presence of an alkali or organic amine, triphenylphosphine, leads to the formation of products $[RhQClA]\cdot nH_2O$ (A - H_2O, pyridine, α-picoline, PPh_3, aniline) and $[RhQAACl]\cdot nH_2O$ (AA – α,α'-dipyridyl, o-phenantroline). Electrochemical investigations of solutions demonstrated the irreversible reduction of Rh(III)→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 $[Rh(H_2Q)_6](OH)_2\cdot 6H_2O$ (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 $[Co(DH)_2\,(HQ)\,(H_2Q)]$.

In the case of oxovanadium combination with the formula $[VOQ(H_2O)]\cdot H_2O$, 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 pH ≈ 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, $CuAB$, Cu_2A_3B, 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 distortioned 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 Cu(L-Ser)(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. Ţucherblat, 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. Ţucherblat) 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 $[CuCu(SalH)_4(H_2O)_2]\cdot 2DMAA$**)**, $[CuSr(SalH)_4(DMAA)_4(H_2O)]$, $[CuBa(SalH)_4(DMAA)_4(H_2O)]$, (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 heterotrinuclear 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 heterotrinuclear 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-oxotrinuclear clusters of iron with alpha- or beta amino acids (AMA) $[Fe_3O(AMA)_6(H_2O)_3](NO_3)_7\cdot nH_2O$ and $[Fe_3O(AMA\text{-}H)_6(H_2O)_3]NO_3\cdot mH_2O$ 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 heterotrinuclear compounds of iron(III) with amino acids, with the tri- or dichloracetic acid, pyromucic acid, on the productivity of some microorganisms (cyannobacteria, ”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. Guțu, N. Ocopnîi, 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. Ştefîrță, 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. Ştefîrță, 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 trichloracetate, 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 where 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 $[Mn_{10}Fe_2O_{12}(CH_3COO)_{12}(CHCl_2COO)_4(H_2O)_4]\cdot 4H_2O$, with a molecular structure. The asymmetric part of the cell unity consists of $[M_3(\mu_3\text{-}O)_3(CHCl_2COO)(CH_3COO)_3(H_2O)]H_2O$ 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 $[Mn^{IV}{}_4O_4]^{8+}$, surrounded by eight atoms (xMn^{III} and (8-x)Fe^{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 carboxyferrocen lead to the formation of $[Fe_3^{III}O(FcCOO)_6(DMF)_3]ClO_4$, 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 $[Ln_2(CNCH_2COO)_6(H_2O)_4]$, (Ln = Eu^{3+}, Nd^{3+}) and polymeric, with the composition $\{[Ln(OOCCH_2CN)_3(HOOCCH_2CN)]\cdot 5H_2O\}_n$, (Ln = Sm^{3+} and Dy^{3+}) (A. Lăzărescu, C. Turtă et al.), $\{FeSr_2(SalH)_2(Sal)_2NO_3(DMAA)_4\}_n$, $[FeBa_2(SalH)_3(Sal)_2\ (DMAA)_4(H_2O)]_n$, $\{[Ba(H_2O)_4Co(Pdc)_2(H_2O)]\cdot 3H_2O\}_n$, ($SalH_2$ = salicylic acid, DMAA = dimethylacetamide, $PDCH_2$ = pirydindicarboxylic 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, CaX2 (X=Cl, Br, I, NCS, NO_3, ClO_4) gave a set of complexes where the ratio Ca: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 Cu^{2+}, Eu^{3+}, Nd^{3+}, Gd^{3+}, Sm^{3+} with Schiff bases were synthesized, obtained as a result of condensation of 2-hydroxy-3-carboxynaphtaldehydes with various amines (aliphatic, aromatic), sulphanylamides, amino acids, thiosemicarbazide etc. with the following chemical composition: $\{Cu(Lig)Ln(NO_3)(H_2O)_x\}$, (Lig = $H_4L^1{}_,$ Ln= Nd, x=6; Eu, x=4; Gd, x= 6; Lig= H_4L^2, Ln= 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 (Ţ. 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. Testemiţanu" (N. Negreaţă, 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 I^st (1962), except for the IX^th edition (1987), which was held in Novosibirsk (Russia). The XVI^th edition of the conference will be held in 2009. Since 1985, this conference is entitled "Physical methods in coordination and supramolecular chemistry". The XXII^th International Ciugaev Conference (2005) in the field of Coordination Chemistry, was also held in Chisinau.

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ADVANCES IN ORGANIC, BIOORGANIC AND NATURAL PRODUCTS CHEMISTRY IN THE INSTITUTE OF CHEMISTRY OF THE ACADEMY OF SCIENCES OF MOLDOVA

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Abstract: This overview deals with the advances in the investigation in the field of organic, bioorganic and natural products chemistry as well as the biologically active compounds in the Institute of Chemistry of the Academy of Sciences of Moldova.

Keywords: organic and bioorganic chemistry, natural products, biologically active substances.

Research in the field of organic and bioorganic chemistry started in 1956, in the Laboratory of Organic Chemistry of the Chemistry Section of the Moldovan Branch of the Academy of Sciences of the former USSR, under the guidance of Professor Gh.V. Lazurievschii. In 1957 the above-mentioned section has been reorganized into two separate ones: of organic and inorganic chemistry. The Institute of Chemistry of the Moldovan Branch of the Academy of Sciences of the USSR has been founded on 15 April 1959, at the same time the section of organic chemistry being transformed into the Laboratory of Chemistry of Natural Compounds. The activity of the newly formed laboratory was focused both on the study of vegetal resources of the republic, and of natural and synthetic organic biologically active compounds. The investigation of two classes of natural organic compounds: alkaloids and terpenoids constituted the main orientation of research at that time. This chemical study has been performed on a large number of spontaneous and cultivated plants, as well as on wastes remaining on the processing of vegetal raw material, both of theoretic and practical value. Over 750 species of local plants were tested for alkaloid′s presence (almost half of Moldova′s florae). As a result, three plants were selected for further studies: periwinkle, meadow-rue and Parma buirush. A high content of alkaloids has been found in Parma buirush (*Carex brevicollis D.C.)*. The discovery of a plant belonging to the *Cyperaceae* family and containing alkaloids, have already represented a great success, as scientists used to consider these plants inadequate as alkaloids sources. The overall extract obtained from *Carex brevicollis* contained 7 alkaloids, three of which were on record, and four being the new ones: brevicollin, brevicarin, dehydrobrevicollin and homobrevicollin. The structure of these alkaloids and the absolute configuration of brevicollin have been established, the synthesis of brevicarin and brevicollin has been performed, as well as their mutual transformations; the biosynthetic pathway for brevicollin has been elucidated and its biological activity has been studied (I.V. Terentieva, P.A. Vember). Brevicollin proved to be an excellent ganglion blocker, possessing also hypotensive activity. It has been introduced onto medicinal practice by the Pharmacologic State Committee of the Ministry of Health of the former USSR. Subsequently, in 1977, brevicollin has been admitted for utilization in the field of veterinary. While studying the alkaloids of Parma buirush, the chemistry of indole has been developed. As brevicollin and brevicarin are derivatives of β-carboline, a synthetic investigation on them has led to the elaboration of a new method of synthesis of β-carboline derivatives. (A.A. Semenov, C.I. Kucicova). A series of new bioactive compounds has been obtained by the condensation of indole and its derivatives with dicarbonyl compounds (G.I. Junghietu). Chisinau became the centre of investigation of indole derivatives; four colloquiums dedicated to the chemistry of indole were organized in Chisinau (1963, 1967, 1971, 1975).

Research related to the chemistry of terpenoids started with the study of compounds, isolated from vegetal wastes generated during the distillation of essential oils from clary sage, lavender, mint, etc. A quite accessible compound has been found – sclareol, a diol isolated from the sage *Salvia sclarea L*. It was found that it is present in the plant in a mixture with its epimer at C-13. The method of their isolation has been elaborated, and their derivatives have been obtained. On the basis of sclareol, nitrogen containing derivatives with spasmolytic and bactericidal properties have been synthesized (D.P. Popa).

Special attention was paid to the study of stereochemistry of a series of labdanic diterpenoids. The absolute configuration at the chiralic C-13 centre was established for various diterpenoids: sclareol, labdanolic acid, manoyl oxides and their derivatives, for which contradictory data were published. (P.F. Vlad). Similar problems have been overcome in the case of elucidation of the geometrical configuration of labile isomeric dienols, the abienols (12-cis and trans; cis- and trans-neo- and iso-abienols) (P.F. Vlad, A.G. Russo, M.N. Colța). Subsequently, these synthesized compounds were discovered in natural sources, as well.

In 1963 systematic studies started, related to superior terpenoids, isolated from a series of plant species belonging to the *Labiatae, Umbeliferae and Compozitae* families. Over 50 polyfunctional new diterpenic compounds possessing complex labdanic and clerodanic structures were extracted from these plants and subjected to detailed studies in order to obtain new physiologically active compounds and solve several taxonomic problems (D.P. Popa, A.M. Reinbold, T.M. Orgheian, L.A. Salei). A series of new compounds were isolated from the *Stachys sylvatica L.*, belonging to the *Labiatae* family, bearing a complex cauranic structure, which were used for the systematics of this plant family. For this reason, taxa were described from the chemical point of view for the first time (D.P. Popa, G.S. Pasecinic).

Wastes obtained after the distillation of essential oil from lavender were used to isolate triterpenic acids: ursolic and oleanolic, as well as the diterpenoid kaurenic acid. On their basis, a series of nitrogen containing derivatives has been synthesized, as potential biologically active compounds. Several of these compounds were used as the stationary optically active phase during gas-liquid analysis (B.N. Kalyan).

The composition of the commercial odorant product ambroxide has been established, all the steps of its obtaining from sclareol having been optimized. On the basis of the neutral non-saponificable part of the oxidation product of sclareol with chromic mixture, the odorant compound ketoxide has been obtained and introduced in practice. The acidic part of the oxidation product, which constituted ~45% of its mass and represented a harmful environmental waste, was used to synthesize the odorant product ambrol, and the technology of its preparation has been introduced. Also, the method of reduction of norambreinolide to sclaradiol was optimized, using instead of potassium borohydride as reducing agent, the *in situ* obtained lithium borohydride, from potassium borohydride and lithium chloride, in isopropanol. This method has also been introduced into production. Regarding the last stage of production of ambroxide– the dehydratation of sclarodiol into ambroxide- two new efficient reagents were proposed: the products of interaction of dimethyl sulfoxide with trimethylsilyl chloride or bromine. As a result, the production of odorant compounds from sclareol became almost wasteless (M.N. Colța, E.A. Vorobieova, N.D. Ungur). The chemical composition of the commercial product ambrial was established (P.F. Vlad). A large number of oxidic odorants with tetrahydrofuranic and tetrahydropiranic decalinic and hydrindanic structures belonging to the norlabdanic series were synthesized (M.N. Colța, N.D. Ungur, A.N. Arîcu). Their study demonstrated that the Ohloff triaxial rule, explaining the presence of ambergris odour in the case of decalinic compounds, did not possess prediction force. A new logico-structural and electron-topological theory was proposed revealing the dependence of amber odour on the structure of compounds. (I.B. Bersuker, A.S. Dimoglo, P.F. Vlad, M.N. Colța). Subsequently, the same approach was used for explanation of the dependence of musk odour on the structure of compounds with this odour. (A.S. Dimoglo, P.F. Vlad, I.B. Bersuker).

On the basis of norambreinolide, a series of derivatives with rearranged carbonic skeleton were synthesized, several of which having a strong amber fragrance (L.A. Zadorojnaia, I.P. Dragalin).

In order to obtain norlabdanic derivatives, which can serve as starting material for drimanic sesquiterpenoids' synthesis, the synthesis of high terpenoids and tobacco aromatizators, the ozonization reactions of a series of labdanoides (sclareol, larixol, neoabienols, 13-epitorulosol, isoabienol and sclareoloxide) were studied in detail. As a result, efficient procedures of obtaining of drimanes, sclareoloxide, norambreinolide and ambreinolide were elaborated (A.N. Arîcu). On the basis of norlabdans and labdans, several dozens of tobacco aromatizing compositions were obtained (M.N. Colța, I.P. Dragalin, G.N. Mironov, A.N. Barbă, A.N. Arîcu, N.D. Ungur, V.N. Kulcițki). Many of them were introduced at the Chisinau Tobacco Factory. For elaboration and introducing of this work, P.F. Vlad and M.N. Colța, along with their collaborators from the Chisinau Tobacco Factory were rewarded with the State Prize in the field of Science, techniques and production in 1996.

In 1965 the Laboratory of Chemistry of Natural Compounds started research on triterpenic glycosides, extracted from cultivated plants (sugar beet, bean, sunflower, cucumber), as well as spontaneous plants. The structures of over 30 triterpenic glycosides of oleanolic and echinocystic acids, hederagenine, soya-sapogenin C and cucurbitacine B were established. These glycosides contain 5-7 sugar units in their molecules. For the first time, L-ribose was found amongst the sugar units of glycosides. A fast method of photometrical determination of bitter compounds, cucurbetacins, in cucumbers was elaborated and introduced in practice, being especially appreciated by selectioneers. (V.Z. Cirva, I.P. Dragalin). Subsequently, starting with 1971, the research was also focused on steroidal glycosides, isolated from various plant species. Steroidal glycosides are categorized into furostanolic and spirostanolic. The anticancer activity of these compounds was studied and it was found that only spirostanolic glycosides possess such an activity (P.C. Chintea). As a reward for the obtained results in glycosides studies, acad. G.V. Lazurievschii and Dr.hab. P. Chintea got the State Prize for science, techniques and production.

In 1975 the laboratory of Chemistry of Natural Compounds has been divided into Laboratory of Chemistry of Steroidal Compounds (ruled by Dr. P.L. Ceban) and Laboratory of Chemistry of Isoprenoides (ruled by Dr. D.P. Popa). The Laboratory of Chemistry of Steroidal Compounds continued the research on steroidal glycosides; several dozens of such compounds were identified. It was discovered that spirostanolic glycosides possess a high fungicide activity against phytotrophic fungi, which attack plants of the *Solanaceae* family (P.C. Chintea, V. Bobeico, N. Maşcenco, S. Şveț). The Laboratory of Chemistry of Isoprenoides continued the studies of polyfunctional diterpenic compounds with labdanic rearranged structure and of kaurenic compounds, as well as the research of products of oxidative transformation of sclareol.

In 1976, a new restructuration of the organic chemistry department took place and research directions were changed, the focus being set on solving a series of applied issues, important for the economy of the state. The Laboratory of Chemistry of Steroidal Compounds was reorganized: the group of researchers, involved in the study of steroidal compounds, managed by P.C. Chintea, has been transferred to the Institute of Genetics of our Academy. The remaining researchers joined to the Laboratory of Chemistry of Isoprenoids, thus forming the Laboratory of Chemistry of Essential Oil Plants (managed by P.F. Vlad). The Laboratory of Chemistry of Isoprenoids was reorganized into the Laboratory of Chemistry of plant's growth and development regulators (ruled by Dr. D.P. Popa).

After reorganization of the organic chemistry department in 1977 the investigations were directed to the obtaining of physiologically active compounds, useful for agriculture, production of essential oils, perfumery and food industry.

The pedo-climatic conditions of Republic of Moldova are favourable for cultivation of many aromatic plants. In parallel with the production of common essential oils from clary sage, lavender, fennel and others, botanists investigated the possibility of introducing into culture of the new local ethero-oleaginous spontaneous plants, as well as acclimatization of several plants brought from abroad. This plan could not be carried out without a significant chemical assistance. The Laboratory of Chemistry of Essential Oil Plants studied the qualitative and quantitative chemical composition of essential oils obtained from *Tagetes signata Bar.*, *Majorana hortensis Moenchi*, several species of absinth (*Artemisia*): *A.Gmelinii Web ex Stechm., A. pontica L., A. Alba Turra, A.haloleuca Bieb.ex Bess, A.balhanorum Krasch,* from *Oryganum heracleoticum L., Perilla fructescens L.*, from a series of hyssop species (*Hyssopus): H.montana, H.meretacens, H.Aristatus, H.canescens şi H.officinalis),* from *Calamintha Mill* (I.P. Dragalin). The chemical composition of the oil obtained from the Vietnamese medicinal plant *Stahlianthus Companulatus* has been studied (N.D. Ungur, Nguen Van Hung). The method for obtaining the anetol from fennicol was elaborated (I.P. Dragalin). The fermentolysis of monoterpenic glycosides obtained from rose plants was studied, and on the basis of this research a new fermentation method was elaborated for obtaining rose oil (P.L. Ceban, A.G. Russo, I.P. Dragalin). A new procedure of sclareol isolation from clary sage concrete was elaborated (M.N. Colța, G.N. Mironov), as well as of isolation of 13-episclareol from its natural mixture with sclareol (P.F. Vlad).

Research in the frames of Laboratory of Chemistry of plant's growth and development regulators was focused on obtaining the new biologically active compounds, which would contribute to the fortification of the adaptation potential of cultivated plants and increase their resistance towards harmful environmental factors. A special attention was directed to analogues of natural phytohormones and their synergists, the most efficient and harmless compounds. Perspective preparations were obtained on the basis of succinic and phtalic acids, terpenic retardants were synthesized, as well as kaurenic derivatives with gibberrillinic activity. A large number of analogues of abscisic acid, a phytohormon regulating various processes of plants development, were obtained. The synthesis of this hormone from ionone has been optimized. Alilcyclic, aromatic and heterocyclic analogues of abscisic acid were obtained as well. It was established that many of them exhibit a high activity as plants growth regulators and are of practical importance. (D.P. Popa, A.M. Reinbold, C.I. Cucicova, G.S. Pasecinic).

In 1991, the Laboratories of Chemistry of Plant's Growth and Development Regulators and Chemistry of Essential Oil Plants have joined into one research unit – the Laboratory of Chemistry of Terpenoids (under the leadership of P.F. Vlad). At present, the research of this lab is directed towards the synthesis of labdanic, norlabdanic and drimanic compounds and the electrophylic cyclization of aliphatic and partially cycled terpenic derivatives by superacid.

In the field of drimanic sesquiterpenoids, the following compounds were synthesized: drim-7-en-11-ol and its acetate, drim-9(11)-en-8α- and 8β-ols, driman-8α,11-diol, drim-7-en-9α,11-diol, drim-7-en-11,12-diol, drim-8-en-7-one, isodrimenine, drim-8-en-11,12-diol-7-one, 6α-acetoxy-drim-8(12),9(11)-diene and related compounds with ketonic groups in the C-6 position (M.N. Colța, C.I. Kucikova, E. Gorincioi, A.N. Arîcu, A.Gh. Ciocîrlan). Drim-8-en-11-oic and drim-8α-acetoxy-11-oic acids were obtained as well (G.N. Mironov). Recently, a group of drimanic diols and tetraols were prepared from drim-7,9(11)-diene (P.F. Vlad, A.Gh. Ciocîrlan, M.N. Colța). At present, the syntheses of nitrogen containing drimanes are performed (P.F. Vlad, C.I. Kucikova, A.N. Arîcu).

The second direction of research deals with the study of electrophylic cyclization of terpenoids. Tetracycloeicozanic compounds with a new carbonic structure were obtained on treatment of labdanoids with conventional acids (P.F. Vlad, M.N. Colța, N.D. Ungur).

Systematic studies were performed in the field of terpene cyclizations with superacids. It was established that labdanic compounds on superacidic treatment give tricyclic isoagatanic diterpenes in high yields. Natural compounds of spongian series were synthesized. The reaction of superacidic cyclization of alcohols, their acetates, of acids and their esters of C_{10}-C_{25} series was studied and it was found that the reaction is chemo- and structural-selective and stereospecific and gives cyclic compounds in high yields. The same regularities of the superacidic cyclization reaction were observed in the case of homo- and *bis*homo- terpenic derivatives. (P.F. Vlad, N.D. Ungur, Nguen van Hung, Nguen van Tuen, V.B. Perutki).

The utilization of this reaction in the sesterterpenic C_{25} series led to tetracyclic scalaranic compounds obtained from aliphatic terpenoids in one step in high yield, with the formation of a record number of 8 asymmetric centres.

Significant results were obtained on the interaction of sesterterpenic and diterpenic α,ω-bifunctionalized compounds with the superacid. In this case, the cyclization is initiated by the protonation of the internal double bond, giving cyclic derivatives containing an isoprene unit in the gem-dimethylic position. This reaction allowed us to perform the biomimetic synthesis of sacculatanic diterpenoids, difficult to obtain in other ways. Interesting results were obtained on the cyclization of terpenylphenylsulfones. When the phenylsulfonic group is situated in the middle of the sesterterpenic aliphatic chain, the superacidic cyclization afforded mixtures of scalaranic, heilantanic and rearranged heilantanic compounds (P.F. Vlad, N.D. Ungur, V.N. Kulcitki, M. Grinco).

In 1959, in the Laboratory of Chemistry of Natural Compounds, a group of researchers was formed, which performed the synthesis of organic compounds. In 1962, this research group was transformed into the Laboratory of Organic Synthesis (ruled by Dr. A.A. Şamşurin). The investigations were oriented towards the synthesis of bioactive compounds with antibacterial, antiviral, antifungal, antihelmintic activity, preservatives for winemaking and veterinary. This was one of the leading laboratories in the former USSR regarding the synthesis and utilization of pheromones for plants protection from pests.

The isolation, characterization and synthesis of the following attractants have been realized: disparliur (forest pests *Porthetria dispar*), propiliur (white American butterfly *Hyphantria cunea*), ghipliur (queen-bee *Apis mellifera* L.), (B.G. Covaleov, M.A, Rehter, L.A. Vlad, N.P. Dormidontova, R.N. Vascan, E.M. Alitmark).

Related to these syntheses, interesting results were obtained in the field of keto-aldehydes. Syntheses of cumarines were carried out, in order to obtain phytoestrogenic compounds. A new synthesis of cumestrol and its derivatives was elaborated, including the stimulator used in the field of veterinary - *STIMOL-410* (A.A. Samsurin, M.Z. Krimer, L.L. Simonova, V.I. Spector, L.P. Sineavskaia, O.M. Radul). A new method of synthesis of pyrocarbonic acid esters was performed, used as a stabilizators for semi-sweet wines. The products of their transformation were studied as well (A.A. Samsurin, O.E. Crivoşcecova, L.V. Curtev). Research related to compounds with juvenile activity was performed. It started with the synthesis of juvenoids known as the “Low mixture” and farnesilic acid derivatives (1968). New diastereospecific syntheses of active compounds and natural juvenile hormones I-III were elaborated. The bioactivity of the synthesized compounds was studied, as well as its dependence on compound’s structure. Interesting data were obtained on testing the activity of several juvenoide compounds against the Colorado beetle (M.Z. Krimer). Contrary to the existent data, is was demonstrated that compound 1-(4-fluorphenoxy)-7-metoxy-3,7-dimethyl-2E-octen (*PREPARATION AC-1*) induces the sterilization of this beetle (M.Z. Krimer, V.I. Spektor, L.L. Simonova).

In 1976, the laboratory of Organic Synthesis was transformed into the laboratory of Chemistry of Preservation compounds (managed by Dr. G.I. Junghietu). The synthesis and investigation of nitrogen-containing heterocycles were started. Investigations related to compounds with preserving properties for fruits, juices, beer, essential oils, and animal food were carried out. For these purposes, the hydroxamic acids were studied, as well as quinoline derivatives and mixed anhydrides of several acids (L.A. Vlad, N.P. Dormidontova). Preservatives for rose petals and fish spawn were proposed (E.P. Stîngaci). As an active preservative for refreshing drinks - *JUGLONE* was proposed (L.A. Vlad). Studies in the field of indole derivatives, isatine and quinoline were carried out. Compounds with antioxidant properties, antiviral and psychotropic properties, useful for medicine were obtained. One of the most efficient compounds was found to be *KETYSAL* – an indole derivative (G.I. Junghietu, E.P. Stîngaci, M.A, Rehter, O.M. Radul). New methods were elaborated for the synthesis of 1,2-dihydroquinolin-4-carboxylic acids, perspective compounds with antioxidant properties for protection of winery materials and preservation of animal gametes.

In 1983 Dr. M.Z. Krimer became the head of this laboratory. In 1985, on the basis of the Laboratory of Chemistry of Preservation compounds the Laboratory Chemistry of Pesticides was created (ruled by Dr. M.Z. Krimer) and a new research direction was chosen: elaboration of new compounds for plants protection and new methods for their production. The main research direction becomes the synthesis and study of 1,2,4-triazole derivatives. New methods for the synthesis of N-alkyl derivatives of 1,2,4-triazole, 1,4-ditiones, *t*-butylmethylketones were elaborated and the conditions of their selective obtaining were ascertained. A new rearrangement of the triazolyl methyl ketones enolacetates was discovered (E.P. Stîngaci, M.A. Rehter, O.M Radul).

In 1991 the laboratory returns to its original name – Laboratory of Organic Synthesis.

The synthetic method and technology for obtaining the systemic fungicide tilt (*PROPICONAZOL*) were elaborated, as well as its structural components: 2,4-dichloroacetophenone, 1,2-pentandiol and 1,2,4-triazol, and the alkylation reaction of 1,2,4-triazols (M.Z. Krimer, G.V. Roitburd, I.B. Kalyan, S.I. Pogrebnoi). A series of hydroxyl-derivatives of 1,2,4-triazols were synthesized (E.P. Stîngaci). Investigations were carried out in order to obtain azols and amides of several aliphatic acids (F.G. Shepeli, M.Z. Krimer, F.Z. Macaev). Novel methods were elaborated for the preparation of cyclohexanolic and cyclopentanolic derivatives, which contain nitrones and ketoximes structural fragments (F.Z. Macaev, I.B. Kalyan).

In 1999 Head of Laboratory of Organic Synthesis becomes Dr. hab. F.Z. Macaev. The main research direction was the synthesis of heteroatomic alkyl, aryl and heteryl aliphatic and cyclic compounds.

Starting from acetophenones, benzoic and salicylic acids, syntheses of five-member heterocycles, contained 1,2,4-triazol, oxadiazol, pyrazol, thiazol, and 1,3-dioxolan fragments, were performed. Initial acetophenones were transformed to corresponding phenacyl bromides, 1,3 –dioxolanes, 2-bromomethyl-2-phenyl-1,3-dioxolanes, and chalkones. It was shown that ketalization of phenacyl bromides gives higher yields of 2-bromomethyl-2-phenyl-1,3-

dioxolanes then bromination of 2-methyl-2-phenyl-1,3-dioxolanes (F.Z. Macaev, S.I. Pogrebnoi, E.P. Stîngaci, L.A. Vlad).

Reaction of phenacyl bromides with benzalguanidine was investigated, and it was shown that the nature of reaction products depends on the ratio of initial reagent: when the ration is equimolar, derivatives of 1,2-diamino-4-phenylimidazole were obtained; using of two equivalents of phenacyl bromide leads to derivatives of imidazo-[1,2α]-imidazole (F.Z. Macaev, S.I. Pogrebnoi, E.P. Stîngaci).

At the first time it was shown that using one-pot reaction it is possible to transform available chalkones to very stable pyrazolines with a high yield. It was shown that derivatives of acetophenones with pyrazolin and oxindol fragments possess an antidepression activity (F.Z. Macaev, S.I. Pogrebnoi, E.P. Stîngaci, L.A. Vlad, F.G. Shepeli, O.M. Radul). Based on hydrazides of benzoic and salicylic acids, the synthesis of 5-aryl-2-thio-1,3,4-oxadiazoles was performed. A number of synthesized compounds possess a high antituberculosis activity (F.Z. Macaev, S.I. Pogrebnoi, E.P.Stîngaci, L.A. Vlad, G.G. Rusu, A.P. Gudima, Z.Yu. Ribkovskaia).

The syntheses of the natural antifidant cryptomerlone and monoterpene carvone were elaborated for the first time. It has been found that effective method for the preparation of common precursor of above compounds is electrochemical anode oxidation of α-pinene (F.Z. Macaev, L.A. Vlad, A.P. Gudima). It was found, that chiral chlorohydrins or quinolines may be selectively obtained from the pinonic acid (F.Z. Macaev, O.M. Radul, A.P. Gudima).

A number of heterocyclic derivatives of 2,2-dimethylcyclobutane, some of which possess the potential *anti*-HIV-1 activity was synthesized (F.Z. Macaev, O.M. Radul, A.P. Gudima). General methods for stereoselective synthesis of optically active biologically active pyretroids and clerodane compounds and of their precursors were developed from (+)-3-carene, and of (-)- and (+)-carvones (F.Z. Macaev, S.I. Pogrebnoi, L.P. Bets). A series of enantiomeric pure derivatives of 2,2-dimethylcyclopropane, cyclohexanones and octalines were prepared in regio- and stereoselective manner. Among heterocyclic analogues of permetrine, perspective compounds were discovered with anti-inflammatory, fungicide, antimicrobial and insecticide properties. A new method for the preparation of clerodane polyfunctional diterpenoids was developed. Stereoselective syntheses of natural biologically active diterpenoids – antifidantes Lupuline C and (-)-dihydroclerodine from (-)-R-carvone was performed. The most important part of the developed method is initial diastereoselective introduction of hexahydro[2,3-*b*]furane fragment on position C-2 of 3-methylcarvone using Mukayma's reaction, and then the selection of conditions for the annulation of cycle A to corresponding octalines with desired stereochemistry at the atom C-10 of clerodane (F.Z. Macaev).

New N-alkyl isatines as well as spirooxindoles were synthesized (F.Z. Macaev, S.I. Pogrebnoi, O.M. Radul, E.P. Stîngaci, N. Sucman).

New functionalized imidazolium salts that can be classified as ionic liquids were synthesized in an attempt to design specific organic solvents. (F.Z. Macaev, E.P.Stîngaci, V. Sargorovschi, L.P. Bets, N.S. Sucman). On the example of (+)-3-Carene, have identified the appropriateness's of Kondacov's reaction and acetoxymethylation using novel imidazolinium ionic liquids. (F.Z. Macaev, L.A. Vlad, L.P. Bets, E.P. Stîngaci, V. Sargorovschi).

Among the asymmetric diamides of malonic acid, compounds capable to increase the myocardial contraction capacity were obtained, which induce blood vessels dilatation and significantly enhance the blood circulation. Several of these compounds were accepted in clinical trials and are currently on the way to be introduced into medical practice (F.Z. Macaev, F.G. Sepeli).

It was find that the nanosized catalytic system (~5-6 nm of γ-Fe_2O_3/CuO),works as an efficient organic phase catalyst (~0.02 mol%) in the one-pot three components Biginelli synthesis (F.Z. Macaev, E.P. Stîngaci, V. Sargorovschi).

Previously unknown *P**-mono, *P*,N*- and *P*,N**-bidentate phosphite ligands based on carenes and pinenes were found to be successful ligands for the Pd-catalysed allylation of 1,3-diphenylallyl acetate with $(Pr)_2NH$, $(CH_2)_4NH$, $PhCH_2NH_2$, $CH_2(CO_2Me)_2$ and 4-Me-$C_6H_4SO_2Na$. Obtained enantioselectivity up to 99% *ee* is the best result among all known optically active phosphites. In the Pd-catalysed deracemization of ethyl (*E*)-1,3-diphenylallyl carbonate, up to 96% enantioselectivity has been achieved. With participation of the novel P^*-chirogenic phosphite-type ligands excellent enantioselectivity was achieved in the Rh-catalysed asymmetric hydrogenation of some α-dehydrocarboxylic acid esters (up to 93-99% *ee*). (F.Z. Macaev, L.A. Vlad, L.P. Bet).

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QUANTUM CHEMISTRY IN MOLDOVA – 50 YEARS

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Abstract. An overview of the main achievements of the Laboratory of Quantum Chemistry of the Institute of Chemistry of the Academy of Sciences of Moldova during the 50 year of its existence is briefly outlined. The main fundamental "non-transient" result obtained in this laboratory is the generalization of the Jahn-Teller effect theory formulated and proved as a *general law of instability of polyatomic systems* and its application to a variety of physical, chemical, and biological problems, including al-range spectroscopy, geometry and spectra of molecular systems, structural phase transitions, ferroelectricity, stereochemistry and crystal chemistry, chemical activation and reactivity, electron transfer in mixed-valence compounds, and electron-conformational transitions in biological systems.

Introduction

Fundamental research in quantum chemistry in Moldova started in 1959 together with the organization of the Institute of Chemistry of the Academy of Sciences of Moldova (IC ASM) (till 1961 it was the Moldavian Branch of the Academy of Sciences of the USSR). Investigations on this subject were initiated by A. V. Ablov, an internationally renowned scientist with a bright vision and deep understanding of the progressive trends in science. At that time quantum chemistry in the Soviet Union was in its embryonic stage suffering from a blow from the ruling authorities for employing the "idealistic" resonance theory. Scared by that atmosphere of ideological dogmas many Soviet chemists tried to avoid direct involvement in quantum theory of electronic structure and chemical bonding. A. V. Ablov ignored these circumstances and took the risk to invite me, a theoretician, to join him in his laboratory and to start quantum-chemical investigation of his experimental results on optical spectra and magnetic properties of transition metal compounds.

At that time I had already my doctoral thesis from Leningrad University and teaching experience from Beltsy Pedagogical Institute. Soon I got my first research student Iu. G. Titova followed later by B. G. Vekhter, S. S. Budnikov, I. Ya. Ogurtsov, S. A. Borshch, V. Z. Polinger, S. S. Stavrov, G. I. Bersuker, M. D. Kaplan, N. N. Gorinchoi, and many others (see the list in [1]). In several years we advanced to the point that in 1964, after I got my next (D. Sc.) degree and some of my coworkers got their PhD degrees, the laboratory of Quantum Chemistry (hereafter LQC) was organized within the Institute of Chemistry.

In recent years the LQC had a bad time. Transit to independence, democracy and free market deprived Republic of Moldova from its decades established sources of rough materials and consummation markets. Lack of investments and very high unemployment further deteriorated the economic situation as a whole. Funding of basic research decreased sharply to the point that salaries went to the level of poverty and the laboratory buildings were not always heated in the winter months. In these conditions many workers of the LQC left the country seeking jobs abroad. From the many Ph. D. and Dr. Hab. of LQC only a small group headed by I. Ya. Ogurtsov survived and kept the LQC alive continuing its research trends. This was possible due to a series of international grants from USA and EU. The LQC is not only alive but has very interesting results in fundamental studies of structure and properties of matter.

50 years is a fair period to make some brief summary of the achievements of this laboratory. A part of the results obtained earlier are reviewed in previous publications [2], and in Ref [1] there is list of a major part of the original publications of the LQC. What follows is an updated brief outline of the main achievements of this lab. The main scientific interests revolve around the central theme known in the literature as the Jahn-Teller Effect (JTE), its generalization being discussed briefly in the next Section. In line of the development of the theory of the JTE and pseudo JTE (PJTE) and their generalizations, numerous applications of the theory to a variety of problems in physics, chemistry, and biology were worked out. These include al-range spectroscopy, structural phase transitions, ferroelectricity, stereochemistry and crystal chemistry, chemical activation and reactivity, electron transfer in mixed-valence compounds, electron-conformational transitions in biological systems, etc. Together with the doctoral theses of people from other research institutions supervised by the members of the LQC the number of PhD prepared in this lab counts for more than 50; 8 of them earned also the degree of "Doctor Habilitat". In view of the very large number of publications of this lab we cite here mostly some books and review articles [1-3, 6-68] that make links to the other (many hundreds of) original publications, occasionally mentioning also original works where necessary. Many of these publications are reviewed and cited in the two recent books [1, 3].

Fundamental achievement: general law of instability of polyatomic systems.

Before going to mention more particular achievements of the LQC I should like to briefly discuss the following question: as a result of half a century work are there any achievements of this laboratory that may be considered as "non-transient", meaning a fundamental, general, and rigorous result that on merits remains in science forever? In my judgment the answer to this question is yes, this laboratory has such a "global" contribution to the theory of structure of matter. This achievement can be formulated as follows: development of *the concept of vibronic interactions.* In the literature this trend is more often cited in its applications aspect as *the Jahn-Teller Effect* (JTE). As a generalization of the concept of vibronic interactions and JTE the *general law of instability of polyatomic systems* was formulated, proved, and confirmed by experimental data.

What is the essence of this result and why may this achievement of the laboratory be considered as fundamental and "non-transient"?

The works on these issues began at the very onset of quantum chemistry investigations at the IC ASM. At that time (1959) there were no studies of the JTE in the Soviet Union and only a couple of papers on this subject published in International journals (including the first one by H. Jahn and E. Teller [4]). The first formulation of the JTE was that *nonlinear molecules in electronically degenerate states are unstable with respect to spontaneous distortions that remove the degeneracy*. This simple statement was shown to lie in the base of a variety of novel effects and applications in physics, chemistry, and biology. The LQC made essential, sometimes seminal, contributions to this field partly discussed briefly in the next sections of this paper. There are many other authors contributing to this field; a review of the trend as a whole can be found in our recent book [3].

But what we claim as a more "global" achievement is the *generalization* of the original JTE and PJTE related to systems with exact degeneracy or near-degeneracy (quasidegeneracy) to *any and all polyatomic systems* in degenerate and non-degenerate states. We proved that the original JTE is just a part of a more general phenomenon that relates possible instabilities and distortions of any polyatomic (molecular or crystalline) system to the presence of two or more electronic states (degenerate or non-degenerate) that become mixed under the nuclear displacements. We formulated a *general law of instability* and distortions of polyatomic systems: *The necessary and sufficient condition of instability and distortions of high-symmetry configurations of polyatomic systems is the presence of two or more electronic states that interact sufficiently strongly under nuclear displacements in the direction of instability.* This result is most general and rigorous; it is based on first principles of quantum mechanics.

The JTE is just a particular case of this law when the energies of the two or more electronic states are degenerate or near-degenerate (in the latter case it is termed PJTE). Obviously, the number of JT systems is rather limited. The formulated above law of instability *includes any system* and (what is essential) *excludes other sources* of instability. The requirement of strong enough interaction between the electronic states limits the cases of possible distortions by the condition of the pseudo JTE, and these states are conventionally termed pseudodegenerate. Thus the formulated law of instability is indeed a global property of matter relevant to all imaginable distortions and symmetry breaking, e.g., chemical reactions, electron-conformational transitions, lattice formation and phase transitions, molecular motors and other biomechanical processes in biology, etc. All of these (and other relevant) phenomena are degeneracy (pseudodegeneracy) controlled making the law of instability a general tool of problem solving on the electronic level, as they can be treated by the extended JTE methodology [3].

An exciting development of this result followed when we found out that there is a similar conclusion in particle physics, namely, that "symmetry breaking is always associated with a degeneracy" [5] (this statement includes also the particle analog of pseudodegeneracy). Relating this result to the above law of instability of polyatomic systems we can state that *Nature tends to avoid degeneracy by means of symmetry breaking.* The "global" meaning of this statement may be hardly neglected.

Tunneling splitting in JT systems

One of our earlier results in the JTE theory was the prediction of the splitting of the vibrational levels of systems with the JTE. Since in many cases the JT distortions produce several equivalent minima of the APES, it occurred to us that if these minima are deep enough and there are localized states in them, there may be a special type of quantum-mechanical tunneling between the minima resulting in specific tunneling splitting of the vibrational levels in the minima [1, 3, 7, 10, 11]. If the system is prepared in one of these minima (which is usually the case), tunneling corresponds to a kind of pulse motions in which the system "jumps" from one minimum of the APES to another, equivalent, but with another direction of the JT distortion, realizing a new kind of molecular motions. This phenomenon was initially predicted in one of the first publications of the LQC in 1960, and it was later multiply conformed experimentally. Together with many important consequences this achievement (after official support by ten research institutions of the USSR) was qualified as a "Scientific Discovery" registered in the USSR in 1978 under No 202 [15]. In further development of the idea of tunneling splitting several students and coworkers of the LQC took part including V. Z. Polinger, B. G. Vekhter, I. Ya, Ogurtsov, and others.

The problem of tunneling splitting acquired a new twist in recent years in relation to the problem of the topological (Berry) phase. The latter emerged initially from the JT $E\otimes e$ problem where, because of the conical intersection on the APES, the electronic wavefunction is not single-valued, and to make the total wavefunction single-valued (as required by quantum mechanics) a special phase factor should be attached to the nuclear wavefunction. This additional phase (often called Berry phase) changes the ordering of the vibronic energy levels of the system and makes the ground state double degenerate. In our works in the 60s the ground state emerged nondegenerate, so there was a problem that remained unexplained for many years. In several recent papers [1, 3, 51] it was shown that if the quadratic terms of vibronic coupling are sufficiently strong, the Berry phase problem disappears as there are four conical intersections instead of one, and the ground state becomes nondegenerate in accordance with our earlier results.

Origin of instability of molecules and crystals

We already mentioned in Section 2 the general law of instability as one of the most fundamental achievements of the LQC. But the way to this result was long and laborious. The starting point was the JTE which states that high-symmetry configurations in degenerate states are unstable with regard to JT active nuclear displacements, and this effect may remain also in cases when instead of exact degeneracy of the electronic states there is near degeneracy (called pseudodegeneracy) provided the energy gap between the interacting states Δ is small enough as compared with the vibronic coupling parameter F and the rigidity of the system K_0. The pseudo JTE was assumed to be a second order perturbation theory effect that may be significant only for very small Δ values. We started by questioning this understanding. Presenting the curvature of the APES in the direction of instability K as a sum of the primary (non-vibronic) part K_0 plus the vibronic (pseudo JT) coupling to excited states K_v, $K=K_0+K_v$, we have shown *K_0 is always positive*, $K_0>0$, and hence a negative curvature (instability) can be obtained only due to the negative PJT contribution K_v provided it is large enough, $|K_v|>K_0$ [1, 3, 28, 39]. If only one excited state |1> contributes to the PJT mixing to the ground state |0> under nuclear displacements Q, $K_v=-F^2/\Delta$, and $F=\langle 0|(\partial H/\partial Q)_0|1\rangle$, so we get a tool of prediction if, where, and why instabilities occur.

The meaning of this result is very significant: $K_0>0$ means that all the instabilities of high-symmetry configuration of any polyatomic system are due to and only to the pseudo JTE. We have also shown that from the interatomic bonding point of view the distortions occur due to the formation of additional covalency between the atoms via the overlap of their orbitals that is zero in the high-symmetry configuration. We used these ideas of instability and distortions to reveal the origin of a variety of phenomena and performed many electronic structure calculations; all of them confirmed numerically the theoretical predictions [1, 3, 22, 39, 52, 57]. Section 2 above and several Sections below discuss some of these results. Most of the works on this topic were performed by V. Z. Polinger, N. N. Gorinchoi, I. Ya. Ogurtsov, F. Chimpoesu, O. V. Yaltichenko and others.

Origin of ferroelectricity. Cooperative JTE.

Works on the PJTE problem brought us in 1964 to the understanding that structural phase transitions in dielectric crystals should be of the same PJT origin [1, 3, 8, 16, 44]. While the cooperative JTE in crystals with JT centers was already revealed at the time, the cooperative PJTE was entirely unknown as the very possibility of a strong local PJTE was not well known and practically ignored.

In the best known ferroelectric crystal $BaTiO_3$, starting with the ionic presentation, the Ti^{4+} ion in the high-symmetry configuration is in the center of the octahedron of O^{2-} ions, and the ground state of the local TiO_6^{8-} cluster is a A_{1g} term formed by occupied linear combinations of the oxygen atomic 2*p* functions, while the first excited term T_{1u} is formed by an one-electron excitation from a t_{1u} molecular orbital to the unoccupied t_{2g} combinations of the $3d_{xy}$ type atomic functions of the Ti^{4+} ion. We succeeded to show that the PJTE $(A_{1g}+T_{1u})\otimes t_{1u}$ results in instability of the centro-symmetric position of the titanium ion, its displacements producing a local dipole moment, and the cooperative interactions of these dipoles leads to the spontaneous polarization of the crystal [8, 44].

The APES for the Ti^{4+} ion has eight equivalent minimum positions at which the ion is displaced along the trigonal axes of the oxygen octahedron, and the energy barriers between them form two types of saddle points which can be thermally overcome. In this picture all the qualitative properties of the $BaTiO_3$ ferroelectric were reproduced including the three phase transitions between the four phases (three ferroelectric phases and the para-phase), the direction of polarization in each of them, and their relative temperatures of occurrence.

The most exciting result was the prediction that only the lowest rhombohedral phase is fully ordered, the other three ones being partially disordered, meaning ordered in some direction and disordered in others. In particular, the cubic para-phase (which is macroscopically not polarized) was predicted to be fully disordered, formed by the thermal averaged positions of the Ti^{4+} ion over the eight equivalent minima. All the predictions of the theory were afterwards multiply confirmed by a variety of experimental data [1, 3, 44]. It is especially suggestive that the PJTE is practically independent of temperature, and hence the Ti^{4+} ion should be displaced along one of the trigonal axis (toward three oxygen atoms) *in all the phases*. This effect is seen explicitly in all the experimental direct measurements. No existing and dominating at the time theories of displacive phase transitions can explain this phenomenon. The works on this subject were realized by B. G. Vekhter, A. A. Muzalevskii, V. P. Zenchenko.

Independently, a series of investigations on the cooperative JTE and structural phase transitions with several applications were published and reviewed in a book on this subject by M. D. Kaplan and B. G. Vekhter [45].

Multimode and multicenter JTE. Mixed-valence compounds

Our LQC attacked the JTE problem from different sides and at different levels. In particular, we treated one of the most difficult JTE problems when there are more that one JT active modes of given symmetry which may take place already when there are more then three atoms in the system, and the number of active modes increases with the number of atoms tending to infinite for active centers in crystals. The latter case is especially important for JT impurity centers in crystals meaning center with a JT or pseudo JT effect. In a series of papers several aspects of this problem were investigated including the influence of the multimode JTE on the vibrational spectrum in infrared and Raman spectroscopy, as well as in ESR spectra [3, 22, 39]. Off-center impurities were also considered in this multimode aspect [19, 30, 39]. Works on these issues were performed by V. Z, Polinger, G. I. Bersuker, and A. Solonenko.

The multicenter JTE is obviously more difficult that the usual one-center one as it includes also the interaction between the centers, but it is also much more complicated than the infinite-center one in crystals where the symmetry of translation essentially and cooperative treatment simplifies the problem. In the QC lab the two-center, tri-center, and four-center problems were successfully solved and a variety of properties predicted, in particular, magnetic properties [24, 39]. Most contributions to this work are due to V. Z. Polinger, L. V. Chibotaru, M. L. Rafalovich, and S. A. Borshch.

In some overlap with the multi-center problem is the one of mixed-valence compounds. The QC laboratory was one of a few in the world to develop the theory of vibronic coupling implication in these systems [1, 3, 23, 42]. For both the general case and specific systems the relation between vibronic coupling constants and the rate of electron transfer between the mixed-valence centers in view of the localization-delocalization alternative was elucidated and their more specific pseudo JTE influence on this process was investigated in view of their optical and magnetic properties. In particular, for tri-center systems the phenomenon of coexistence of localized and delocalized states was revealed for the first time. A similar effect was found in four-center systems. The problem of multi-level centers and the so-called double-exchange interaction was also advanced significantly. As model systems, for some aspects of the problem tri-center and four-center ferredoxins were studied [1, 3, 42]. Works on these issues were performed by S. A. Borshch, I. N. Kotov, L. V. Chibotaru, I. Ya. Ogurtsov, and B. S. Tsukerblat.

Chemical activation and reactivity

Among the many chemical and biological applications of the JTE carried out in our lab chemical activation by coordination occupies a special place. We succeeded to reveal the intimate mechanism on why and how the weak interaction of a small molecule with the coordination center of a catalyst or enzyme results in its becoming more chemically active (acquiring larger reactivity) in interaction with other species, and we obtained analytical formulas for estimation of the reduction of the activation energy in such catalyst enhanced reactions [1, 3, 32, 57]. The basic idea of our approach is based on the understanding that the main effect of coordination is orbital charge transfer, and that the bondings in the coordinated molecule is weakened by charge transfer to its antibonding molecular orbitals (MO) or from the bonding MO's realized via the vibronic coupling of these MO's to the nuclear framework. The solution of this problem was essentially simplified by using the introduced earlier in our lab orbital vibronic constants [22] which are now used also in a variety of other problems. We applied the theory of vibronic activation by coordination to quite a number of activation problems, mostly to activation of diatomics by transition metal systems including biological systems (e. g., activation of oxygen by hemoproteins [38]). Contribution to this part of works are due mostly to S. S Budnikov, S. P. Svitin, I.Ogurtsov, N. N. Gorinchoi, I. Balan, V.Mirzac, and others.

Most related to the catalyst problem is the activation of a molecule by the JTE or pseudo JTE. It was shown that these effects lower the activation energy of reactions that proceed in the direction of JT or pseudo JT active coordinates. The latter are determined by the degeneracy of the electronic state in the presence of the JTE or by the symmetry of the active excited state in case of pseudo JTE [1, 3, 48].

Applications to biological systems

In application of the vibronic theory molecular systems we focused our attention also to active centers in biological systems. Transition metal centers and other prosthetic groups are of special interest in application of the JTE and the pseudo JTE for two reasons: (1) they possess degenerate or sufficiently close electronic energy levels and (2) their environment is relatively very soft to distortions (they have size dependent soft modes). Our treatment of several biological problems with the vibronic theory confirmed these statements [1, 3, 38].

One of these problems was the origin of the trigger mechanism of hemoglobin oxygenation. It was shown earlier that the hemoglobin's fast absorption of oxygen in an oxygen environment and its release of the oxygen in no-oxygen environment is due, respectively, to the out-of-plan (without oxygen) and in-plan (with coordinated oxygen) positions of the iron atom with respect to the porphyrin ring in the hemoprotein center, and the in-plan motion triggers electron-conformational changes resulting in the four-center cooperative absorption oxygen in the former case and its release in the latter one. We proved that the out-of plane displacement of the iron atom is due to the pseudo JTE, and its in-plan return by oxygenation is due to the quenching of this effect by coordination of the oxygen molecule [38].

This electronic mechanism improves our understanding of biological processes and provide us with tools to control them.

In the case of cytochrome P-450 which has a similar hemoprotein as an active center oxygen coordination produces the same quenching the pseudo JTE and the iron atom moving in-plan, but because of another environment this iron atom motion results in a breakdown of a hydrogen bond and an excess electron occupying an antibonding orbital of the oxygen molecule thus strongly weakening the O—O bonding.

The pseudo JTE is also instrumental in explaining the geometries of small ligand coordination to hemoproteins and their behavior in flash photolysis [38]. Most of the works on this subject is due to S. S. Stavrov and I. P. Dicusar.

Hidden JTE

Further developments of the JTE theory lead us to the so-called *hidden JTE*. We have shown that when molecular systems are distorted, but there are no apparent degeneracies or close in energy states to claim pseudo JT interaction *the JTE are "hidden" in the excited states* of the undistorted configuration, even when the energy gap to these states is very large. For the example of the ozone molecule (which has no degenerate ground state, neither in the distorted obtuse-triangular nor in the undistorted regular triangular configurations, and it has no low-lying excited states) the distortion is shown to emerge from the JTE in the excited E state situated at ~8.3 eV above the ground state. The JT stabilization energy is more than ~9 eV which makes the distorted configuration the lowest in energy [60, 63]. For molecular systems with half-closed-shell electronic configurations e^2 and t^3 (formed by degenerate orbitals e and t), which produce totally symmetric charge distribution and are not subject to the JTE, distortions were shown to occur due to a *strong pseudo JT mixing of two excited states*. Again, the pseudo JT stabilization energy in these cases is larger than the energy gap to the ground state, and the distortion is accompanied by *orbital disproportionation.* In some systems this produces two coexisting states, low-spin distorted and high-spin undistorted, and a novel phenomenon: *JT-induced spin-crossover*. Distinguished from the known spin-crossover in transition metal compounds the JT-induced spin-crossover takes place in a large variety of molecular systems from different classes including organic compounds, and it has a much lower rate of relaxation between the two states; this makes them candidates for single-molecule materials for electronic devices. Ab initio calculations of the hidden JTE were performed on a series of molecular systems from different classes [62, 64, 65]. These works were carried out in cooperation with the Theoretical and Computational Chemistry group of the University of Texas at Austin.

Theory of physical methods of investigation

Quite a number of works were devoted to the theory of a variety of physical methods, especially for systems with the JTE. These include first of all spectroscopy in all ranges of wavelengths including band shapes and zero-phonon lines of optical absorption and spectroscopy, birefringence, infrared and Raman spectra, ESR , gamma-resonance (Mossbauer) spectroscopy, as well as magnetic susceptibility, diffraction of X-rays and electrons, and others [18, 21, 29, 31, 33, 36, 40]. Many members of the LQC contributed to this trend including B. G. Vekhter, I. Ya. Ogurtsov, V. Z. Polinger, S. A. Borshch, L. A. Kazantseva, V.L. Ostrovskii, V.P. Khlopin, Iu. V. Shaparev, and Iu. E. Perlin.

Electronic structure calculations and molecular modelling

In the earlier years of existence the QC laboratory had no sufficient computers for electronic structure calculations, so the earlier works with such calculations were performed using analytical methods and semiempirical calculations and more emphasize was put on novel qualitative results and their physical meaning. For quite a number of small to moderate molecular systems electronic structure calculations were used to reveal the origin of the chemical bonding, reactivity, and spectra [12, 48]. In further development of the semiempirical methods some improvements were introduced and appropriate computer programs worked out. In particular, a method of fragmentary calculations was suggested [53]. Of particular interest was the semiempirical quasirelativistic approach which happened to be the first application of relativistic theory to MO LCAO calculations [14]. Ab initio methods were worked and applied to calculations of the PJTE [28, 55], as well as hidden JTE and origin of distortions of linear molecules [62, 65], and to evaluate important chemical processes, e.g., to reveal the mechanism of activation of oxygen on transition metal coordination systems [59, 60]. These works were carried out with Iu. G. Titova, S. S. Budnikov, B. A. Leizerov, M. A. Baraga, A. S. Dimoglo, S. M. Bardina, F. A. Spataru, I.Ya.Ogurtsov, L. Baciu, N. N. Gorinchoi, and V. Z. Polinger.

In more recent years a method combined quantum-classical calculations of large metallobiochemical systems was worked out and applied to specific calculations in collaboration with the Theoretical and Computational Chemistry group of the University of Texas at Austin. In this method the active site is calculated in the usual quantum-chemical (QM) approximations, whereas the larger (biological) part is evaluated by means of molecular modelling (MM) with a special interface between them. Distinguished from other QM/MM methods worked out earlier by other authors, our method takes into account the charge transfer (CT) between the QM and MM parts which is most important when the QM part contains transition metals. Our QM/MM/CT method is the only one that is able to take into account this charge transfer [53].

Stereochemistry and crystal chemistry

Obviously, the JTE has direct influence on the formation of molecular shapes, crystal lattices, and other properties of polyatomic systems controlled by the electronic structure. A variety of such problems were considered in QC laboratory among which we mention here the phenomenon of *plasticity* of the coordination sphere around some transition metals, formation of distortion isomers, and the origin of the active and inert lone pairs [1, 3, 13]. The plasticity effect came out to be very useful in understanding the origin of different coordination symmetries for the same transition metal (mostly Cu(II)) in the same first coordination sphere. We have shown that such differences take place due to the JTE which makes the coordination sphere "soft" to the influence of the rest of the lattice. The publication on this effect [13] got a record number of references (more than 500).

A method of computer-based prediction, screening, and design of biological activity

In a more practical aspect, the so-called electron-conformational (EC) method of computer-based prediction of biological activity in drug design and toxicology was worked out in the LQC and applied to a large number of relevant problems [41, 56, 68]. Distinguished from other methods with the same goal known mostly as quantitative structure-activity relationships (QSAR), the EC method uses the quantum-chemical calculated electronic structure of conformations as the unique descriptor of their activity in the interaction with the bioreceptor and does not employ statistics at the stage of pharmacophore and toxicophore evaluation, thus making the results most reliable (within the accuracy and completeness of the training set). Supplemented with an empirical parameterization of the anti-pharmacophore (and other) influence of out-of-pharmacophore groups, the EC method yields predictions of the activity quantitatively, while the pharmacophore (or toxicophore) itself, presented in the form of a numerical matrix of electronic structure parameters, can be conveniently used also for screening new compounds with respect to the activity under consideration. Works on this topic were carried out by A. S. Dimoglo, M. Iu. Gorbachov, I. N. Choban, I. Ya. Ogurtsov, N. N. Gorinchoi,

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THE SCHOOL OF ECOLOGICAL CHEMISTRY FOUNDED BY ACADEMICIAN GHEORGHE DUCA

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Abstract. This review details the most important achievements in the field of ecological chemistry and environmental protection, obtained at the State University of Moldova and Institute of Chemistry of the Academy of Sciences of Moldova. The main research directions are described, as well as main scientific laboratories and centres of these two institutions.

Keywords: ecological chemistry, redox catalysis, activated carbons, environmental pollution.

Scientific research in the field of ecological chemistry and physico-chemical mechanisms which occur in the environment were initiated in the frames of the *Department of Physical Chemistry*, by prof. A. Sîciov. A very important part of scientific research performed in the field of oxidation-reduction catalytic processes was carried out in the frameworks of the Physical Chemistry department, by prof. V. Isac. Intensification of this research field led to the formation, in 1988, of the scientific laboratory *Applied and Ecological Chemistry*, one the initiative of acad. Gh. Duca. In the 80's, under the direction of prof. A. Sîciov, research was performed in the field of chemical and photochemical oxidation-reduction processes, related to transformations in model and real systems of hydroxy acids, phenols, several pesticides; also, the role of hydrogen peroxide and variable valence metal ions in these processes was determined (A. Sîciov, Gh. Duca, M. Gonța, L. Romanciuc).

On the basis of the obtained experimental results, the monography "Catalytic reactions and environmental protection" was edited [3]. Beside the study of processes of transformation of various compounds in aquatic systems, investigations concerning transformations of nitrites, nitrates and formation of N-nitrosamines were initiated in the early 80's (Gh. Duca, M. Gonța).

The research directions in the frames of the SL of *Applied and Ecological Chemistry* were always up-to-date. However, in order to widen the possibility of solving environmental problems, training of highly qualified specialists in the field of ecological chemistry was necessary.

Therefore, on the initiative of acad. Gh. Duca, the *Department of Industrial and Ecological Chemistry* was founded at the State University of Moldova, in the frames of the Faculty of Chemistry and Chemical Technology. This was the first department in the country, in the field of ecological chemistry and environmental protection, which started preparing students and PhD's at the specialty *Environmental protection and rational utilization of natural resources.*

The first manual of ecological chemistry was edited in 1994, and subsequently translated in three languages [1]. In 1996, the *Centre of scientific researches in Applied and Ecological Chemistry (CSRAEC)* was founded, comprising 4 scientific laboratories. Research performed at the department, in the frames of CSRAEC laboratories, was directed towards *Chemistry and Technology of Industrial Processes and Treatment of Water and Wastes* and was crowned with important elaborations, such as:

- Oxidation theory of waters chemical self purification process and of seasonal dynamics of natural waters redox state
- Theory of fluid reactors of nitrogen compounds transformation using support-immobilized microorganisms
- Theory of the redox state of the environment
- Methods of physico-chemical and biochemical treatment of solid waste and waste waters
- Methods of inhibition of formation of N-nitrosamines using reductons
- Mechanisms of catalytic and photochemical oxidation of organic compounds with oxygen, hydrogen peroxide and free radicals.

Scientific Laboratory „Ecological chemistry of aquatic systems" (PhD V. Gladchi, PhD N. Goreacev, PhD L. Romanciuc)

One of the most important particularities of the environment consists in the fact that changes usually occur at rates exceeding those of development of control and prognostication methods. Often, ecologically unfavourable phenomena are only ascertained, without the possibility of preventing them. In order to reduce this discrepancy, is required a new method of treating the processes which happen in the environment, taking into account that this is a chemical-physical-biological whole and unique system. Therefore, the necessity of knowing the chemical, physico-chemical and biochemical processes of interaction between living organism and the environment, appears to be crucial in order to provide a qualified description and management of the equilibrium state of ecosystems, given the increased anthropogenic activity.

For an adequate estimation of the ecological state of natural waters, various research methods must be used, which include studying physical, chemical and biological processes which occur in aquatic ecosystems. Chemical processes in the aquatic medium, which are related to the oxidation of some compounds, and the reduction of others, occur catalytically or under the influence of solar irradiation. The catalysts in such processes are ions and complex compounds of transition metals, present in natural waters.

Among oxidizing equivalents present in aquatic systems, the most important are the dissolved oxygen and hydrogen peroxide [1,2]. The specifics of these oxidants is their quite low reactivity, thus the majority of them needs to be activated using metal ions, such as copper and iron. Although redox-catalytic processes in aquatic systems are numerous and various, all of them are based on a limited number of typical reactions. The most efficient method of estimating the mechanisms of chemical processes in the aquatic environment, is their modelling, i.e. separate study in laboratory conditions using a certain number of parameters which can be experimentally determined. The study of mechanisms of transformation of various compounds in the frames of these model systems allows explaining the processes which take place in natural ecosystems, and suggests methods of diminution of their pollution.

Transformations of many chemical compounds in the aquatic medium are accompanied by the formation of free radicals which actively participate in processes of chemical self purification of natural waters. The equilibrium of oxidation and reduction processes form a special state of the aquatic medium – *the redox state*, notion proposed by us in collaboration with Russian scientists [3-6]. It consists in detecting the oxidation and reduction flows, as function of the intensity of oxidation and reduction processes in the aquatic medium. The oxidative state is determined by the presence of hydrogen peroxide, while the reducing state – by the presence of reducing compounds, which can be easily oxidized by H_2O_2.

Taking into consideration all mentioned above statements, the necessity of introducing and implementing new methods for characterization of natural waters state and estimation of their self purification capacity is of great importance. Therefore, during several last years, our attention was focused on research of kinetic laws related to chemical and photochemical self purification of aquatic systems, in the presence of increased amounts of various pollutants. Our investigations demonstrated that these processes have an important role in the totality of self purification processes occurring in natural waters [4,7].

Kinetic treatment of laws of chemical self purification process offer a unique opportunity to evidence the parameters which determine chemical transformations of pollutants by their interaction with other elements of the aquatic medium. This treatment doesn’t exclude utilization of traditional hydrochemical and biological methods used for ascertaining of natural waters quality and their dynamic characteristics.

For many years, we have collaborated with researchers from the Institute of Chemical Physics of the Academy of Science of Russia, in the field of studying the chemical self purification processes of aquatic medium, including the possible mechanisms of redox-catalytic transformations of pollutants, which involve dissolved oxygen and its active forms – hydrogen peroxide and OH radicals.

Initially, researches were performed in the frames of various model systems, and further the methods of determination of various kinetic parameters were widely approved for various aquatic objects of the Republic, in order to perform the ecological monitoring of natural waters. Methods of active redox components determination and of their seasonal dynamics in natural waters were elaborated, optimized and implemented: hydrogen peroxide, OH radicals, inhibition capacity of natural waters towards processing involving OH radicals. For the first time, these methods were applied for the estimation of the state of rivers Nistru and Prut.

The elaboration of kinetic methods for the complex estimation of the state of environmental aquatic objects is based upon the following fundamental principles.

An important oxidant in the aquatic environment is the dissolved oxygen, which is a quite inert substance in usual conditions. The oxygen cycle in water represents a fundamental factor which assures a normal activity of living organisms, and it is closely linked with other biogeochemical cycles. In the case of dissolved oxygen participation in chemical self purification processes of water, its reduction leads to the formation of several products, which posses high reactivity, and contribute to a more efficient occurrence of these processes.

The presence of hydrogen peroxide in natural waters is very important for self purification processes. It practically represents a carrier of oxidizing equivalents in the aquatic medium, being an intermediate product of reduction of molecular oxygen to water. Hydrogen peroxide accompanies the majority of redox transformations of H_2O and O_2, which proves its huge importance for the aquatic environment.

Catalytic activation of O_2 and H_2O_2 in real conditions may take place if reduced forms of transition metals ions are present in water – Fe(II) and Cu(I), which are catalysts for this process. Complex ions of iron and copper interact with H_2O_2 to give hydroxyl radicals, which posses a significant chemical and biological activity, as compared to other products of oxygen monoelectronic activation.

In the case when the penetration of hydrogen peroxide into natural waters is higher than the penetration of reducing agents, the concentration of hydrogen peroxide is higher than the stationary concentration of reductants. In this case, natural waters posses an oxidizing environment. However, if the stationary concentration of reductants is higher than that of H_2O_2, a reducing environment is installed, which leads to the diminution of self purification capacity of the aquatic environment. In this case, utilization of titration methods for the determination of redox equivalents will lead to the discovery of reductants instead of the oxidant. The reducing state is temporary, due to the presence in waters of dissolved oxygen, which will trigger the oxidation of all reducing equivalents [3].

The phenomenon of existence and importance of free radicals in natural waters is not widely discussed and studied. It is known [4] that the stationary concentration of OH radicals, the most active oxidant in natural waters, is quite low ($\approx 10^{-15} - 10^{-17}$M), but due to its high reactivity, it plays a very important role in regulating the composition and self purification of the aquatic environment.

The method of determination of the stationary concentration of OH radicals [7] consists in the determination of the ratio between two kinetic parameters – rate of initiation and effective constant of OH radicals' disappearance as a result of their interaction with the components of the aquatic medium.

Therefore, application of kinetic parameters, determination of the redox state of natural waters by the hydrogen peroxide content, their inhibition capacity and stationary OH radicals concentration, estimates the dynamic equilibrium between the oxidizing and reducing equivalents in natural waters, and may serve as an integral parameter of assessing the redox-catalytic balance inside the aquatic reservoir, the intensity of self purification processes involving OH radicals and to characterize the ecological state of the water reservoir.

The method of application of kinetic parameters conjunctively with traditional hydrological parameters was approved in the Republic of Moldova and is currently applied for the estimation of chemical composition and self purification processes in the waters of the Nistru river [8-10].

Obtained results show that a seasonal change in the redox state is characteristic for the waters of Nistru river. The general tendency for the autumn-spring period is the decrease of hydrogen peroxide concentration and creation of an unstable, or even quasi-reducing state of waters, from the point of view of redox equivalents – of hydrogen peroxide and reductants of peroxidasic type. During summer, the content of hydrogen peroxide increases up to 10^{-6}M. However, this increase is characteristic only for the sector Naslavcea-Cosăuți, while hydrogen peroxide is totally absent in the sector Boşernița-Dubăsari, downstream the dam.

The decrease of the H_2O_2 concentration during September-November, its insufficiency in March may be explained, on one hand, by the decrease of photosynthetical activity, the predominant role in H_2O_2formation in natural waters being solar radiation (which induces the formation of the superoxide radical anion $O_2^{-\cdot}$, the precursor of H_2O_2). On the other hand, in autumn decreases the temperature of waters, which is one of the physico-chemical parameters which influence the rate of redox-catalytic processes.

The values of registered H_2O_2 concentrations are mostly close to10^{-7} M, which is insufficient for an efficient realization of chemical self purification processes in waters. Beside these conclusions, it should be mentioned that processes of chemical self purification involving OH radicals, occur effectively in the waters of Nistru during summer, which can contribute to the increase of water pollution.

Obtained results evidenced that Nistru river waters continue to be polluted by reducing compounds which decrease the content of hydrogen peroxide in the aquatic reservoir, thus creating conditions for the instauration of a reducing environment of aquatic ecosystems – an unfavourable state for living organisms. The degradation of Nistru waters are due to the increased level of pollution of influents waters, as well as of domestic waters evacuated from riparian localities, and waters accumulated before the Naslavcea and Dubăsari dams.

These scientific results are only the beginning of a series of investigations regarding aquatic objects of the Republic of Moldova, which are now extending on Nistru influents– rivers Răut, Ichel, Bîc and Botna.

The investigations performed up to now, and those that are in progress, confirm that application of kinetic parameters in estimation of the state of aquatic objects represent a necessary addition to traditionally determined hydrochemical parameters. In the case of critical situations of various aquatic objects (perishing of fish, overflowing of huge amounts of pollutants etc.), the application of methods for the determination of hydrogen peroxide in water, of the inhibition capacity and of the stationary concentration of free radicals may become necessary for an immediate response to improve the situation, as well as for prognostication and pollution prevention.

Scientific Laboratory Redox-catalysis in water and foodstuffs

During last three decades, numerous investigations were performed for hazard assessment of persistent carcinogenic substances, which are harmful for humans. Among the large number of such compounds, N-nitroso compounds (NNC) are of special interest, 80% of which possess carcinogenic action and induce malign tumours in almost all human and animal organs.

N-nitroso compounds are formed quite easily inside the human body, in foodstuffs and tobacco smoke. The synthesis of these compounds occurs, predominantly, from secondary amines and nitrites or nitrogen oxides.

Scientific research in the field of carcinogenesis of these compounds, initiated in the 80's, developed in several directions up to date: (i)- monitoring of known NNC sources in the environment and foodstuffs, (ii) – determination of mechanisms of carcinogens formation and (iii)- elaboration of methods for the prevention of appearance and spreading of carcinogenic agents.

Therefore, one of the scientific directions is the *Transformation of nitrites, nitrates, formation of N-nitroso amines and utilization of inhibitors in redox processes* (acad. Gh. Duca, Dr. hab. M. Gonța, PhD I. Stepanov, PhD I. Subotin and PhD D. Porubin).

The study of kinetics and mechanisms of NNA formation on various environmental objects is of great importance for a correct understanding of the negative effects of NNA on living organisms [15]. Elaboration of several methods of inhibition of secondary amines nitrosation leads to the diminution of NNA concentration, which can be formed *in vitro* as well as *in vivo*. One of the most important results in this area is the elaboration of methods of inhibition of NNA formation using natural reductons.

The mechanism of inhibition of amines (aliphatic and cyclic) and amides nitrosation, using reductants obtained from secondary winery products (DFH_4, dimethyl ester of dihydroxyfumaric acid and DFH_3Na) was studied [10]. As a result of computational estimation of model systems used for nitrosation of various substrates with nitrite ions, species concentrations were determined and it was found that the concentration of the nitrosating agent N_2O_3 is almost twice greater than the concentration of NO^+. Te rate constants were calculated for the process of inhibition of MORF nitrosation using various reductants, obtained from secondary winery products, which may be presented as follows: $k_{inh}^{DFH}=1,8\ M^{-1}s^{-1} > k_{inh}^{EDMD}=1,4\ M^{-1}s^{-1} > k_{inh}^{(+)\text{-}Ct}=1,01\ M^{-1}s^{-1} > k_{inh}^{DFH3Na}=0,74\ M^{-1}s^{-1} > k_{inh}^{EDMT}=0,25\ M^{-1}s^{-1}$.

It was established that the formation of tobacco specific N-nitroso amines during fermentation is determined by technological processing, tobacco type, and may be inhibited by using dipotassium tartrate [14]. The short duration of the tobacco fermentation process determines a low content of TSNA in cigarettes produced in Moldova, while its sauceing, for longer periods and at higher temperatures, leads to the increase of TSNA in American cigarettes.

Inhibition activity of DFH_4 and DFH_3Na was determined, related to the process of nitrosation of metabolites formed in the gastric juice, at proteolysis of albumin and casein in the presence of various enzymes (pepsin, trypsin, chemotrypsin) and at nitrosation of nornicotine *in vivo* [16] . Analysis of the content of non-hydrolysed protein substrate showed that sodium hydrogen dihydroxyfumarate, used as an inhibitor of the nitrosation of the formed metabolites, doesn't influence the activity of specific enzymes. It was determined that DFH_3Na decreases the rate of formation of MetHb at oxidation of HBO_2 with nitrite ions, by decreasing the acceleration factor with the increase of reductons' concentration. The mechanism of action of sodium hydrogen dihydroxyfumarate on the process of oxyhaemoglobin oxidation with nitrite ions, was ascertained, and it was found that it is based on the interaction of the $OH^{\bullet}$ and $HO_2^{\bullet}$ radicals.

Using the DPPH-radical and the $ABTS^{+\cdot}$-cation-radical, the antioxidant/antiradical activities were determined for reductons obtained from secondary winery products, and it was found that the antiradical power of DFH_4 and DFH_3Na is comparable to the antiradical power of (+)-catechin and quercitin.

Also, research regarding *treatment of natural waters from nitrites and nitrates* was performed, using electrochemical methods (Gh. Duca, M. Gonța, V. Matveevici and V. Iambarțev), due to the fact that one of the most important source of nitrosation agents in natural waters are the NO_3^- ions. The main objective of these investigations was to achieve the maximal admissible concentration for nitrite and nitrate ions, during treatment of model systems, as well as natural waters. Results obtained in scientific studies showed that in the case of treatment of natural waters using the electrochemical method with soluble anodes of aluminium, iron and magnesium, the effect of diminution of nitrates and nitrites depends of the pH value, the intensity of the current and the amount of electricity [11].

Treatment conditions were optimized in order to achieve the MAC for nitrites and nitrates. As opposed to aluminium, the efficiency of treatment with soluble magnesium anodes is higher at a lower electricity amount (180-600 C), and the increase of Q (600-900 C) leads to a maximal efficiency in the case of treatment using soluble aluminium anodes. During electrochemical dissolving of aluminium electrode, additional monovalent aluminium particles are obtained, which are quite active when formed and participate in the process of nitrates reduction.

However, the increase of reduction of NO_3^- and NO_2^- occurs only till the optimal value of current density is reached. At a further increase of current density, the effect of NO_3^- reduction decreases, due to the increase of the anode potential. Therefore, at high values of anode potential, the elimination of oxygen due to water decomposition occurs concomitantly with electrochemical dissolving of aluminium. It was found that in the pre-anodic zone, the reduction of nitrites to free nitrogen or inferior nitrogen oxides occurs concomitantly with the reaction of reduction of nitrite and nitrates.

In 2006 in the frames of the Redox-catalysis laboratory, investigations related to *treatment of waste waters containing textile colorants* are continuously performed (Gh. Duca, M. Gonța, V. Matveevici and V. Iambarțev).

Textile industry is one of the most polluting industries, due to high amounts of waste waters evacuated into the environment. The mean value of chemical dose of oxygen (CDO) and of biochemical dose of oxygen (BDO_5) is in the range 11700-250 mg O/L and 3500-100 mg O_2/L. Treatment of such waste waters is quite difficult. Traditional methods for treatment of textile waste waters are inefficient, due to the large variety of these compounds in waste waters, as well as to their high concentrations. Destructive methods are far more efficient, when as a result of oxidation or reduction of dyes molecules, products are formed with smaller molecular weights, which may be adsorbed on activated carbons, or eliminated by a continuous oxidation at biological treatment stations.

Therefore, we initiated the study of the process of diminution of textile (direct and active) colorants concentrations from model solutions, during their combined treatment with aluminium coagulant and catalytic oxidation of dyes using hydrogen peroxide. The process was investigated as function of: coagulant amount, initial dyes concentration, treatment time, oxidant concentration.

As a result of scientific investigations, the conditions of waste waters treatment were optimized. It was found that the effect of diminution of direct dyes concentration at treatment of solutions with coagulants was 94-96%, and most efficiently direct dyes were eliminated from solutions with initial concentration of 200 mg/L and higher, which are characteristic to textile waste waters. However, it was demonstrated that a two-stage treatment of waste waters is more efficient. At first, it is necessary to decrease the concentration of direct dyes down to 8-12 mg/L during the first stage, and then to decrease it further during the second treatment stage (until the admissible concentration for evacuation in water reservoirs is reached) by adsorption of activated carbons, of by catalytic oxidation with hydrogen peroxide in the presence of iron(II) ions. In the case of optimal combination of coagulation with catalytic oxidation using hydrogen peroxide, the effect of diminution of direct dyes from model solutions with initial concentrations of 200 mg/L increases up to 97-98%, while the amount of coagulant and formed sediment decreases two folds. The method of catalytic oxidation has advantages, as compared to that of adsorption on activated carbons, as it leads to an advanced degradation and mineralization of organic dyes molecules, forming simple nontoxic compounds such as carbon dioxide and water, and some simple organic compounds, such as aldehydes, organic acids etc., which are already biodegradable.

Utilization of the catalytic oxidation method alone leads to the degradation and mineralization of direct colorants only from model solutions and waste waters with a low content of these dyes (50 mg/L at most).

In the case of active dyes, utilization of the coagulation method during the first treatment stage is inefficient (only 10-15% of the initial dye amount is eliminated using aluminium coagulants). Therefore, the oxidation method using hydrogen peroxide is applied in order to achieve a more significant decrease of dyes concentration in model solutions and waste waters. Results showed that using hydrogen peroxide in model solutions with initial concentrations of around 150-160 mg/L leads to an oxidation and mineralization effect of 78-84%. Remaining concentration of formed compounds may be decreased to that admissible by activated carbon adsorption. This treatment method allows the diminution of active dyes concentration from model solution in the case when iron(II) ions are used as catalysts. If ultraviolet irradiation is used to catalyze this process, the effect of oxidation and mineralization of dyes remains the same for dyes concentration of 50 mg/L. If the dye concentration increases, the effect of hydrogen peroxide oxidation at presence of UV irradiation decreases and the process becomes inefficient.

It is widely known that grape processing generates around 20% of wastes, which pollute the environment. However, these secondary winery products may be used to obtain various valuable compounds. Therefore, researchers of the department initiated scientific investigations in the field of *optimization of the process of obtaining of reductons from secondary winery products* (Gh. Duca, M. Gonța, A. Mereuța, I. Guțu and N. Marchitan). Scientific results led to the elaboration of a new, easier procedure of obtaining tartaric acid, which broadens the field of utilization of raw material, which contains tartaric compounds, increases the final product purity, assures a reduced consumption of chemical reagents and contains two know-how elements [13]. As opposed to the classical procedure, the proposed technology excludes the stage of calcium tartrate obtaining, due to the application of reactive extraction, which allows performing a selective extraction of tartaric acid from the aqueous solution using an extragent, such as th anionic resin "Amberlite LA-2" dissolved in an organic solvent – butyl acetate, which allows increasing the output and the purity of the final product. The crystallization of tartaric acid from the azeotrope mixture, which is formed when an organic solvent (in which tartaric acid is almost insoluble) is introduced into the water solution, is performed at the same time with the distillation of water from the mixture, thus decreasing the crystallization time, and increasing the purity rate. Installations of extraction, crystallization and drying of TA were elaborated. The pilot installation for the production of tartaric acid was mounted, and the technological regulation of production of tartaric acid from calcium tartrate was elaborated. Technical prescriptions were approved for the tartaric raw material (calcium tartrate, calcaric sediments, etc.); technical prescriptions for the final product (tartaric acid) were also elaborated.

Procedures of obtaining dialkyl tartrates, sodium dihydroxyfumarate [12] and dimethyl dihydroxyfumarate were elaborated; these compounds are important reductons suggested for utilization in the cosmetic industry. Cosmetic creams were obtained on the basis of diethyl tartrate and their reological properties were compared to the blank, according to the following parameters: viscosity, adhesion, shear tension; the compatibility of diethyl tartrate with the basic raw material was assessed, and it was demonstrated that this preparation cab be used for the production of cosmetic creams. On the basis of obtained experimental data, it was shown that substitution of lanoline with diethyl tartrate may be considered an admissible procedure, and that the diethyl tartrate containing cream is more stable in time than the lanoline containing cream.

The processes of extraction of tartaric acid from winery wastes were optimized, using solid anionites impregnated with amines, using the tertiary amine – tri-n-octylamine and the secondary amine lauryl-trialkyl-methylamine. It was found that solid and liquid anionites of Amberlite type, exhibit the highest performance: 93-96%. Tartaric acid was transformed into alkyl esters, and these were transformed into hydrazones and thiosemicarbazide derivatives. On the basis of tartaric acid dihydrazide, synthesized from dimethyl- or diethyl tartrate, the bishydrazones of salicylic acid and 5-nitrofurfurol were obtained. New bishydrazones of the 2-R-phenyl – 1,3- dioxolan - 4,5 – dicarboxylic acids and bis-thiosemicarbazides were synthesized. Synthesized compounds are potentially biologically active. Bis-hydrazones of salicylic acid and bis-thiosemicarbazide derivatives are of interest as complex formatting compounds with heavy metals.

Scientific laboratory „Electrochemical processes and clean technologies"(PhD O. Covaliov, V. Covaliov, V. Neno, V. Jalbă)

Researches in the frames of the laboratory of „Electrochemical processes and clean technologies" (1996-2008), address many scientific issues. One of the most significant problems for our country in this field is the cyanide pollution of waters. In order to solve this issue, a new economically advantageous procedure was elaborated, for the neutralization and utilization of wastes generated by the gelatine-tannin treatment of wines, which contain cyanide formed due to wines demetallyzation. This procedure is performed by separating the bentonite from the yeasts, using electroflotation and selective treatment of iron cyanides (Prussian blue) in alkaline medium, which gives micro fertilizers with nanodisperse structure and prolonged action, fungicide preparations, corrosion converters, new pigments and/or reagents for wines demetallyzation [24].

To produce the intensification of water treatment from persistent organic pollutants, new technical principles were elaborated for obtaining highly dispersed compounds of titanium oxides with nanostructural characteristics, by regulating their disperse phases and photocatalytic properties. New methods were elaborated for the deposition of multicomponent boron-containing catalytic layers on porous ceramic supports, and subsequent boron dissolving, for their concomitant utilization with nanodispersed metal oxides in the process of photocatalytic destruction of pollutants. A multi-functional electro-photocatalytic laboratory scale reactor was built, with high capacity of treatment and destruction of persistent organic pollutants of benzothiazol class [28].

Researchers studied the kinetic processes and the mechanism of photocatalytic transformations, in stages, of benzothiazol macromolecules, as well as of one derivative of benzothiazol, on the basis of modern physico-chemical methods. The following technical solutions were elaborated and tested on pilot scale, some of them with no analogues:

- new principle of treatment of waste waters containing sparingly biodegradable polyphenols using photocatalytic hydrolysis, and UV radiation, in order to improve the efficiency of the biochemical purification of water and the generated amount of biogas;
- new method of methanogenic synthesis of vitamin B_{12} in the composition of sediments which are formed during anaerobic treatment of waste waters;
- method of concentration and purification of biogas-contained methane, for its more efficient utilization;
- technology for obtaining nanostructured micro-fertilizers on the basis of biologically active metals («metals of life») for their introduction into soil;
- construction of the biochemical reactor on the basis of standard vessels existent at factories, with an automated system of controlling anaerobic fermentation [27].

Also, scientist of this laboratory developed a technology of microbial degradation of cyanides from wastes generated by gelatine-tannin treating of wine, concomitantly with soil enrichment with elements important for plants nutrition. Thus, these compounds were first solubilised using the waste generated by sugar production, in order to accomplish a faster and more complete microbial degradation of these compounds. A technology of obtaining combined fertilizers in various doses was elaborated and tested. This method allowed increasing the productivity of green mass by 14,1-15,0 centners/ha [22].

Scientists of this laboratory also elaborated other methods for destroying wastes generated by the gelatine-tannin treatment of wine: the oxido-thermal method and the utilization of sediments as nitrogen fertilizers, for selecting and assuring the implementation of the most effective method of those mentioned above, to eliminate the environmental hazard and to assure a direct economical success [23].

As to the treatment of waste waters, the particularities of magneto-hydrodynamical conditions of pseudo fluidization of aquatic medium were studied, related to processes of destruction of organic compounds with concomitant action of UV radiation. The magnetic field influences the increase of the efficiency of destruction of organic compounds by an additional action on the molecular structure of organic compounds. It was found that the values of CDO and CDO_5 of treated water decreases from 835 mg O_2/L and 378 mg O_2/L to 108 mg O_2/L and 37 mg O_2/L, respectively. At the same time, occurs the destruction of molecules of magnesium and calcium carbonates and bicarbonates, which determine water hardness. It was determined that the hardness of the water treated in such a way, decreases from 6,72 mg·equiv/L to 3,8 mg·equiv/L. The energy used on the account of UV irradiation constitutes 0,01-0,03 kW·h/m^3. The bacteriological action of UV light on water is exhibited by the formation of peroxides (H_2O_2), ozone O_3, as well as of active radicals, such as O^{2-}, HO_2^- etc. [21].

The influence of the anodic material on phenolic compounds transformation was studied, in conditions of electrochemical generation of active chlorine. The investigation of the process of electrogeneration of active chlorine, including NaClO, $NaClO_3$ and dissolved Cl_2, using broad graphite electrodes, showed that when the current intensity is of 2-5 A/dm^2, the output doesn't exceed 70-75%. Thus, the increase of output as function of the current (ή) was performed up to 93-95%, but the process occurred with the increase of hydraulic resistance. In order to eliminate this phenomenon, a new method of electrogeneration of active chlorine was suggested, where magnetite particles were introduced in a permanent magnetic field, formed by spherical particles of barium hexaferrite [5].

Scientists performed investigations regarding galvanochemical processes of production of aluminium containing coagulants. The mechanism of this process, which occurs on the account of internal electrolysis of the galvanic pair aluminium-carbon, was studied. The standard potentials of aluminium and caked coal are equal to $\varphi_0^{Al} = -1{,}662$ V and $\varphi_0^{C} = +0{,}792$ V, respectively, thus $\Delta\varphi \approx 2V$. This significant difference between potentials allows creating conditions when, during the contact of these materials, aluminium transforms into the anode and decomposes quite fast: $Al^0 - 3e^- \rightarrow Al^{3+}$. In the case of graphite, water electrolysis is possible, with oxygen involvement, giving hydroxide ions (OH^-): $H_2O + 1/2O - 2e \rightarrow 2\ OH^-$ which hydrolyze the Al^{3+} ions, forming intermediate complexes such as $[Al(OH)]^{2+} \rightarrow [Al(OH)_2]^+$ etc. In the presence of chlorine or fluorine ions, aluminium hydroxychloride is formed, with the general formula $Al_2(OH)_nCl_{6-n}$, known as an active coagulant. Coagulation characteristics of synthesized aluminium hydroxychloride were studied, and 6-8 fold increased efficiency was discovered, as compared to coagulation properties of aluminium sulphate, currently used in practices [26].

Many of the realizations achieved in the laboratory of *Electrochemical processes and clean technologies* were implemented, such as the technology of production of biogas – implemented at the winemaking factory Vinăria Bardar, which is an automated, semi-industrial installation for biogas production with a 35 m^3 capacity. Currently, the technology of detoxification of the sediment resulted during the gelatine-tannin treatment of wine is being implemented, as well as obtaining of new products, based on laboratory experimental installations.

Laboratory of scientific research „Atmosphere protection” (acad. Gh. Duca, PhD A. Crăciun)

Atmosphere protection is an important problem, and also a large area of investigation of ecological chemistry. Since 1996, researchers of the laboratory performed a series of investigations in order to diminish toxic emissions into the atmosphere during the activity of thermo-energetic aggregates and internal combustion motors:

- hydrogenation during combustion of hydrocarbon fuel;
- investigation of combustion of naphtha-water emulsion;
- investigation of combustion of natural gas using catalysts;
- utilization of electrical field to influence the flame during natural bas combustion;
- influence of the homogeneous catalyst on the efficiency of gasoline and diesel combustion.

A scientific project was accomplished in the frameworks of the laboratory, regarding the elaboration and investigation of high efficiency, environmentally clean plastic lubricant materials, on the basis of regenerable material – colza seed oil.

Also, applicative elaborations and investigations were performed, such as: hydrogenation during the combustion of hydrocarbonic fuel; investigation of combustion of naphtha-water emulsion and elaboration of installations for obtaining of naphtha-water emulsion. Combustion of this emulsion reduces the naphtha consumption by 10-12%, while atmospheric emissions are lower than admissible concentrations [17].

In order to perform the study of catalytic natural gas combustion, were elaborated the composition and technology of catalyst deposition of ceramic cell-type blocks, which are subsequently used in burners for natural gas burning.

The mixture gas-air is bubbled through catalytic layers, deposited on cell-type ceramics, and then burned. As a result of catalyst utilization, atmospheric emissions of carbon monoxide decreased 1,8 - 1,9 fold, and of nitrogen oxides - 1,6-2,5 fold [18].

Investigations related to the influence of the homogeneous catalyst on the efficiency of burning of gasoline and diesel, in internal combustion motors, were conducted using the catalyst “BIO-friendly” (SUA). As a result of these researches, it was established that environmental reduction of exhaust gases concentrations 1.5 – 1.9 fold in the case of diesel motors, leads to the diminution of grime content, which is a carrier of carcinogenic aromatic hydrocarbons. Due to its high efficiency (1,4-2,0 fold decrease of CO concentrations in exhaust gases, CH - 1,5-1,7 fold, NO_x - 1,3-1,6 fold, as well as reduction of gasoline consumption by 10%, and of diesel by 15% and absence of carcinogenic and mutagenic substances in its composition), the homogenous catalyst may be recommended as an additive for gasoline and diesel [19].

Utilization of electric field in order to influence the flame of natural gas combustion allows obtaining the following effects: increase of the flame temperature from 1100 to 1190^{o}C; reduction of CO concentration in burned gases from 1,2% to 116 ppm (0,12%). Utilization of this technology leads to a 5% saving of fuel [20].

Elaborations and investigations of high efficiency environmentally clean plastic lubricant materials on the basis of regenerable material (colza seed oil) led to obtaining plastic polyfunctional lubricants: for articulations with equal angular rates; for cold deformation processing of metals; electroconducting, which outrank prototypes used in Russia, Ukraine and some European countries.

Conducted scientific studies allowed elaborating pilot installations for obtaining of naphtha-water emulsion, for catalytic burning of natural gas, for studies related to the influence of electrical field on the flame of natural gas burning, for production of four samples of plastic lubricants.

Research in the field of ecological chemistry started at the *Institute of Chemistry the ASM* at the beginning of the 70's, when the laboratory „Mineral resources and the chemistry of water" was created.

For over 30 years, water quality of main aquatic resources of the Rep. Moldova has been studied, such as rivers Danube, Nistru, Prut, Răut, Bâc, accumulation lakes Dubăsari, Costeşti-Stânca, Cuciurgan, Ghidighici, Taraclia, Ialpug, Cahul etc. The results of these researches allowed establishing of processes and mechanisms of interaction of chemical components in the aquatic resources, as function of many factors, such as: temperature, reaction medium, dissolved oxygen concentration, anthropic pressing, turbidity, water flow rate, ionic force etc. (V. Ropot, M. Sandu, R. Lozan, T. Lupascu, G. Stratulat, V. Rusu, I. Dranca et al.) [29].

Also, investigations were performed on the processes and mechanisms of immobilization, migration and transformation of heavy metals, organic and inorganic compounds of nitrogen and phosphorus in the system water – matters, in suspensions – bottom depositions in the main aquatic resources of the Republic of Moldova (V. Rusu, T. Lupascu, L. Postolache) [30].

The obtained results formed the basis of evidencing the main laws of formation of natural waters quality, which are especially important for predicting water quality, theoretical ascertainment and implementation of surface waters potabilization technologies.

The quality of waste waters, generated by the main economical unities of the republic, was studied. The processes and mechanisms of coagulation, decantation, flotation, oxidation, adsorption of organic and inorganic pollutants, discovered in waste waters, on carbonic and mineral adsorbents, were investigated. The obtained results were used for the elaboration of technologies of purification of waste waters generated by agro-alimentary and textile factories. The most relevant results in this field are the elaborated technologies, which were implemented at the winemaking factory in Bălți, which allowed the purification of waste waters generated during wine distillation. Application of this technology allows obtaining tartaric acid and construction materials from the sediments formed after decantation of mineral adsorbents. A significant share of research in this field was performed under the direction of the regretted chemist and ecologist, Ph doctor in chemistry, Valeriu Ropot [31].

Another elaborated and implemented technology is the technology of treatment of waste waters generated at texture colouring sections of textile factories. Purified waste waters may be recycled into the technological process of texture colouring, thus saving potable water sources (T. Lupascu, M. Ciobanu, N. Timbaliuc) [32].

Provision of world population with high quality drinking water was always one of the most important goals to be achieved by humanity, from any point of view. This constitutes a significant problem for the Republic of Moldova, as well, considering that our country possesses limited amount of drinking water originating from surface and underground water sources.

Considering all stated above, the issue of elaboration of technologies for potabilization of surface and underground waters remains, as always, one of the main research objectives of the *Ecological Chemistry* laboratory of the Institute of Chemistry the ASM. During the years, research was performed in order to optimize the technologies of surface and underground waters potabilization. The chemical indices of water quality were studied following the treatment stages of the potabilization process of the Nistru and Prut waters. It was found that the currently applied technologies don't provide a high and stable quality of drinking water. Investigations showed that following the existent technological flux at potabilization stations, drinking water contains small amounts of organic compounds of chlorine, nitrogen and phosphorus. This leads to the conclusion that drinking waters contains small amounts of pesticides, trihalogenomethane etc.

The techniques leading to the enhancement of drinking water quality were studied, namely the substitution of the chlorination process with that of ozonation and the process of adsorption of persistent organic pollutants traces by their filtration on columns of activated carbons, obtained from fruit stones and nutshells. The obtained results demonstrated that the utilization of mentioned above processes allow obtaining high quality drinking water (V. Ropot, T. Lupascu, M. Nicolau) [33].

Underground waters of our republic play an important role in the provision of population and economical agents with drinking water, especially in rural zones. However, unfortunately, the analyses performed in order to establish the quality of underground waters evidenced that over 50 percent of these waters don't correspond to the standards of drinking water, and are characterized by an increased content of fixed residue, total hardness, fluorine, iron, ammonia, hydrogen sulphide, methane, chlorides, sulphates, nitrates, nitrites, manganese etc.

The presence of hydrogen sulphide in underground waters used for provision of the population induces various affection of human health. According to sanitary standards set for drinking water, sulphide ions must be absent. Analysis of scientific literature shows that there are several techniques and technologies in the world, dealing with the purification of underground waters of hydrogen sulfide. The most frequently used is the method of oxidizing sulphide ions by aeration in the presence of solid supports, including activated carbons. The main disadvantage of this technology consists in the fact that it results in the formation of colloidal sulphur, which clogs up the pores of the adsorbents, thus diminishing its catalytic activity. Also, heavy colloidal sulphur is hard to be removed through decantation and filtration.

During the last 15 years, the laboratory of Ecological Chemistry of the Institute of Chemistry the ASM deals with scientific research regarding the technologies of purification of underground waters from hydrogen sulphide and its salts. The analysis of gathered data allowed evidencing and selecting a catalyst based on activated carbons obtained from peach stones, with copper ions impregnated on its surface.

Utilization of mentioned above catalyst allows oxidizing the sulphur ions into thiosulphates, sulphates, sulphites, thus avoiding the formation of colloidal sulphur. This procedure is a global scale novelty, which was patented (R. Nastas, T. Lupascu, V. Rusu, M. Tcaci, Gh. Duca) [34]. At present, the scientist of the laboratory carry out scientific research which would allow obtaining catalyst that would oxidize sulphur ions in sulphate, avoiding the stages forming intermediate compounds. These investigations are performed in the frames of the project entitled „Optimization of technological processes of potabilization of surface and underground waters" which is part of the State Program entitled „Scientific and management research of water quality", headed by academician Gh. Duca. Sustainable economical and social development without the determination of environmental quality enforces an adequate waste management, without exhaustion of natural resources.

One very acute problem of ecological chemistry consists in rational valorisation of secondary products derived from grapes and fruit processing. In the Republic of Moldova, as the result of grapes processing, dozens of thousands of tons of grape seeds are obtained, which contain up to 16% oils, 14% tannins and other precious products.

Processing of peaches, plums, apricots, also results in thousands of tons of stones, which contain up to 5 – 7 % oil. Nutshells are obtained, as well, in amounts of hundreds of tones following the separation of nutmeat. All these are valuable raw materials for various valuable products necessary for the national economy.

During last 20 years, the scientists of the laboratory of *Ecological Chemistry* perform scientific research in order to elaborate technologies for the production of activated carbons from fruit stones, grape seeds and nutshells. As a result of performed investigations, were elaborated and patented dozens of procedures of activated carbons production using physico-chemical, chemical and mixed activation methods. The structural parameters, adsorption capacity and surface chemistry of activated carbons were estimated. Obtained results demonstrated that quality indices of local activated carbons are superior, or at least equivalent to those imported. Obtained activated carbons were tested in order to establish the possibility of their utilization for treatment of surface, underground and waste waters, as well as for the detoxification of human body. It was found that these activated carbons are extremely fitted for solving issues of ecological chemistry, namely for the protection of the environment and human health. On the basis of mentioned scientific research, 3 theses of dr. hab. and 3 theses of Ph doctor were proved (T. Lupascu, R. Nastas, V. Botan, V. Goncear, V. Rusu, M. Tcaci, M. Ciobanu, O. Petuhov) [35].

As mentioned above, grape seeds contain increased tannins amounts, which represent a series of natural compounds with polyphenolic structure. The interest towards these compounds is due to their antioxidant properties, i.e. these compounds trap free radicals, thus protecting the human organism from various diseases, such as cancer and cerebral ictus. The majority of enotannins are soluble in ethylic alcohol and insoluble in water. This hindrances the utilization of enotannins in various field, including pharmaceutics. The specialists of Ecological Chemistry Laboratory elaborated and patented a procedure of hydrosolubilization of enotannins. Using the method of mass spectrometry, it was found that the procedure consists in breaking catechin polymers of enotannins. As the result of this procedure, a new product was obtained, formed from monomers, dimers, trimers of catechin, polydentate carboxylic acids, peroxidic compounds etc. Microbiological, pharmacological and toxicological investigations, performed in the frameworks of the project „New preparations from grape seeds for medicine, veterinary and agriculture" and „Evaluation of activity of medicinal and agricultural preparations obtained on the basis of the biologically active compound Enoxil in clinical and field trials" in the frames of the State Program „Processing and utilization of winery wastes and obtaining of new compounds" directed by acad. Gh. Duca, demonstrated that Enoxil is not toxic, and possesses significant antifungal and antibacterial properties. On the basis of the active compound Enoxil, the medicinal preparations Enoxil-M and Enoxil-A were elaborated and tested in clinical and field conditions. Field trials showed that the preparation Enoxil-A increases the resistance of agricultural cultures by 60% towards the action of root rot, and of vine – by two folds, towards grey rot (T. Lupascu, Gh. Duca, L. Lupascu, P. Vlad, R. Nastas, G. Lupascu, V. Rudic, V. Crivceanschi, V. Gonciar, V. Ciobanu etc.) [36].

Clinical trials of the medicinal preparations Enoxil-M produced at „Farmaco" enterprise demonstrated a positive effect in the treatment of diseases induced by fungi and bacteria, of plagues provoked by thermal and surgical lesions.

Researchers of the laboratory of Chemical Ecology have been preoccupied by the utilization of wastes generated at the calcite mines in the vicinity of Chişinău for almost 20 years. As a result of these studies, 5 compositions of construction materials, with calcite powder as the main component, were elaborated and patented. The obtained construction materials are 30% cheaper as compared to analogical imported materials, and are qualitatively equal to them. Industrial scale production of new construction materials is carried out at the „Monolit" enterprise in Chişinău (T. Lupascu, V. Botan, V. Ungureanu) [37].

Investigations of mineral resources of Republic of Moldova (diatomites, bentonites, tripoles etc.) started in 1962 in the frameworks of the laboratory of Mineral resources, as it was called then. In 1972, it was transformed into the laboratory of Mineral resources and chemistry of water. These investigations continue in the present, in the frames of the Ecological Chemistry laboratory, which is the successor of the laboratory of Mineral resources and chemistry of water since 1992. During these years were performed studies of physical, physico-chemical and chemical properties of intact mineral adsorbents, as well as of those modified through chemical and thermal procedures (M. Cherdivarenco, V. Ropot, V. Rusu, A. Moftuliac, G. Stratulat) [38].

Sorption and cationic exchange properties of intact and modified adsorbents were studied. Humic acids, fulvic and carboxylic acids, natural and synthetic colorants etc. were used as adsorbates. The following cations were studied: Fe(II), Fe(III), Al(III), and Cu(II). The obtained results were used in surface waters potabilization technologies and waste waters purification technologies.

During last several years, special procedures led to obtaining of a wide spectrum of oligomers of aluminium oxy-hydroxy complexes, with charges ranging from $[Al_2(OH)_2(H_2O)_8]^{4+}$ to Keggin ion $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$. These oligomers possess properties of molecular sieves with pores bigger than of common zeolites, and a wide range of practical utility (V. Rusu, L. Postolache).

The continuous increase of the mean atmospheric temperature in immediate soil proximity, as well as of sea and ocean waters represents a universally accepted statement during last decades.

The mean air temperature in the vicinity of Earth surface increased by $0{,}74 \pm 0{,}18^{o}C$ during the last century. Global warming has a negative impact in various fields. Due to this phenomenon, glaciers and snow melt, leading to the increase of sea level, and "swallowing" by water of new soil surfaces, which are already insufficient for a proper food provision of the world population.

Temperature increase will lead to the migration of deserts towards more dump areas and, respectively, to the disturbance of the ecological equilibrium, established for thousands of years, including in the world of plants and animals species. Evidently, as a result of these changes, the physical and psychical state of man will be altered.

In order to diminish the negative effects of global warming, scientist seek new alternative sources of energy. Solar energy is the most perspective, and may be used in many different ways. The oldest and most common method is obtaining of biomass during photosynthesis. Mankind always used wood as an energy source. From the point of view of carbon cycle, this energy is environmental friendly, because plants developed using atmospheric carbon dioxide, and it is again emitted during plants burning, and again absorbed during photosynthesis. Biomass may be also used as raw material for obtaining biogas through chemical methods of anaerobic fermentation, and of biodiesel, bioethanol through chemical procedures and aerobic fermentations.

One of the global problems to be solved by mankind is obtaining hydrogen from water using solar energy. In order to solve this issue, billions of dollars and euro are currently spent. As a result, hydrogen will become one of the main "green" energy sources, necessary for mankind existence. Of course, today fundamental investigations are carried out in this field, in order to solve the problems of optimization of photolysis processes using various nanocatalysts, depositing, transportation and utilization of hydrogen.

Recently, such investigations were initiated at the *Centre of Physical Chemistry and Nanocomposites* at the Institute of Chemistry the ASM, directed by acad. Gh. Duca. We are confident in the future results of our scientists in this area.

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PHYSICAL METHODS IN CHEMISTRY INVESTIGATIONS OF THE CHEMISTRY INSTITUTE OF ASM

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Abstract. The following classes of compounds are presented: terpenes, cyclic nitrogen compounds, dioximates, carboxylates etc., which have been studied with the participation of experts on physical methods of research - IR, UV-Vis, Atomic, Mössbauer spectroscopy, as well as Mass-spectrometry and Nuclear Magnetic Resonance in the IC ASM. Also, a number of significant scientific results obtained in collaboration of chemists and specialists in physical methods are described.

Keywords: IR, UV-Vis, Atomic, NMR, Mössbauer spectroscopy, mass-spectrometry

Introduction

Many different modern physical methods are widely used for an ample characterization of new chemical substances synthesized in Institute of Chemistry of the ASM. Among them there are X-rays, Infrared, UV-Vis, NMR, ESR, Mössbauer spectroscopy, TG, Mass-spectrometry, Magnetochemisry, Spectral analysis etc. All these methods have been provided with necessary equipment and high skilled specialists. Over time the group of X-rays analysis was transferred in IFA ASM maintaining effective scientific collaboration.

Contribution of physical methods in chemistry investigations

IR, UV-Vis Spectroscopy

The idea to organize a spectroscopic group appeared as early as 1958 in the inorganic chemistry department of the Academy of Sciences of Moldova SSR, headed by Professor A.V. Ablov. At first, only the method of UV-VIS - spectroscopy was used to study the coordinative compounds of cobalt. As a result of these investigations, were discovered several new dioximates of Co (III) with a hydroxyl group (OH) in the intern sphere.

During the period from 1956 to 1958 eight scientific articles were published and one thesis entitled „Absorption of light by coordination compounds of trivalent cobalt" was proved by M.P. Filippov.

Further, the IR spectroscopy method was studied, which gave the opportunity to investigate the properties of coordination compounds in low frequency region. By the year of the establishment of the Institute of Chemistry of AS MSSR (1959) the spectroscopic team collaborated with all institute divisions.

Since the formation of the Centre of Automation and Metrology, the cooperation of the spectroscopic group was expanded to all institutions with an experimental destination. In addition to obtaining UV-Vis and IR spectra (annual ≈ 3000 spectra), the common scientific studies were conducted on topics of concerned institutes (Institute of Plant Physiology and Biochemistry, Institute of Applied Physics etc.). Shortly after, they published about 25 scientific articles.

A fruitful collaboration with the Winemaking Institute also took place: different methods of spectral analysis of wine, brandies and other wine products had been developed. The results of these investigations were presented in 13 publications, including methods of prevention of microcrystal tones, disorder of albumin and hydrogen sulphide or saponification.

In the Centre of Automation and Metrology the spectroscopic group collaborated with German company Zeiss Jena (GDR) and some Soviet Union institutes.

During the same period, some methods of investigation of pectin were developed according to household work contracts.

As a result, in 1989 the group leader of the spectroscopic team M.P. Filippov proved his Doctor habilitate thesis in chemistry [1]. Publications - 68 articles.

Mass-spectrometry

Mass-spectrometry (MS) is a widely used method for studying of gaseous substances. This method enables obtaining characteristic information about an investigated object, as it isn't affected by other effects (solvent, crystal lattice, interaction between molecules) during the study.

The development of mass-spectrometry in the Institute of Chemistry of ASM began with the purchase of installations MX-1303 (1968) and MX-1320 (1976). The objects of study were traditional for IC ASM and were dictated by the scientific topics of the Institute laboratories.

Most of organic substances are considered to be good objects for mass spectrometry studies. MS is particularly important in the investigation of natural substances, because processes of their preparation, separation and identification are very difficult. By studying the mass spectra of diterpenic alcohols of abienols, which are characterized by a high liability and common properties, interesting data have been obtained on their identification and development of methods for their efficient extraction and synthesis. It was found that MS can serve as a quick and adequate analysis of natural substances [2].

Izatine and its derivatives represent another class of organic substances studied with MS. The investigation of deuteride compounds gave the opportunity to suggest behaviour lows of this class of substances under the action of electron impact [3,4].

In the field of inorganic chemistry an ample study of coordination compounds was performed: monooximates, dioximates of Ni (II), Cu (II) and Pd (II) [5]; coordination compounds of 3d metal with Schiff bases, derivatives of thio- and selenocarbasides [6-12], of various metal (s, p, d, f) carboxylates [9-12]. As a result of these studies, various schemes were suggested for the general fragmentation under the impact of electrons, and were proven that there was a close correlation between the substances in the crystalline and gas states. Transition metal carboxylates (3d) proved to be more labile in the mass spectrometry study and suffer of different regrouping, as a result of which different polynuclear structures were detected. Mass-spectrometry data were used as points of reference to predict routes of synthesis of new substances with nontrivial nuclei [13,14].

Atomic spectroscopy for solving scientific and practical tasks

The laboratory of atomic spectroscopy was founded in 1979. The following analysis methods are carried out in this laboratory: atomic spectroscopy methods (atomic absorption, flame photometry, emission spectral analysis), molecular spectroscopy methods (photo colorimetric method) and chemical methods (volumetric, gravimetric method).

Utilization of the entire set of methods provides the most complete picture of the chemical composition of the analyzed samples. About 50 different parameters can be defined in the laboratory, more than half of which is done by the atomic absorption method. In addition, the emission spectral analysis provides an overview spectrum, where about 40 elements can be simultaneously determined semi-quantitatively, and about 20 items quantitatively.

These laboratory features are widely used by research institutes of the Academy of Sciences to solve various scientific and applied problems.

Among the major problems that were dealt with by the laboratory of atomic spectroscopy together with the Institute of ASM and other scientific organizations, the following tasks should be mentioned:

- regional analysis of ground and surface water;
- changes in micro-and macro-composition of plants, with their feeding and treating of various drugs;
- study of the soil, rocks and sediments composition;
- analysis of the effectiveness of water purification by various methods (electroflotation process, use of diatomite, activated charcoal etc.);
- analysis of various complex compounds;
- optimization of conditions for synthesis of propolis.

Among the applications, addressed to Moldovan economic agents, the following should be noted:

- study of the micro-and macro-components impact on wines and brandies quality, and methods to improve them;
- analysis of drugs quality;
- the influence of chemical composition on glass quality;
- study of underground waters stability;
- analysis of food products quality;
- analysis of the quality of drinking and mineral water;
- study of the slag composition from smelters, metal and alloys, sand, clay, etc. for industrial enterprises in Moldova.

For over 30 years, the laboratory of atomic spectroscopy participated in solving of a broad range of scientific problems for scientific organizations in other countries (SU, Moscow; SU Chernovtsy; Institute of Oceanology, Odessa; Institute of Glass, Romania). In collaboration with leading laboratories from other countries, it successfully participated in the certification of standard samples of soil, carried out by the Institute of Geochemistry in Irkutsk.

The laboratory is accredited by the Standards Department of the Republic of Moldova.

Mössbauer Spectroscopy (SM) method

Mössbauer spectroscopy operates in the Institute of Chemistry of ASM since 1975. From that date until present time all studies were conducted on isotope Fe-57. The five parameters of the Mossbauer spectroscopy are: the isomer shift, quadrupol splitting, magnetic hyperfine interaction, probability of Mössbauer Effect and peaks asymmetry (Fig. 1).

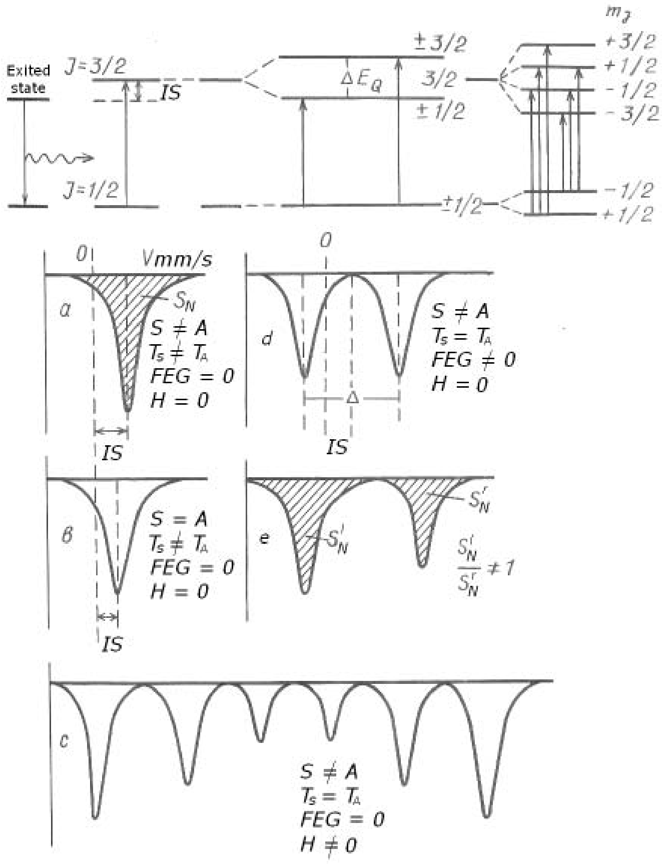


Fig. 1. Mössbauer Spectra Parameters: IS = Isomer shift; ΔE_Qor Δ = Quadrupole splitting; Probability of effect, S_N; Asymmetry of picks A = (S^l norm/S^r_N) # 1; Hyperfine magnetic interaction, H#0.

The values of obtained parameters provide researchers information about electronic structure of the Mössbauer nucleus environment and dynamic oscillations of an atom in the molecule crystal lattice. Many classes of chemicals, objects of solid body physics, biology samples as well as some archaeological items have been studied by Mossbauer spectroscopy. Different coordination compounds, ion changers, absorbents, oxides, etc. are studied among chemical substances.

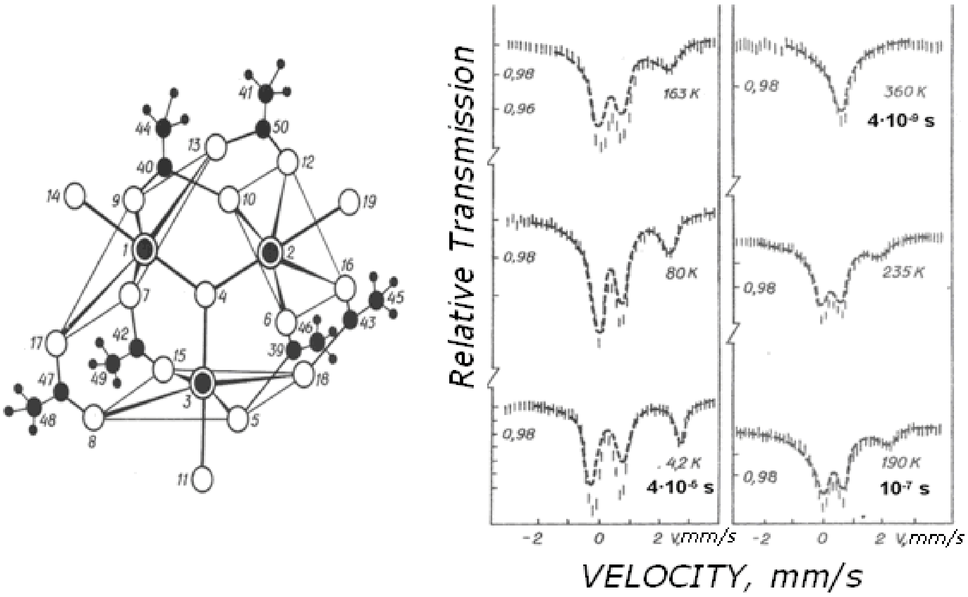


Fig. 2. Molecular structure of the cluster $[Fe_3O(O_2CCF_3)_6(H_2O)_3].3.5H_2O$ [16] and the Mössbauer spectra of iron acetate with mixed valence at different temperatures [15].

Next, several obtained scientific results will be detailed, which are of particular interest and that were the most cited in scientific literature worldwide.

An article was published on Mössbauer spectra of iron acetate of mixed valence in 1973 [15]. The temperature dependence of Mössbauer spectra of the complex $[Fe^{III}_2Fe^{II}O(CH_3COO)_6(H_2O)_3].2H_2O$ (Fig.2) shows that at low temperatures (4.2 - 80 K) the spectrum has 3 peaks of different intensity, which were sufficient approximated with two doublets with intensities of 2:1.

The parameters of Mössbauer spectrum indicates the presence of Fe(III) ions in a high spin state S = 5/2 (more intensive doublet) and Fe(II) ions S = 2 (less intensive doublet) corresponding with excellent data analysis of the complex chemical composition. With temperature increasing the spectrum radically changes and at 360 K spectrum is approximated with a very broad singlet that can be fitted as a doublet with a small quadrupol splitting. This change of Mossbauer spectrum form was interpreted by three groups of researchers [15,17,18]. They based on dynamic delocalization model of type electron space-time for a three centres system. According to this model, the spectrum depends on the ratio of an electron presence around a nucleus (τ_e) and the characteristic measuring time of the method (τ_o). In the case of Mossbauer spectroscopy for isotope Fe-57 ($\tau_o = 1\cdot10^{-7}$s).

At ($\tau_e >> \tau_o$) all states of Mössbauer nuclei will be presented in Mossbauer spectroscopy, and at ($\tau_e << \tau_o$) it will be a spectrum of an average state (taking into account the stoichiometric data). If $\tau_e \sim \tau_o$ the spectrum shape will be kind of a "trough" with the absorption of gamma rays from the most negative relative velocity to the most positive in the system of the several Mossbauer isotope states. The simulation of experimental spectra with theoretical some led to the following τ_e values: $2{,}4\cdot10^{-6}$ s at 17 K and $2{,}5\cdot10^{-9}$ s at 296 K. Further studies conducted in the inorganic chemistry sector of the IC ASM on iron carboxylates of mixed valence resulted in the following conclusions: the X-rays study demonstrated that iron carboxylates of mixed valence have the μ_3-oxo triangular structure; there is an antiferomagnetic interaction between iron ions; electron delocaliyation of the space-time type takes place, and its speed depends on temperature as well as the donor-acceptor nature of ligands from the internal and external cluster sphere that enables the routing of this process. For iron ions in the triangle with a high symmetry and a more equivalent position, a dynamic electron delocalization with a higher speed can be observed. It should be mentioned that „intermolecular" electron transfer occurs „slow" in iron polycluster carboxylates of mixed valence, synthesized by "stitching" of μ_3-oxo-iron acetate (III) with μ_3-oxo-iron acetate of mixed valence. [19]

Another pioneer achievement in the class of iron carboxylates was the synthesis and study of tetranuclear iron carboxylates - hexaaqua-tetrakis (μ-trifluoroacetato-trifluoroacetato(O,O')) - μ_3 - dioxo - tetrafier(III) trihydrate [19,20]. As a result, it was determined that the structure of this carboxylate had a form of "butterfly" (X-ray method) (Fig.3).

From Mössbauer spectroscopy data it clearly apperas that the electronic structure of Fe(III) ions of high spin is arranged in groups of two with different values of electric field gradient (EFG) around the nucleus. Magnetic properties are characterized by antiferomagnetic interaction between paramagnetic ions of trivalent iron with the following values of the magnetic exchange parameters $J_{(perimeter)} = -18$ cm^{-1}, $J_{13} = -10$ cm^{-1} and $J_{24} = -24.7$ cm^{-1}. For the first time, an original method was offered to describe the component parts of a Mossbauer spectrum which presents a superposition of component spectra at the temperature dependence of dynamic parameter $<x^2>$ (average squared projection amplitude of nucleus or atom oscillations, from direction of gamma ray spread) estimated from Mossbauer spectra and data of X-ray sample analysis at different temperatures [19].

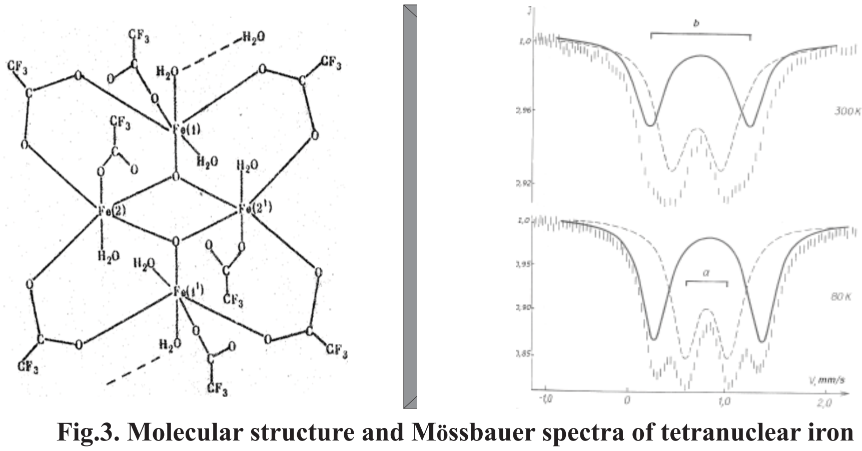


Fig.3. Molecular structure and Mössbauer spectra of tetranuclear iron carboxyl ate $[Fe_4O_2(O_2CCF_3)_8(H_2O)_6]\cdot2H_2O$ [20].

In 2003-2004 [21,22] it was synthesised and studied heterotetranuclear μ_3-dioxo iron tricloracetate, that contained three iron(III) and one Eu(III) ions, $[Fe_3EuO_2(CCl_3COO)_8H_2O(THF)_3]\cdot THF$, and had similar structure with other metal carboxylates of "butterfly" type (Fig.4.). The tetranuclear molecule presents a structure of "butterfly" with two Fe_2Eu

triangles and with a common aspect Eu···Fe. Metals are linked by two μ_3-oxo centres and eight carboxylic ligands. Each metal atom is surrounded only by oxygen atoms: six for iron and eight for europium. Fe(3) coordinates both oxygen-μ_3 atoms, while Fe(1) and Fe(2) bonds only one - O(1) and O(2) respectively. Axial coordination positions of Fe(1) and Fe (2) are occupied by oxygen atom of THF. Unlike Fe(2), the atom of Fe(1) coordinates a molecule of water.

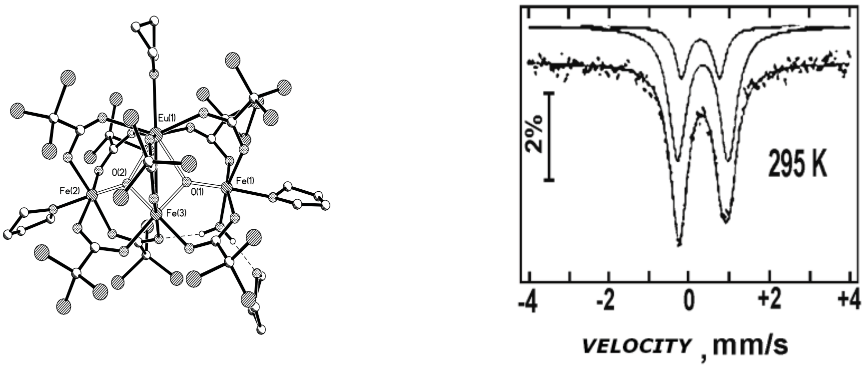


Fig. 4. Molecular structure and Mossbauer spectra of the complex $[Fe_3EuO_2(CCl_3COO)_8H_2O(THF)_3]$ associated with two THF solvent molecules [21,22].

All equatorial oxygen atoms come from carboxylic groups, which are coordinated in *syn-syn* form. Thus, the surrounding of three iron atoms in complex is slightly different. A water molecule forms two hydrogen bonds with the oxygen atoms of a solvated THF and a carboxylic ligand. It is assumed that the last play the role of the second bridge-ligand, which is missing between atoms of Fe(1) and Fe(2).

Later was obtained and characterized a complete set of compounds of this series, where Eu(III) ions were substituted with La^{III}, Ce^{III}, Pr^{III}, Nd^{III}, Sm^{III}, Gd^{III}, Tb^{III}, Ho^{III}, Er^{III} and Yb^{III} ions. According to the parameters of Mossbauer spectra of these compounds, where Ln = Eu, Ce, Pr, Nd, Sm, it was found that electronic states of two Fe(III) configurations (those "butterflies wings", Fe1 and Fe2) are close by symmetry as well as summary density of the electron cloud around the nuclei and also differs from the position of iron "head-tail", Fe3. At temperatures below 15 K, the Mossbauer spectra of such complexes have a form of doublet corresponding to paramagnetic Fe(III) ions (S = 5/2) and a sextet (Zeeman spectrum) indicating the presence of magnetic ordering around the other Fe (III) atoms position.

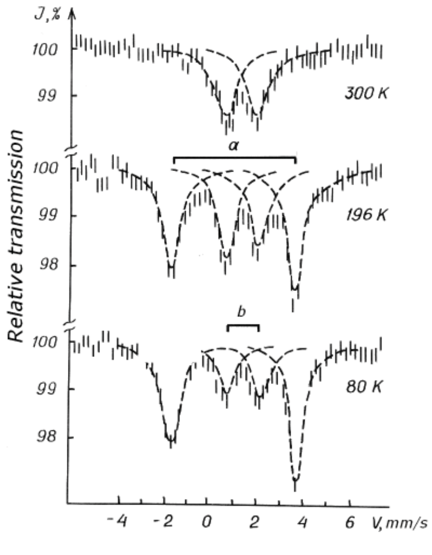


Fig.5. Mössbauer spectra of thiosemicarbazone $Cat[Fe(R\text{-}thasa)_2]$.nSolv at different temperatures.

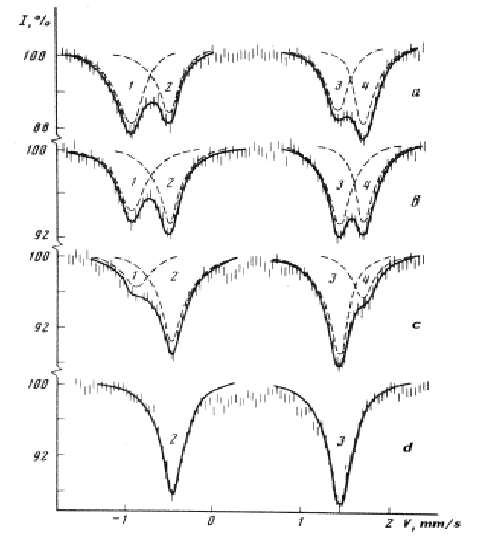


Fig.6. The time and temperature dependence of Mossbauer spectra of $[Fe(DfgH)(Dfg)Py_2]$ ·nSolv.
a-c At the initial moment of giving off;
d – After standing at 300 K during long time.

Another interesting phenomenon studied extensively in IC ASM with Mossbauer spectroscopy is the effect of spin transition ("cross-over") in iron(III) thiosemicarbasone, with the composition Cat[Fe(R-thasa)2]·nSolv, where Cat = cation, R = different electron-donor or electron-acceptor radicals. In this class of substances $^6A_1 \leftrightarrow {}^2T_2$ transition is achieved. It can be observed (Fig.5) that the Mössbauer spectra change at different temperatures in a rather long set of coordination compounds of this class of substances [23-26]. At low temperatures (about 80 K) the spectrum contains one or two doublets, but at high temperatures there is only a single doublet. The parameters of Mössbauer spectra correspond to iron(III) ions in low spin state (S = 1/2, with large values of quadrupole splitting ΔE_Q) and to iron ions in the state of uncoupled spin (S = 5/2, with small values of quadrupole splitting ΔE_Q).

The topic of dioximates was developed throw synthesis and Mössbauer spectroscopy (MS) investigations of a whole range of compounds with coordinative core $Fe^{II}N_4A_2$, where A = N, As, P, C [23, 27,28]. An intermolecular red-ox process with participation of oxime takes place in solid samples of iron(III) alpha-benzyldioximates with ketones. MS measurements of solid samples at different temperatures and variable time (Fig. 6.) allowed studying the kinetics of an intermolecular red-ox reaction with transfer of electron from ligand to Fe(III).

The studied reaction kinetics Ligand $\overset{\bar{e}}{\rightsquigarrow}$ Fe(III) → Fe(II) is characterized by the formal order of this transformation kinetics n = 0.50, K = 0.070 h^{-1}, activation energy $\Delta E^* \sim 111$ kJ/mol, and the pre-exponential coefficient $Z = 8.10^{17}$ which is in the limits of other topochimical reaction. Through this study it was demonstrated the possibility of using MS in the investigation of topochemical reactions.

MS was used to study the formation of complexes with active groups of ionic exchange resins. The treatment of different types of such substances (КУ-2, КВ-2, АН-31, АВ-17, ЭДЭ-10П, АН-2ФНб АВ-16Г et al.) with salts of iron ions, subjecting them to various other actions (thermal processing, variation of environmental acidity, pH, etc.) and then their studying with Mossbauer spectroscopy gave the opportunity to demonstrate the formation of chemical bounds Fe - Donor from groups of ionic exchange resins, or redox transformations in their composition, as well as dynamics of complex oscillations in their generator phase [29-31].

The scientific results obtained using Mössbauer spectroscopy became a part of 4 doctor habilitat theses in science [19,28,31,32] and more than 15 PhD thesis [22, 23,25-27, 29, 30, 33-38 et al.] thereby contributing to increasing the professional level of researchers.

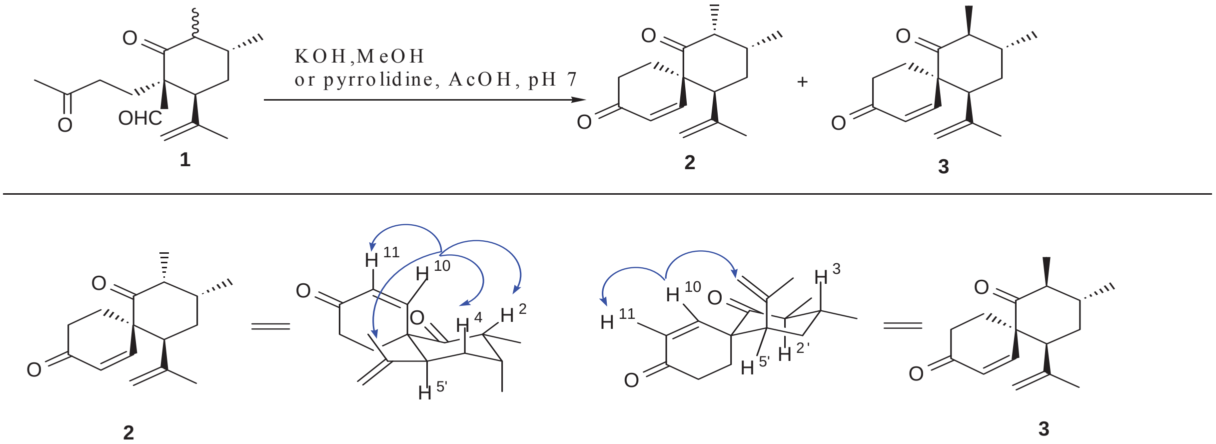
Nuclear Magnetic Resonance (NMR)

Method of nuclear magnetic resonance (NMR) began operating in IC ASM in 1975. Main users of this method have been and are specialists in organic chemistry, who use it to control the purity of synthesized substances and to determine their structure.

NMR group has actively participated in caring out of many scientific themes of the laboratories from IC AŞM and from academic Departments. One of the interesting topics was the polymer synthesis inclusive graft polymers for different areas. Especially it should be mentioned the polymers for optoelectronics - field developed in collaboration with physicists of IAF of ASM and centre of optoelectronics of Moldova State University (MSU).

At the Department of Organic Chemistry of MSU, 300 monomers of styrene with active functional groups in benzene ring (NH_2, NCO, NCS) wee studied. All of them have been used to obtain new polymers. The main control methods of reactions of synthesis have been IR, UV-Vis, NMR spectral methods. The obtained scientific results were presented at various scientific forums and published in specialized journals.

IR, UV-Vis and NMR spectra of these compounds (267 monomers) were interpreted and presented in the form of atlases [39,40]. In 1985, a monograph of nitrogen-containing vinylarenes was published [41].

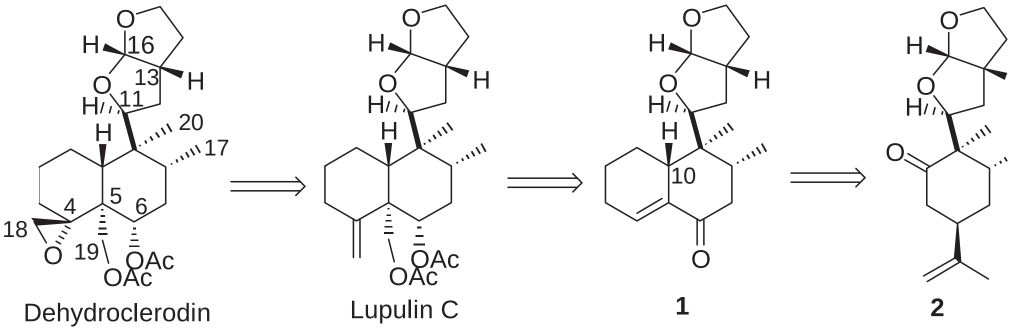


Scheme1. The transformation of the decalin moiety in different conditions.

The construction of the decalin moiety in clerodines via Robinson annulation has been studied. As the part of this investigation, the structure of compounds **2,3** (scheme 1) were elucidated by 2D-NMR, more concretely – by Nuclear Overhauser Effect (NOE) in NMR method. This technique permits elucidating the spin polarization from one nuclear spin to another, through space (not through bonds) and it is used to determine the structure of complicated organic molecules. Furthermore, the distance can be derived from the observed NOEs, so that the precise, three-dimensional structure of the molecule can be reconstructed. Lower one example is presented.

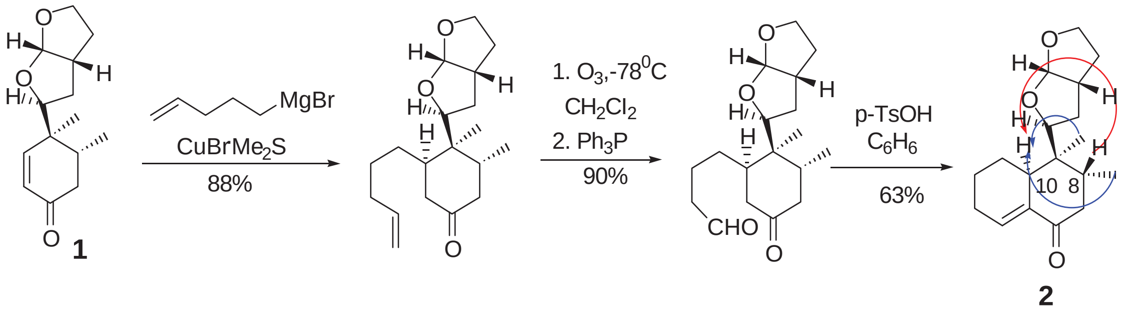
A clear NOE difference interaction was observed between H10 and H2, H4 and the CH_3 at the isopropenyl group, which suggests structure **2**. The equatorial position of isopropenyl group was further proven by the coupling constants of H5', which were 13.6 Hz and 3,5 Hz respectively, indicating an axial-axial and axial-equatorial coupling. In compound **3,** a clear NOE difference was observed between H10 and H11 and the CH_2 of the isopropenyl group, but no NOE difference was observed for H2 and H4. This indicated an axial position of the isopropenyl group, which was supported by the small coupling constants of H5' [42].

In continuation of decalin direction the construction of natural antifeedants Dehydroclerodanin and Lupulin-C via 1,4 and 1,2-additions reactions has been studied (scheme 2).

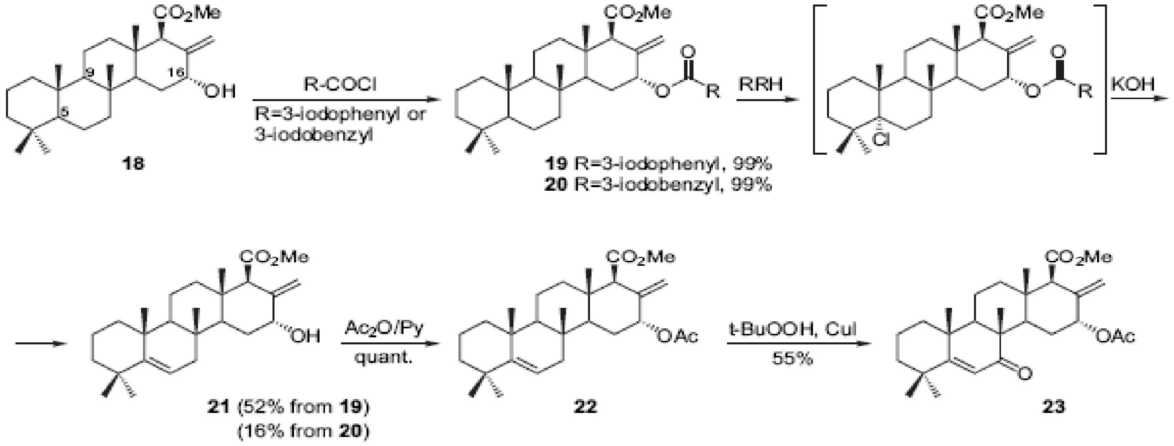


Annulation via a 1,4-addition

The structure of methyl 18αH-scalar-16α-hydroxy-5(6),17(25)-dien-19-oate (**21**) (scheme 3) was determine by high resolution mass spectrometry and a detailed 2D-NMR analysis.



Scheme 2. The transformation of dehydroclerodin to cyclized decalin 2.



Scheme 3. The transformations of scalarane sesquiterpene in different conditions.

For the construction of ring A, a four carbon fragment had been introduced at C10. The configuration at C10 was determined in the cyclized decalin **2** by NMR, where no NOE between H-10 and H-8 could be detected, whereas a clear NOE was observed between H-10 and both the methyl groups at C8 and C9, which is indicative for an α-position of this proton [43].

Scalarane sesquiterpenes represent an interesting class of organic substances which was studed with the participation of our institute's specialists in organic chemistry. The functionalization of the B-ring of the scalarane framework has been achieved for the first time by a radical relay halogenation (RRH) synthetic method. Lower some theoretical considerations explaining the course of RRH reaction are presented.

First of all, the molecular formula $C_{26}H_{40}O_3$, deduced by the sodiated ion peak at *m/z* 423 (M+Na) in the HRESIMS spectrum, exhibited the expected additional unsaturation degree with respect to the starting product - Methyl 18αH-scalar-16α-hydroxy-17(25)-en-19-oate (**18**).

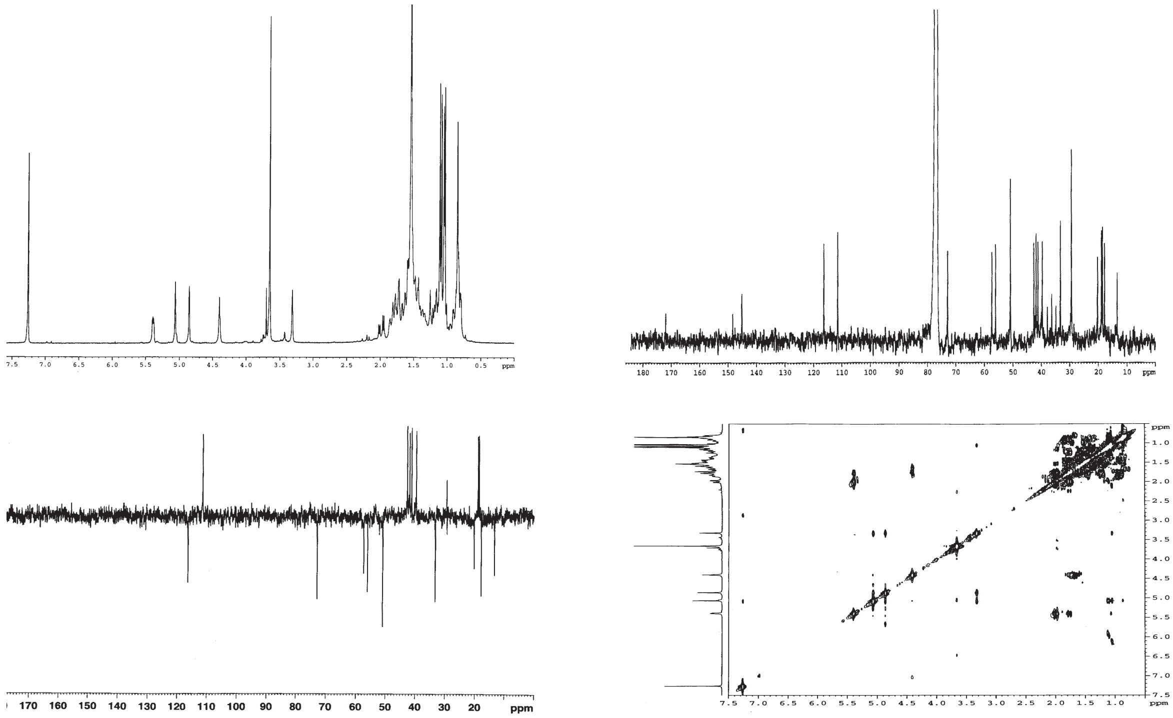


Fig. 7. The 1H, 13C, ^{13}C NMR DEPT, and 2D-NMR ^{1}H-^{1}H COSY NMR spectra of 21.

Analysis of ^{1}H and ^{13}C NMR spectra of **21** [Fig.7 in[44]] in comparison with those of **18** [45,46] showed that the difference was in the presence of a trisubstituted double bond [δ_C 148.1 (s) and 116.4 (d); δ_H 5.39 (m)] in the scalarane skeleton of **21**. The ^{1}H–^{1}H COSY spectrum indicated that the olefinic proton at δ 5.39 (H-6) was correlated to a methylene (H_2-7) resonating at δ 1.77 (m) and 1.99 (dd, *J*=17.5) linked to a quaternary carbon, according to the position of the double by the down-field shifted ^{13}C values of both β-methyl groups C-21 (δ 29.4 in 21, δ 21.3 in 18) and C-23 (δ 20.3 in **21**, δ 16.2 in **18**) of the scalarane framework, due to the different steric arrangement of ring B and absence of the γ-*gauche* effect of C-6. All proton and carbon resonances, assigned by 2D-NMR (^{1}H–^{1}H COSY, HMQC, and HMBC) experiments as reported in Section 4, were in agreement with the proposed structure **21**. Once its structure was proved, ester **21** was subsequently used to functionalize the ring B of the scalaranic framework.

Conclusions

Physical methods of study are an integral part of modern chemistry and will continue to play a greater role in achieving important scientific results.

Recently, the Centre "Physical Chemistry and Nanocomposites" was created in the frames of the Institute of Chemistry of the ASM.

The main objectives of the Centre are:

- Research in the fields in quantum chemistry, chemical kinetics, nanocomposites, analytical chemistry, hydrogen production and storing, bioinorganics, according to the scientific fields of the laboratories of the centre.
- Modern analyses for (Elemental analysis – C,H.N,S, metals; IR (250-4000 cm^{-1}); UV/Vis (380-780 nm); RMN (^{1}H, ^{19}F, ^{13}C, ^{15}N,^{31}P, ^{119}Sn,^{59}Co etc); RNG (^{57}Fe, ^{119m}Sn); mass-spectrometry; thermal differentiated analysis; atomic absorption analysis; magnetochemistry; electronic microscopy, at the needs of chemistry related institutions, involved in institutional projects, state programs, grants.

- Special courses regarding physical methods in chemistry for universities students, master students, PhD students and for lecturers and scientists during refresher courses.
- Practical work and production practices on the basis of physical methods in chemistry for young researchers and lecturers during refresher courses.
- Training of highly qualified scientific staff through PD courses and postdoctoral education in the field of physical and physical-chemical research methods.

The centre is endowed with modern equipment. During 2007-2008 the following equipment was purchased: NMR spectrometer 400 MHz (NRM 400), Gamma nuclear resonance Spectrometer (Mössbauer Spectrometer), a system for the determination of materials specific area and pores volume, FTIR Spectrometer, UV/Vis Spectrometer, Elemental analyzer, SF E-100 Stopped Flow Spectrometer, КФК-2 Colorimeter, magnetic stirrers with heating, electronic weights, rotavapors.

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FLOW INJECTION ANALYSIS SYSTEM COUPLED WITH ICP-EOS FOR DETERMINATION OF SOME METALLIC ELEMENTS IN DRINKING WATER

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Abstract: The European Drinking Water Directive (98/83/EC), transposed in Romanian Legislation as Low 458/2002, amended by Low 311/2004, imposes the limit of concentration for metallic elements in water intended for human consumption. The toxic metals arsenic and selenium are among these elements and the limit value is 10 µg/L. In the paper there are presented the working conditions for determination of As and Se from drinking water using modern techniques based on the flow injection-hydride generation with the inductively coupled plasma atomic emission spectrometry (FIAS-ICP-EOS). The analyses were performed on Optima 5300 DV Perkin Elmer equipment with FIAS 400 Flow Injection System, Perkin Elmer type. For the hydride generation two types of solution were used: 10% (v/v) HCl as a carrier solution and 0.2 % $NaBH_4$ in 0.05%NaOH solution as a reducing agent [1]. The treatment step of the samples and standard solutions consisted in reducing with mixed solutions of KI and ascorbic acid in acidic condition (HCl) for As and only with HCl and high temperature for Se [2,3]. The paper contains the characteristic parameters of the methods, such as: low detection limit, quantification limit, repeatability, precision, recovery, which were evaluated using Certified Reference Materials for each element.

Keywords: drinking water, As, Se, hydride analyses, ICP-EOS.

Introduction

Nowadays the determination of trace elements in drinking water is a matter of real interest because of the role of water in the human metabolism and the consequences of ingestion for human health. The European Drinking Water Directive (98/83/EC), transposed in Romanian Legislation as Low 458/2002, amended by Low 311/2004, imposes the limits of concentration for metallic elements in water intended for human consumption. The toxic metals arsenic and selenium are among these elements and the limit value is 10 µg/L.

Arsenic may be found in water which has flowed through arsenic-rich rocks. Severe health effects have been observed in populations drinking arsenic-rich water over long periods, in countries worldwide. Chronic arsenic poisoning, as occurs after long-term exposure through drinking water is very different to acute poisoning. Immediate symptoms of an acute poisoning typically include vomiting, oesophageal and abdominal pains, and bloody “rice water” diarrhoea. Chelation therapy may be effective in acute poisoning but should not be used against long-term poisoning. Long-term exposure to arsenic via drinking-water causes cancer of the skin, lungs, urinary bladder, and kidney, as well as other skin changes such as pigmentation changes and thickening (hyperkeratosis). Increased risks of lung and bladder cancer as well as arsenic-associated skin lesions have been observed at drinking-water arsenic concentrations of less than 0.05 mg/L. Absorption of arsenic through the skin is minimal and thus hand-washing, bathing, laundry, etc. with water containing arsenic do not pose human health risk [4].

Selenium is toxic within large amounts, but trace amounts of it are necessary for the cellular function in most, if not all, animals, forming active centres of the enzymes glutathione peroxidase and thioredoxin reductase. Although selenium is an essential trace element, it is toxic if taken in excess. Exceeding the Tolerable Upper Intake Level of 400 micrograms per day can lead to selenosis [5]. Symptoms of selenosis include a garlic odour on the breath, gastrointestinal disorders, hair loss, sloughing of nails, fatigue, irritability and neurological damages. Extreme cases of selenosis can result in cirrhosis of the liver, pulmonary oedema and death [5]. Elemental selenium and most metallic selenides have relatively low toxicities because of their low bioavailability. By contrast, selenates and selenites are very toxic, having an oxidant mode of action similar to that of arsenic trioxide. The chronic toxic dose of selenite for human beings is about 2400 to 3000 micrograms of selenium per day for a long time [6]. Hydrogen selenide is an extremely toxic, corrosive gas. Selenium poisoning of water systems may result whenever new agricultural runoff courses through normally dry undeveloped lands. This process leaches natural soluble selenium compounds (such as selenates) into the water, which may then be concentrated in new “wetlands” as the water evaporates.

Accurate measurement of arsenic in drinking-water at levels relevant to health requires laboratory analysis, using sophisticated and expensive techniques and facilities while trained staff not easily available in many parts of the world. Analytical quality control and external validation remain problematic. Field test kits can detect high levels of these elements but are typically unreliable at lower concentrations of concern for human health.

Usually, these elements can be detected using UV-VIS spectrometry, AAS [15], atomic absorption spectrometry coupled with FIAS technique [7], GF-AAS [8,9], ICP-EOS [10,11], ICP-MS [12,13], HG-ICP-MS [14] TXRF[15], LC-

MS[16], HPLC-ICP-MS [17,18]. In the paper there are presented the working conditions for determination of As and Se from drinking water using modern techniques based on the flow injection-hydride generation with the inductively coupled plasma atomic emission spectrometry (FIAS-ICP-EOS). The methods applied with this modern technique have low detection limits (As – 0.21 ÷ 0.59 µg/L, Se – 0.21 µg/L), situated under the limit values imposed by legislation.

Experimental Section

Apparatus: Flow Injection Hydride Generation System FIAS 400 with Inductively Coupled Plasma Optical Emission Spectrometer ICP-EOS type Optima 5300 DV Perkin Elmer, Analytical Balance Kern ABT 220-50M, Bandelin Sonorex Water Bath (only heating function).

Reagents: Merck solution for calibration (1000 mg As/L; 1000 mg Se/L, ICP standards), 100 mg/L multielement Perkin Elmer SRM, hydrochloric acid (37%, Merck quality), potassium iodide (99,995% purity, Merck quality), L-ascorbic acid (>99%, Sigma-Aldrich quality); sodium borohydride (>96%, Merck quality), sodium hydroxide (pellets, Gr for analysis, Merck quality), argon 99,996% purity, nitrogen 99,999% purity (Linde-Gas quality), ultrapure water.

Procedure: The water samples (drinking water, groundwater, surface water) and standard solutions for As and Se determinations should be pre-reduced prior the analysis (table 1). For each set of standards a blank sample using the same procedure was prepared. For the hydride vapour generation two types of solution were used: 10% (v/v) HCl as a carrier solution and 0.2 % $NaBH_4$ (w/v) in 0.05%NaOH (w/v) solution as a reducing agent, which should be freshly prepared.

Table 1

Pre-treatment step for the As and Se determinations with FIAS-ICP-EOS

Element	Reduction	Pre-treatment procedure for each standard solution and sample
As	As^{5+} to As^{3+}	5 mL 5% (w/v) potassium iodide and 5% (w/v) ascorbic acid, 45 minutes at room temperature.
Se	Se^{6+} to Se^{4+}	2 mL HCl concentrated, heated on a water bath at 90ºC for 20 minutes.

The operational parameters for the spectrometer, plasma, FIAS and data processing are presented in Table 2.

Table 2

Parameters for FIAS-ICP-EOS

Spectrometer parameters			
As Wavelengths:	193.696, 188.979, 197.197 nm	Replicates	3 times
Se Wavelength:	196.026 nm	Purge Gas Flow	normal
		Transient Read Delay	0.0 sec
Integration time:	0.05 sec	Transient Read Time	15.0 sec

Plasma parameters			
Plasma flow rate	15 L/min	Power RF	1350 W
Auxiliary flow rate	0.2 L/min	Plasma View	Axial
Nebuliser flow rate	0.5 L/min	View distance	15.0 mm

Flow Injection Programme

Step	Time (s)	Pump 1 (U/min)	Pump 2 (U/min)	Valve	Read
Prefil	15	80	100	Fill	-
1	10	80	100	Fill	-
2	15	80	100	Inject	On

Spectral Peak Processing		Time Processing	
Peak Algorithm :	Peak Height	Peak Algorithm :	Peak Height
Points per peak :	3 points	Smoothing points :	19 points
Spectral corrections :	None		

The hydride technique involves the reaction of acidified aqueous samples with a reducing agent, such as sodium borohydride. This reaction generates a volatile hydride which is transported to a quartz cell by means of an argon carrier gas. In the quartz cell, the hydrides are converted to gaseous metal atoms, which are then transported in plasma by argon gas. Plasma generation of the ICP-EOS spectrometer requires argon gas as fuel. Nitrogen gas is used only for the cooling system of the equipment. The purity of all reagents used is critical when determining low levels of hydride elements. Table 1 summarizes preceding treatments for the As and Se determinations with FIAS-ICP-EOS.

ICP-EOS uses specific wavelengths to detect metallic elements; the methods applied with this equipment are perfectly able to measure accurately an analyte in the presence of interferences.

In order to evaluate the performances of the methods some standard solutions for As and Se using Certified Reference Material (1000 mg/L, Certipur ICP Standard, traceable to SRM from NIST) were prepared during the experimental tests. For the recovery test a multielement SRM type Perkin Elmer Quality Control Standard 21 was used, with 100 mg/L As and Se. To establish the performance parameters of the methods, the tests indicated in Table 3 were performed.

Table 3

Performed tests used for performance parameters of the methods

Linearity	**LOD and LOQ**	**Test for the homogeneity of the variance**	**Repeatability precision, recovery**
10 standard solutions between 2 µg/L ÷ 20 µg/L 1 mL; 2 mL; 3 mL; 4 mL; 5 mL; 6 mL; 7 mL; 8 mL; 9 mL and 10 mL from 0.1 mg/L to 50 mL with 10% HCl.	10 independent blank solutions measured each of them once.	- 10 independent standard solutions of 2 µg/L concentration;	- 10 independent standard solutions of 15 µg/L concentration.
		- 10 independent standard solutions of 20 µg/L concentration.	- 5 independent standard solutions of 5 µg/L, 15 µg/L and 20 µg/L concentrations (Perkin Elmer QCS 21).

The mathematical relations and the admissible range or value for some important parameters, such as: bias, coefficient of variation (relative standard deviation) and recovery are presented in Table 4.

Two aspects are important for Internal Quality Control: the analysis of "control materials", such as CRM or spiked samples, to monitor the trueness (recovery) and replication of analysis to monitor the precision. Both aspects form a part of statistical control, a tool for monitoring the accuracy of an analytical system. Recovery studies were performed to the same matrix type (drinking water) at different levels of analyte concentration [19].

Table 4

Mathematical equations used for evaluation of recovery, precision and bias

Recovery, %	**Bias, %**	**Relative standard deviation, %**
$\bar{\eta}$ (%) = $\frac{\overline{x_f}-\overline{x_b}}{\overline{x_a}}$ 100, %, $\overline{x_f}$ = mean value of fortified samples, µg/L; $\overline{x_b}$ = mean value of unfortified samples, µg/L; $\overline{x_a}$ = concentration of added standard solution, µg/L. For 10 µg/L mean recovery = 60-115% [20,22]	Bias = $\frac{x_f - x_a}{x_a}\times 100$, % Bias value < t(99,9) =2.82 [21,22]	RSD = $\frac{S_r}{\bar{x}}\times 100$, S_r = standard deviation of concentrations, µg/L; $\bar{x}$ = mean value of concentrations, µg/L. for 10 µg/L, acceptable RSD values: Horwitz, 22.6 -33 %; AOAC Peer Verified Methods, 15 -21% [20,22]

Results and discussion

The working range for As and Se determination using FIAS-ICP-EOS is linear between 2 and 20 µg/L for all tested wavelengths. In the tests for the homogeneity of the variance, PG values are lower than Fischer-Snedecor's "F" value. The values of coefficient of variation (As: 1.77% for λ=193.696 nm, 2.77% for λ =197.197 nm and 1.39% for λ =188.979 nm; Se: λ =197.197 nm), lower than 3%, situate the test methods as good analytical methods. The detection limits (LOD) and quantification limits (LOQ) allow the detection of As and Se from drinking water samples at the normed level of concentration (Table 5).

Table 5

Linearity, LOD and LOQ

As, Λ=193.696 nm		
$y = -138.13 + 764\cdot x$ linear equation	$B = 764 \mu g^{-1} L$ *sensitivity, the slope of the calibration curve*	$s^2_1 = 0.89E+08$, $s^2_{10} = 3.9E+08$, $PG = s^2_{10}/ s^2_1 = 4.39 < F_{9,9;0,99} = 5.35$
$S_{Y1} = 149$ µg/L *residual standard deviation*	$S_{x01} = 0.19$ µg/L *method of standard deviation*	$V_{x01} = 1.77$ %, *coefficient of variation*
R=0.9995 Correlation coefficient, accepted values R≥0.997	$\bar{x} = 0.214$ µg/L, $\sigma_{blank} = 0.04$ µg/L **LOD** = 0.33 µg/L, **LOQ** = 0.61 µg/L	
As, Λ=197.197 nm		
$y = -100.4 + 461.17\cdot x$ linear equation	$b = 461.17 \mu g^{-1} L$ *sensitivity, the slope of the calibration curve*	$s^2_1 = 0.55 E+07$, $s^2_{10} = 2.72 E+07$, $PG = s^2_{10}/ s^2_1 = 4.96 < F_{9,9;0,99} = 5.35$
$S_{Y1} = 140.45$ µg/L *residual standard deviation*	$S_{x01} = 0.30$ µg/L *method of standard deviation*	$V_{x01} = 2.77$ %, *coefficient of variation*
R=0.999 Correlation coefficient, accepted values R≥0.997	$\bar{x} = 0.256$ µg/L, $\sigma_{blank} = 0.11$ µg/L **LOD** = 0.59 µg/L, **LOQ** = 1.34 µg/L	
As, Λ=188.979 nm		
$y = -75.4 + 587.96\cdot x$ linear equation	$b = 587.96 \mu g^{-1} L$ *sensitivity, the slope of the calibration curve*	$s^2_1 = 0.12E+08$, $s^2_{10} = 0.61E+08$, $PG = s^2_{10}/ s^2_1 = 5.06 < F_{9,9;0,99} = 5.35$
$S_{Y1} = 90.15$ µg/L *residual standard deviation*	$S_{x01} = 0.15$ µg/L *method of standard deviation*	$V_{x01} = 1.39$ %, *coefficient of variation*
R=0.9995 Correlation coefficient, accepted values R≥0.997	$\bar{x} = 0.122$ µg/L, $\sigma_{blank} = 0.03$ µg/L **LOD** = 0.21 µg/L, **LOQ** = 0.41 µg/L	
Se, Λ=197.197 nm		
$y = -47.73 + 487.81\cdot x$ linear equation	$b = 487.81 \mu g^{-1} L$ *sensitivity, the slope of the calibration curve*	$s^2_1 = 4.27 E+06$, $s^2_{10} = 18.26 E+06$, $PG = s^2_{10}/ s^2_1 = 4.28 < F_{9,9;0,99} = 5.35$
$S_{Y1} = 101.54$ µg/L *residual standard deviation*	$S_{x01} = 0.21$ µg/L *method of standard deviation*	$V_{x01} = 1.89$ %, *coefficient of variation*
R=0.9995 Correlation coefficient, accepted values R≥0.997	$\bar{x} = 0.095$ µg/L, $\sigma_{blank} = 0.034$ µg/L **LOD** = 0.21 µg/L, **LOQ** = 0.43 µg/L	

In figures 1 and 2 the evolutions in time of peak height for As (Λ=193.696 nm) and Se are presented. The method measures the high of the peaks for each standard solution and processes the data in order to obtain a calibration curve.

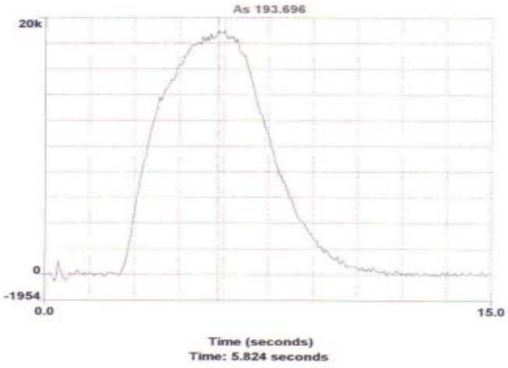

Fig. 1. Peak configuration for As (Λ=193.696 nm)

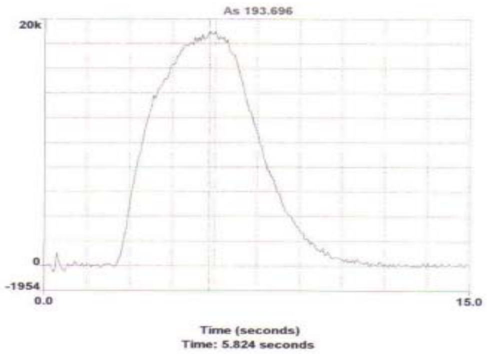

Fig. 2. Peak configuration for Se

The Bias values are situated under the limit value for both elements and all wavelengths. The limit value is 2.82% for 99% confidence level and 9 freedom degrees. For 10 µg/L level of concentration, the recovery percentage must be situated within 60 and 115 % range. In the Tables 6 and 7 all the obtained values of recovery percentage for different types of standard solutions respect needed requirement.

Table 6

Precision and bias data on SRM Merck

Parameter	ARSEN			SELENIUM
	Λ=193.696 nm	**Λ=197.197 nm**	**Λ=188.979 nm**	**Λ=197.197 nm**
RSD_r, %	1.87	2.03	1.02	1.40
Bias, %	1.99	0.99	2.50	1.59

Table 7

Recovery data on SRM Perkin Elmer

Parameter	ARSEN			SELENIUM
	Λ=193.696 nm	**Λ=197.197 nm**	**Λ=188.979 nm**	**Λ=197.197 nm**
5 µg/L				
$\bar{x}_f \pm s_{xf}$, µg/L	5.40 ± 0.20	5.38 ± 0.23	5.04 ± 0.25	4.54 ± 0.19
$\eta_m \pm s_\eta$, %	103.74 ± 3.92	102.39 ± 4.64	98.43 ± 5.07	88.93 ± 3.83
15 µg/L				
$\bar{x}_f \pm s_{xf}$, µg/L	15.36 ± 0.56	15.33 ± 0.51	15.43 ± 0.58	14.52 ± 0.12
$\eta_m \pm s_\eta$, %	100.98 ± 3.74	100.48 ± 3.42	102.04 ± 3.85	96.15 ± 0.79
20 µg/L				
$\bar{x}_f \pm s_{xf}$, µg/L	20.98 ± 0.07	21.14 ± 0.11	21.14 ± 0.11	20.02 ± 0.23
$\eta_m \pm s_\eta$, %	102.16 ± 1.96	104.44 ± 0.55	105.09 ± 0.53	99.62 ± 1.16

Conclusions

Single-laboratory validation is a valuable source of data usable to demonstrate the fitness-for-purpose of an analytical method. Also, the statistical interpretation of the experimental results prove that the proposed methods applied with FIAS-ICP-EOS equipment can be successfully used for the analytical control of the As and Se from drinking water, groundwater and surface water. Arsenic determination can be performed at three different wavelengths, 193.696 nm, 197.197 nm and 188.979 nm, the experimental data showed small differences for the obtained performance parameters. Selenium can be determined at 197.197 nm.

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DETOXIFICATION OF PESTICIDES POLLUTED SOIL BY ADSORBTION ON ACTIVATED CARBONS

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Abstract. The paper emphasizes a very severe social-ecological problem, related to the contamination of soils by pesticides and fodder micotoxins. The authors suggest the utilization of a carbon adsorption based method of purification of soils contaminated with traces of pesticides. It is demonstrated that this method of soil rehabilitation leads to an 80% crop increase, allowing the production of environmentally clean plant products. The utilization of special activated carbons "Ptitsesorb" leads to a 30-40% decrease of necessary combined fodder in chickens breeding.

Keywords: pesticides, soil, activated carbon, detoxification.

One of the major threats to the biosphere is the decrease of soil fertility and total exhaust of agricultural fields as a result of technogenic activity. The soils of agricultural areas constitute only 6 % of the total land surface, and almost 40% of it belongs to Russia. Considering the fact that over 10 billion people will be living on Earth by the end of the XXIst century, primordial attention should be focused on the protection and rehabilitation of soils.

The large scale utilization of various chemicals, including pesticides, in local and world agricultural practice lead to the aggravation of medical-environmental matters caused by the pollution of plant cultivation and zootechny products, and of the entire biosphere, in general. To date, the number of poisonous chemicals used in various countries is close to thousand; approximately three hundred of them are widely used. In these conditions, it is absolutely necessary to possess methods and sources which would allow the elimination of the harmful action of pesticides on cultured and wild plants and get environmentally clean production of phytotechny and zootechny [1].

Considering the solving of environmental issues of the agro-industrial complex, activated carbons (AC) are characterized by several advantages, such as selectivity of sorption of organic toxicants, universality of sorption properties, high adsorptive capacity, hydrophobicity, convenient preparation form (granules, powder) and low cost (1,5-2,0 USD/kg).

Table 1

Efficiency of recovery of soil fertility, polluted with herbicides traces, using modified AC in doses of 100 kg/ha

Trace amounts of herbicides in soil	Culture	Index of preserved crop of test-cultures, % of polluted control
Chlorsulphuron, 0,2 g/ha	Cucumber	16 – 20
	Beet	58 – 63
	Radish	23 – 28
Terbacil, 1,4 kg/ha	Cucumber	23 – 27
	Beet	64 – 69
	Radish	30 – 39
Picloram, 2g/ha	Cucumber	22 – 24
Simazine, 50 g/ha	Tomato	22 – 26
Chlorsulphuron, 0,4 g/ha	Tomato	98 – 100
	Beet	98 – 99
	Radish	98 – 100

Regardless of the actuality of this issue, carbonic adsorbents haven't been produced for soil detoxification until recently. Therefore, the authors presented a theoretical argumentation of the requirements for the porous structure and preparative forms of AC used particularly for agro-sorption, and also the technologies of its introduction into soil.

It is disclosed that agro-sorbents must possess a micropores volume of not less than 0,2-0,3 cm^3/g and a significant development of thin pores (0,4–0,6 nm), allowing a strong retention of pesticides molecules, and also the products of its destruction, and the transporting porosity must be well developed in order to provide a good adsorption kinetics of these compounds [2].

Experimental results obtained in a synthetic environment laboratory using various types and concentrations (corresponding to real trace amounts) of herbicides in soils, are presented in table 1. According to these data, activated carbons are indeed a universal tool for the recovery of fertility of polluted soil, regardless of the type and trace amount of herbicide, increasing crop yield by 20-100 %.

Another significant result of AC adsorption based soil detoxification consists in collecting environmentally clean production of plants and vegetables. The data presented in tables 2 and 3 were obtained during comparative experimental studies on agricultural crops cultured according to the usual technology and using carbonic adsorbents. According to these data, the utilization of activated carbons on polluted areas in doses up to 100 kg/ha (in the case of cultured barley, up to 200 kg/ha) leads to a sharp decrease, and in several cases – to a total elimination, of herbicides accumulation in the products of plants and vegetable growing.

Table 2

Accumulation of herbicides by agricultural cultures

Dose of herbicide, kg/ha	Dose of AC, kg/ha	Test-culture	Amount of herbicide in the crop, μg/kg
Treflan – 1	-	Tomato	28
Treflan – 1	100	Tomato	0,6
Treflan – 1	-	Carrot	95
Treflan – 1	100	Carrot	Not found
2,4-D – 5	-	Barley	220
2,4-D – 5	200	Barley	Not found
2,4-D – 10	-	Barley	670
2,4-D – 10	200	Barley	Not found
2,4-D – 2,4 – Dichlorphenoxy acetic acid			

Table 3

Accumulation of atrazine by corn

Dose of AC, kg/ha	In the green mass per ensile, μg/kg, using the atrazine dose, kg/ha			In the grains, μg/kg, using the atrazine dose, kg/ha		
	8	***16***	***32***	***8***	***16***	***32***
0	2	5	13	7	11	29
50	Not found	Not found	1	Not found	1	2
100	Not found	Not found	Not found	Not found	Not found	Not found

On the basis of these data, in 2000 the State Commission of the Russian Federation registered the activated carbons “Agrosorb-1”, “Agrosorb-1G” and “Jiznedar”, and allowed their practical utilization as soil melioration agents in large-sized Russian agricultural enterprises, as well as in individual households for recovery of soil fertility and acquirement of environmentally clean plant production (state registration № 13-9089-0332-1, 13-9090(9962-9966)-0132-1).

Summarizing the described above work, we should mention the significant economical and environmental-economical effects due to the recovery of fertility of pesticides polluted soil, evidenced by the increase of crop yield of respective cultures, by the return of polluted areas in the sowing cycle and acquirement of dietetic products of plants and vegetables growing. According to the data of the Research Institute of Phytopathology of the Russian Academy of Agricultural Sciences, the potential environmental-economical effect of soil detoxification rises up to 300 USD per ha and could constitute around 20 bill. USD/year (considering the prices of 1999) in the Moscow region, alone. The importance of this is even greater, as all available data indicate that pesticide pollution in doses which inhibit cultured plants growth is evidenced on 50 mill. ha of fields. In particular, in the Krasnodar region, characterized by a very intense agriculture, the area of agricultural fields where pesticide pollution exceeds admissible limits constitutes over 240 thousands ha. In the case of intense implementation of AC in agricultural practices during the following years, the amount of AC required by the Krasnodar region alone will constitute around 25–30 thousands tones/year [1].

The technogenic and demographic loads increasingly influence environmental pollution. Naturally, the production of environmentally clean food, including the products of zootechny, swine-breeding, aviculture, encounters increasing difficulties. The fodder necessary for animal breeding is polluted by xenobiotics in a controlled manner (for example during pesticide treatment of plants), but also accidently (for example in the case of micotoxins affection of grains during storage and processing). It has to be mentioned that accidental, uncontrolled pollution of fodder is continuously increasing, and it is often detected only after the perishing of animals and birds.

In order to neutralize the harmful influence of polluted fodder on the efficiency of animal breeding and aviculture, various mineral and organic additives are widely used (such as “Micosorb”, “Biosorb” etc.), which always solve only one, very specific task. However, globalisation sets new requirements for such an important branch, as combined fodder production, therefore a wide utilization of special activated carbons is imperative for animal breeding and aviculture [3].

Lately, issues related to chicken breeding gained increasing significance, considered as one of the most dynamic branch of meat production. In most cases, micotoxins and other xenobiotics are constantly discovered in fodder materials for agricultural animals and birds, and even small concentrations of these substances significantly affect specialized aviary enterprises.

The efficiency of AC “Ptitsesorb”, used as a detoxifying agent at chicken aviaries in the case of utilization of combined fodder contaminated by various micotoxins was confirmed in the Institute of Aviculture (in Sergyev Posad)in 2005 (Tab. 4) by its addition in a dose of 0,5% mass.

Table 4

Efficiency of “Ptitsesorb” AC in the case of utilization of combined fodders, contaminated by several micotoxins (DON – 3,2 μg/kg, T-2 – 121 μg/kg, B1 – 9,5 μg/kg)

Groups	Safety of birds number,%	Combined fodder consumption for 1 kg of mass augmentation, kg	Decrease of production consumption, %
BR with dose of toxins 133,7 μg/kg	86	2,06	-
BR with dose of toxins 133 μg/kg + 0,5% AC	90-93	1,91-1,93	30-40

Note: BR – basic ration.

A significant increase in birds safety and mean daily mass augmentation of chickens was observed when 0,5% of “Ptitsesorb“ AC was included into trichotecene micotoxins infected fodder ration; the birds commenced a better usage of the ration nutrients, which caused enhancement of most production indices of chicken breeding, as compared to chicken which consumed analogical fodder with no added AC.

Thus, as presented in table 4, the AC “Ptitsesorb” produced by the ESMU “Neorganica”, included into birds ratio in doses of 0,5–1,0%, determined a 30–40% decrease of production costs, caused by the negative influence of fodder micotoxins.

Obtained data prove that fodder producing companies ought to use AC on large scale not only to increase economical indices of a given branch plant growing, zootechny, aviculture, hatchery, but also to confer new quality characteristics to the food consumed by people, in terms of its environmental cleanness, thus enhancing people’s life quality.

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SORPTION OF Cu^{2+} IONS ONTO DIATOMITE CONSTITUENTS

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Abstract: Studies of the sorption capacity towards Cu^{2+} ions of diatomite from the Ghidirim location of RM, as well as of the extracted clay phase are presented. Separated clay fraction from diatomic material is clean enough, and especially is rich in montmorillonite. Maximum sorption capacity for studied clay fraction is achieved by rising the temperature of calcination treatment up to 200°C. At higher temperatures the lattice of montmorillonite is contracted and its sorption capacity towards Cu^{2+} ions decreases strongly.

Keywords: diatomite, sorption of Cu^{2+} ions.

Introduction

Elimination of heavy metals from water is an important public health issue. Proposed methods for the removal of heavy metals include chemical precipitation, membrane filtration, ion exchange, alum coagulation, and adsorption. Adsorption is considered a reliable process that can be used to remedy a mixture of contaminants with low concentration. An efficient material that can be used, especially at a low cost, is diatomite or diatomaceous earth. Its physical and chemical properties such as high porosity, high permeability, small particle size, and large surface area, makes diatomite suitable for a wide range of industrial applications. Recently, many attempts have been made to increase sorption capacity of natural adsorbents toward heavy metals by chemical modification of their surface [1-5]. Despite the efforts made to utilize diatomite as an adsorbent, more studies on increasing its adsorption capacity are needed. In the Republic of Moldova significant deposits of diatomaceous earth are localized along course of the Dniester, on the sector Naslavcea – Camenca. Recently studies demonstrated that the mineral phase of the diatomite from the Ghidirim location contains a number of clay minerals, like montmorillonite (in a mixture with insignificant quantities of slightly chloritized montmorillonite), illite and kaolinite [6]. The diatomite contains also non-clay components as fine dispersed quartz and amorphous material, the more probable sources of which are opal, amorphous alumosilicates, aluminum and iron hydroxides. For extension of the field of application of diatomites, as well as intensification of their usage efficiency, the common procedures are the modification of the surface chemistry or the concentration of the diatomic phase by the elimination of impurities existing in the diatomic raw material. More often, the question is mooted to cleanse the diatomic phase of all other phases, including clay minerals [3-5]. In fact, the clay minerals which are present in the diatomic formations may be of a special interest for certain usage. Consequently, when the question is mooted to cleanse the diatomic formations, the formulation should also include the proceeding of reutilization of the clay components.

Current work includes studies of the separated clay fraction from the Ghidirim diatomite with the purpose to be utilized as mineral adsorbent for the removal of heavy metals from water.

Experimental

The diatomite from the Ghidirim location of RM was used for investigations. X-ray analysis was performed using the DRON-1 X-ray installation with CoKα radiation. Isotherm experiments were conducted by adding 0,5 g of adsorbent into a varied concentration of solution $CuSO_4$ in a cleaned stoppered glass bottle, and shaking in an isothermal shaker at 22°C for 24 h. The volume of adsorbate solutions was fixed at 50 mL. After equilibrium time, residual Cu^{2+} ions were analyzed by using atomic absorption spectrophotometer.

Results and discussions

Extraction of the clay fraction from the diatomite

Extraction of the clay minerals from the studied diatomite was performed using the method of sizing by settling in liquid media (distilled water) [7]. The procedure insures “mild” conditions for the extraction of clay constituents without their denaturing or destroying. For the extraction of different constituents from solid materials (soils, sediments, clay formations) are applied various chemical reagents (acids, bases, complexons etc.), however the degree of selectivity and effects on other components should be well-argued by individual investigations of each type of solid material [7]. Aqueous extraction applied in these studies are more easily to perform and, though sizing by settling in liquid media does not insure a complete extraction of all clay constituents from diatomite, such procedure, what is more importantly, does not alter natural chemical composition of clays.

X-ray analysis of the clay fraction extracted from the diatomite shows “clean” and distinctly reflexions (peaks) of the clay minerals and their veraciously behavior on thermal treatment [6]. The presence of montmorillonite, illite and kaolinit in separated clay fraction is uniquely demonstrated. The initial diatomic material contains some non-clay components, as fine dispersed quartz and amorphous material, the more probable sources of which are opal, amorphous alumosilicates, aluminum and iron hydroxides. Though some quantities of fine-dispersed quartz also penetrate into the separated clay fraction, these quantities are matchless smaller compared to those which are contained in the initial diatomic material. It is very importantly that the separated clay fraction does not contain amorphous material extracted from the initial diatomic material.

Thus, the applied procedure of clay fraction separation by sizing settling in liquid media proves to be very useful enabling possibilities for more accurate identification of the clay constituents of diatomic material. Also, along with an accurate diagnostics of the clay minerals, it is very important that the applied procedure allows to separate very clean clay fraction especially rich in montmorillonite, which can be utilized itself as mineral adsorbent for practical purposes.

Sorption of Cu^{2+} ions from water solution

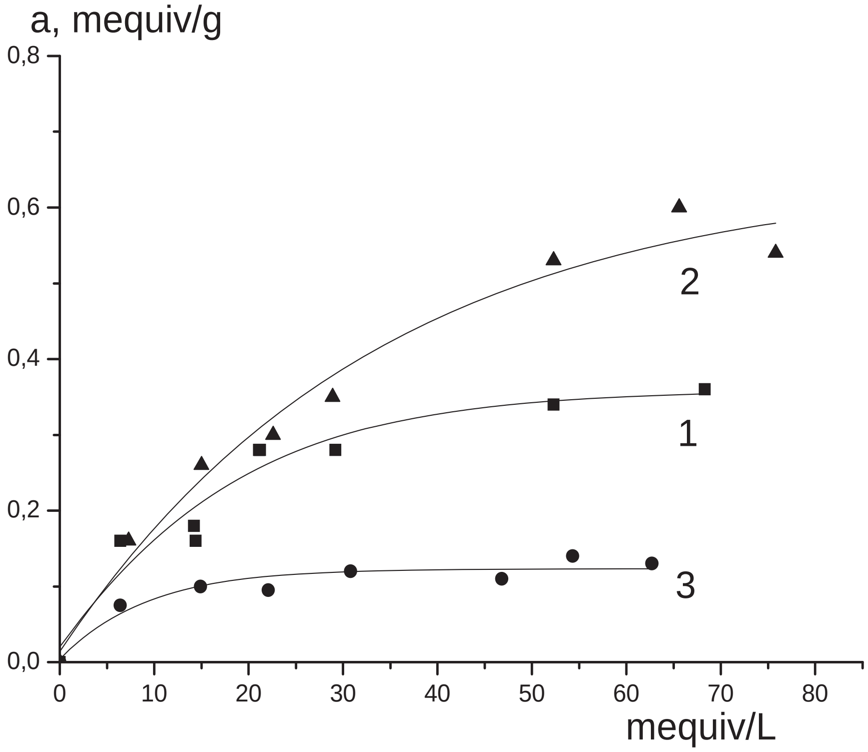

Fig. 1. Sorption isotherms of Cu^{2+} ions onto initial (integral) diatomic material (1), onto separated clay fraction (2), and onto non-clay fraction remained after separation of clays from diatomic material (3). Samples dried at 105°C.

Initial (integral) diatomic material, separated clay fraction and non-clay fraction remained after separation of clays from diatomic material were tested as adsorbents for Cu^{2+} removal from water solution. Figure 1 presents sorption isotherms onto these samples dried beforehand at 105°C.

Sorption capacity for initial (integral) diatomic material reaches 0,35 miliequivalents of Cu^{2+} ions per gram of adsorbent (or ~11,2 mg Cu^{2+}/g). Sorption capacity for extracted clay fraction from diatomic material reaches 0,57 miliequivalents of Cu^{2+} ions per gram of adsorbent (or ~18,2 mg Cu^{2+}/g). Thus, the sorption capacity of the extracted clay fraction is higher than that of initial (integral) diatomic material by about 1,6 times. Sorption capacity of non-clay fraction is lesser, and reaches only 0,12 miliequivalents of Cu^{2+} ions per gram of adsorbent (~3,8 mg Cu^{2+}/g), i.e. less than by about 3 and 5 times, as compared to that for integral diatomic material or extracted clay fraction. To be mentioned, that separated clay fraction from diatomic material is clean enough, and especially is rich in montmorillonite. This mineral possesses more higher sorption properties towards heavy metals than other clay minerals [1]. Non-clay fraction (remained after separation of clays from studied diatomite) is composed of fine dispersed quartz and amorphous material, the more probable sources of which are opal, amorphous alumosilicates, aluminum and iron hydroxides [6]. In this case, initial (integral) diatomite represents properly summary structure of the diatomic material including clay fraction on the background of the diatomic formation (non-clay components).

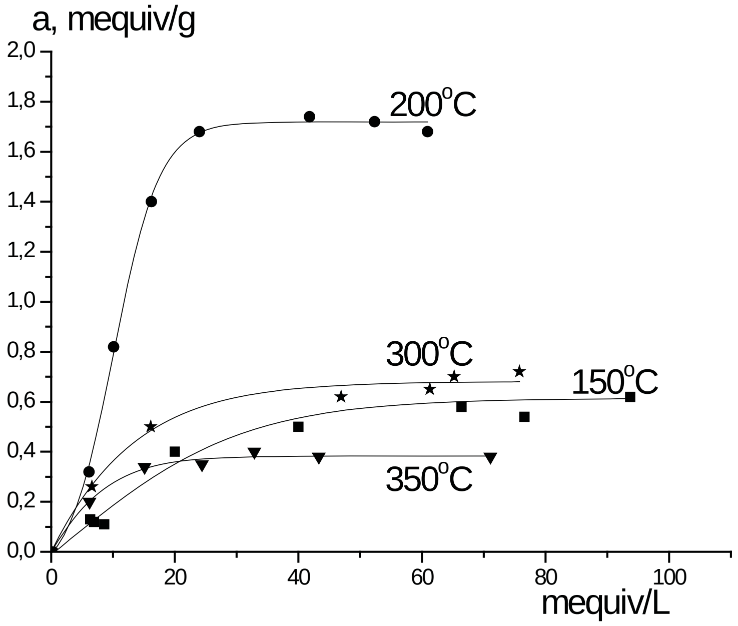

Fig. 2. Sorption isotherms of Cu^{2+} ions onto separated clay fraction. Samples calcined at 150, 200, 300 and 350°C.

Fig. 2 presents sorption isotherms of Cu^{2+} ions onto separated clay fraction calcinated beforehand at different temperatures. Calcination treatment at 200°C increases sorption capacity of clay fraction by about 3 times as compared to that for sample dried at 105 °C, and reaches ~1,8 miliequivalents of Cu^{2+} ions per gram of adsorbent (~58 mg Cu^{2+}/g). After calcination treatment at 300°C, sorption capacity of clay fraction decreases to ~0,7 miliequivalents of Cu^{2+} ions per gram of adsorbent (~22 mg Cu^{2+}/g), nevertheless this value exceeds by about 2 times sorption capacity of initial (integral) diatomic material.

Spectral analysis used to investigate the hydroxyl species and acid sites on diatomite surface shows the presence of the Lewis and Brønsted acid sites, and various hydroxyl species, including isolated hydroxyl groups, H-bonded hydroxyl groups and physically adsorbed water [2]. The Lewis acid sites in diatomite samples are considered to be resulted from the clay impurities, and the Brønsted acid sites are considered to be resulted from surface silanol groups (≡Si-OH) of diatomaceous silica associated with the physically adsorbed water by hydrogen bond. In fact, silanol groups are present also on the edges of the tetrahedral layers of clay minerals, being for montmorillonite an important source of the surface charge and Brønsted acid sites [8]. Delimitation of the Lewis and Brønsted acid sites in diatomite samples as is considered by [2] seems to be equivocal, and to conclude about the role of the surface chemistry of such complex materials as diatomaceous formations it is necessarily to separate adequately its constituents.

To be mentioned, that itself sorption process onto clay minerals is too complex, and can occur in the several forms, selective (specific or non-exchangeable sorption) and non-selective (exchangeable) sorption [1, 8]. In the case of non-selective sorption, clay minerals adsorb ions through exchangeable cations, also certain quantities of ions are electrostatically bound to the surface as counter ions in the diffusion layer which is formed because of the surface charge. Selectively adsorbed ions form inner-sphere complexes with surface hydroxide sites and are primarily bound to the surface of clay minerals by chemical bond. Such bond depends upon the structure of the surface chemistry and exhibits different behavior from electrostatic bonding.

As was mentioned, separated clay fraction from diatomic material studied in this work is clean enough, and especially is rich in montmorillonite. Therefore, it is reasonably to consider that registered dynamics of sorption capacity towards Cu^{2+} ions reflects properly dynamics of modification of the surface structure of montmorillonite during calcination treatment.

At moderate temperatures (e.g. up to 105°C, at which in this work clay fraction was dried beforehand), sorption process onto montmorillonite can occur both as selective (specific) sorption and non-selective (exchangeable) sorption. Specific to clay minerals is the presence of isomorphous substitutions in their lattice, e.g. in montmorillonite Al^{3+} may be substituted for Mg^{2+} in the octahedral layer. This gives rise to an unbalanced negative charge which is compensated for by adsorption on the surface of cations. These cations are exchangeable and are coordinated to water. The water molecules exhibit the peculiar property of being strongly dissociated, at least when the amount of adsorbed water is at the double layer level or less [9-11]. The enhanced dissociation is ascribed to the polarization effect of the cations to which they are coordinated. In consequence, the surface concentration of mobile protons is increased which is responsible for the Brønsted acidity:

$$Me^{n+}(OH_2)_{n-1} \rightarrow Me(OH)_{n-1}^{+} + (n-1)H^{+}$$

This type of acidity is considered dominating and the acid strength increases on dehydrating. Maximum sorption capacity for studied clay fraction in this work is achieved by rising the temperature of calcination treatment up to 200°C. At higher temperatures the lattice of montmorillonite is contracted as evidenced from X-ray analysis [6], and its sorption capacity towards Cu^{2+} ions decreases strongly.

Conclusions

Studies of the sorption capacity towards Cu^{2+} ions of diatomite from the Ghidirim location of RM, as well as of the extracted clay phase are presented. Separated clay fraction from diatomic material is clean enough, and especially is rich in montmorillonite. Maximum sorption capacity for studied clay fraction is achieved by rising the temperature of calcination treatment up to 200°C. At higher temperatures the lattice of montmorillonite is contracted and its sorption capacity towards Cu^{2+} ions decreases strongly.

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SOLUTION OF PROBLEM OF SUPPLYING THE POPULATION WITH QUALITY DRINKING WATER

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Abstract: The reasons of poor quality of the drinking water, submitted to consumers have been analyzed. The new concept of supplying the population with high quality drinking water is offered. Qualitative and safe for health drinking water is produced on site of its consumption (using the installations for well-room type). The ways for solving of legislative, organization and technical problems required for realization of the proposed concept are considered.

Keywords: high quality drinking water, supplying of the population, concept.

Introduction

The problem of supplying the population with quality drinking water, safe for human health, is especially socially significant since its solution directly affects the degree of ecological and epidemiological safety of many regions. The question on the quality of drinking water has long ago stepped over national frontiers and has taken a global nature. The priority in its statement belongs, first of all, to native scientists: to Academician of the Academy of Sciences of the USSR S.V.Iakovlev and to Academician of the Academy of Sciences of the UkrSSR L.A.Kulskij.

In numerous works they recognized that a society had come to understanding of the importance of the problem of drinking water quality. The hygienic congress on drinking water in Brussels in 1853 accepted the first standard regulating quality of drinking water on 9 parameters which could be authentically determined in conditions of laboratories of water supply plants and rendered obvious influence on the human health. Such parameters were normalized on organoleptic parameters of water quality and on its scale-forming properties. Further, aroused the necessity of bringing to conformity the technologies of preparation of drinking water to quality of water in a source of water supply at a legislative level.

The new concept of supplying the population with high quality drinking water

Real realization of such approach is DSTU 4808:2007 standard [1]. Alongside with basic researches in this area at its development the special attention was given to achievements in practice of water-preparation. DSTU 4808:2007 standard is the first normative document in Ukraine from a series of the standards guaranteeing the supplying of the population by high-quality drinking water. It incorporates essentially new approaches [2] of supplying of the population by high-quality drinking water with use as a source of water supply waters with a various degree of impurities. They consist in, that consumption of water for the economic - household purposes and for drink (including meal preparation) is precisely differentiated, and include:

- Creation and putting into practice of the uniform interconnected system of State Standards on drinking water, safe for human health, namely four standards: on drinking water supply sources; tap water of sanitary-and-hygienic purposes; drinking water of the increased quality; the packed water.
- The providing of the population with high-quality and safe for health drinking water in volumes, sufficient for satisfaction of physiological needs of the person, is carried out on a place of its production using installations of well-room type. Such drinking water is obtained mainly from underground waters protected against anthropogenic influence or from tap water.
- Water of the centralized water supply is produced mainly for sanitary-and-hygienic needs that almost in 100 times exceed physiological person need. In this case it is obtained mainly from the water of surface sources.
- For settlements and villages where the centralized water supply is absent, installations of well-room type are used for production of drinking water of the high quality from surface and underground water sources.
- In regions where there are no sources of low mineralized waters, drinking water of the improved quality could be received from sea and mineralized waters by their desalination.

Practical implementation of this concept is taking into account that specifically developed technical measures should be based on the complex knowledge about the factors affecting the quality of drinking water. Among these factors the following should be taken as the first priority: inequality in regional supply of quality sources of water which results in the necessity for finding alternative water sources; a strong tendency for the worsening of water quality in traditional sources of drinking water supply; secondary contamination of water at water treatment facilities and in the water system; the necessity of rapid response to the quality of the initial water at the time of obtaining drinking water; new possibilities of obtaining drinking water due to the use of modern technologies; the impact of the conditions of water supply on its quality and, certainly, the state of the water system. At the same time, one of the main areas of work aimed at supply of the population with water meet to high standards is the use for assessing the quality of the final products of new approaches making it possible to credibly evaluate water suitability for its consumption. Introduction of such techniques to the standards provides not only a possibility to monitor the consumer's quality of the water being used, but to create incentives for the introduction of technical solutions securing nontoxicity of drinking water and its physiological full value.

The basic sources of drinking water production are surface and underground waters. The majority of surface waters are characterized by a high level of biological and chemical pollution, in particular, surface-active substances, mineral oil, phenols etc.

In Ukraine centralized water supply is realized mainly due to use surface water sources (about 70%), the most of which are strongly polluted. About 35% of wastewaters enter water bodies without treatment and the untreated ones that are not in compliance with sanitary standards–39%. This is a reason for a stable tendency for deterioration of the ecological state of water bodies both in terms of sanitary-chemical and microbiological indicators. [3,4]. The research carried out as early as in 1994–1997 [5] demonstrated that each 4–5th samples of water from the water bodies, which formally refer to categories I and II does not meet hygienic standards by sanitary-chemical indicators and every 3–4th sample does not meet microbiological indicators. Organic compounds, suspended substances, oil products, phenols, synthetic SAS, heavy metals, etc. have remained priority pollutants for many years. Among disease pathogens salmonellas, eteroviruses, etc. are determined in water most often [5]. Monitoring results of the quality of the surface waters in the sites of water intakes of Ukraine's drinking water systems are evidence of the fact that the concentration of priority harmful chemical substances approaches the maximum admissible concentration (MAC) and in some cases even exceed them. Under such situation the possibility of obtaining quality drinking water become complicated since the existing water treatment systems effectively do not secure a barrier function as for technogenic chemical substances–they enter drinking water by transit. In 1994–1997 all surface water sources of Ukraine by the level of pollution approached the 3rd quality class and in terms of the international classification–class 4–5 [5]. And in this case the composition of the treatment facilities and technology of water treatment up to now have remained invariable.

The striking example of such a situation was detection in water supply systems of micromycetes (Fig.1).

Fig. 1. Micromycetes isolated from tap water of the city Kiev, *Aspergillus niger, Cladosporium cladosporioides*

Such mushrooms go as transit through existing water treatment facilities and essentially influence on disease incidence of the population.

The high level of pollution of drinking water supply sources has forced to think about a cardinal problem: whether approach of GOST 2874-82 «Drinking Water» to determination of quality of drinking water is true. GOST 2874-82 provides, that safety of water for human health can be estimated under the additive scheme based on values of MAC of pollution of the same class of danger. Thus it is not taken into account influences of synergism effect of impurities on toxicity of water.

Complex approach to the analysis of drinking water

The method of water biotesting recently developed by the A.V. Dumansky Institute of Colloid and Water Chemistry of National Academy of Sciences of Ukraine (ICWC) has made it possible to approach the issue of determining the degree of drinking water toxicity based, in principle, on new approaches.

On the basis of long-term researches the complex approach to the analysis of drinking water is developed by methods of analytical chemistry, microbiology and biotesting which allow revealing a degree of influence of water impurity on human health. Thus, full physiological value of drinking water is also determined. According to modern criteria drinking water is considered qualitative if it does not contain toxic substances of any origin, and the content of impurities includes an optimum set of the elements necessary for maintenance of functional activity of a human body. Based on this, classification of quality of drinking water on a degree of its toxicity including three categories is offered: safe, not safe and hazardous. Thus, the following circumstances are taken into account. First, at an environment about 60000 substances are present, which besides are transformed. Second, various compounds show synergism effect in toxicity of water which in many cases is not investigated. Clearly, that, even possessing reliable techniques of analysis, it is practically impossible to determine the concentration of each of them in real terms.

Results of complex testing of surface water, underground waters, chlorinated tap water and the tap water purified with use of installations such as "Vega", are given in Table 1.

Table 1

Comparative characteristic of quality of waters by results of complex testing

No	Water origin	Index of total toxicity (ITT)	Index of cytotoxicity (ICT)	Index of genotoxicity (IGT)	Cumulative Index of toxicity (CIT)	Category
1.	Surface waters (Dnepr river)	20	20	10	50	Not safe
2.	Underground waters	10	0	0	10	Safe
3.	Tap chlorinated water	60	45	65	170	Hazardous
4.	Tap water after treatment on "Vega" installation	10	5	5	20	Safe

As follows from Table 1, chlorination of water results in a sharp increase of its toxicity. The underground (artesian) waters, sampled from 9 well-room type of wells of Kiev in which both, the cytotoxicity and genotoxicity are absent, are safe for human health. Treatment of toxic tap water at "Vega" type installation (fig. 2,3) secure its deep purification that is due to removal of extremely toxic chloro-organic compounds.

Fig.2. Installation "Vega" with productivity of 20 liters per hour

Fig.3. Multifunctional module installation "Vega-3UM" with productivity of 5000 liters per hour

Installations of such type have been developed, tested and successfully work in Kharkov, Barvinkovo (Kharkov region), Lviv, Yalta, Donetsk, Novoazovsk (Donetsk region), Mukachevo (Zakarpatye region), Pologi (Zaporozhye region) and in other sites.

It would seem that by packaging qualitative drinking water from the several reliably tested sources it is possible to solve a problem of supplying of the population with qualitative drinking water. However, the carried out researches have shown, that at storage and transportation of water its toxicity increased over time and the biomass development occurs especially at the temperature over 20^{o}C. Besides the toxicity of water can be caused by an addition of unsafe preserving agents at its packaging. It is confirmed by data of Table 2, in which the data on quality of packed waters produced in Ukraine and Russia are given.

Table 2

Complex assessment of quality of the bottled waters on cyto-and genotoxicity parameters (2008)

No	Brand of bottled water	GP (geno-toxicity parameters M ‰)	GP (geno - toxicity parameters 2N ‰)	IC (Index cyto-toxicity)
1.	Morshynska	0	0	2,21
2.	Semeina	0	0,33	2,65
3	Bonaqa*	0	0,33	3,09
4.	St.Mirgorod	0	0,33	3,98
5	Arhyz*	0,33	0	3,09
6	-Selen*	0	0,66	3,94
7	Auqa minerale*	0,33	0,33	3,98
8	Waterhall *	0	0,99	5,70
9	Rokadovskaya	0	0,66	7,52
10.	Ordana	0,33	1	10,33
11.	Voda pytna	0,66	0,99	10,48
12.	Bebivita	0,66	0,99	10,56
13.	Vitel	0,33	1,67	10,62
14.	Hipp	0,67	1,34	11,75
15.	Demidovskaya*	0,99	1,33	11,40
16	Pushkarskaya jivaya*	0,99	1,33	11,84
17.	Svyatoi istochnik*	0,33	2,01	14,16
18.	Sophiya Kiev	0,99	1,33	16,11
19.	Prozora	0,33	2,01	16,14
20	Shishkin les*	1,66	1,33	16,24
21	Senezskaya*	0,99	2,34	16,23
22.	Doktor	1,67	2,34	18,14
23	Auqa-areal*	1,67	2,67	20,61
24.	Kalipso	1,67	3	20,35
25.	Humana	1,67	3	20,35
26.	Novoterskaya gornaya*	1,67	3	23,25
27.	SPA	2,01	3,66	22,14
28.	Znamenivskaya	2,01	3,66	22,12
29.	Piligrim*	2,34	4	28,07
30.	Contrex	3	4	27,34
31.	Gornaya vershina*	Test- organisms	died	

* - Water brands of Russia production.

1-4 –category “Safe water”, meets to high quality drinking water;

5-19 – category “Not safe water”, causes cytogenetic changes in cells of tests - organisms. It is undesirable for drinking use;

20-30 – category “Hazardous water”, makes strong cyto-and genotoxicity action on tests - organisms. It is unsuitable for drinking use.

As follows from Table 2, only four trademarks of packed drinking waters, available in retail network, are safe for human health.

Practical realization of the concept

For practical realization of the concept, it is necessary:

- its approval at the state level and its adoption as a first-priority program of action in the field of population water supply;
- development and endorsement in the nearest future of new State Standards for tap, drinking, and bottled water;
- adoption of enactments, which would ensure unconditional fulfillment of State Standards in the field of population water supply by all entities of economic activity irrespective of ownership forms;

– determination and implementation of first-priority and promising (for the nearest 5 years) of measures for the construction and equipment of water pump well rooms in Ukraine's regions.

Today, according to the aim to expand the realization of the new concept of supplying the population with qualitative drinking water, the Ministry of Housing and Municipal Economy of Ukraine together with A.V. Dumansky Institute of Colloid and Water Chemistry of National Academy of Sciences of Ukraine, have developed complex programs on introduction of installations of well-room type such as "Vega" in the Kherson, Sumy, Zhitomir regions, and in cities: Novograd-Volynsk and Borispol.

For operative quality assurance of the produced drinking water in ICWC has been developed the portable laboratory " Aqua-test " intended for the control of presence of the most widespread pollution of surface and underground waters (30 components) (fig. 4).

Fig. 4. Portable laboratory "Aqua-test" for monitoring water quality.

The principle of laboratory work rationally combines low cost and wide functionalities.

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MONITORING OF THE EURASIAN NATURAL MINERAL WATERS OF CHLORIDE-HYDROCARBONATE TYPE

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Abstract: Mineral waters of Russia, the CIS countries (Ukraine, Belarus, Moldova, Armenia, Azerbaijan, Georgia and Uzbekistan) and EU (Germany, France, Italy, Spain and some East European countries) carried to Chloride-Hydrocarbonate type have been investigated in this work. The analytical dependences connecting, entered by authors, characteristic parameters of structure of waters ($\overline{Э}$, *B*, *Φ*, *R*) with independent variables of ionic structure and concentration are resulted.

Keywords: mineral waters, mathematical model, monitoring.

Introduction

Natural mineral waters concern to the major natural resources widely applied in medicine, food and a number of other branches of manufacture. The expansion of geography of developing deposits, extractions and pouring of mineral waters has led to the necessity of developing the system of monitoring and estimated parameters of quality of various waters on their origin and properties.

In this case the issue is on the development of mathematical model of water-salt systems of mineral waters on the basis of which it is possible to spend identification of regional mineral waters of various genesis and structure on their conformity to widely known (standard) mineral waters. Standard waters are presented to Russia in the state standard of GOST 13273-88 " Mineral, drinking, medical waters and medical table."

Now there are different ways of classification of mineral waters on a chemical compound. However the general model of classification of the mineral waters allowing quantitative estimation of conformity of regional mineral waters to reference waters of certain types, groups and classes has not been developed until now.

The purpose of this work consisted in the establishment of the quantitative dependences connecting certain estimated parameters with the mineralization and ionic structure of natural mineral waters of Chloride-Hydrocarbonate type. Mineral waters of Russia, the CIS countries and EU which are closest to the mineral waters included in State standard – GOST 13273-88 in terms of their ionic structure have been investigated in this work.

Methodical part

As the estimated parameters applied for the identification of waters of various origin and structure we had been introduced the representations about characteristic parameters of structure of waters and their interrelations with a chemical compound and the general mineralization of mineral waters.

As the initial parameters accepted for the mathematical description of structure of water-salt systems of mineral waters, following values have been entered:

1. $\overline{M}$ - The general mineralization of water, g/dm^3.

Value $\overline{M}$ is function of two independent variables C_N and ${}^{X_{Cl'}}\!/_{X_{HNO_3'}}$, where C_N – equivalent (normal) concentration, eqv/dm^3 and ${}^{X_{Cl'}}\!/_{X_{HNO_3'}}$ - the attitude of equivalent shares anions Cl' and HCO_3', forming the certain type of mineral water.

2. $\overline{Э}$ - Gram-equivalent of salt system of mineral water, g/eqv, counted from a known parity in chemistry:

$$\overline{M} = \overline{Э} \cdot C_N \,, \tag{1}$$

The value $\overline{Э}$ is accepted by us as the first characteristic parameter defining the type of mineral water and allowing to have investigated mineral waters of various ionic structures in the certain sequence.

The value $\overline{Э}$ can be calculated on the parity:

$$\overline{Э} = a({}^{X_{Cl'}}\!/_{X_{HNO_3'}})^b \,, \tag{2}$$

where *a* and *b* – are the constants corresponding to mineral waters of one type.

The estimation of an accessory of investigated water to the certain group of standard waters was performed by means of the function B, entered by us and connected with value $\overline{Э}$ by the parity:

$$B = \frac{\overline{\text{Э}}^2}{2}, \text{ g}^2/\text{eqv}^2 \tag{3}$$

Using the representations of quantum mechanics it is possible to assume, that the square of a characteristic parameter $\overline{\text{Э}}$ of a solution is a measure of probability of conformity of an investigated solution to the some, are mainly determined (standard), to a solution.

In this case the square of a characteristic parameter $\overline{\text{Э}}$ can be presented in the form of the second characteristic parameter which we have marked by symbol *B*.

In general the dependence of group value *B* on the structure of solutions of the mineral waters forming the separate group of waters can be represented in the form of the parity:

$$B = \frac{a^2}{2} \cdot \left(X_{Cl'} / X_{HNO_3'} \right)^{2b} \tag{4}$$

The analytical dependences presented by the equation (4) for two bordering groups on structure of waters allow solving a problem about the establishment of border of water division into different groups. Solving of this task is reduced to finding the value $X_{Cl'} / X_{HNO_3'}$ by joint solving of the system of two equations of the function *B* on the parity:

$$X_{Cl'} / X_{HNO_3'} = 10^{\frac{\lg a' - \lg a''}{b'' - b'}}, \tag{5}$$

where indexes ‘ and “ - correspond to vicinal groups of mineral waters.

In order to estimate the belonging of separately taken mineral water to a certain classe of waters which are a part of group of standard waters, we have presented the third characteristic parameter *Ф* which represents the first derivative function *B* on argument $X_{Cl'} / X_{HNO_3'}$.

Value *Ф* can be calculated from the parity:

$$\Phi = y'[B] = A\left(X_{Cl'} / X_{HNO_3'} \right)^{D}, \tag{6}$$

where *A* and *D* – the constants accordingly equal: $a^2 \cdot b$ и $2b-1$.

The values A and D characterize the mineral waters with the close values of the value $X_{Cl'} / X_{HNO_3'}$, forming a separate class of certain group of mineral waters.

A logarithmic conversion of the equation (6) allows to receive the equation of linear regression and to continue processing the results by methods of mathematical statistics. In this work, the base computer program «Statistic-6» was applied.

The fourth characteristic parameter of mineral waters structure estimates the water-salt system in the form of function *R* of two independent variables C_N and $X_{Cl'} / X_{HNO_3'}$, which is the second derivative of function $\overline{M}$, described by the equation (1).

The differentiation of function $[\overline{M}(C_N, \frac{X_{Cl'}}{X_{HCO_3'}})]$, which is the complex function, has led to the parity:

$$R = y''[\overline{M}_i] = [\overline{\text{Э}}]''[C_N + \frac{2}{b-1}(\frac{X_{Cl'}}{X_{HCO_3'}})], \tag{7}$$

where $[\overline{\text{Э}}]''$ - the second derivative of value $\overline{\text{Э}}$, corresponding expression

$$[\overline{\text{Э}}]'' = ab(b-1)(\frac{X_{Cl'}}{X_{HNO_3'}})^{(b-2)} \tag{8}$$

Thus, the natural mineral waters corresponding to ascertained group of standard waters according to GOST 13273-88, should have strictly fixed quantitative characteristic parameters: $\overline{\text{Э}}$, *B*, *Ф* and *R*, which will allow to estimate an accessory of investigated mineral water to the certain group ($\overline{\text{Э}}$ and *B*) and to a concrete class of waters of the given group on structure (*Ф*) and concentration (*R*) [1].

Results and Discussion

For natural Chloride-Hydrocarbonate waters included in XXII group of GOST 13273-88, we obtained the following dependences.

$$\overline{\text{Э}} = 70,71\left({X_{Cl'}}/{X_{HNO_3'}}\right)^{-0,0762}, \qquad (9)$$

$$B = 2498\left({X_{Cl'}}/{X_{HNO_3'}}\right)^{-0,1524}, \qquad (10)$$

$$\Phi = -381\left({X_{Cl'}}/{X_{HNO_3'}}\right)^{-1,1524} \qquad (11)$$

The analysis of the equations (9) - (11) has shown that mineral waters of the Chloride-Hydrocarbonate type, which belong according to GOST 13273-88 to XXII group, can be actually assigned to an independent group of waters characterized by group parameters $\overline{\text{Э}}$ and *B*, according to equal values: 70,71 and -0,0762.

We established the borders of division of waters into groups between waters of Hydrocarbonate and Chloride-Hydrocarbonate types, and also of Chloride-Hydrocarbonate and Chloride types on value ${X_{Cl'}}/{X_{HNO_3'}}$. Researches have shown, that the border of division in the first case is defined by the value ${X_{Cl'}}/{X_{HNO_3'}}$, equal to 0,218 and corresponds to the content of ions in a solution of 78,2 % of mg-eqv. In the second case these value are equal, accordingly: 3,624 and 21,6 % of mg- eqv.

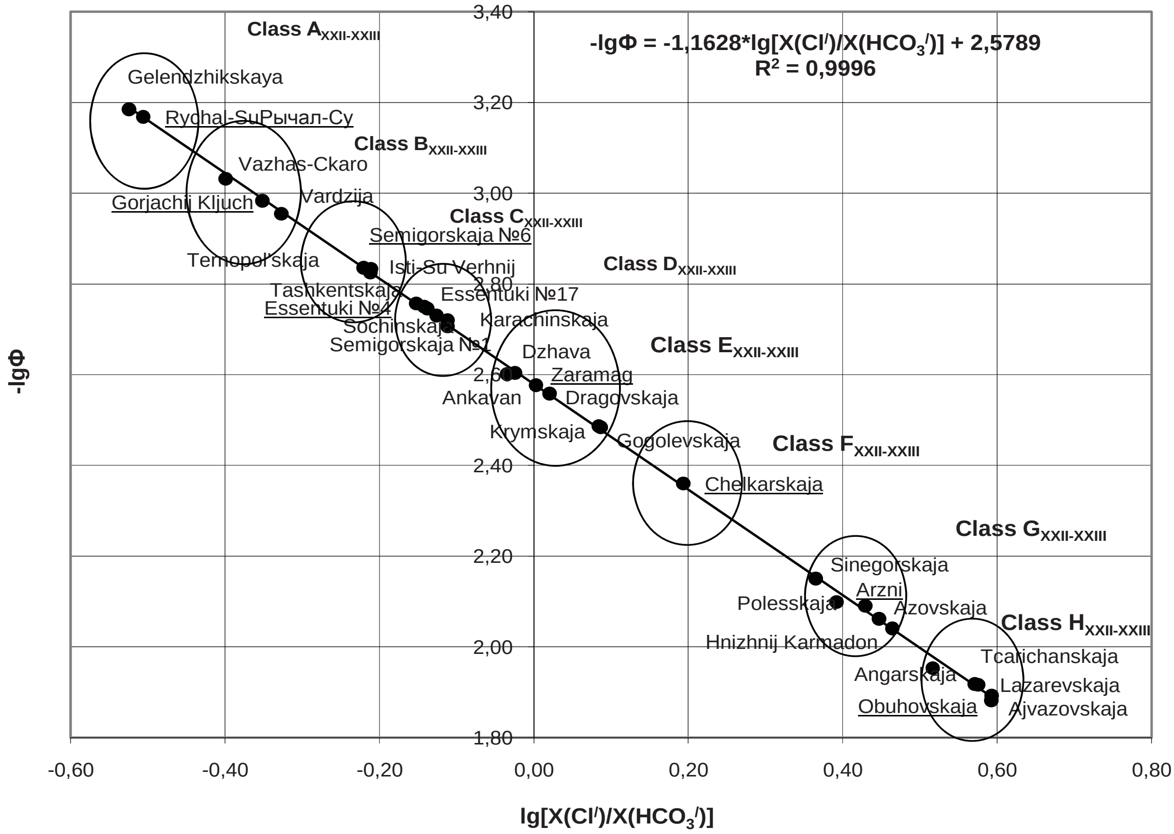

Figure 1. Graphic dependence of function “$-\lg\Phi_i \; f[\lg({X_{Cl'}}/{X_{HNO_3'}})_i]$” for mineral waters XXII-XXIII of group according to the specified classification.

Figure 1 presents the graphic dependence of function “$-\lg\Phi_i \; f[\lg({X_{Cl'}}/{X_{HNO_3'}})_i]$” for standard waters of Chloride-Hydrocarbonate type, included in XXII- XXIII group (GOST 13273-88).

Analytical expression of the equation of linear regress corresponds to expression

$$-\lg \Phi_i\,(\pm 0{,}007) = -1{,}163(\pm 0{,}006)\lg({}^{X_{Cl'}}\!/\!_{X_{HNO_3'}})_i + 2{,}579(\pm 0{,}002), \tag{12}$$

$$R^2 = 0{,}9996$$

From figure 1 follows, that separate representatives of mineral waters of Chloride-Hydrocarbonate type, assigned to XXII-XXIII groups, can be divided according to the size of the characteristic parameter Φ_i into half-groups (classes) in process of change of the value Φ_i:

1. The class *A* – Rychal-Su (Russia), Gelendzhikskaja (Russia);
2. The class *B* – Vazhas-Ckaro (Georgia), Gorjachij Kljuch (Russia), Vardzija (Georgia);
3. The class *C* – Ternopol'skaja (Ukraine), Semigorskaja №6 (Russia), Isti-Su Verhnij (Azerbaijan),
4. The class *D* – Tashkentskaja (Uzbekistan), Essentuki №4 and №17 (Russia), Karachinskaja (Russia), Semigorskaja №1 (Russia), Sochinskaja (Russia);
5. The class *E* – Dzhava (Georgia), Ankavan (Armenia), Zaramag (Russia), Dragovskaja, Gogolevskaja and Krymskaja (Ukraine);
6. The class *F* – Chelkarskaja (Kazakhstan);
7. The class *G* – Polesskaja (Ukraine), Sinegorskaja, Azovskaja (Russia);
8. The class *H* – Lazarevskaja, Obuhovskaja (Russia), Arzni (Armenia), Ajvazovskaja (Ukraine).

In figure 1, mineral waters inside a circle represent the separate subgroups (classes) generated on the basis of close values of value ${}^{X_{Cl'}}\!/\!_{X_{HNO_3'}}$.

Mineral waters are characterized within the limits of each class by the value of the characteristic parameter *R*, defining general mineralization (or concentration) of separately taken natural water.

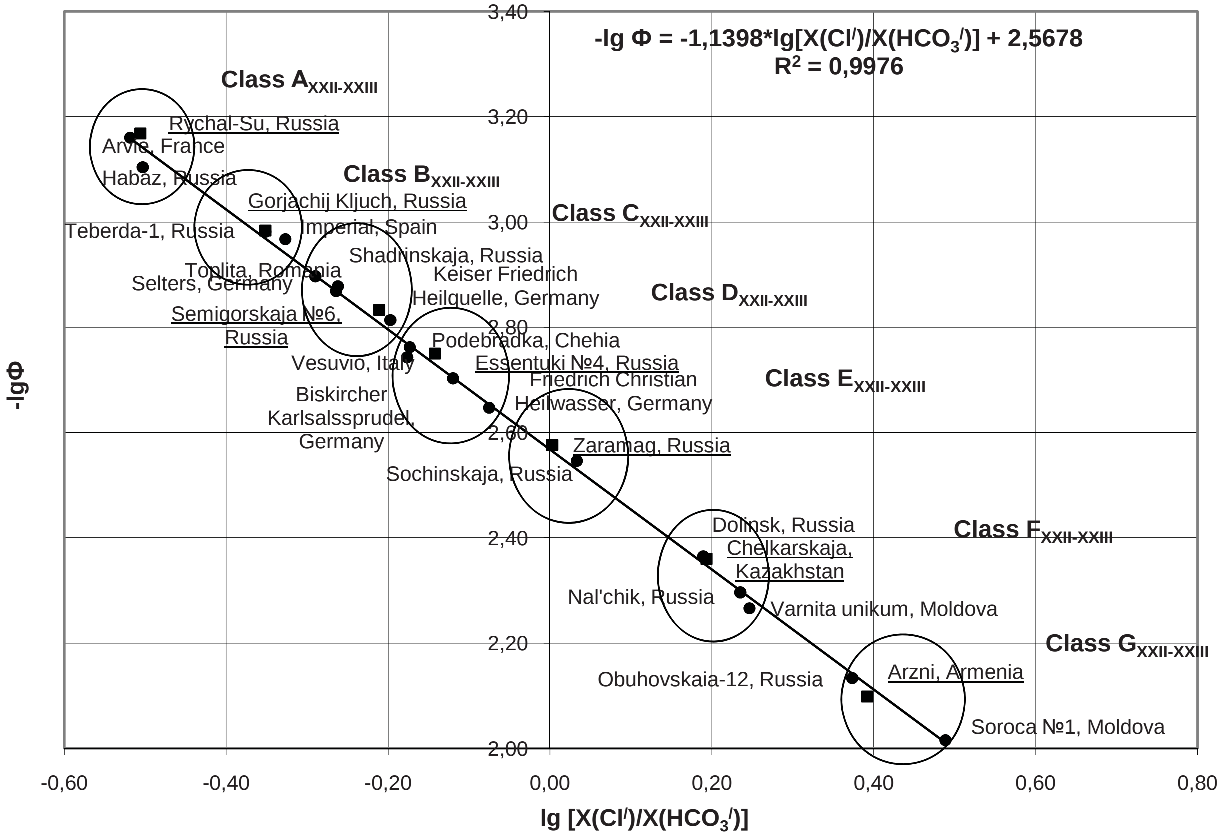

Figure 2. Graphic dependence of function " $-\lg \Phi_i\ \text{-}\ f[\lg({}^{X_{Cl'}}\!/\!_{X_{HNO_3'}})_i]$ **" for the Eurasian regional mineralized waters.**

In figures 2 and 3 are given the graphic dependences of logarithmic function "$-\lg \Phi_i$ - $f[\lg({X_{Cl'}}/{X_{HNO_3'}})_i]^{''}$" for regional Eurasian natural waters: mineral (fig.2) and waters with low mineralization with concentration less than 1 g/dm^3 (fig.3).

Analytical expressions of logarithmic functions for the specified waters correspond to the equations:

$$(2)\ -\lg \Phi = -1{,}144\lg({X_{Cl'}}/{X_{HNO_3'}}) + 2{,}5685,\quad R^2 = 0{,}9976 \tag{13}$$

and

$$(3)\ -\lg \Phi = -1{,}1345\lg({X_{Cl'}}/{X_{HNO_3'}}) + 2{,}547,\quad R^2 = 0{,}9962 \tag{14}$$

The comparison of values of factors *A* and *D* for the standard and Eurasian regional mineral waters given by the equations (12) - (14) has shown their full practical concurrence. The generalized statistical processing of the obtained data for the Eurasian and standard waters has shown, that the factor of correlation of the equations is in all cases within the limits of $r = 0{,}995 - 0{,}999$ and the error of calculations did not exceed the standard deviations of 5 %-s' level of a confidential interval.

The analysis of settlement data of a characteristic parameter of structure *Φ* from analytical dependences (13) and (14) has shown, that natural mineral waters of different sources of the Eurasian continent, regardless of their geographical position, form families of waters with close values of ionic structure ${X_{Cl'}}/{X_{HNO_3'}}$, which testifies to unity of genesis of water-containing layers and mineral waters.

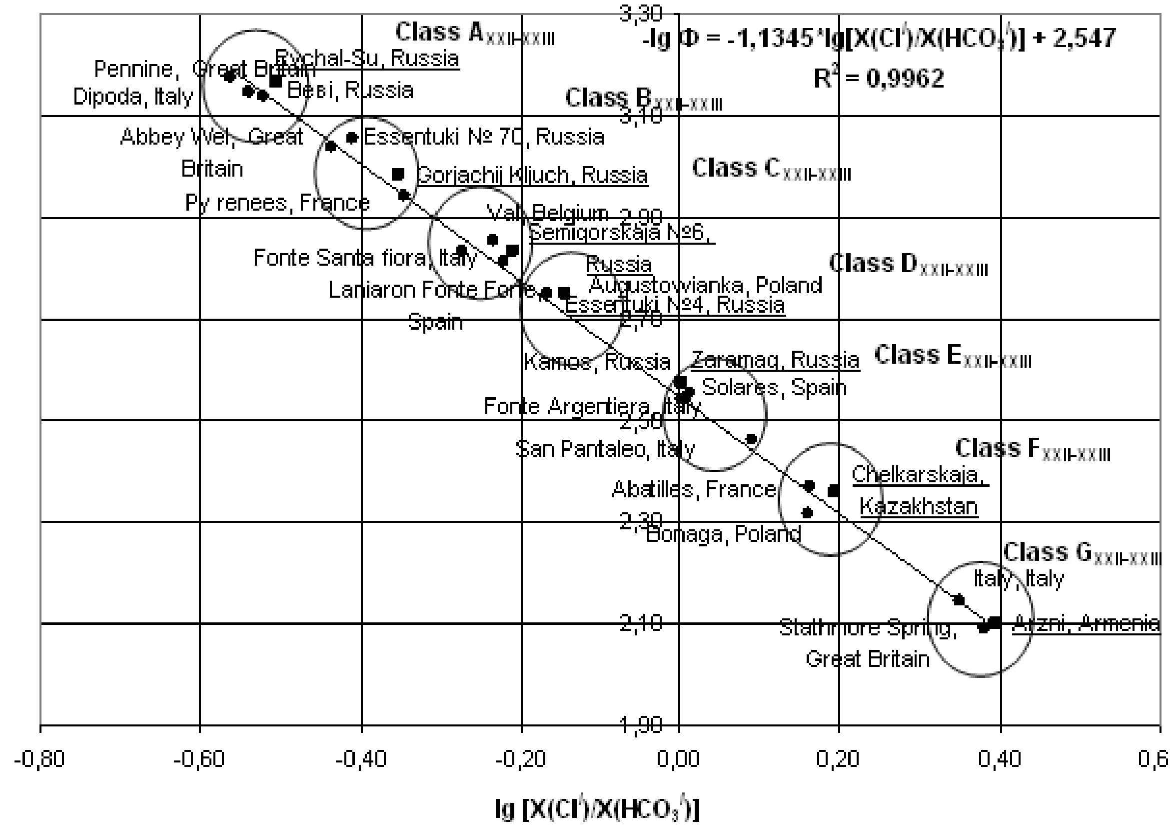

Figure 3. Graphic dependence of function "$-\lg \Phi_i$ - $f[\lg({X_{Cl'}}/{X_{HNO_3'}})_i]^{''}$" for the Eurasian regional waters with low mineralization.

At the same time, it is necessary to note that the mineral waters assigned to one class, have various mineralizations, at significant time periods, which in our opinion is due to various conditions of the physical and chemical processes proceeding at their formation and various sources of receipt in water-containing layers H_2O and CO_2 [2-4].

Conclusions

As a result of the estimation of structure of Eurasian natural mineral waters and waters with low mineralization of Chloride-Hydrocarbonate type, using the characteristic parameters $\overline{\text{Э}}$, B, Φ and R, the following conclusions may be drawn.

a) Characteristic parameters $\overline{\text{Э}}$, B, Φ and R allow to perform the identification of any mineral water on conformity to reference waters, regardless of the geographical location of the source, with a high degree of reliability;

b) Values of characteristic parameters of the mineral water counted on initial data of the chemical analysis of structure, can serve as a quantitative estimation of quality of mineral water and may be used for the organization of the system of national and interstate waters monitoring;

c) Characteristic parameters of waters structure can be used for the examination of quality and conformity of mineral water to the passport characteristics of declared analogue of standard water, and also for the establishment of source location;

d) The expansion of geography of finding the sources of the mineral waters identified on their conformity to reference mineral waters on characteristic parameters $\overline{Y}$, B, Φ and R allows rational utilization of regional natural water resources and promote the social development of territory of location the sources of mineral waters which were disregarded before.

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SYNTHESIS, CRYSTAL STRUCTURE, AND SPECTRAL AND MAGNETIC PROPERTIES OF CHLORO-BRIDGED CHAIN COMPLEX OF DINUCLEAR RUTHENIUM(II,III) 3,4,5-TRIETHOXYBENZOATE

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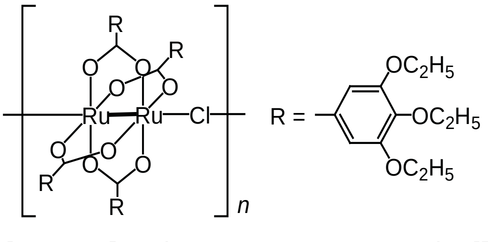
Abstract: A chloro-bridged chain complex constructed from paddlewheel-type dinuclear ruthenium(II,III) carboxylate units, $[Ru_2\{3,4,5\text{-}(C_2H_5O)_3C_6H_2CO_2\}_4Cl]_n\cdot 1.2nC_2H_5OH$ ($\mathbf{1}\cdot 1.2nC_2H_5OH$), was synthesized and characterized by elemental analysis and IR and UV-vis spectroscopies. The single-crystal X-ray analysis showed that the complex forms a zig-zag chain structure, in which the chloro ligands bridge the dinuclear units at the axial positions with the Ru1–Cl–Ru2 angle of 120.38(7)°. A broad band around 1144 nm and a band at 475 nm were observed in the diffused reflectance spectra and ascribed to a $\delta\rightarrow\delta^*$ and a $\pi(RuO, Ru_2)\rightarrow\pi^*(Ru_2)$ transitions, respectively. Temperature-dependence of magnetic susceptibility showed that the antiferromagnetic interaction between the dinuclear units is weak ($zJ = -0.8$ cm^{-1}) with D value of 60 cm^{-1}.

Keywords: dinuclear ruthenium(II,III) carboxylate; magnetic property; chloro-bridged complex; polymeric complex.

1. Introduction

There have been considerable interests in the coordination chemistry of paddlewheel-type dinuclear ruthenium(II,III) carboxylates $[Ru_2(O_2CR)^4]^+$, which are paramagnetic with three unpaired electrons on the $\pi^{*2}\delta^{*1}$ orbitals in the metal–metal bonds and with large zero-field splitting (ZFS) [1–4]. It is known that dinuclear ruthenium carboxylates form one-dimensional polymeric compounds with some bidentate bridging ligands L, $[Ru_2(O_2CR)_4L]_nX_n$(X=monoanion). We found that magnetic interaction between the dinuclear units is antiferromagnetic and the strength of the interaction depends on the bridging ligand L [5,6]. Recently, we reported magnetic properties of polymeric compounds of ruthenium(II,III) 3,4,5-trioctanoxybenzoates, $[Ru_2\{3,4,5\text{-}(C_8H_{17}O)_3C_6H_2CO_2\}_4Y]_n$ ($Y = Cl^-, OCN^-$) with liquid crystalline properties [7]. However, their structures have never been elucidated by X-ray crystal structure analysis because of their liquid-crystalline properties themselves. In this study, we prepared a chain complexes of ruthenium(II,III) 3,4,5-triethoxybenzoate with chloro bridging ligand, $[Ru_2\{3,4,5\text{-}(C_2H_5O)_3C_6H_2CO_2\}_4Cl]_n\cdot 1.2nC_2H_5OH$ ($\mathbf{1}\cdot 1.2nC_2H_5OH$) in the hope of obtaining single-crystals suitable for X-ray structure analysis.



Scheme 1. $[\mathbf{Ru_2\{3,4,5\text{-}(C_2H_5O)_3C_6H_2CO_2\}_4Cl]_n}$.

The obtained complex was characterized by elemental analysis and IR and UV-vis spectra, and temperature dependence of magnetic susceptibilities. The X-ray crystal structure analysis was performed for this complex.

2. Results and Discussion

Crystals of a chloro-bridged polymeric complex of dinuclear ruthenium(II,III) 3,4,5-triethoxybenzoate, $[Ru_2\{3,4,5\text{-}(C_2H_5O)_3C_6H_2CO_2\}_4Cl]_n\cdot 1.2nC_2H_5OH$ ($\mathbf{1}\cdot 1.2nC_2H_5OH$), were formed from a reaction of a precursor complex, $[Ru_2(O_2CC_2H_5)_4Cl]_n$, and 3,4,5-triethoxybenzoic acid in ethanol. The formation of the mixed-valence dinuclear ruthenium(II,III) 3,4,5-triethoxybenzoate with a metal-metal bond was confirmed by the infrared and electronic spectra, and single-crystal X-ray structure analysis.

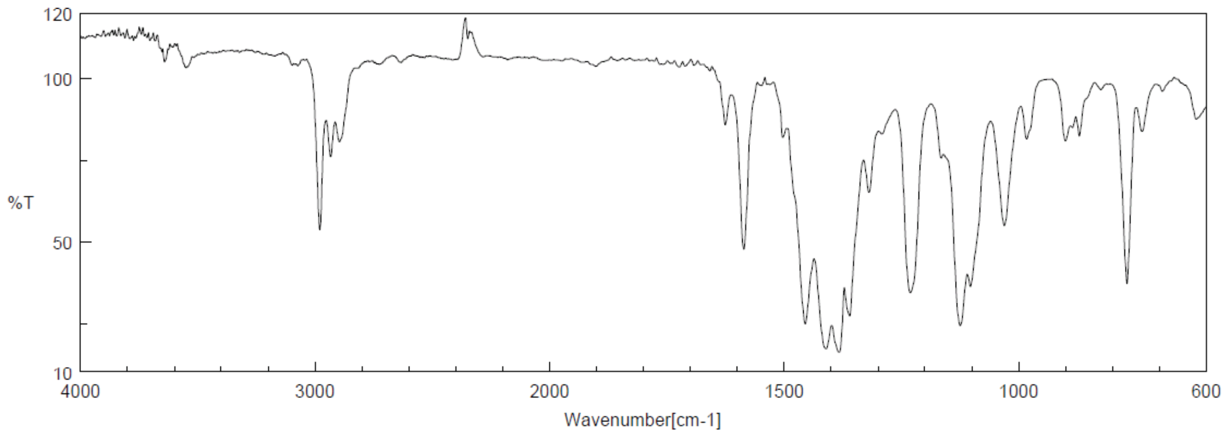


Figure 1. Infrared spectra of [Ru$_2${3,4,5-(C$_2$H$_5$O)$_3$C$_6$H$_2$CO$_2$}$_4$Cl]$_n$·1·1.2nC$_2$H$_5$OH (1·1.2nC$_2$H$_5$OH).

In the infrared spectrum, two strong bands at 1455 and 1383 cm^{-1} assignable to asymmetrical and symmetrical stretching vibrations of the carboxyl groups, respectively (Fig. 1). The strong bands at 1411 and 1360 cm^{-1} may be attributed to δ(CH$_2$) and δ_s(CH$_3$) in the ethoxy groups, respectively. The stretching vibrations of aromatic ring were observed at 1586 and 1503 cm^{-1}, and a weak band of ν(Ar–H) at 3074 cm^{-1}. Moreover, stretching modes at 3642 and 3550 cm^{-1} and bending mode at 1626 cm^{-1} due to the hydroxyl groups of ethanol molecules were observed. A thermogravimetric analysis showed that **1**·1.2nC$_2$H$_5$OH releases the ethanol molecules from room temperature to ca. 75 °C and decomposes from ca. 300 °C (Fig. 2). These results suggest that the ethanol molecules in the crystals of **1**·1.2nC$_2$H$_5$OH are lost at room temperature.

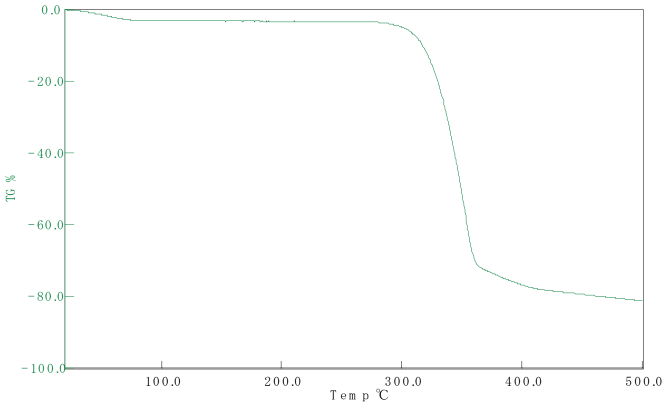


Figure 2. Thermogravimetric analysis of [Ru$_2${3,4,5-(C$_2$H$_5$O)$_3$C$_6$H$_2$CO$_2$}$_4$Cl]$_n$·1.2nC$_2$H$_5$OH (1·1.2nC$_2$H$_5$OH).

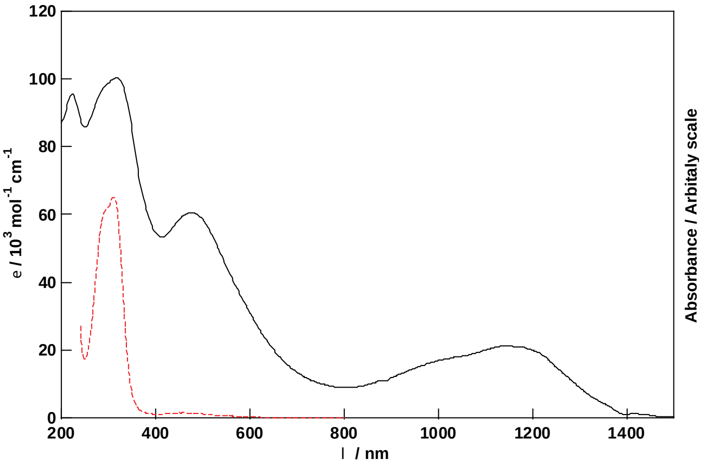


Figure 3. Electronic spectra of [Ru$_2${3,4,5-(C$_2$H$_5$O)$_3$C$_6$H$_2$CO$_2$}$_4$Cl]$_n$·1.2nC$_2$H$_5$OH (1·1.2nC$_2$H$_5$OH) in solid (solid line) and CH$_2$Cl$_2$ (dashed line).

The electronic spectra of **1**·1.2$n$$C_2H_5OH$ are shown in Fig. 3. The paddlewheel-type dinuclear structure of **1** can be considered to be maintained in CH_2Cl_2 solution, because the spectrum in the solution is similar to that in solid. A weak broad absorption band around 1144 nm in solid is typical for ruthenium(II,III) carboxylates and can be attributed to a δ→δ* transition within ruthenium(II,III) dinuclear core [8]. A medium band at 475 nm may be due to π(RuO, Ru_2)→π*(Ru_2) transition [9,10].

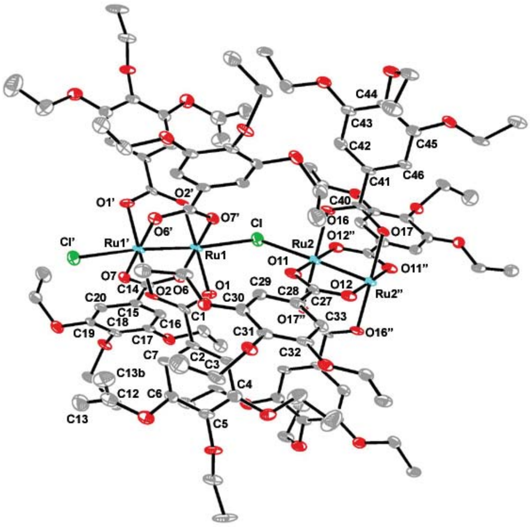


Figure 4. ORTEP drawing of the structure of [Ru_2{3,4,5-$(C_2H_5O)_3C_6H_2CO_2$}$_4$Cl]$_n$·1.2$n$$C_2H_5OH$ (1·1.2$n$$C_2H_5OH$) showing the 50% probability thermal ellipsoids. Hydrogen atoms and ethanol molecules are omitted for clarity. Symmetry codes: prime: 3–*x*, 2–*y*, –1–*z*; double prime: 4–*x*, 2–*y*, –1–*z*.

Table 1

Selected bond distances (Å) and angles (°) with esds in parentheses for [Ru_2{3,4,5-$(C_2H_5O)_3C_6H_2CO_2$}$_4$Cl]$_n$·1.2$n$$C_2H_5OH$ (1·1.2$n$$C_2H_5OH$).

Ru1–Ru1^{i}	2.2907(12)	Ru2–Ru2^{ii}	2.2922(11)
Ru1–Cl	2.5580(19)	Ru2–Cl	2.5748(17)
Ru1–O1	2.040(4)	Ru2–O11	2.038(4)
Ru1–O2^{i}	2.029(4)	Ru2–O12^{ii}	2.037(4)
Ru1–O6	2.026(4)	Ru2–O16	2.045(4)
Ru1–O7^{i}	2.013(4)	Ru2–O17^{ii}	2.024(4)
Ru1^{i}–Ru1–Cl	174.04(5)	Ru2^{ii}–Ru2–Cl	170.70(5)
Ru1^{i}–Ru1–O1	90.64(14)	Ru2^{ii}–Ru2–O11	90.35(13)
Ru1^{i}–Ru1–O2^{i}	88.26(13)	Ru2^{ii}–Ru2–O12^{ii}	88.54(13)
Ru1^{i}–Ru1–O6	89.47(13)	Ru2^{ii}–Ru2–O16	90.13(12)
Ru1^{i}–Ru1–O7^{i}	89.35(13)	Ru2^{ii}–Ru2–O17^{ii}	88.91(12)
Cl–Ru1–O1	95.06(14)	Cl–Ru2–O11	97.70(14)
Cl–Ru1–O2^{i}	86.05(13)	Cl–Ru2–O12^{ii}	83.44(13)
Cl–Ru1–O6	92.29(14)	Cl–Ru2–O16	94.66(12)
Cl–Ru1–O7^{i}	88.97(13)	Cl–Ru2–O17^{ii}	86.45(12)
O1–Ru1–O2^{i}	178.80(19)	O11–Ru2–O12^{ii}	178.81(18)
O1–Ru1–O6	89.50(17)	O11–Ru2–O16	88.86(18)
O1–Ru1–O7^{i}	89.58(16)	O11–Ru2–O17^{ii}	90.03(18)
O2^{i}–Ru1–O6	90.00(17)	O12^{ii}–Ru2–O16	90.70(18)
O2^{i}–Ru1–O7^{i}	90.90(17)	O12^{ii}–Ru2–O17^{ii}	90.39(18)
O6–Ru1–O7^{i}	178.50(19)	O16–Ru2–O17^{ii}	178.52(17)
Ru1–Cl–Ru2	120.38(7)		

Symmetry codes: (i) 3–*x*, 2–*y*, –1–*z*; (ii) 4–*x*, 2–*y*, –1–*z*.

A band at 318 nm and a shoulder around 289 nm may be due to transitions within the carboxylato ligand. In CH_2Cl_2 solution, large molar absorbance coefficients of the corresponding band at 310 nm and shoulder around 294 nm were observed. These are similar to the band at 272 nm and shoulder around 296 nm of 3,4,5-triethoxybenzoic acid in CH_2Cl_2 solution.

The single-crystal X-ray analysis at 90 K shows a chain structure of **1**·1.2*n*C_2H_5OH, of which the axial positions of the paddlewheel-type dinuclear ruthenium core are occupied by chloro ligands. The ORTEP diagram is shown in Fig. 4 and the selected bond distances and angles are listed in Table 1. There are two crystallographically independent halves of the dinuclear units. Each of the dinuclear units has an inversion centers on the midpoint of the Ru–Ru bond.

The chloro ligands bridge the dinuclear units alternately to form a zig-zag chain molecule along *a*-axis. The Ru–Cl–Ru angle is **1**·1.2*n*C_2H_5OH (120.38(7)°). The Ru–Ru (2.291(1) and 2.292(1) Å) and Ru–Cl (2.558(2) and 2.575(2) Å) lengths of **1**·1.2*n*C_2H_5OH are normal as this kind of chloro-bridged chain complexes of dinuclear ruthenium(II,III) carboxylates [2]. The 3D network of **1**·1.2*n*C_2H_5OH is build up by van der Waals interactions and hydrogen bondings, which are C–H···O interactions between the ethoxy groups and C–H···π interaction between the ethoxy group and the phenyl ring along the *b*-axis, and involve ethanol molecules along the *c*-axis. The hydrogen bonding geometry is shown in Fig.5 and Table 2.

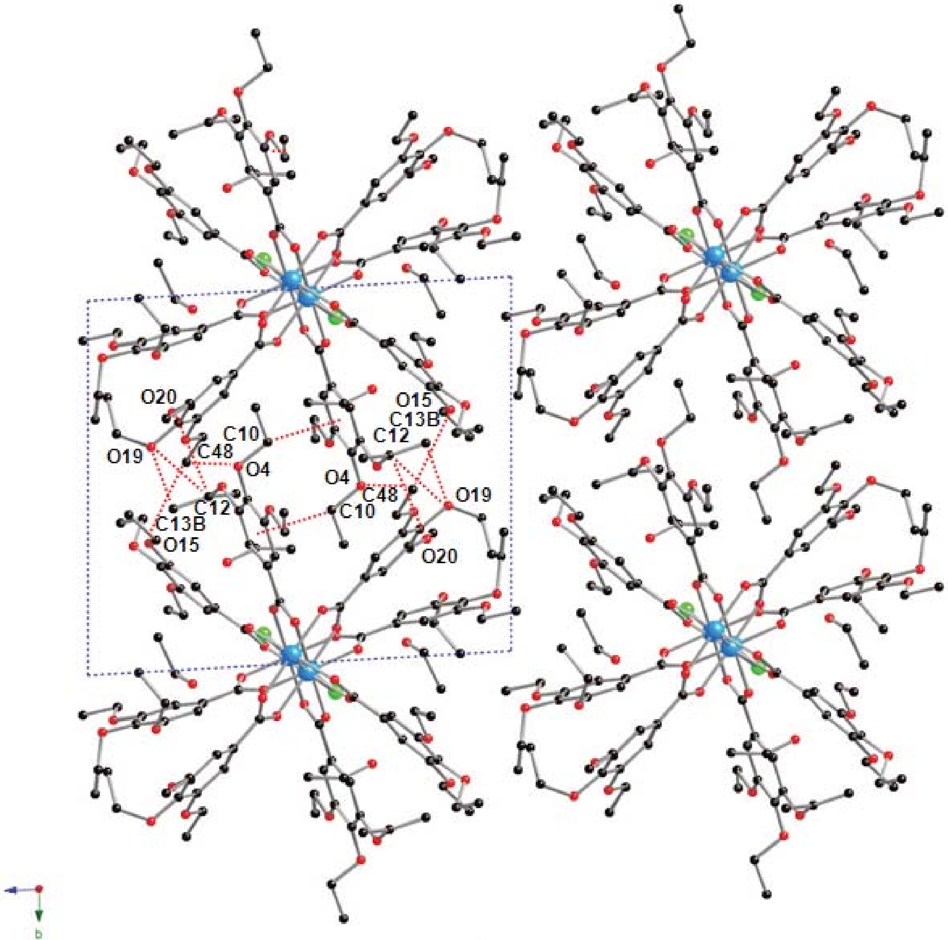


Figure 5. Packing diagram of $[Ru_2\{3,4,5-(C_2H_5O)_3C_6H_2CO_2\}_4Cl]_n$·1.2*n*$C_2H_5OH$ (1·1.2*n*C_2H_5OH) along a-axis. Hydrogen atoms are omitted for clarity. Dashed lines show hydrogen-bonds between one chain molecule and the peripheral chains.

Table 2

Hydrogen bond geometry.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
$C10^i$–$H10B^i$···$\pi^{[a]}$	0.99	2.69	3.463	135
$C12^{ii}$–$H12B^{ii}$···O19	0.99	2.65	3.549(9)	151
$C12^{ii}$–$H12B^{ii}$···O20	0.99	2.72	3.469(9)	133
C13–H13A···O31	0.98	2.31	2.81(3)	110
$C13B^{ii}$–$H13F^{ii}$···O19	0.98	2.69	3.12(4)	107

C16–H16A···O30	0.95	2.44	3.388(8)	177
C48^{iii}–H48A^{iii}···O4	0.98	2.46	3.416(9)	165
C48^{iii}–H48B^{iii}···O15	0.98	2.63	3.412(9)	137
C51^{iv}–H51B^{iv}···O30	0.99	2.69	3.637(8)	159
C61^{v}–H61C^{v}···O9	0.98	2.74	3.582(9)	144
O30–H30A[b]···Cl	0.84	3.53[b]	3.297(5)	67[b]
O31^{vi}–H31A[b]···Cl	0.84	3.50[b]	3.06(3)	53[b]

[a] Centroid of phenyl ring with C2, C3, C4, C5, C6, and C7. [b] These hydrogen atoms are incorrectly positioned because it isn't located by D-Fourier synthesis.

Symmetry codes: (i) 3–*x*, 3–*y*, –1–*z*; (ii) 1+*x*, –1+*y*, *z*; (iii) *x*, 1+*y*, *z*; (iv) 4–*x*, 2–*y*, –1–*z*; (v) 3–*x*, 2–*y*, –*z*; (vi) 3–*x*, 2–*y*, –1–*z*.

Temperature dependence of the magnetic susceptibilities and effective magnetic moments is shown in Fig. 6.

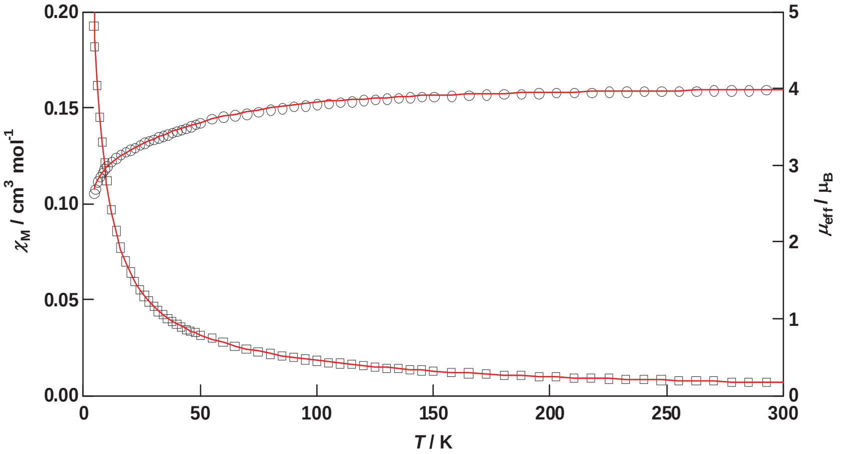


Figure 6. Temperature dependence of magnetic susceptibilities (squares) and effective magnetic moments (circles) of $[Ru_2\{3,4,5\text{-}(C_2H_5O)_3C_6H_2CO_2\}_4Cl]_n\cdot 1.2nC_2H_5OH$ ($\mathbf{1}\cdot 1.2nC_2H_5OH$).

The magnetic moment of $\mathbf{1}\cdot 1.2nC_2H_5OH$ is 3.99 μ_B at 300 K per dinuclear ruthenium(II,III) unit, which is slightly higher than the spin-only value of $S = 3/2$ (3.87 μ_B). The magnetic moment gradually decreases with lowering of temperature until reaching 2.63 μ_B at 4.5 K, being typical of chain complexes of dinuclear ruthenium(II,III) carboxylates [2,4]. The magnetic data were analyzed by a molecular field approximation considering the ZFS effect to estimate the magnitude of the antiferromagnetic interaction [11–13]. This approximation has been commonly applied for dinuclear ruthenium(II,III) carboxylates using the following equations:

$$\chi' = \chi / \{1 - (2zJ / Ng^2\mu_B^{\,2})\chi\}$$
$$\chi = (\chi_{//} + 2\chi_{\perp}) / 3$$
$$\chi_{//} = (Ng^2\mu_B^{\,2} / kT)[1 + 9\exp(-2D / kT)] / 4\{1 + \exp(-2D / kT)\}$$
$$\chi_{\perp} = (Ng^2\mu_B^{\,2} / kT)[4 + (3kT / D)\{1 - \exp(-2D / kT)\}] / 4\{1 + \exp(-2D / kT)\}$$

where zJ is the exchange integral multiplied by the number of interacting neighbors, χ is the magnetic susceptibility of the individual dinuclear unit, and D is the ZFS parameter. The D parameter was fixed at 60 cm^{-1} which is a normal value for dinuclear ruthenium(II,III) carboxylates [2]. The g value was treated as isotropic. Best fitting curve was obtained with the parameters; $zJ = -0.8$ cm^{-1}, $g = 2.08$. This results show that a weak antiferromagnetic interaction is operating between the dinuclear ruthenium units, being consistent with the small Ru–Cl–Ru angle and the long Ru–Cl lengths of $\mathbf{1}\cdot 1.2nC_2H_5OH$.

Conclusions

By using the ethoxy derivative of 3,4,5-trialkoxybenzoate, a chain complex, $[Ru_2\{3,4,5\text{-}(C_2H_5O)_3C_6H_2CO_2\}_4Cl]_n\cdot 1.2nC_2H_5OH$, was successfully isolated as single-crystals which enabled us to determine the crystal structure by X-ray structure analysis. The crystal structure revealed a zig-zag one-dimensional chain with an alternated arrangement of dinuclear ruthenium units and chloro ions. In accordance with the structural feature, a weak antiferromagnetic interaction was observed for the present complex.

3. Experimental

Synthesis: $[Ru_2(O_2CC_2H_5)_4Cl]_n$ and 3,4,5-triethoxybenzoic acid were prepared by literature methods [14,15]. Other reagents and solvents were obtained from commercial sources and were used without further purification.

$[Ru_2(O_2CC_2H_5)_4Cl]_n$ (105 mg, 0.198 mmol) and 3,4,5-triethoxybenzoic acid (500 mg, 1.966 mmol) were refluxed in 5 ml of ethanol for 24 hours. The mixture was left at room temperature to give red-brown crystals. The crystals were filtered, washed with 1 ml of 1–pentanol and 5 ml of hexane, and dried in air. Yield: 223 mg (84%). Anal. Found: C, 50.09; H, 6.00%. Calcd for $C_{52}H_{68}ClO_{20}Ru_2\cdot 1.2C_2H_5OH$: C, 50.03; H, 5.80%. IR (KBr): $\nu(C_2H_5\text{–}OH)$ 3642, 3550, $\nu(Ar\text{–}H)$ 3074, $\nu_{as}(CH_3)$ 2979, $\nu_{as}(CH_2)$ 2933, $\nu_s(CH_3)$ 2896, $\delta(C_2H_5\text{–}OH)$ 1626, $\nu(Ar)$ 1586, 1503, $\nu_{as}(CO_2^-)$ 1455, $\delta(CH_2)$ 1411, $\nu_s(CO_2^-)$ 1383, $\delta_s(CH_3)$ 1360 cm^{-1}. Diffuse reflectance spectrum: λ_{max} 222, 289sh, 318, 475, 1025sh, 1144 nm. UV-vis: λ_{max} (ε / mol^{-1} cm^{-1}, in CH_2Cl_2) 294sh (61000), 310 (65000), 460 (1400) nm.

Measurements: Thermogravimetric analysis was performed over a range of 20—500 °C at a heating rate of 10 °C/min in a nitrogen flow of 100 ml/min on a Seiko TG/DTA 220U. Elemental analyses for carbon, hydrogen, and nitrogen were done using a Thermo-Finnigan FLASH EA1112 analyzer. Infrared spectra were measured with a JASCO MFT-2000 FT-IR Spectrometer in the 4000—600 cm^{-1} region. Electronic spectra were measured with a Shimadzu UV-vis-NIR Recording Spectrophotometer (Model UV-3100). Magnetic susceptibilities were measured with a Quantum Design MPMS-5S SQUID susceptometer operating at a magnetic field of 0.5 T over a range of 4.5—300 K. The susceptibilities were corrected for the diamagnetism of the constituent atoms using Pascal's constants. The effective magnetic moments were calculated from the equation $\mu_{eff} = 2.828\sqrt{\chi_M T}$, where χ_M is the molar magnetic susceptibility per mole of dinuclear ruthenium(II,III) unit.

X-Ray Crystallography: Diffraction data were collected on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation at 90 K and indexed using the SMART software. Crystal data and details concerning data collection are given in Table 3. The cell parameters were refined by full-matrix least-squares on F^2. Integrated intensity information for each reflections was obtained and corrected using the SAINT+ program package including the reduction program SAINT and the empirical absorption correction program SADABS. The structure was solved using the SHELXTL program. The ruthenium atoms were positioned by a Patterson synthesis, and the residual non-hydrogen atoms were located by D-Fourier synthesis. All of non-hydrogen atoms were refined by full-matrix least-squares on F^2 with restrain for the distances between C12 and C13b, and between C9 and C63. The ethanol molecule constructed from O31, C62, and C63 was refined with an occupancy rate of 0.208. The hydrogen atoms were inserted at their ideal positions and fixed there. CCDC 727560 for **1**$\cdot 1.2nC_2H_5OH$ contains supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB12 1EZ, UK; fax: (internet.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 3

Crystallographic data for $[Ru_2\{3,4,5\text{-}(C_2H_5O)_3C_6H_2CO_2\}_4Cl]_n\cdot 1.2nC_2H_5OH$ ($1\cdot 1.2nC_2H_5OH$).

Formula	$C_{54.42}H_{75.25}ClO_{21.21}Ru_2$
Formula weight	1306.33
Temperature / K	90
Crystal dimensions / mm	0.58 × 0.12 × 0.08
Crystal system	Triclinic
Space group	$P\bar{1}$
a / Å	13.076(4)
b / Å	14.479(4)
c / Å	16.051(4)
α / °	86.527(5)
β / °	88.824(6)
γ / °	78.889(5)
V / $Å^3$	2976.5(13)
Z	2
$d_{calcd.}$ /gcm^{-3}	1.458
μ / mm^{-1}	0.629
$F(000)$	1353

No. of reflections collected	18477
No. of independent reflections	13112
θ range / °	1.44 to 28.48
Data / Restraints / Parameters	13112 / 2 / 741
Goodness-of-fit on F^2	0.923
R_1, wR_2 $[I > 2\sigma(I)]$[a]	0.0705, 0.1562
R_1, wR_2 (all data)	0.1228, 0.1728
$(\Delta/\sigma)_{max}$	0.001
$(\Delta\rho)_{max}$ / eÅ^{-3}	2.473
$(\Delta\rho)_{min}$ / eÅ^{-3}	–2.134
Diffractometer	Bruker SMART APEX CCD

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $R_w = [\Sigma\omega(F_o^2-F_c^2)_2/\Sigma\omega(F_o^2)_2]^{1/2}$.

4. Acknowledgements

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SYNTHESIS OF TRIPHENYLAMINE-BASED RHOMBIMINE MACROCYCLE BY [2+2] CYCLOCONDENSATION REACTION BETWEEN (1R,2R)-DIAMINOCYCLOHEXANE AND 4,4’-DIFORMYL TRIPHENYLAMINE

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Abstract. A Schiff base macrocycle with persistent rhomboidal shape was synthesized in excellent yield through [2+2] condensation reaction between (R,R)-1,2-diaminocyclohexane and 4,4’-diformyltriphenylamine. The dimeric macrocylic structure was proved by electrospray ionization mass spectrometry (ESI-MS), ^{1}H-NMR, and FTIR spectroscopy. The complexation properties were evidenced by UV absorption.

Keywords: triphenylamine group, Schiff base macrocycle, rhombimine.

Introduction

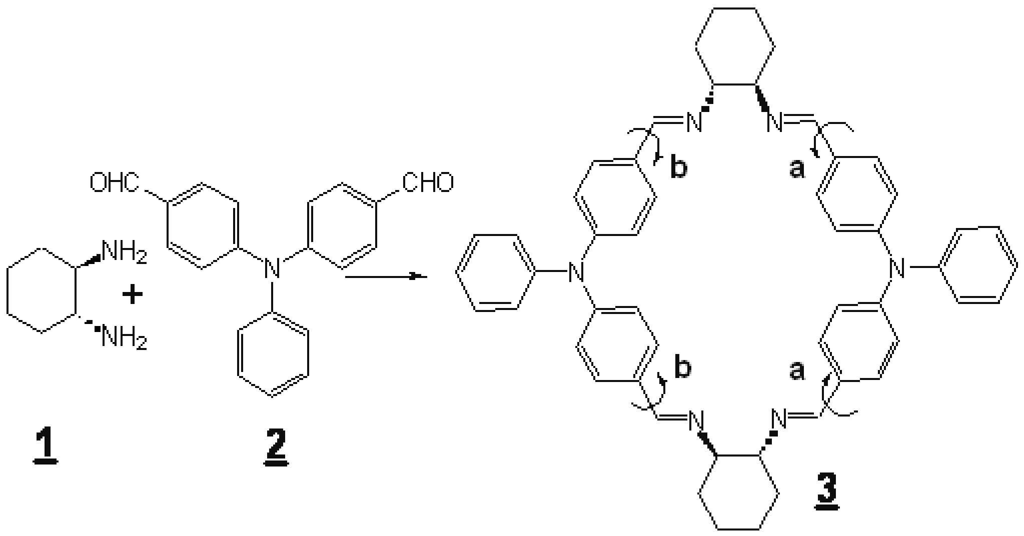
Imine macrocycles [1] derived from (R,R)-1,2-diaminocyclohexane [2-6] and aromatic dialdehydes have been extensively studied in the last years due to their exotic shapes and potential applications in supramolecular chemistry and materials science. Depending on dialdehyde geometry imine macrocycles with different persistent shapes, such as chiral trianglimines [2a,b,e,3a,b,4a-c,e,f,5a-c,6], rhombimines [2c,h,4c,f,5b,6] rectanglimines [2f] and spherands [2h] are obtained.

Arylamine-based polymers have attracted much attention due to their unique properties that allow them to have potential application in organic electronics, photonics and spintronics [7-9]. Particularly, triphenylamine–based polymers have good hole-transporting properties, high light-emitting efficiency, photoconductivity and photorefractivity, large two-photon absorption cross sections and stabilization effect of high-spin polyradicals in organic magnets. Due to the good electron-donating nature of triphenylamine (TPA), its polymers have been widely used as hole-transporting materials for a number of applications, such as xerography, organic field-effect transistors, photorefractive systems, light emitting diodes etc [10-12]. These interesting properties are associated with presence of TPA unit that contains the nitrogen center (the electroactive site) linked to three electron-rich phenyl groups in a propeller-like geometry [13]. Triphenylamine-based oligomers with dendrimer or star-shaped architectures have been synthesized for various applications as organic light emitting materials or field-effect transistors and two-photon related applications but only a cyclic TPA dimer was reported until now [14]. This compound was synthesized in very low yield (9%) by McMurry coupling reaction from 4,4’-diformyltriphenylamine and have the two TPA units coupled at 4,4’ positions by two ethylene bridges. The supramolecular structure is columnar with cyclic dimer stacked each on other that allows a high hole mobility.

The aim of this communication is to present synthesis of a Schiff base macrocycle by [2+2] cyclocondensation of 4,4’-formyl TPA with (R,R)-1,2-diaminocyclohexane and its spectral data and properties.

Results and discussion

Previously, we have studied synthesis of some Schiff base polymers by solution polycondensation of 3,6-*bis*formyl N-alkyll carbazole and 4,4’-*bis*formyl triphenylamine with aromatic diamines [15-17]. Both dialdehyde comonomers have a bent structure with in plane-projected angle between the two Ar-CHO close by 120°. When diamine partner has also a bent structure, i.e. 3,6-diamino N-alkyl carbazole, formation of macrocycles of different shapes and dimensions has been evidenced [16]. Another diamine, (R,R)-1,2-diaminocyclohexane, has a rigid and bent structure and in plane-projected angle between C-NH$_2$ functions close to 60° and was much used in combination with suitable dialdehydes to obtain cyclic compounds of different forms and dimensions [2-6]. There is only a short communication about synthesis of a rhombimine based on 4,4’-*bis*formyl triphenylamine without a detailed study of its properties and spectral data [2g]. The aim of this communication is to present our results regarding synthesis and some properties of rhombimine (**3**) (Scheme 1). Condensation of **1** with **2**, in dichloromethane at room temperature or under reflux, yielded the rhombimine **3** in nearly quantitative yield whithout the use of dehydrating conditions and without any external template. It is noteworthy that the [2+2] macrocycle is the only cyclic compound observed by ESI-MS spectroscopy in the crude product of condensation reaction. The pure product was obtained by recrystallization from N,N-dimethylformamide as colorless powder. The structure of the compound was confirmed by ^{1}H-NMR, EIS-MS, FTIR, UV spectroscopy.



Scheme 1. Synthesis of rhombimine 3 (CH_2Cl_2, reflux, 5 hr).

The ^{1}H-NMR spectrum of macrocycle **3** after recrystallization from DMF is consistent with the proposed structure in Scheme 1, showing a singlet signal at 7.91 ppm for the four imine protons. The assignments of other signals are presented in Figure 1 and signal integrals are in good agreement with number of protons. Some signals positioned at 7.26, 2.96 and 2.88 ppm (labeled on Figure) come from $CHCl_3$ and DMF traces. There are no signals for –CHO or $–NH_2$ end groups. When a $CDCl_3$ solution of **3** was left several days at room temperature its proton NMR spectrum showed significant modifications (Figure 2). So, new signals appeared for imine (8.11-8.13 ppm), aromatic (7.42-7.44 ppm) and -CH-N= diamine (3.35 ppm) protons. The intensities of the new signals integrals are correlated between them. We assume this behavior to an *anti-syn* isomerization process that takes place in solution by a ring inversion induced by a concerted rotation around two (**a** case) or four (**a** and **b**) imine bonds. So, by dissolution **3** in DMF and heating then at reflux temperature, a colorless fine powder in *anti* form resulted. It was observed that the conformer *anti* spontaneously isomerizes to *syn-anti* or *all syn* isomers with one or both N-Ph moieties in syn arrangement if it is immediately cooled in chloroform (Figure 3).

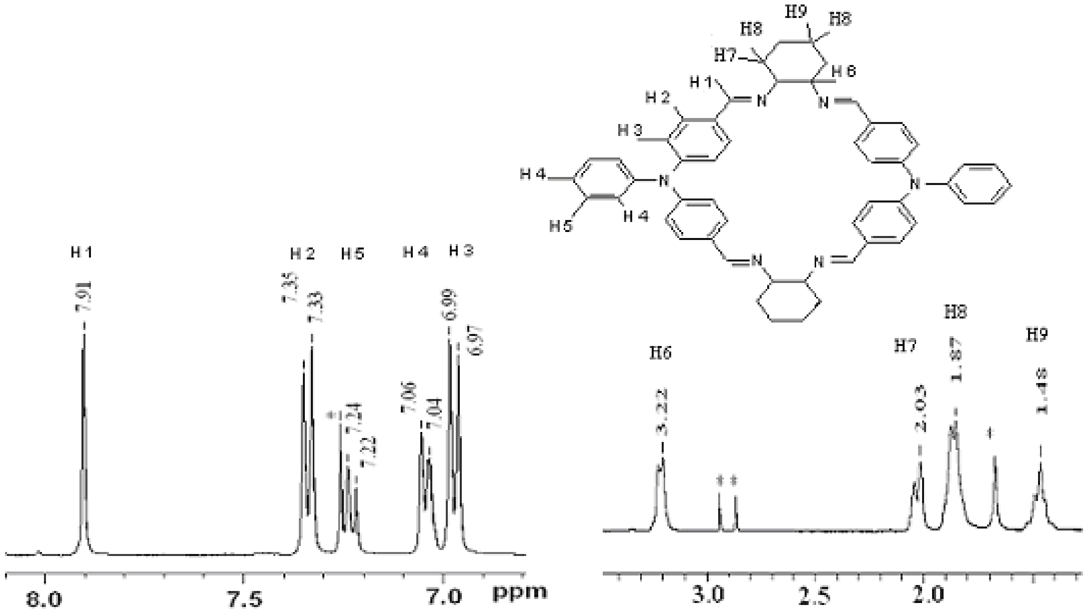


Figure 1. ^{1}H-NMR ($CDCl_3$) spectrum of 3 after recrystallization from N,N-dimethylformamide.

The isomerization is not completely and a mixture of three isomers results. The crude product obtained from synthesis shows a NMR spectrum rather similar with that presented in Figure 2. Another imine macrocyle based on **1** and 3,6-*bis*formyl N-ethyl carbazole displayed the same temperature dependence of the NMR spectrum [4c].

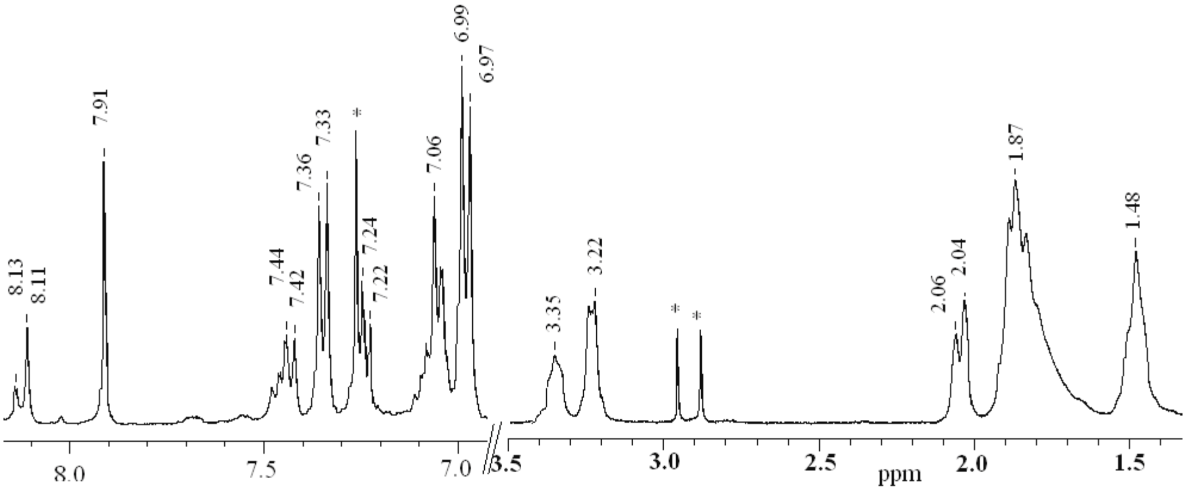


Figure 2. ^{1}H-NMR spectrum (CDCl$_3$) of 3 (presented in Figure 1) registered again but after several days.

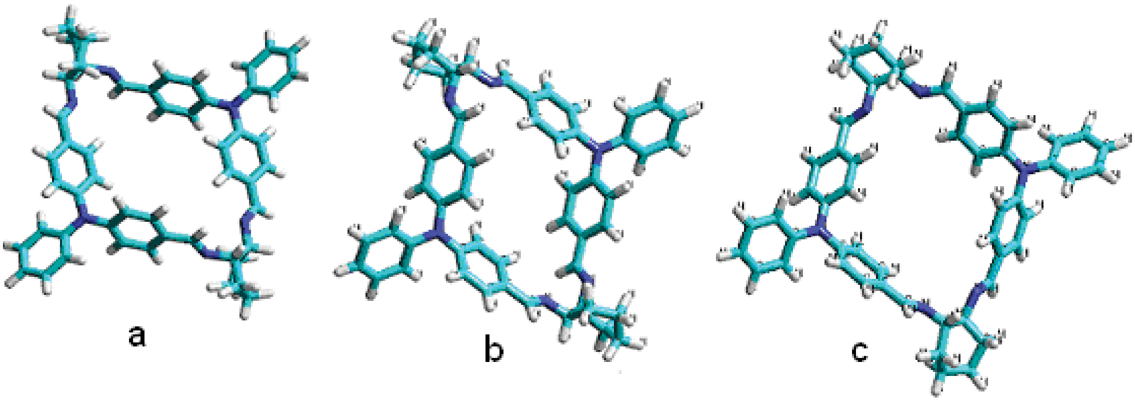


Figure 3. Models illustrating a) *all-anti* isomer, b) *all-syn* isomer and c) *syn-anti* isomer.

Having in mind the reversibility of imine condensation reaction, the first thing done was to check if an expansion of macrocycle is responsible for NMR spectrum changes. The ESI-MS spectra of **3** recorded after recrystallization and after preserving in chloroform solution for several days were identically, with the molecular ion peak at 759.3 Da and fragmentation ions peak 380.15 Da, what is consistent with the structure proposed in Scheme 1. Therefore, the modifications observed by NMR spectroscopy could be assigned only to an isomerization process and if the sample is protected against moisture or acid traces the isomerization is not accompanied by hydrolysis.

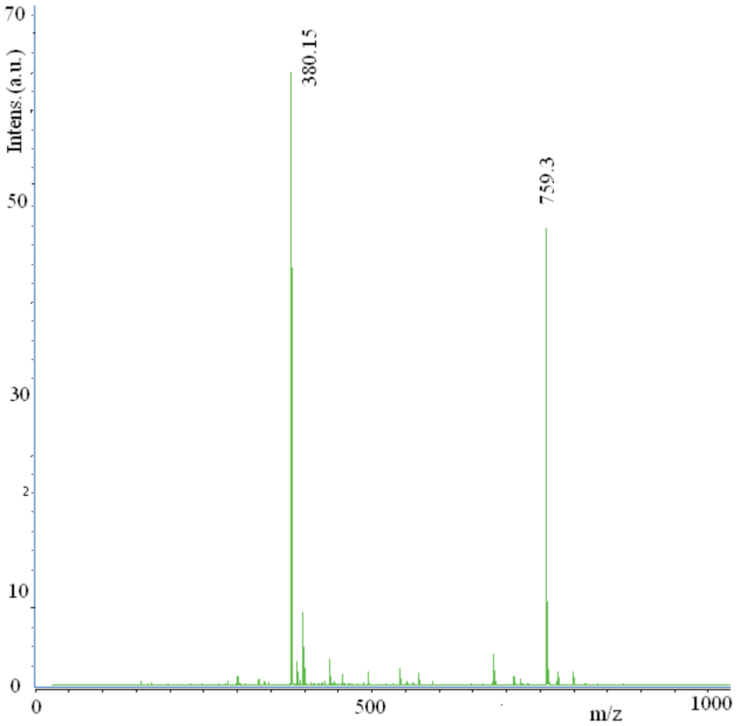


Figure 4. ESI-MS of product obtained from cyclocondensation reaction between 1 and 2.

The FTIR spectrum of **3** does not show any absorption for aldehyde C=O (1680 cm^{-1}) and amine N-H (3390 and 3315 cm^{-1}) stretches, while absorption bands characteristic to the new groups C=N (1634 cm^{-1}) and C=C (1607 and 1507 cm^{-1}) are present. The absorption bands localized between 697 and 837 cm^{-1} (ν C-H aromatic from benzene rings), 1268-1286 cm^{-1} (the stretching vibration of tertiary amine) and 2856-2930 (C-H aliphatic from cyclohexane) are present.

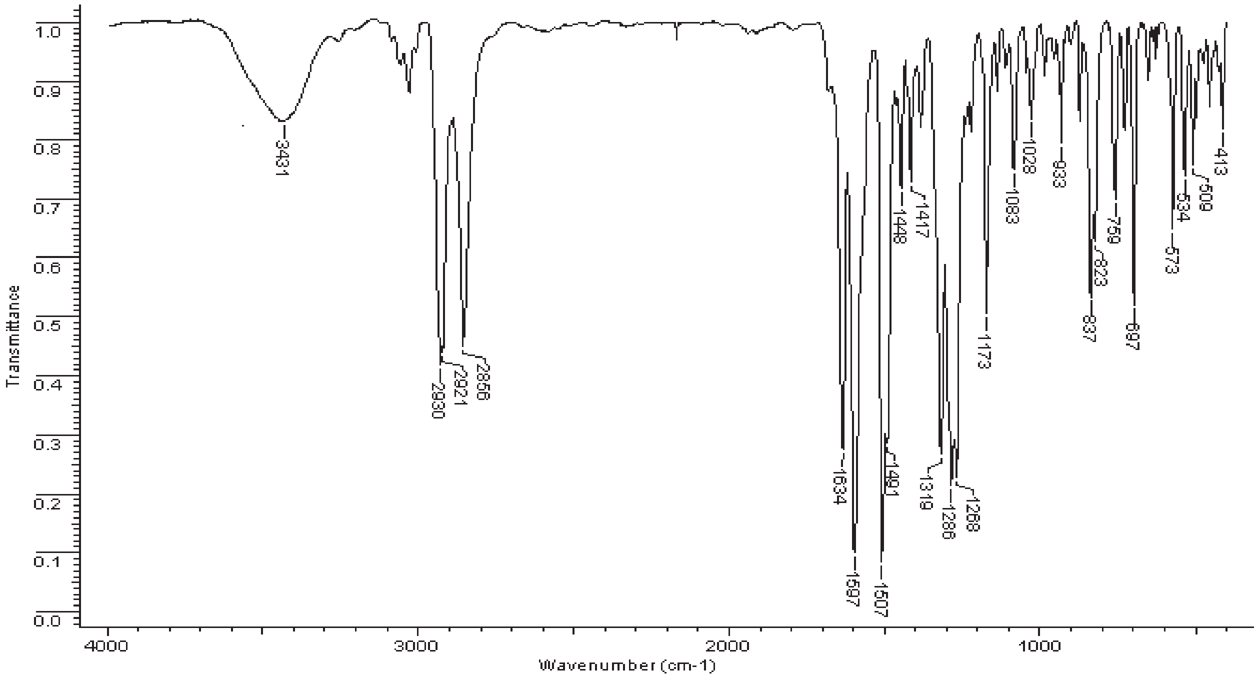


Figure 5. FTIR (KBr pellet) spectrum of 3.

When a chloroform solution of **3** was treated with $SnCl_2.2H_2O$ in acetonitrile, the UV-*vis* spectrum showed a bathocromic shift (Figure 6). The macrocycle showed absorptions situated at 334 and 394 nm. The addition of transitional metal salt to **3** showed changes in the electronic spectrum, the peaks at 334 and 394 nm are slightly hypsochromically shifted and their intensity is diminished while a new absorption at 444 nm that increased with the quantity of the salt was observed. The cations were complexed by azomethine bonds leading to more planar structures.

The **3** has a high thermal thermostability due to the imine structure and absence of end groups, the onset degradation temperature was observed at 348 °C and thermal destruction took place in two steps (340 - 448 °C and weight loss = 23.2% and 448 - 590 °C, weight loss = 46.3%). An endothermic peak observed at 340 °C was assigned to melting of **3**. The DSC runs showed no transitions between –40-300 °C.

In summary, a Schiff base macrocycle with rhomboidal shape was synthesized by [2+2] cyclocondensation reaction of 4,4'-*bis*formyl triphenylamine with (R,R)-1,2-diaminocyclohexane. ^{1}H-NMR spectroscopy indicated that macrocycle adopt different conformations in solution as result of *anti-syn* isomerization process that takes place by a ring inversion induced by a concerted rotation around imine bonds. The macrocycle can bind cations and change its absorption spectrum.

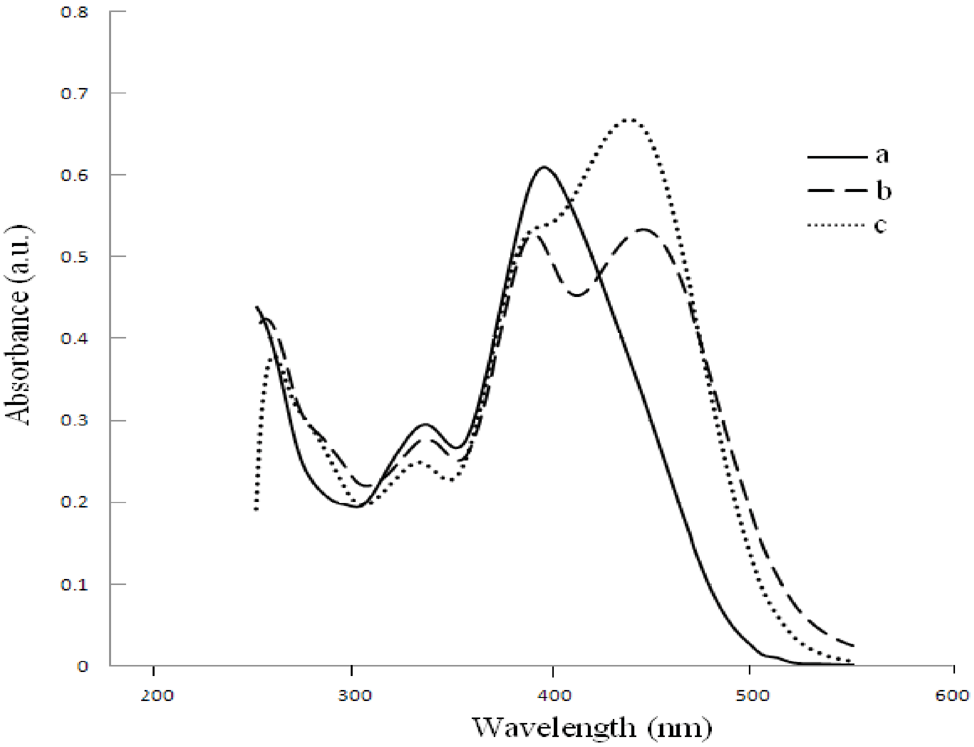


Figure 6: UV-vis spectra change of 3 during the addition of $SnCl_2$: (a) 0, (b) 3/$SnCl_2$=1/1 molar ratio and (c) 3/ $SnCl_2$=1/2 molar ratio. (solvent: dichloromethane/acetonitrile =1/1) [3]=1.10^{-5} M.

Experimental

Materials

Triphenylamine (Aldrich, 97%) and (1R,2R)-trans-1,2-diaminocyclohexane (**1**) (Aldrich, 98%) were used as received. Solvents were purchased from Aldrich source and were dried using the usual procedures. All manipulations of air/moisture-sensitive materials were handled under nitrogen atmosphere. 4,4'-Diformyl triphenylamine (**2**) was synthesized by formylation of triphenylamine in presence of high excess of $POCl_3$/DMF mixture.

Rhombimine 3

A solution of dialdehyde **2** (0.4457 g, 1.48 mmol) in dichloromethane (5 ml) was added to a solution of (*1R,2R*)-*trans*-1,2-diaminocyclohexane **1** (0.1691 g, 1.48 mmol) in 15 ml dried CH_2Cl_2 (20 mL) at room temperature and stirred for 5 hours under gentle reflux. The solvent was evaporated and the residue was crystallized from N,N-dimethylformamide giving colorless fine powder of **3** in 85.7 % yield (0.48 g). Mp=325 °C (with decomposition).

Instrumentations

The FT-IR spectra were recorded in KBr pellets on a Bruker Vertex 70 spectrometer, while UV-Vis absorption spectra were obtained on a Specord 200 Analytik Jena spectrophotometer using 10 mm quartz cells. ^{1}H-NMR spectra were recorded at room temperature on a Bruker Avance DRX-400 spectrometer (400 MHz) as solutions in $CDCl_3$ and chemical shifts are reported in ppm and referenced to TMS as internal standard. ESI-MS analysis was performed using an AG-QTOF instrument and methanol/chloroform as solvent. Thermal gravimetric analysis (TGA) was performed by means of a Mettler Toledo TGA-SDTA 851e device, in N_2 atmosphere, with a flow of 20 ml/min, and a heating speed of 10 K/min (25-850 ^{0}C range). DSC measurements were performed with a Mettler DSC-12E apparatus, in nitrogen.

Acknowledgments

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INELASTIC NEUTRON SCATTERING, EPR AND SPIN CHIRALITY IN SPIN-FRUSTRATED V_3 and Cu_3 NANOMAGNETS WITH DZIALOSHINSKY-MORIYA EXCHANGE

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Abstract. The inelastic neutron scattering (INS) and EPR transitions are considered for the spin-frustrated V_3 and Cu_3 nanomagnets. It is shown that the DM exchange and distortions determine the Q-dependence and redistribution of the intensities of the intra- and inter-doublet INS transitions in the 2(S=1/2) states as well as the intensities of the EPR transitions. The peculiarities of the INS and EPR spectra of the V_3 ring of V_{15} quantum molecular magnet and EPR spectra of the V_3 and Cu_3 nanomagnets are described by the isosceles Heisenberg model with the DM exchange. Spin chirality and spin structure of the Cu_3 and V_3 nanomagnets with the Dzialoshinsky-Moriya (DM) exchange interaction are analyzed in the vector and scalar spin chirality models. The vector chirality model describes the field, orientation and deformation dependence of the spin chirality κ_n. The spin chirality is formed by the DM interaction and depends on the sign of the DM parameter G_z. The DM exchange and distortions determine the degree of chirality $\kappa_n<1$ in the isosceles clusters.

1. Introduction

Metal clusters have attracted significant interest as molecular magnets [1], possible components for molecule-based quantum computation [2-4], as well as active centers of biological systems [5]. In the equilateral Cu_3 and V_3 clusters, ($J_{ij}=J_0$), the Heisenberg antiferromagnetic ($J_0>0$) exchange interaction $H_0=\sum J_0\mathbf{S}_i\mathbf{S}_j$ leads to the spin-frustrated ground state 2(S=1/2) and excited S=3/2 state [6, 7]. These trinuclear clusters are the simplest magnetic systems which allow one to investigate the effects of the Dzialoshinsky-Moriya [8, 9] (DM) exchange $H_{DM}=\sum\mathbf{G}_{ij}[\mathbf{S}_i\times\mathbf{S}_j]$ and distortions, anisotropy of magnetic and spectroscopic characteristics [6, 7], the spin-frustration, spin chirality, spin reorientation, and quantum magnetization. Large DM exchange in the Cu_3 trimers with large J (>150 cm^{-1}) was found and described in the DM(z) model with the DM parameters G_z=5, 15-47 cm^{-1} (G_z/J_{av}=0.155-0.225) [6,7, 10-17]. For the equilateral clusters with large J_0, the DM exchange results in zero-field splitting (ZFS) $2\Delta_{DM}{}^0=|G_z|\sqrt{3}$ of the 2(S=1/2) ground state (GS), and determines the anisotropy of magnetic and spectroscopic characteristics [6, 7, 10-17]. In the isosceles DM clusters with $J_{13}=J_{23}\neq J_{12}$, the ZFS 2Δ of the 2(S=1/2) states is determined by G_z and δ-distortion [6, 7]. The DM mixing of the spin states in the Cu_3 clusters with large J and G, and the origin of the DM exchange parameters were considered in ref [18].

The DM exchange is also active in the clusters with small Heisenberg and DM parameters such as the {Cu_3} [19-21] and [V_3] [22] nanomagnets, as well as the V_3 ring of V_{15} quantum molecular nanomagnet [23-33, 2a]. These trimers with small J (J=1.7-3.4cm^{-1}=2.4-4.8K) have attracted much attention as molecular magnets [2a, 19-33]. The effect of quantum magnetization, owing to the spin-frustrated 2(S=1/2) doublets, was observed first in the V_3 ring of V_{15} [23, 24], and later in the [V_3] [22] and {Cu_3} [19, 20] nanomagnets. These clusters are characterized by the crossing of the |3/2,-3/2> and |1/2,-1/2> levels at level-crossing (LC) field H_{LC} ($H_{LC}=3J/2g\mu_B$) and tunneling gaps Δ_{ij} at H_{LC}. The ZFS, tunneling gaps, quantum magnetization and EPR spectra of the V_3 ring of V_{15} were explained in the equilateral DM model with the non-zero G_z and G_x, G_y parameters (G=0.05-0.2K) [23-33].

The microscopic origin of this 2Δ-gap of the spin-frustrated 2(S=1/2) states of the V_3 ring of V_{15} is a subject of discussion until now [33, 34]. The DM exchange coupling in the V_3 ring of V_{15} was proposed [23-33, 3a] for the explanation of the 2Δ-gap and quantum magnetization. On the other hand, this 2Δ-gap was described by the isotropic pure Heisenberg scalene triangle model ($J_{12}\neq J_{13}\neq J_{23}$) [34] on the basis of the observed inelastic neutron scattering (INS) spectra [34]. At the same time, recent EPR investigations [33] of the V_3 ring of V_{15} show the angle dependence of the resonance fields, which was discussed in the equilateral DM exchange model [33]. The correlations between the INS and EPR spectra, chirality and geometry of the V_3 clusters require the joint analysis of the INS and EPR spectra in the trimeric DM models. The influence of the DM exchange on the INS transitions was not considered in the Heisenberg spin models of the INS transitions [35-37].

The DM exchange, the ground state (GS) spin chirality and the tunneling gaps at LC field H_{LC}, play the principal role in explaining the quantum magnetization in the {Cu_3} [19, 20] and [V_3] [22] DM nanomagnets ($G_n\approx$0.5K). The spin chirality in the {Cu_3} DM nanomagnets was proposed as the parameter for electric control over a single molecular spin system which allows manipulation with the spin triangles as elements for molecule-based quantum computation [19-21]. However, the spin chirality of the Cu_3 and V_3 clusters with the DM exchange, the correlation between chirality and tunneling gaps, the dependence of spin chirality on magnetic field and distortions were not considered.

The aim of the paper is the consideration of i) the INS and EPR transitions in the V_3 clusters with the DM exchange, and application of the DM exchange models for the explanation of the observed INS and EPR spectra of the V_3 and Cu_3 nanomagnets, and ii) the influence of the DM exchange on the spin chirality of the V_3 and Cu_3 nanomagnets, the field and deformation dependence of the spin chirality

2. The DM exchange splitting and mixing of spin states

The Hamiltonian of the distorted V_3 and Cu_3 clusters

$$H=(J_{12}\boldsymbol{S}_1\boldsymbol{S}_2+J_{23}\boldsymbol{S}_2\boldsymbol{S}_3+J_{13}\boldsymbol{S}_1\boldsymbol{S}_3)+H_{DM}+H_{ZFS}+\sum\mu_B\boldsymbol{S}_i\boldsymbol{g}_i\boldsymbol{H} \qquad (1)$$

describes the isotropic Heisenberg exchange H_0, the DM exchange [8, 9]

$$H_{DM}=\sum\boldsymbol{G}_{ij}[\boldsymbol{S}_i\times\boldsymbol{S}_j], \qquad (2)$$

ZFS of the S=3/2 state ($H_{ZFS}=D_0[S_Z^2-S(S+1)/3]$) and Zeeman interaction, *ij*=12, 23, 31.

In the equilateral cluster, the DM(z) coupling $H_{DM}(z)=\Sigma G_{ij,z}[\boldsymbol{S}_i\times\boldsymbol{S}_j]_z$ splits the spin-frustrated 2(S=1/2) states on the two doublets with the energy $E_{1,2=}-d_z$, $E_{3,4=}d_z$; $d_z=\frac{1}{2}G_z\sqrt{3}$ [6,7]. The spin eigenfunctions $[u_+(-1/2), u_-(1/2)]$ and $[u_-(-1/2), u_+(1/2)]$, which diagonalize the $H_{DM}(z)$ model in the representation φ_0, φ_1 of the intermediate spins (S_{12}=0 and 1 in $\varphi_{S_{12}}(S,M)$) are the following:

$u_+(-1/2)=|1,-1/2>=-[\varphi_0(-1/2)+i\varphi_1(-1/2)]/\sqrt{2}=i[|\downarrow\downarrow\uparrow>+\omega|\uparrow\downarrow\downarrow>+\omega^2|\downarrow\uparrow\downarrow>]/\sqrt{3}$, (3)
$u_-(+1/2)=|-1,1/2>=[\varphi_0(1/2)-i\varphi_1(1/2)]/\sqrt{2}=-i[[|\uparrow\uparrow\downarrow>+\omega|\uparrow\downarrow\uparrow>+\omega^2|\downarrow\uparrow\uparrow>]/\sqrt{3}$;
$u_-(-1/2)=|-1,-1/2>=[\varphi_0(-1/2)-i\varphi_1(-1/2)]/\sqrt{2}=i[|\downarrow\downarrow\uparrow>+\omega^2|\uparrow\downarrow\downarrow>+\omega|\downarrow\uparrow\downarrow>]/\sqrt{3}$,
$u_+(+1/2)=|1,1/2>=-[\varphi_0(1/2)+i\varphi_1(1/2)]/\sqrt{2}=-i[[|\uparrow\uparrow\downarrow>+\omega^2|\uparrow\downarrow\uparrow>+\omega|\downarrow\uparrow\uparrow>]/\sqrt{3}$.

$\omega=e^{2\pi i/3}$, up and down arrows represent the up and down spins, respectively, for S_i. In the case of the existence of the G_x, G_y and G_z DM parameters [18b], the correlations between the in-plain components G_x, G_y of the DM vectors $\boldsymbol{G}_{ij}$ in the pair X_{ij}, Y_{ij}, Z_{ij} and the cluster *X, Y*, Z right-handed coordinate system have the form

$$G_{12,X}=G_{12,X_{12}}=G_x, G_{12,Y}=G_{12,Y_{12}}=G_y, \qquad G_{23,X}=-\tfrac{1}{2}(G_x+\sqrt{3}G_y),$$
$$G_{23,Y}=\tfrac{1}{2}(\sqrt{3}G_x-G_y), G_{31,X}=-\tfrac{1}{2}(G_x-\sqrt{3}G_y), G_{31,Y}=-\tfrac{1}{2}(\sqrt{3}G_x+G_y). \qquad (4)$$

The pair DM parameters are equal in the equilateral system, $G_{ij,X_{ij}}=G_x$, $G_{ij,Y_{ij}}=G_y$.

The *Z* components of the pair $\boldsymbol{G}_{ij}$ DM vector parameters are oriented perpendicular to the plain of the cluster $G_{12,Z}=G_{23,Z}=G_{31,Z}=G_z$, $Z_{ij}\|Z$. The in-plain (G_x, G_y) DM exchange results in the mixing of the S=1/2 and S=3/2 states [25, 27-33, 18-22], which plays significant role in the V_3 and Cu_3 nanomagnets [18-33]. The group-theoretical analysis of the DM mixing in the V_3 ring of V_{15} was considered in refs [30, 31]. The matrix elements of the DM exchange mixing of the S=1/2 and Φ(3/2) states have the form

$$<u_\pm(\pm1/2)\,\|\,\Phi(\pm3/2)>=(3i\sqrt{2}/4)G_\pm, <u_\pm(\mp1/2)\,\|\,\Phi(\pm1/2)>=(i\sqrt{6}/4)G_\pm,$$
$$<u_\pm(\mp1/2)\,\|\,\Phi(\mp3/2)>=0, \qquad <u_\pm(\pm1/2)\,\|\,\Phi(\mp1/2)>=0. \qquad (5)$$

where $G_\pm=(G_x\pm iG_y)/\sqrt{2}$. The energy levels of the equilateral $[V_3]$ cluster (J=4.8K, G_z=-0.5K, G_x=0.5K, G_y=0), the spin chirality, ZFS, and the DM mixing are shown in Fig.1, $H=H_z$. The lowest zero-field (ZF) state for $G_z<0$ is the $[u_-(-1/2), u_+(+1/2)]$ doublet. The DM exchange (G_x) results in the tunneling gap Δ_{12}' in the ground branch at LC field H_{LC1} and simple level crossing ($\Delta_{23}'=0$) in the excited state at H_{LC2} for $G_z<0$, Fig. 1.

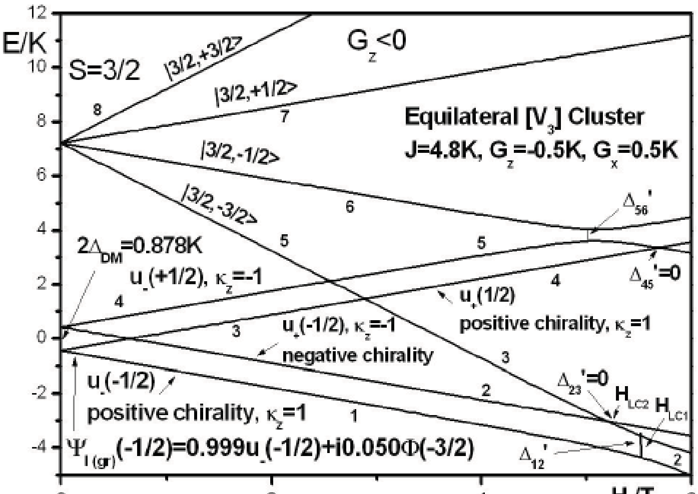

Fig. 1. The energy levels scheme, spin chirality, the DM exchange mixing and tunneling gaps in the equilateral V_3 cluster. J=4.8K, G_z=-0.5K, G_x=0.5K, G_y=0.

The isosceles {Cu$_3$} nanomagnets [19, 20] with small J (J_{12}= 4.52 K, J_{13}=J_{23}=4.04 K) were characterized by the strong in-plain and out-of-plain DM(x,y,z) exchange coupling $|G_z|=G_x=G_y=0.53$K; $G_z/J_{av}=0126$, $G/J_{av}=0.218$ [20]. Fig. 2 shows the energy levels scheme, tunneling gaps, the INS and EPR transitions for this Cu$_3$ nanomagnet with different G_z parameters: G_z= +0.53K (dashed lines) and G_z=-0.53K (solid lines), g_{av}=2.06. For H<2T, the splittings do not depend on the sign of G_z. The in-plain (G_x, G_y) DM spin mixing results in the large tunneling gap Δ_{12}' in the ground branch at LC field H_{LC1} and small tunneling gap Δ_{23}' at H_{LC2} in the excited state for $G_z<0$, Fig. 2, solid. In the case $G_z>0$, small tunneling gap Δ_{12}' in the ground branch at LC field H_{LC1} and large tunneling gap Δ_{23}' in the excited branch at H_{LC2} take place, Fig. 2, dash.

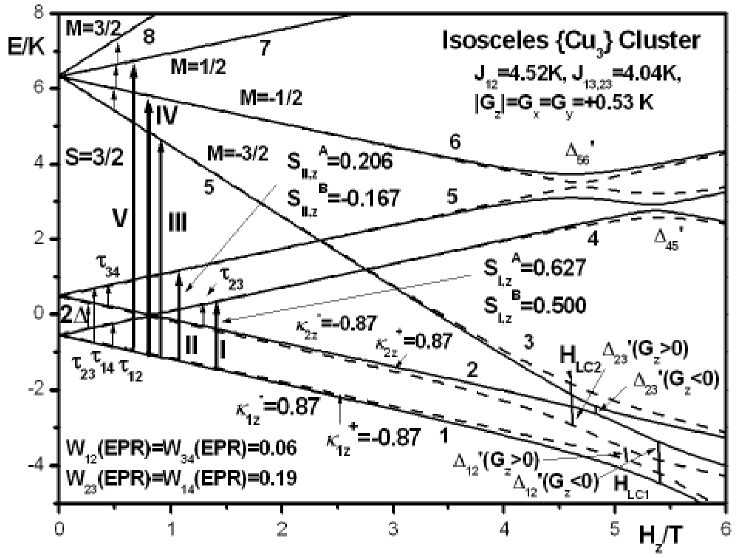

Fig. 2. Spin levels, the INS and EPR transitions, tunneling gaps in the isosceles Cu$_3$ nanomagnet.

3. Intensities of INS transitions in isosceles clusters with DM exchange

The expressions for the differential magnetic cross-section of INS, the intensities of the INS transitions in the Heisenberg clusters were presented in refs [34-37]. The INS transitions are determined by the spin structure factors $S_N(\mathbf{Q})$ [36], where $\boldsymbol{Q}$ is the scattering vector. The scheme of the INS transitions for the V$_3$ and Cu$_3$ isosceles nanomagnets is shown in Fig. 2. The analysis [34] of the observed INS transitions in the V$_3$ ring of V$_{15}$ in the scalene Heisenberg model (G_n=0) results in the intensity ratios (III:IV:V)=3:2:1 for the transitions III, IV and V (Fig. 2). The Q-dependence of these transitions was described [34] very well by the equations I_{III}=1/2[1-sin(QR)/QR], I_{IV}=1/3[1-sin(QR)/QR], I_V=1/6[1-sin(QR)/QR], $I_{III}+I_{IV}+I_V$~[1-sin(QR)/QR]. For description of the Q-dependent intensity of the intra-doublet INS transition I (Fig. 2) of a scalene trimer with ground state $\Omega_0(\pm1/2)= a\varphi_0(\pm1/2)+b\varphi_1(\pm1/2))$, the equation $I_I=I_0F^2(Q)$ $[a^2+⅓b^2$(1-sin(QR)/QR)] was proposed [34].

The consideration of the spin structure factors shows that the scalene Heisenberg model (G_n=0) cannot describe the Q-dependence of the INS transition I [39]. The analysis of the INS and EPR spectra requires the taking in account the DM exchange.

The calculations of the INS for the isosceles DM trimer result in the structure factors for the INS transitions I-V (Fig. 2) in magnetic field $H=H_z$

$$S_I' = 1/2+(G_z^2/8\Delta^2)\ [1-4\cos(\mathbf{QR}_{23})], \tag{6}$$
$$S_{II}' = 1/3[1-\cos(\mathbf{QR}_{12})]-(G_z^2/8\Delta^2)\ [1-4\cos(\mathbf{QR}_{23})],$$
$$S_{III}'= 1/2[1-\cos(\mathbf{QR}_{12})],\ S_{IV}'= 1/3[1-\cos(\mathbf{QR}_{12})],\ \ S_V'= 1/6[1-\cos(\mathbf{QR}_{12})],$$

$\Delta=(\delta^2+d_z^2)^{1/2}=½[(J_{12}–J_{23})^2+3G_z^2]^{1/2}$. The structure factors for the transitions I and II at high field H⊥Z are reduced to their values in the pure Heisenberg model, since high transverse magnetic field $H_\perp$ suppresses the effect of the DM exchange. The average structure factors $S_{N,av}'= S_N'$ for the INS transitions in the IS trimer have the form:

$$S_I'= 1/2+(G_z^2/24\Delta^2)\ [1- 4\sin(QR)/QR], \tag{7}$$
$$S_{II}'=1/3[1-\sin(QR)/QR]-(G_z^2/24\Delta^2)[1-4\sin(QR)/QR],$$
$$S_{III}'=1/2[1-\sin(QR)/QR],\ \ S_{IV}'=1/3[1-\sin(QR)/QR],\ \ S_V'=1/6[1-\sin(QR)/QR].$$

In the absence of the DM exchange (G_z=0), the structure factor S_I' (7) of the INS transition I (Fig. 2) is reduced to the Q-independent form S_I'=1/2; the structure factor S_{II}' (7) of the INS transition II is reduced to S_{II}'=1/3[1-sin(QR)/QR], the structure factors of the Heisenberg isosceles trimer. Eq (7) shows significant influence of the DM exchange on the intensities of the intra-doublet transition I ($S_I'= [S_I^A-S_I^B\sin(QR)/QR)$ and doublet-doublet transition II ($S_{II}' =[S_{II}^A-S_{II}^B\sin(QR)/QR]$). Thus, the S_I^B term of the DM exchange origin $S_I^B=\Delta S_I^B=(G_z^2/6\Delta^2)$ (7) results in the Q-dependence of the transition I [$S_I^B=S_{I,0}^B+\Delta S_I^B$, $S_{I,0}^B=0$]. The DM exchange switches on and increases the Q-dependence of the INS transition I and, at the same time, decreases the Q-dependence of transition II. The redistribution of the intensities of the INS transitions II and I, which is controlled by the DM exchange and distortions (the $[G_z/\Delta]^2$ term in (7)), takes place with the conservation rule $S_I^A+S_{II}^A=S_{I,0}^A+S_{II,0}^A$ for the Q-independent terms, and $S_I^B+S_{II}^B=S_{I,0}^B+S_{II,0}^B$ for the Q-dependent terms.

Calculated values of the S_I^A, S_{II}^A and S_I^B, S_{II}^B coefficients of the Q-independent and Q-dependent terms, respectively, of the averaged structure factors $S_I'=S_I^A-S_I^B\sin(QR)/QR$ and $S_{II}'=S_{II}^A-S_{II}^B\sin(QR)/QR$ of the INS transitions I and II, are shown in Fig. 2 for the set of the Heisenberg and DM parameters of the Cu_3 nanomagnet, which were determined [19, 20] in the magnetization and EPR experiment. The values of the structure factors in Fig. 2 [$S_{Iz}^A=0.627$ ($S_{I0}^A=0.5$), $S_{Iz}^B=0.500$ ($S_{I0}^B=0$); $S_{IIz}^A=0.206$ ($S_{II0}^A=0.333$), $S_{IIz}^B=-0.167$ ($S_{II0}^B=+0.333$)] show significant influence of the DM exchange on the intensities of the INS transitions.

The Q-dependence of the transitions I and II allows one to experimentally determine the $|G_z/2\Delta|$ relation. Thus, the experimentally observed Q-dependence of the transition I in the V_3 ring of V_{15} was described [34] by the Q-independent term ($a^2+b^2/3)=0.6$) and Q-dependent term [$-0.2\sin(QR)/QR$] [34]. For case, where the Q-dependence of the INS transition I is determined by Eq (7), the comparison with the coefficient [$(G_z/\Delta)^2/6$] in the Q-dependent term in S_I' (7) leads to the estimate $G_z/2\Delta\approx0.55$. Since $2\Delta\approx0.31$K and $J_{av}=2.46$K [34], this estimate results in $G_z\approx0.17$K and $\delta=0.06$K. In this case, the Q-independent term in the structure factor S_I' (7) of transition I is $S_I^A\approx0.55$. This value is close to the Q-independent term 0.6 for I in [34], that allows one to explain qualitatively the observation [34] that the overall intensity of peak I is significantly smaller than the sum of (III+IV+V).

In the isosceles [V_3] clusters, the DM exchange results in i) the Q-dependence of the spin structure factor S_I of the INS intra-doublet transition I (the coefficient S_I^B in S_I) and ii) the redistribution of the Q-independent S_I^A and S_{II}^A parts, as well as the Q-dependent, S_I^B and S_{II}^B, parts of the intensities of the INS transitions I and II with the conservation of the summary intensities of these two transitions: $S_I^A+S_{II}^A=S_{I,0}^A+S_{II,0}^A=5/6$ {$S_I^B+S_{II}^B=S_{I,0}^B+S_{II,0}^B=1/3$}.

4. EPR transitions in isosceles clusters with DM exchange

In the pure Heisenberg isosceles model, only intra-doublet 1→2(3) and 3(2)→4 EPR transitions are allowed for $H=H_z\|Z$ and $H(\perp Z)=H_\perp$ ($W_{1\to2(3)}=W_{3(2)\to4}=0.25$, $W_{14}=W_{23}=0$). For the isosceles trimer with the DM exchange, the relative intensities of the allowed EPR transitions (τ_{13}, τ_{24}, τ_{23}, τ_{14} in Fig. 2, $\hbar\nu>2\Delta$) for $H=H_z$ are determined by the equation $W_{13}=W_{24}=\delta^2/4\Delta^2$; $W_{14}=W_{23}=d_z^2/4\Delta^2$ [6, 7]. At high transverse magnetic field, $h_x>>\Delta$, the effect of the DM exchange is suppressed: $W_{13,x}'=W_{24,x}'=0.25$, $W_{14,x}=W_{23,x}=0$. Fig. 3 shows the frequency dependences [(ν_{ij}/γ_g)-H] of the resonance fields for the 2(S=1/2) states of the isosceles trimer with the DM exchange, $\gamma_g=g\mu_B/\hbar$.

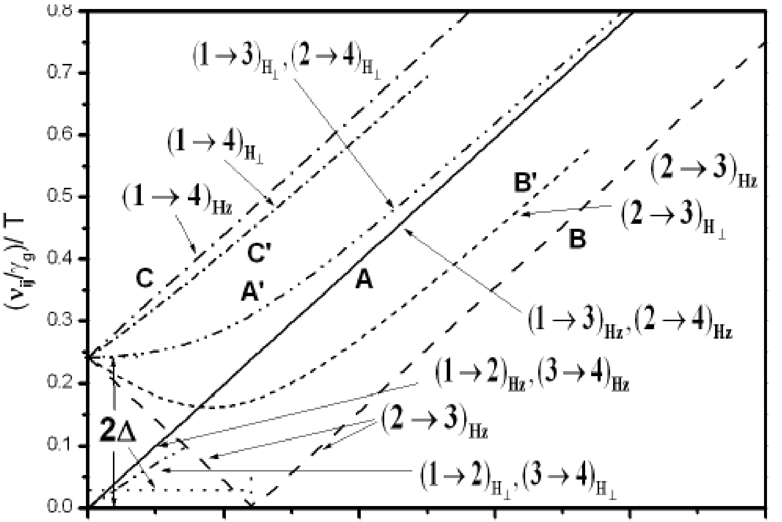

Fig. 3 Frequency (ν/γ_g) –field (H) diagram for $H_z\|Z$ and $H_x\perp Z$.

The straight A (solid), B (dash), and C (dash-dot) lines show the resonance conditions for the transitions $(1\to3)_{Hz}$, $(2\to4)_{Hz}$ [$W_{13,Hz}'=W_{24,Hz}'=0.14$] for $\hbar\nu>2\Delta_{SC}$ {$(1\to2)_{Hz}$, $(3\to4)_{Hz}$ (for $\hbar\nu<2\Delta_{SC}$)}, $(2\to3)_{Hz}$ and $(1\to4)_{Hz}$, [$W_{23,Hz}'=W_{14,Hz}'=0.11$], respectively, at magnetic field $H_z\|Z$. The A′ (dash-dot-dot) {B′ (shot dash)} [C′ (shot dash-dot)] curve shows the resonance conditions for the resonance fields for the EPR transitions $(1\to3)_{Hx}$, $(2\to4)_{Hx}$ {$(2\to3)_{Hx}$} [$(1\to4)_{Hx}$] at magnetic field $H\perp Z$. The non-linear field dependence A′, B′ (Fig. 3) of the frequency dependences ν(H) of the resonance fields at magnetic field $H\perp Z$ is characteristic for the DM exchange in the trimer. The low-frequency

EPR spectra [33] of the V_3 ring of V_{15} quantum molecular magnet were explained by the authors [33] in the equilateral DM model. The inter-doublet EPR transitions 1→4 and 2→3 and the intra-doublet 1→3 and 2→4 transitions with weak intensity for $H=H_z$ were observed in [33] (Fig. 2b[33]), as well as the linear magnetic behavior of the resonance frequencies for H||Z and non-linear magnetic behavior at H┴Z (Fig. 2a [33]) induced by the DM exchange. The observation of the inter-doublet $(1\rightarrow4)_z$ and $(2\rightarrow3)_z$ EPR transitions and linear {non-linear} ν-H magnetic behavior for H||Z {H┴Z} is the evidence of the presence of the DM exchange in V_3 ring (Fig. 2. B,C {A′}). At the same time, the intra-doublet low-frequencies $(1\rightarrow3)_z$ and $(2\rightarrow4)_z$ transitions are forbidden for the equilateral DM model and are allowed for the isosceles V_3 ring, Figs. 2, 3 ($W_{13}=W_{24}=\delta^2/4\Delta^2$). The observation of the $\tau_{13z,}\tau_{24z}$ as well as the $\tau_{14z,}\tau_{23z}$ EPR transitions on the V_3 ring of V_{15} [33] shows that this V_3 ring has the symmetry of the isosceles triangle (not equilateral) with the DM exchange. The observed correlation ($W_{13}\approx W_{24}<W_{14}\approx W_{23}$) between the intensities of the EPR transitions [33] corresponds to the relation $\delta<G_z\sqrt{3}$ in the isosceles DM model. The analysis of the calculated INS and EPR transitions [39] for the equilateral V_3 cluster and comparison with the observed INS [34] and EPR [33] transitions shows that the equilateral DM model cannot describe the EPR and INS spectra of the V_3 ring of V_{15}, the isosceles δ-distortion should be included in the consideration. The EPR spectra of the V_3 [22] and Cu3 [19, 20] nanomagnet also are described in the isosceles DM model.

5. Spin chirality of the Cu_3 and V_3 nanomagnets with DM exchange

Recently, the spin chirality of the $\{Cu_3\}$ DM nanomagnet was proposed as the parameter for the manipulation with the spin triangles as units for molecule-based quantum gates [19-21]. The spin chirality of the magnetic systems is usually considered in the scalar chirality model and in the vector chirality model. The spin chirality in the $\{Cu_3\}$ nanomagnet was considered [21], using the scalar chirality operator C_z

$$C_z = (4/\sqrt{3})\mathbf{S}_1 \cdot [\mathbf{S}_2 \times \mathbf{S}_3]. \tag{8}$$

The matrix elements of $\boldsymbol{C}_z$ in the $u_\pm(\pm1/2)$ basis (3) have the form

$$\chi_+ =< u_+(\pm1/2)\,|\,\hat{C}_z\,|\,u_+(\pm1/2)>=1, \qquad \chi_- =< u_-(\pm1/2)\,|\,\hat{C}_z\,|\,u_-(\pm1/2)>=-1. \tag{9}$$

The operator C_z splits the 2(S=1/2) set on the states $u_+(M_S)$ and $u_-(M_S)$ characterized by the projections $M_L=\pm1$ of the pseudoorbital moment L and does not act on the spin moments M_S, $M_S=\pm1/2$. The scalar chirality $\chi=\pm1$ pseudospin coincides with $M_L=\pm1$.

In the case of the vector chirality [38] which can be defined for the $S_i=1/2$ trimer as

$$\boldsymbol{K}_z=(2/\sqrt{3})\{[\mathbf{S}_1\mathrm{x}\mathbf{S}_2]_z+[\mathbf{S}_2\mathrm{x}\mathbf{S}_3]_z+[\mathbf{S}_3\mathrm{x}\mathbf{S}_1]_z\}, \tag{10}$$

the chirality vector $\boldsymbol{K}_z$ is parallel to Z-axis with amplitude +1 or -1, since the matrix elements of $\boldsymbol{K}_z$ in the $u_\pm(\pm1/2)$ basis have the form

$$\kappa_z =< u_\pm(\pm1/2)\,|\,\hat{\mathbf{K}}_z\,|\,u_\pm(\pm1/2)>=1, \qquad \kappa_z =< u_\pm(\mp1/2)\,|\,\hat{\mathbf{K}}_z\,|\,u_\pm(\mp1/2)>=-1. \tag{11}$$

The chirality is the sign of the projection of the spin vector onto the orbital momentum vector: negative is left, positive is right. In the positive (right) chiral states $u_+(1/2)$ and $u_-(-1/2)$ with $\kappa_z=+1$ (11), the direction of the spin moment (M_S) coincides with the direction of the pseudoorbital moment (M_L): thus, $M_L=-1$, $M_S=-1/2$, and the total pseudoangular moment is $M_J=M_L+M_S=-3/2$ for $u_-(-1/2)$; $M_L=+1$, $M_S=+1/2$, $M_J=M_L+M_S=3/2$ for $u_+(1/2)$. In the negative (left) chiral states $u_+(-1/2)$ and $u_-(1/2)$, $\kappa_z=-1$, the directions of M_S and M_L are opposite: thus, $M_L=-1$, $M_S=1/2$, $M_J=-1/2$ for $u_-(1/2)$; for $u_+(-1/2)$ - $M_L=+1$, $M_S=-1/2$, $M_J=+1/2$. The two states with M=-1/2 in Fig. 1 posses different vector spin chirality: In the case $G_z<0$, the GS is the positive (right) chiral state $u_-(-1/2)$, $\kappa_z=+1$, $M_L=\chi_{1z}^-=-1$, which exhibits the in-plain (G_x, G_y) DM exchange repulsion from the |3/2, -3/2> state that results in the tunneling gap Δ_{12}' at LC field H_{LC1} in the ground branch, Fig. 1. The first excited negative chiral state $u_+(-1/2)$, $\kappa_z=-1$ does not exhibit the DM mixing with the |3/2,-3/2> state, that results in the simple crossing ($\Delta_{23}'=0$) at H_{LC2}, Fig. 1. The equilateral trimers with $G_z>0$ and left chiral GS $u_+(-1/2)$, $\kappa_z=-1$, $\chi_{1z}^+==1$, posses the simple crossing ($\Delta_{12}'=0$) at LC field H_{LC1} in the ground branch and the tunneling gap Δ_{23}' at LC field H_{LC2} in the excited state. These correlations are consistent with the results of the group-theoretical analysis [30].

The DM exchange H_{DM} forms the chiral states of the DM trimer, the sign of G_z determines the vector spin chirality κ_z of the ground and excited states. The spin chirality of the pure Heisenberg states ($G_{ij}=0$) is equal to zero.

Fig. 4 shows the spin chirality κ_1 of the ground state and κ_2 of the first excited state of the equilateral V_3 cluster with the exchange parameters $J_0=4.8$K, $G_z=\pm0.5$K, $G_{x,y}=0$, in magnetic field $H=H_z\|Z$ (κ_{1z}) and $H=H_x\perp Z$ (κ_{1x}, κ_{2x}). κ_{1n}^+ and κ_{1n}^- correspond to $G_z>0$ and $G_z<0$, respectively. The spin chirality in the DM(z) model (Fig. 4, short-dash-dot) does not depend on H_z for $H_z<H_{LC}$: i) $\kappa_{1z,0}^-=+1$ for the positive chiral ground state $u_-(-1/2)$, $G_z<0$, and ii) $\kappa_{1z,0}^+=-1$ for the negative chiral ground state $u_+(-1/2)$, $G_z>0$.

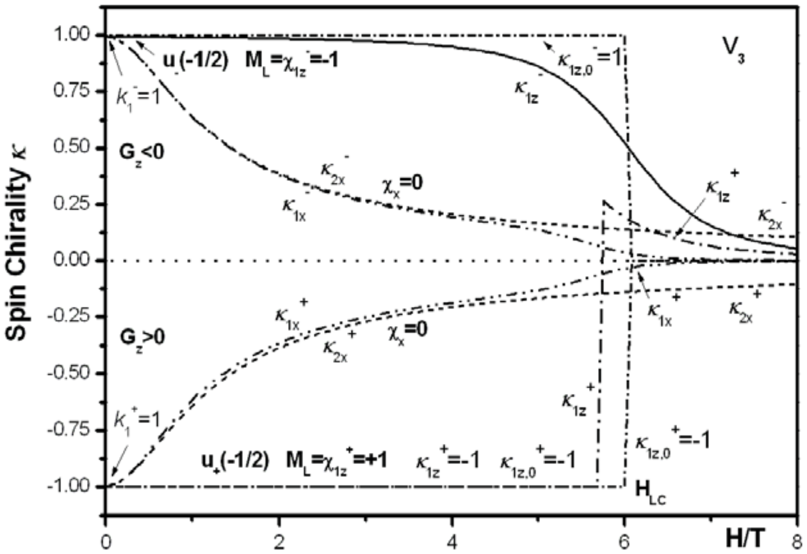

Fig. 4 Field dependence of the spin chirality of the equilateral V_3 cluster.

Chirality $\kappa_{1z,0}$ changes sharply to the value $\kappa_{1z0}=0$ ($M_{gr}=-3/2$) at LC field $H=H_{LC}$. Fig. 4 also shows the field dependence of the spin chirality of the V_3 cluster ($J_0=4.8K$, $G_z=\pm0.5K$) with the in-plane ($G_x=0.5K$) DM mixing. Positive chirality $\kappa_{1z}^{-}=+1$ of the ground $u_-(-1/2)$ state ($G_z<0$) changes smoothly to the value $\kappa_{1z}=0$ after the avoided crossing (Fig. 4) due to the G_x DM mixing in accord with Fig. 1. In the case $G_z>0$, $G_x\neq0$, negative chirality $\kappa_{1z}^{+}=-1$ of the ground $u_+(-1/2)$ state is field-independent for $H_z<H_{LC}$ and then κ_{1z}^{+} changes abruptly at H_{LC} (Fig. 4) due to the simple level crossing. The states of the different vector chirality $\boldsymbol{\kappa}$ are characterized by the same scalar χ pseudospin: $u_-(1/2)$, $\kappa_z=-1$, $\chi=-1$ and $u_-(-1/2)$, $\kappa_z=+1$, $\chi=-1$.

In the case of the transverse field $H_x\perp Z$, the vector chirality operator K_z describes the projection of the spin chirality vector on the magnetic field. Eq (12) describes the field dependence $\kappa_{1x}(H_x)$ and $\kappa_{2x}(H_x)$ of the vector spin chirality of the ground and first excited states

$$\kappa_{1x}=\kappa_{2x}=\pm|d_z|/\sqrt{d_z^2+h_x^2}\,, \tag{12}$$

the sign + (-) corresponds to $G_z<0$ ($G_z>0$), $h_x=½g\mu_BH_x$, Fig. 4. In the case $G_z<0$, the ZF chirality of the ground and first excited states (10) is positive and equal to 1: $\kappa_{1x}^{-}=\kappa_{2x}^{-}=1$, as in the field H_z, Fig. 4. In the case $G_z>0$, the ZF chirality is negative $\kappa_{1x}^{+}=\kappa_{2x}^{+}=-1$, Fig. 4. In the DM(z) model, the vector spin chirality $\kappa_{1x}(H_x)$ of the ground state changes abruptly to the value $\kappa_{1x}=0$ at H_{LC} since $\kappa(S=3/2)=0$.

In the transverse magnetic field H_x, the scalar chirality is equal to zero, $\chi=0$.

In the isosceles trimer (Fig. 2), the vector spin chirality for the states with $M=-1/2$ in magnetic field $H=H_z$ has the form $\kappa_z=|d_z|/\Delta$, $\kappa_z'=-|d_z|/\Delta$, $\Delta=(\delta^2+d_z^2)^{1/2}$, $\delta=½(J_{12}-J_{23})$. The Heisenberg δ–distortion reduces the exchange symmetry of the system, destroys the spin chirality and, together with d_z, determines the degree $\kappa_z=|d_z|/\Delta$ of the positive [negative] chirality of the states of the isosceles DM clusters. For $G_z<0$, the two lowest states with $M=-1/2$ in Fig 2 are characterized by the positive $\kappa_{1z}^{-}=0.87$ and negative $\kappa_{2z}^{-}=-0.87$ vector chirality, respectively. The dominant positive chiral GS ($G_z<0$) in Fig. 2 corresponds to the large tunneling gap Δ_{12}' in the ground branch at H_{LC1} and small gap Δ_{23}' in the excited branch at H_{LC2}. The dominant negative chiral GS ($G_z>0$) corresponds to small tunneling gap Δ_{12}' in the ground branch at H_{LC1} and large gap Δ_{23}' in the excited branch at H_{LC2}. Since the intensities of the inter- and intra-doublet EPR transitions in Fig. 2 have the form $W_{14}=W_{23}=(d_z/2\Delta)^2$, $W_{12}=W_{34}=(\delta/2\Delta)^2$, there is a direct correlation between the spin chirality κ_z in the isosceles cluster, on the one side, and the intensities of the EPR and INS (see Eqs (6), (7)) transitions, on the other side,

$$W_{14}=W_{23}=\kappa_z^2/4;\ W_{12}=W_{34}=(1-\kappa_z^2)/4. \tag{13}$$

$$S_I=1/2+(\kappa_z^2/6)[1-4\cos(\mathbf{QR}_{23})], \tag{14}$$

$$S_{II}=1/3[1-\cos(\mathbf{QR}_{12})]-(\kappa_z^2/6)[1-4\cos(\mathbf{QR}_{23})];$$

$$S_I'=1/2+(\kappa_z^2/18)[1-4\sin(QR)/QR],\ S_{II}'=1/3[1-\sin(QR)/QR]-(\kappa_z^2/18)[1-4\sin(QR)/QR].$$

The degree of chirality $\kappa_z=|d_z|/\Delta$ may be determined from the EPR and INS experiments. The scalar chirality $\chi(H_z)$ of the $M=-1/2$ state in Fig.4 have the opposite sign in comparison with κ_z, $\chi_{1z}=-|d_z|/\Delta$, $\chi_{2z}=d_z|/\Delta$.

In the case of the transverse magnetic field, $H=H_x$, the field and deformation dependence of the vector chirality of the isosceles Cu_3 cluster has the form

$$\kappa_{1x}=|d_z|/[(\delta+h_x)^2+d_z^2]^{1/2}\,,\quad \kappa_{2x}=|d_z|/[(\delta-h_x)^2+d_z^2]^{1/2}. \tag{15}$$

The vector chirality correlate with the intensities of the inter-doublet EPR transitions $(1\rightarrow4)_x$ and $(2\rightarrow3)_x$ in the transverse field $H=H_x$,

$$W'_{14}(H_\perp)=\kappa^2_{1x}/4, \qquad W'_{23}(H_\perp)=\kappa^2_{2x}/4. \tag{16}$$

The scalar chirality in the field $H_\perp$ is equal to zero.

The operator of the vector chirality $\boldsymbol{K}_z$ describes the spin chirality of the S=1/2 states in the Cu_3 and V_3 nanomagnets, its field, orientation and distortion dependence. The operator of the scalar chirality $\boldsymbol{C}_z$ describes the pseudoorbital moment $\chi=M_L$; $\chi=0$ in the transverse field $H_\perp$.

6. Conclusion

The DM exchange results in i) the Q-dependence of the structure factor S_I of the INS intra-doublet transition I and ii) redistribution of the Q-independent (Q-dependent) parts of the intensities factors of the intra-doublet I and doublet-doublet II INS transitions with the conservation of the summary Q-independent (Q-dependent) intensities of these two transitions. For the intra-doublet and doublet-doublet transitions, the changes and redistribution of the intensities of the INS transitions I and II, on the one hand, and the intensities of the EPR transitions, on the other hand, have the same origin: they are controlled by the DM exchange and distortions (the $[G_z/\Delta]^2$ terms). The joint consideration of the INS and EPR transitions in the V_3 clusters in the Heisenberg plus DM exchange models shows that the Q-dependence of the INS transitions, peak positions and EPR transitions in the V_3 ring of V_{15} quantum molecular magnet as well as EPR transitions in the V_3 and Cu_3 nanomagnets can be explained in the isosceles model with the DM exchange.

The vector chirality model describes the field, deformation and orientation dependence of the spin chirality κ_n of the Cu_3 and V_3 nanomagnets with DM exchange. The spin chirality is formed by the DM interaction, depends on the sign of the DM parameter G_z and is equal to zero for the pure Heisenberg clusters. The DM exchange and distortions determine the degree of chirality $\kappa_n<1$ in the isosceles clusters. The spin chirality κ_n correlates with the intensities of the EPR and INS transitions.

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BITEMPLATE SYNTHESIS OF MESOPOROUS SILICAS WITH THIOUREA GROUPS

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Abstract. Mesoporous silicas with the thiourea functional group $\equiv Si(CH_2)_3NHC(S)NHC_2H_5$ have been synthesized by monotemplate and bitemplate route (bitemplate is cetylpyridinium chloride as micelle-forming surfactant and monoethanolamide of saturated *n*-aliphatic acid as non-micelle-forming surfactant). The influence of a number of factors on mesoporous silicas structure has been studied: alkoxysilanes and surfactants concentration, and as well as the nature of medium in hydrothermal treatment of mesophases. The optimum conditions under which functionalized mesoporous silicas have possessing highly ordered hexagonal structure have been found. The surface area of mesoporous silicas synthesized using optimum bitemplate solubilization composition reaches 1055-1350 m^2/g and sorption volume and pore diameter are 0.75-0.95 cm^3/g and 2.5-2.9 nm respectively.

Keywords: mesoporous silicas, bitemplate synthesis, thiourea functional group.

Introduction

Mesoporous silicas with complexing groups are usually obtained by modification of synthesized samples surface [1-5]. More promising alternative is the introduction of functional groups directly during template synthesis. It conducts to reduction of the number of synthesis steps. Besides, it gives the opportunity to introduce different functional groups (at desired ratios) into the silica surface layer simultaneously. Earlier, the papers [6-16] have already shown the possibility of production of functionalized mesoporous silicas which were obtained in the one-pot template synthesis by using tetraalkoxysilanes, trifunctional silanes and various surfactants such as 1-dodecylamine, cetyltrimethylammonium bromide, and triblock polymers. However, in many cases after template extraction the final products had a less-ordered spatial structure and a relatively low specific surface area [8, 17, 18]. It is worth mentioning about the effect of bitemplate solubilization composition on the perfection degree of a spacial structure of mesoporous silicas [19]. Therefore, in this work bitemplate synthesis method was used for the production of functionalized mesoporous silicas. As a bitemplate the solubilization composition generated by mixed solubilization type has been used: the solubilizer was efficient micelle-forming surfactant (cetylpyridinium chloride, C_{16}PyCl) and the solubilizate was slightly soluble in water non-micelle-forming surfactant (monoethanolamide of saturated *n*-aliphatic acid with hydrocarbon radical length C_{12} (EAC$_{12}$) and C_{14} (EAC$_{14}$)). In contrast to [19] where the source of silicon dioxide was sodium metasilicate, tetraethoxysilane was used in this work. As a trifunctional silane was used $(C_2H_5O)_3Si(CH_2)_3NHC(S)NHC_2H_5$ (ETUS) enabling to embed into surface layer such complexing group as the thiourea which is important from practical point of view. The appearance of such group in the surface layer of mesoporous silicas enables to utilize them as highly efficient and selective sorbents of heavy and noble metals [20].

Experimental

As initial materials were used: tetraethoxysilane, $Si(OC_2H_5)_4$ (TEOS, 98%); cetylpyridinium chloride $[CH_3(CH_2)_{15}N(C_5H_5)]Cl$ (99.9%); ethanol; 25% solution NH_4OH (all reagents “Aldrich”). Monoethanolamides of saturated *n*-aliphatic acid (EAC$_m$) with *m* carbon atoms 12 and 14 were prepared by the known procedure [21] using reaction of methyl esters of alkylcarboxylic acids with monoethanolamine $RC(O)OCH_3 + H_2NC_2H_4OH \rightarrow RC(O)NHC_2H_4OH + CH_3OH$. For bitemplate synthesis the solubilization solution has been prepared as a preliminary using certain concentrations of the solubilizer (C_{16}PyCl) and the solubilizate (EAC$_{12}$ or EAC$_{14}$). The trifunctional silane with thiourea groups - $(C_2H_5O)_3Si(CH_2)_3NHC(S)NHC_2H_5$, ETUS - was synthesized according to [22]. 0.01M solution HCl in etanol was prepared by adding to 96% etanol of the calculated amount of concentrated hydrochloric acid.

The synthesis of organosilica samples was carried out using the following method. In the case of **FMS-1** (TEOS/ETUS = 10:1) to the solution 0.00885 mole C_{16}PyCl in water (175 cm^3) at stirring were added 0.0019 mole ETUS dissolved in ethanol (130 cm^3), then 0.019 mole TEOS. After 10 min. of constant stirring, 57.8 cm^3 of NH_4OH was added drop by drop. Approximately in two minutes from a clear solution the precipitation dropped out. It was to stand at ambient temperature for 48 h. The resulting white precipitate was exposed to hydrothermal treatment (HTT) at 80±2ºC for 24 h. Then the solid sample was filtered and dried in air for 48 h. The surfactant was extracted from obtained white powder material by help of 0.01M HCl solution in ethanol which was boiled for 3 h (at the rate of 45 см^3 of solvent and

1g of sample). The operation was repeated three times and after that the sample was dried in vacuum at 110°C for 4 h. The sample denoted as **FMS-2M** (TEOS/ETUS = 5:1) was synthesized in the similr way.

In the case of **FMS-3** (C_{16}PyCl/(TEOS+ETUS) = 1:2.36) the stirring of the suspension was sustained for 2 hours and then it was kept at ambient temperature for 2 days. The white precipitate was exposed to HTT at 80±2ºC for 3 days in mother liquor (**M**) or in water (**H**). Then it was filtered and dried in air for 48 h. The surfactant was extracted as mentioned above. The samples **FMS-4M** and **FMS-4H** were synthesized in the same way, but C_{16}PyCl/(TEOS+ETUS) = 1:4.

The bitemplate synthesis of samples was carried out analogous using the solubilization composition of C_{16}PyCl and EAC_m. The solubility of EAC_m in water at 20ºC is 9 mg/l (for m = 12) and 2 mg/l (for m = 14). The conditions of synthesis are listed in Table 1. In the case of **FMS-5M** (TEOS/ETUS = 10:1) to the solution 0.00885 mole C_{16}PyCl and 0.000885 mole EAC_{12} (80 cm^3 of ethanol and 175 cm^3 of water) at stirring were added 0.0019 mole ETUS dissolved in ethanol (50 cm^3), then 0.019 mole TEOS. After 10 min. of constant stirring, 57.8 cm^3 of NH_4OH was added drop by drop. In two minutes from a clear solution the precipitation dropped out. The stirring of the suspension was sustained for 2 hours and then it was kept at ambient temperature for 3-4 days without stirring. The white precipitate was exposed to HTT at 80±2ºC for 72 h. Then it was filtered and dried in air for 48 h. The surfactant was extracted from obtained white powder material by help of 0.01M HCl solution in ethanol which was boiled for 3 h (at the rate of 45 cм^3 of solvent and 1g of sample). The operation was repeated three times and after that the sample was dried in vacuum at 110°C for 4 h.

The elemental analysis was performed in Analytical Laboratory of the Institute of Organic Chemistry (NASU, Kyiv). The X-Ray diffraction powder patterns were collected on a DRON-4-07 diffractometer ($Cu_{K\alpha}$-radiation). The DRIFT spectra were recorded on the Thermo Nicolet Nexus FT-IR in the region of 4000-400 cm^{-1} at 8 cm^{-1} resolution by using the Spectra Tech collector diffuse reflectance accessory at room temperature. The samples were mixed up with KBr (1:30), and that mixture was used to fill the DRIFT sample cup before measurements.

SEM photomicrographs of samples were obtained with a Tesla BS301 scanning electron microscope. TEM image was obtained on a JEM 2010 microscope operating at 200 kV for which the sample was dispersed in ethanol by supersonic treatment and then the drop was deposited on a grid with a holey carbon film.

The nitrogen adsorption isotherms were measured by the "Kelvin-1042" adsorption analyzer. Before the measurements, the samples were outgassed at 383 K in the helium atmosphere for 2h. The BET specific surface area [23] was calculated in the range of relative pressure range between 0.05 and 0.35. The total volume of pore (V_s) was determined from the amount of nitrogen which was adsorbed at the relative pressure of 0.99 [23]. The pore size distributions were determined by using the Barrett, Joyner and Halenda (BJH) approach [24].

Results and discussion

The preparation of mesoporous silicas which contained $\equiv Si(CH_2)_3NHC(S)NHC_2H_5$ functional groups in the surface layer was carried out by using of the traditional template method [19, 25, 26]. During synthesis the following conditions have been varied (Table 1): alkoxysilanes concentration, the carbon chain length in solubilizate (EAC_m, *m* = 12 or 14), its concentration and the medium, where HNN was performed – mother solution (**FMS-M** samples) or

Table 1

Structural and structural-adsorption characteristics of functionalized mesoporous silicas

Sample	Molar Ratio of Reaction Mixture	Initial Form		Removed Form			$S_{sp,}$ m^2/g	V_s, cm^3/g	d, nm
		d_{100}, nm	a_0, nm	d_{100}, nm	a_0, nm	I^a, sec^{-1} (a.u.)			
C_{16}PyCl/TEOS/ETUS (Monotemplate Systems)									
FMS-1M	1/2.15/0.21	3.65	4.22	3.67	4.23	12880	1132	0.62	2.5
FMS-2M	1/2.15/0.43	3.67	4.23	3.53	4.08	18500	1172	0.60	2.9
FMS-3M	1/2.15/0.21	3.76	4.34	3.93	4.53	24240	1058	0.66	2.5
FMS-3H	1/2.15/0.21	3.76	4.34	3.76	4.34	24090	1132	0.87	2.5
FMS-4M	1/3.64/0.36	3.84	4.44	3.84	4.44	23960	1372	0.79	2.5
FMS-4H	1/3.64/0.36	3.84	4.44	3.93	4.53	22420	1064	0.62	2.5
C_{16}PyCl/EAC_m/TEOS/ETUS (Bitemplate Systems)									
FMS-5M	1/0.10/2.15/0.21	3.76	4.34	3.84	4.44	27020	1045	0.60	2.5
FMS-5.1M	1/0.15/2.15/0.21	-	-	3.68	4.25	17100	-	-	-
FMS-5.2M	1/0.33/3.62/0.36	3.68	4.25	3.84	4.44	9100	1036	0.66	2.5
FMS-5.2H	1/0.33/3.62/0.36	3.68	4.25	4.02	4.64	9410	-	-	-
FMS-6M	1/0.05/2.15/0.21	3.84	4.44	3.84	4.44	27690	1352	0.75	2.5
FMS-6H	1/0.05/2.15/0.21	3.84	4.44	4.02	4.64	23980	1055	0.95	2.9

FMS-6.1H	1/0.14/3.64/0.36	3.68	4.25	3.93	4.53	9710	-	-	-
FMS-6.2H	1/0.14/3.64/0.72	3.84	4.44	3.84	4.44	15280	-	-	-

[a] Intensity of the first reflex in X-ray diffraction pattern.

water (**FMS-H** samples). The obtained powder samples, as shown in Fig. 1, represent the aggregates of practical spherical particles with the size of about 0.5 µm. The data of element analysis, which was performed for nitrogen and sulfur, shows that the content of functional groups in the synthesized samples has been closed to 1.2 mmol/g (if TEOS/ETMS ratio (mol.) in the initial solution was 10:1 and when it was closed to 1.8 mmol/g (if that ratio was 10:2).

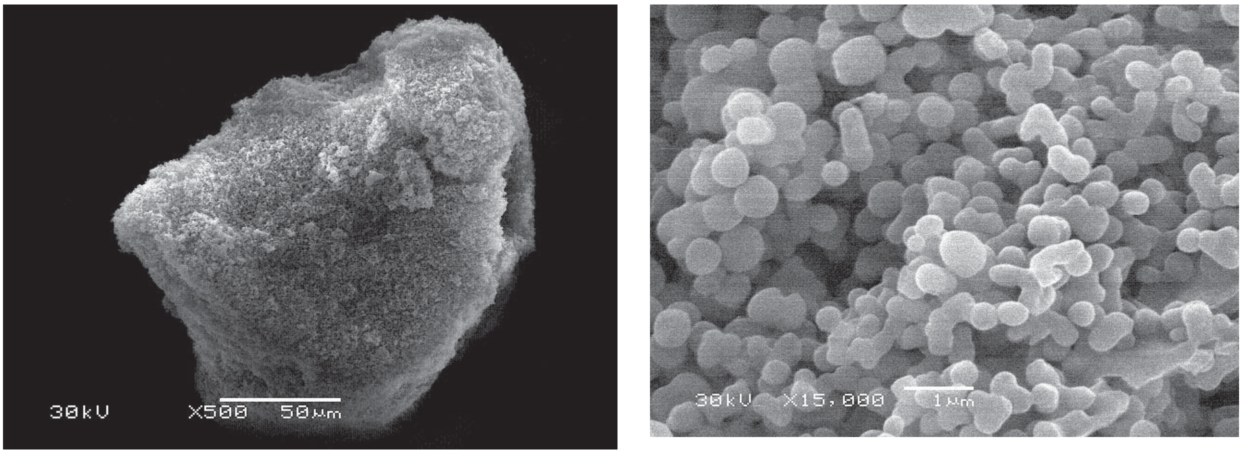

Figure 1. Micrographs of FMS-1M sample obtained by SEM.

The IR spectra of the initial trifunctional silane with thiourea group, cetylpyridinium chloride, monoethanolamides and the samples denoted as **FMS-5M, FMS-6M** and **FMS-6H** are shown in Fig. 2. The IR spectra of other mesoporous silicas that were obtained after template extraction are identical. All of them have the most intensive absorption band with high frequency shoulder in the region of 1050-1200 cm^{-1}. Its appearance can be attributed to formation of the three-dimensional siloxane framework which contains the carbofunctional groups [27]. Also the IR spectra of all samples has a sharp medium-intensity absorption band about 1560 cm^{-1}, which can be attributed to $\nu_{as}(NCN)$ vibration of the thiourea fragment –NH–C(S)–NH– [28]. This fact is also confirmed by the existence of an intensive and broad absorption band $\nu(NH)$ about 3300 cm^{-1}, which is typical of initial ETUS (Fig. 2). Possibly this band is overlapped by another one – the absorption band of $\nu(OH)$ vibration of water, since IR spectra of all the obtained samples contains a small-intensity absorption band at ~1630 cm^{-1}, which may be ascribed to $\delta(H_2O)$. Furthermore, in the region of 2800-3000 cm^{-1} one can identify well-defined absorption bands of valence vibrations of alkyl radicals C–H bonds, but absorption bands which are typical to such templates, are not present in the IR spectra (Fig. 2). Therefore, one can assume that during HTT and extraction the practically full removal of templating agents from mesophases takes place and the sulfur-containing functional groups destruction does not take place in the surface layer. The similar situation has also been observed for mesoporous silicas with thiourea group that were obtained by using $C_{16}PyCl$ only [29]. However, in this case, in accordance with the data of ^{13}C CP/MAS NMR spectroscopy, the samples contain insignificant amount of template.

The X-ray diffraction patterns of synthesized samples usually have 3-4 reflexes in the region of small angles (Fig. 3), that testifies to formation of MCM-41-type spatial structure. This statement is confirmed by micrographs of these samples that are obtained by TEM (Fig. 4) – they contain clearly formed regions with hexagonally ordered structure.

The preliminary investigation was shown while performing HTT, independently from the medium – was it water or mother liquor – the relative intensity of all of the reflexes slightly increased and at the same time the first reflex narrowed a little bit. Therefore, HTT allows to obtain samples with more ordered structure. One can see the same effect at the time of HTT's increase from 1 to 3 days (Table 1, **FMS-1M** and **FMS-3M** samples accordingly). This follows from the final estimate of structural characteristics of samples, which were emanated from their X-ray diffraction patterns (Fig. 3), where the main attention was paid not to the increase of the first reflex intensity, but to the increase of all further reflexes' intensity, their number, resolution and symmetry. Therefore, HTT for the rest of samples was 3 days.

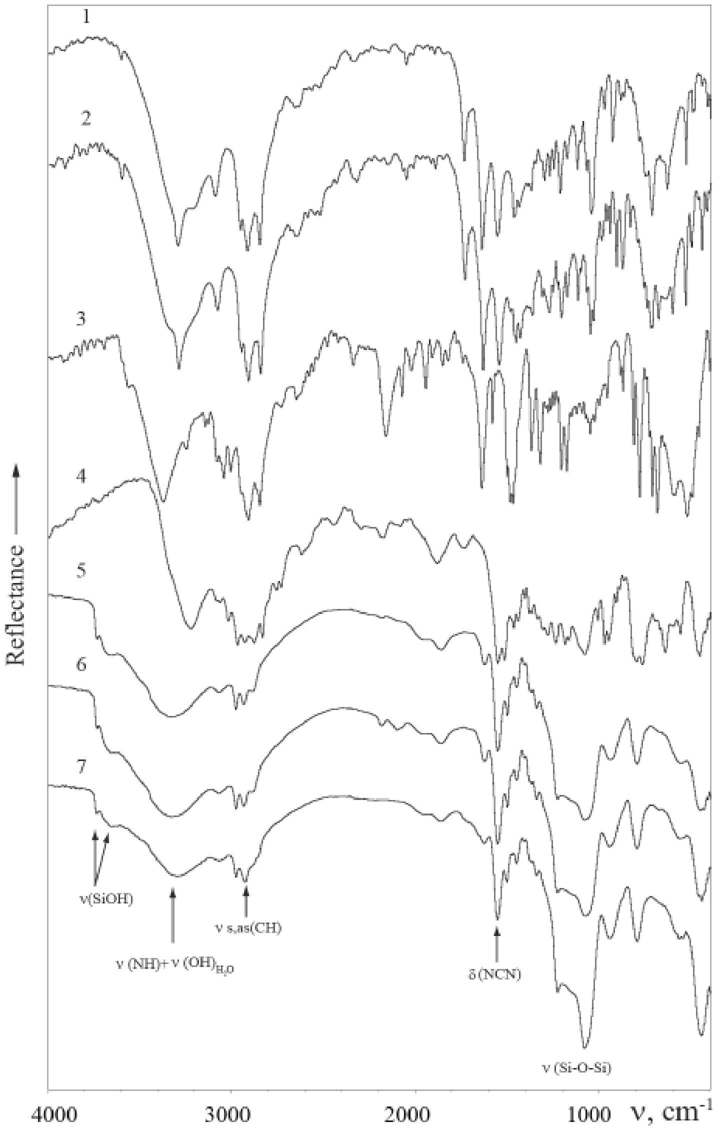

Figure 2. IR spectra of initial reagents: EAC$_{12}$ (1), EAC$_{14}$ (2), C$_{16}$PyCl (3), ETMS (4) and resulting samples: FMS-5M, FMS-6M и FMS-6H (5, 6 and 7 respectively).

The comparison of X-ray diffraction patterns (Fig. 3) for samples that were syntezied using monotemplate variant with those which were obtained by application of bitemplate variant demonstrates, that the usage of template solubilization composition of combined type raises the perfection degree of spatial structure of the final functionalized material. The effect of bitemplate solubilization composition evinces in the formation of more perfect spatial mesophases on the initial stage of synthesis. This effect is likely connected with an increase in strength, density, and rigidity of micelles which is due to interaction between C$_{16}$PyCl and solubilized monoethanolamide molecules, as well as to decrease in the surface charge density of micelles which in its turn is resulted by the dominant localization of monoethanolamide molecules between C$_{16}$PyCl hydrocarbon chains in the region of polar groups [30]. This effect of changing structure of template micelles is more manifested for reacting systems of EAC$_{14}$ (Table 1, **FMS-3M** and **FMS-6M**, **FMS-3H** and **FMS-6H** samples).

As for the molar ratio of templating substances, for it the region which is close to the saturation of micelles with a solubilizate is more preferable. Higher content of solubilizate content results likely in the formation of excessively hard and dense micelles, which weakens the co-organization of reacting system components in the interface into a single spatial structure with framework-forming substance. As a result, this leads to the deterioration of material spatial structure (Table 1, **FMS-5** and **FMS-6** samples).

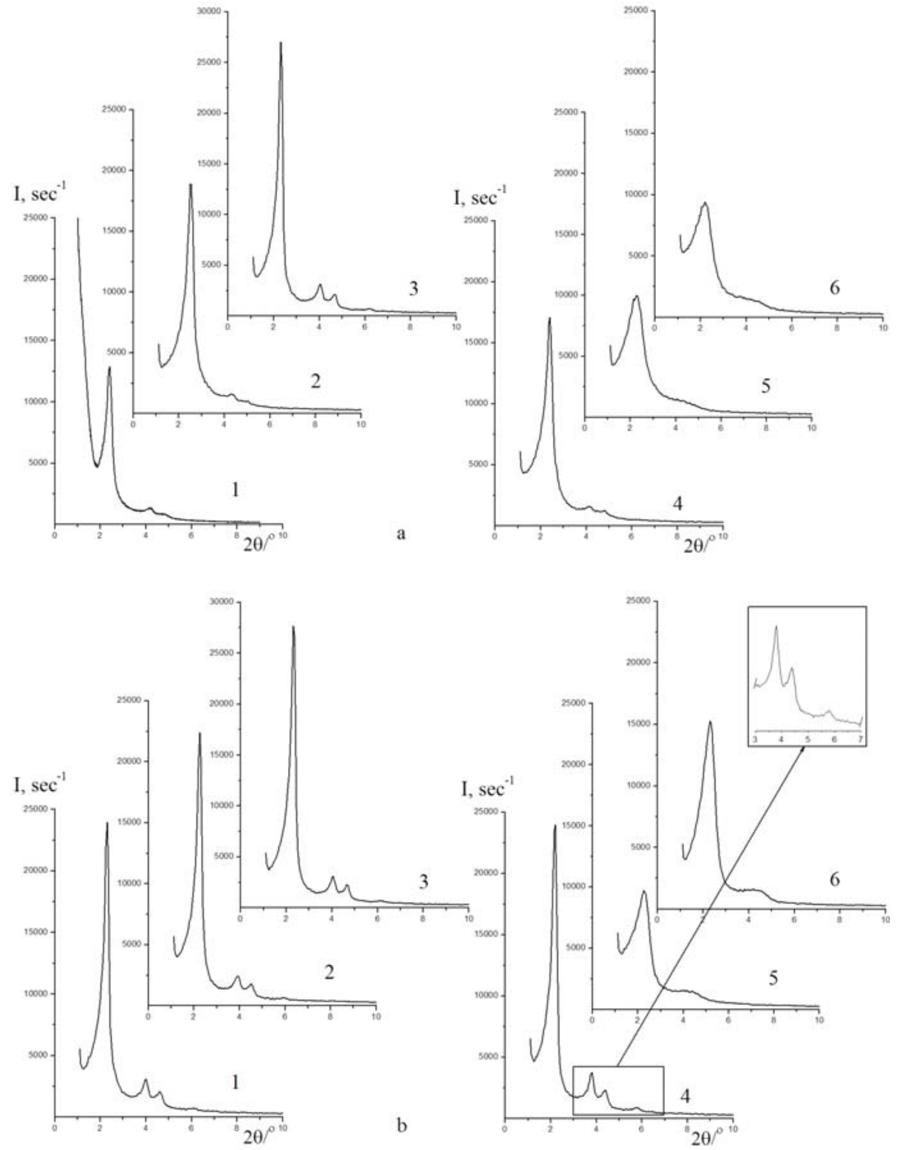

Figure 3. X-ray diffraction patterns of functionalized mesoporous silicas: (a) 1- FMS-1M; 2 - FMS-2M; 3 - FMS-5M; 4 - FMS-5.1M; 5 - FMS-5.2M; 6 - FMS-5.2H and (b) 1 - FMS-4M; 2 - FMS-4H; 3 - FMS-6M; 4 - FMS-6H; 5 – FMS-6.1H; 6 - FMS-6.2H.

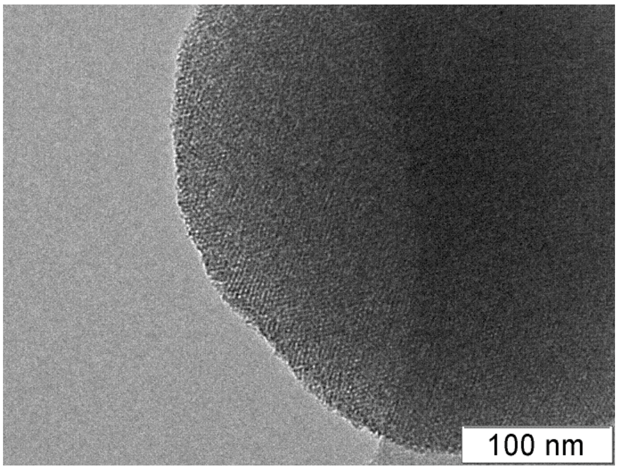

Figure 4. TEM micrograph of FMS-2M sample.

Fig. 5 shows the nitrogen adsorption-desorption isotherms for the samples which did not contain template. All of them have S-like bend in the region of relative pressures 0.1–0.4. They may be ascribed to type IV under the IUPAC classification [31].

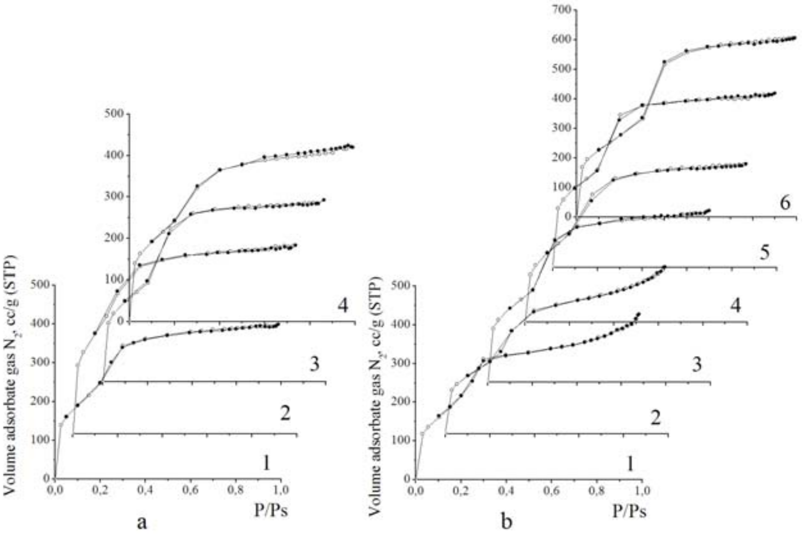

Figure 5. Isotherms of nitrogen adsorption(○) – desorption(●) of synthesized mesoporous samples: (a) 1-FMS-1M; 2 FMS-2M; 3 - FMS-5M; 4 – FMS-5.2M and (b) 1 - FMS-3M; 2 - FMS-3H; 3 - FMS-4M; 4 - FMS-4H; 5 FMS-6M; 6 - FMS-6H.

However, the hysteresis loop is not presented on these isotherms. The Table 1 presents parameters of the porous structure of synthesized samples which were calculated by usage of the obtained isotherms. This table also shows that the effect from introduction of the second template agent (EAC_m) is of different character and is determined by the length of its carbon chain. Thus, in the case of EAC_{12} the change of porous structure parameters is not observed practically (cf. **FMS-5M** and **FMS-3M** samples in Table 1). However, in the case of EAC_{14} the increase of practically all the parameters of porous structure is observed (cf. **FMS-6M** and **FMS-3M** samples in Table 1). In last case the same effect is observed by replacing mother liquor for water at HTT of mesophases (cf. **FMS-6H** and **FMS-3H** samples in Table 1). Therefore, the formation of more ordering spatial structure conduces to the increase of structural-adsorption characteristics of material as well. At the same time it is obvious that the rising concentration just of the second templating agent EAC_m in the reacting solution (Table 1, **FMS-5.1M** sample) or rising of its concentration with alkoxysilane concentration results as a rule in the formation of less ordered structure (Fig. 3).

Hence, this paper shows that the use of bitemplate solubilization composition which is based on micelle-forming surfactant (C_{16}PyCl) and non-micelle-forming surfactant (monoethanolamides of saturated *n*-aliphatic acid ($EAC_{12,14}$)) improves structural and structural-adsorption characteristics of resulting functionalized material. Among the studied systems the most effective one is bitemplate solubilization composition EAC_{14}/C_{16}PyCl with the molar ratio of 0.05/1. It may be forecasted that this effect will be observed for other variants of the bitemplate synthesis of functionalized mesoporous silicas as well.

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CATALYTIC PROPERTY OF DOUBLE LAYERED PEROVSKITES $A_2MM'O_6$ FOR RADIOLYTICAL SPLIT OF WATER

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Abstract: This paper deals with a study of water splitting by gamma rays in the presence of some double perovskites $A_2MM'O_6$ and also $Sr_2Fe_{1-x}Ta_{1+x}O_6$. The irradiation is performed using ^{60}Co as a source with $3 \cdot 10^4$ Ci activity and 8.3 kGy/h dose rate, which simulated the radioactive wastes, resulted from reprocessing of spent nuclear fuel elements much more active: 10^8-10^9 Ci. The stable products of radiolysis, as well as the other chemical species are measured by mass spectrometry. The calculated radiation yield (GH_2) generally decreases in the order: $Sr_2Fe_{1-x}Ta_{1+x}O_6$ (x=0.5; 0.4; 0.3; 0.1) > Ca_2AlTaO_6 > Sr_2AlTaO_6 > Ba_2AlTaO_6, under the given experimental conditions; the yield was higher in the presence of these catalysts than in their absence.

Keywords: catalytic effect, double perovskites, hydrogen production, water radiolysis.

Introduction

Photocatalytic water splitting in the presence of perovskites has received an extensive attention, as it can provide a clean and renewable source for hydrogen fuel. A variety of photocatalysts have been reported as active in water splitting process. In particular, 2D-layered photocatalysts are of great interest, because of the possibility to modify the chemical composition as well as microstructure by means of ion exchange or interaction.

Experimental results show that the 2D-layered perovskite oxide should be more favorable for water reducing due to the particular layered structure and the easy formation of large surface areas.

However, the application of these chemical compounds for pure water splitting was not successful, although a lot of cocatalysts were used, such as NiO, RuO_2 and Pt, to improve the activity of the 2D-layered photocatalyst [1].

Yao and Ye developed studies on $CsLaSrNb_2NiO_9$ and also on $K_2Sr_{1.5}TaO_{10}$ as photocatalysts in pure water splitting, even in the absence of any cocatalyst. Their studies pointed out that the new active catalysts for pure water splitting based on 2D-layered tantalate are stronger than those corresponding to niobate [2].

Li *et al.* investigated the photocatalytic properties of water splitting over a series of perovskite-type compounds $A_2MM'O_6$ (A=Ca, Sr, Ba; M=Ni, Co, Zn, Mg; M'= Mo, W). Although H_2 and O_2 evolution was observed under ultraviolet or visible light irradiation in the presence of CH_3OH or $AgNO_3$ as sacrificial reagents, it has been found that most of these compounds suffer instability in aqueous solution under light irradiation and only Ca_2NiWO_6 remained chemically stable [3].

The ideal catalyst should not react with the solvent used, resist to the action of light or nuclear radiations and did not catalyze the water decomposition at room temperature developing hydrogen.

The present paper is a continuation of some former studies regarding hydrogen output from water radiolysis in the presence of some solid catalysts. Here are investigated the catalytic properties of new double perovskites seria with the stoichiometry $A_2^{2+}M^{3+}M^{5+}O_6$ (A=Ca, Ba, Sr; M=Al; M'=Ta) and also $Sr_2Fe_{1-x}Ta_{1+x}O_6$ (x = 0.1; 0.3; 0.4; 0.5) in water splitting process, under gamma-rays irradiation emitted by a ^{60}Co source [4, 5].

Experimental Section

Sample Preparation and Characterization

Polycrystalline samples $A_2^{2+}M^{3+}M^{5+}O_6$ were synthesized by solid state reaction, from a stoichiometric mixture of ACO_3 ($SrCO_3$, $BaCO_3$), CaO, B_2O_3 (Al, Fe) and Ta_2O_5 with a purity ranging between 99.99 and 99.999%. These carbonates and oxides were dried at 120°C for 2 h before weighing. Afterwards, they were thoroughly mixed, placed in Al_2O_3 crucibles and heated at 950 °C, for 6 h [6].

Other determinations showed that a thermal treatment at higher temperatures (~1500°C) of these catalysts reduce their catalytic activity due to a higher crystallization degree. [7]

Structural properties

Structural characterization of these catalysts after the thermal treatment was accomplished using an Infrared spectrometer Jasco FT/IR–660 Plus. FT-IR spectra were registered between 4000 cm^{-1}-400 cm^{-1}, on the KBr tablets. Vibrational behavior of doubles perovskites is complex due to the fact that crystalline cell has two polyhedrons MO_6, each of them with metallic cations with different size and charge.

FT-IR spectra showed two strong adsorption bands, one in the 800-600 cm^{-1} domain due to the stretching vibration of $M'O_6$ polyhedrons and another one of low energy usually split at 450 cm^{-1} arrogated to the MO_6 polyhedrons distortion. Also, the formation of the perovskitic phase at 950 °C was noticed [8].

It is well known that the tolerance factor ŕ determines the crystal structure of perovskites AMO_3. Only for ŕ close to unity is a cubic perovskites structure obtained. For $f \neq 1$ a tilt and rotation of the oxygen octahedral is obtained, compensating for the misfit of the ionic radii of the involved A and M cations. The deviation of the tolerance factor from the ideal value $f=1$ can be used as a measure for the internal strain in perovskites induced by the different radii of the A and M cations. This can be seen from the definition of ŕ given by:

$$f = \frac{r_A + r_O}{\sqrt{2}(\langle r_M \rangle + r_O)} \tag{1}$$

where $\langle r_B \rangle$ denotes the average ionic radius for the ions on the M site. For $f<1$, the strain is compensated by a tilt and rotation of the oxygen octahedra. This results in a deviation of the M-O-M bond angles from the ideal value of 180°. For $0.96 \leq f \leq 1$ the connected pattern of the oxygen octahedral is rhombohedral, whereas it is orthorhombic for lower values of f. For $f>1.06$, a hexagonal structure is expected which is classified by the stacking sequence of the MO_6 octahedra [9, 10].

It was discussed the change of tolerance factor f and its influence on the structure for the system A_2AlTaO_6 (A=Ca, Ba, Sr) and $Sr_2Fe_{1-x}Ta_{1+x}O_6$ (x=0.1; 0.3; 0.4; 0.5). Tolerance factors were calculated using SPuDS simulation software.

Table 1

The tolerance factor of $A_2MM'O_6$ series (A= Ca, Ba, Sr)

Compound (t_{sint})	f	Structure	Structure Lattice. parameters [Å]	Space group
Ca_2AlTaO_6 950°C	0.9626	Monoclinic	a=5.3780 b=5.4154 c=7.6248	$P_{21/n}$
Ba_2AlTaO_6 950°C	1.0790	Hexagonal	a=5.7155 c=13.9510	$P6_{3/mmc}$
Sr_2AlTaO_6 950°C	1.0178	Cubic	a=7.795	Fm-3m
$Sr_2Fe_{1-x}Ta_{1+x}O_6$ 950°C	0.9825	Rhombohedric	a=5.6204 b=5.6161 c=7.9266	P_{bmn}

It can be notice that while Sr_2AlTaO_6 compound with ŕ=1.0178 is cubic, Ca_2AlTaO_6 compound with ŕ=0.9626 is strongly distorted forming a monoclinic system. In the case of Ba_2AlTaO_6 it can be considered that the size of Ba^{2+} cation will determine a strong deformation of the ideal crystallographic cell forming a hexagonal system.

Water decomposition

In the 30 ml glass vials different quantities of each catalyst were introduced and 5 ml of double distilled water were added. Each vial was tightly closed with rubber cork and outside paraffined to hinder the release of gaseous radiolysis product. These vials were γ-irradiated in different experimental conditions, under different dose rates, at IFIN-Bucharest. A blank sample for comparison was also prepared under the same conditions but without the addition of the catalyst.

The radiolysis products but also other chemical species having 14 and 28 mass numbers (corresponding to N and N_2) were analyzed by mass spectrometry, using an original connection device between the irradiated sample and the spectrometer, based on a metallic capillary.

Hiden Analytical mass spectrometer was first calibrated with the hydrogen resulted from a total chemical reaction:

$$Zn + 2\,HCl_{dil} \rightarrow ZnCl_2 + H_2 \tag{2}$$

This means that 1.08 g Zn corresponds to 0.01 mole H_2 which further correspond to peak intensity (in arbitrary units) of $1.58 \cdot 10^7$ in the mass spectrum, for the species having the mass number 2.

A vacuum of about $2 \cdot 10^{-6}$ torr was reached inside of ionization chamber of mass spectrometer before each measurement, in order to avoid the contamination risk for the following vial with the chemical species of the previous sample. Computer plots the obtained experimental results as spectra, in the coordinates: Mass number = f (Peak intensity).

Results and discussion:

It's generally known that the radiolysis of water leads to the formation of different chemical species, such as: H_2, O_2, H_2O_2, $HO^\bullet$, O, $HO_2^\bullet$ etc. via a number of reactions outlined below, as:

$$\rightsquigarrow H_2O \rightarrow H_2O^* \rightarrow H^\bullet + HO^\bullet \tag{3}$$

$$\rightsquigarrow H_2O \rightarrow H_2O^+ + e^- \tag{4}$$

$$H_2O + e^- \rightarrow H_2O^- \tag{5}$$

$$H_2O^+ + H_2O^- \rightarrow 2H_2O^* \rightarrow 2H^\bullet + 2HO^\bullet \tag{6}$$

$$H^\bullet + H^\bullet \rightarrow H_2 \tag{7}$$

$$HO^\bullet + HO^\bullet \rightarrow HO_2^\bullet + H^\bullet \tag{8}$$

$$H^\bullet + O \rightarrow HO^\bullet \tag{9}$$

$$HO_2^\bullet + HO_2^\bullet \rightarrow H_2O_2 + O_2 \ldots \tag{10}$$

Radiolytic yield of hydrogen, GH_2 (number of transformed or appeared molecules for 100eV absorbed energy, by γ-ray irradiation) was calculated using a formula deduced from the Henglein expression [11]:

$$G_{H_2} = \frac{b \cdot I_x}{D \cdot t \cdot \rho \cdot I_{et}} \cdot 9.66 \cdot 10^6 \tag{11}$$

where:

$D \cdot t = D_a$ – is the absorbed dose (1J/kg or $6.24 \cdot 10^{15}$ eV/g) (12)

ρ - the density of irradiated material (g/cm^3),

b - hydrogen amount determined from the calibration of the mass spectrometer (mole H_2/1kg H_2O)

I_{et} - is peak intensity value of molecular hydrogen resulted from the mass spectrometer calibration reaction

I_x - is peak intensity value of molecular hydrogen resulted from the catalyzed water radiolysis

Several species ($H^\bullet$, $HO^\bullet$, $HO_2^\bullet$, and H_2O_2) were found in the mass spectra, but the radiolytic yield was determined only for molecular hydrogen.

The experimental results and also the catalysts efficiency in water radiolysis process were shown by the radiolytic yield values of the molecular hydrogen in several working conditions (Figures 1, 2).

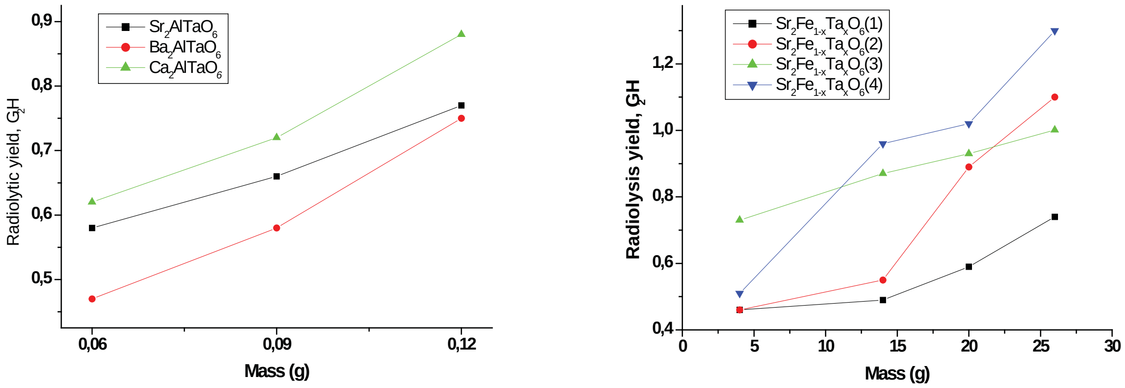

Figure 1. Radiolytic yield vs catalysts mass (x = 0.1; 0.3; 0.4; 0.5).

Experimental data pointed out that radiolytic yields of molecular hydrogen increased when the absorbed dose (for a given quantity of catalyst) or perovskites mass (for the same dose) were increased.

The subsequent action of the gamma rays produces a radiolytical split of water, releasing a radiolytic yield GH_2 higher than that produced from pure water splitting in the absence of the catalyst (0.43), irradiated in the same conditions as the samples with catalyst.

Furthermore the FT-IR spectra were achieved on some of the catalysts before and after irradiation (Figure 3), to prove the catalytic effect of these solid masses in radiolytical split of water molecules. There were not observed any changes in their structure. FT-IR spectra were achieved in the same conditions, on tablets containing KBr dried for 24 h at 120°C.

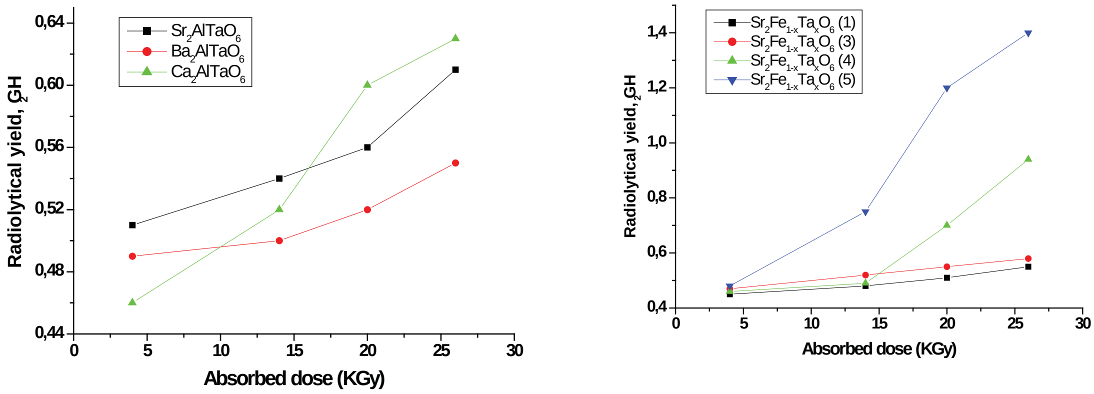

Figure 2. Radiolytic yield vs. absorbed dose (x = 0.1; 0.3; 0.4; 0.5).

Explaining the catalytic effect

Perovskite oxides contain large concentrations of oxygen vacancies, this being a consequence of the cation stoichiometries and valence.

It can be considered that the neutral water molecule will fill these oxide vacancies. Anionic vacancies ($V_O^{\cdot\cdot}$) are acting as Lewis acid and the water molecules as Lewis base.

$$V_O^{\cdot\cdot} + \mathbf{O}_O^x + H_2O \leftrightarrow 2\,OH_O^{\cdot} \qquad (13)$$

From experimental data it was noticed that the double perovskite Ca_2AlTaO_6 had a higher catalytic effect comparing with Ba_2AlTaO_6 and Sr_2AlTaO_6. This might be explained on the base of ionic radii variation ($rCa^{2+} < rSr^{2+} < r\,Ba^{2+}$). A smaller ionic radius will determine a higher number of anionic vacancy ($V_O^{\cdot\cdot}$). Also, Ca^{2+} has a higher polarizing action on the water molecules, due to his smaller ionic radius.

The changes in stoichiometry that occur on annealing water in the perovskite structure can also be summarized:

$$A_2AlTaO_6 + x\,H_2O \rightarrow A_2AlTaO_{6-x}(OH)_{2x} \qquad (14)$$

$$Sr_2Fe_{1-x}Ta_{1+x}O_6 + x\,H_2O \rightarrow Sr_2Fe_{1-x}Ta_{1+x}O_{6-x}(OH)_{2x} \qquad (15)$$

In the case of $Sr_2Fe_{1-x}Ta_{1+x}O_6$ it might be consider that the catalytic effect increases with x value due of a greater number of anionic vacancies [12-16].

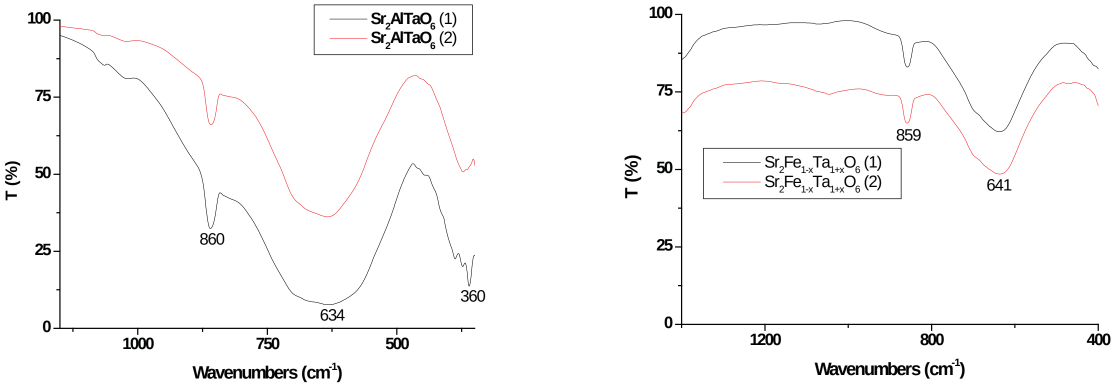

Figure 3. FTIR spectra of Sr_2AlTaO_6 and $Sr_2Fe_{1-x}Ta_{1+x}O_6$ (x=0.1), (1) before and (2) after irradiation.

Conclusion

The present paper has been directed towards the evaluation of the catalytic properties of some double perovkites A_2AlTaO_6 with different interlayer cations (A=Ca, Ba, Sr) and $Sr_2Fe_{1-x}Ta_{1+x}O_6$ (x=01; 0.3; 0.4; 0.5) for pure water splitting under γ-rays irradiation.

It was noticed that the double perovskites with A= Ca has a higher catalytic effect in water splitting and also the ones with $Sr_2Fe_{1-x}Ta_{1+x}O_6$ formula, where x=0.5.

Double perovskites $Sr_2Fe_{1-x}Ta_{1+x}O_6$ have a more important catalytic effect comparing with A_2AlTaO_6 (A=Ca, Ba, Sr).

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ACTIVATION OF ACETYLENE BY COORDINATION TO BIS-TRIPHENYLPHOSPHINE COMPLEX OF Pt(0): DFT STUDY

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Abstract: The present work is devoted to the theoretical study of the activation of the acetylene molecule coordinated in the $[Pt(PPh_3)_2C_2H_2]$ complex. By means of DFT calculations it is shown that the geometrical and electronic characteristics of the C_2H_2 are essentially changed due to its coordination. The subsequent detailed analysis of the molecular orbitals (MO) of the active valence zone of this complex allows one to make important conclusion that this activation is being realized mainly due to the orbital back donation of 5*d*-electronic density from one of the occupied MOs of the complex $[Pt(PPh_3)_2]$ to the unoccupied antibonding π*-MO of C_2H_2.

Keywords: chemical activation, quantum-chemical calculations, DFT method.

1. Introduction

Halogen derivatives of acetylene are very important in practical (industrial) use as monomers in plastics manufacturing. They are usually obtained by means of reactions between hydrogen halogenides and various transition metals complexes with coordinated (activated) acetylene molecules. Activation of acetylene by coordination to transition metals is thus the main chemical process in one of the most important chemical industries [1, 2].

Under the *chemical activation of molecules by coordination* it is implied the modification of their electronic and nuclear structures which leads to their higher chemical reactivity. Among qualitative models for representation of the metal-unsaturated hydrocarbon bonding the Dewar-Chatt-Duncanson diorbital scheme [3] is more conventional. According to this approach the carbon-metal bond in the transition metals complexes of acetylene is provided by two bonding MOs: the first MO of a σ character is formed through the overlap between one of the empty metal d-orbitals and the bonding π-MO of acetylene, and the second one of a π-type is formed by one of the filled d_π orbitals of the metal and the empty antibonding π* orbital of acetylene. The formation of the σ bond leads to the transfer of electronic density from the acetylene to the metal (σ-type donation, Δq_σ), while the π bond provides the opposite charge transfer from the metal to the antibonding π*-MO of acetylene (π-type back donation, Δq_π).

A more general definition of the ligand bonding, in which *mono-orbital, diorbital and multiorbital* metal-ligand bonds are distinguished, was suggested by Bersuker in the monograph [4]. In the MO terminology "*the multiplicity of the orbital bonding (mono-, di-, and multiorbital) equals the number of complex-ligand bonding MOs uncompensated by the antibonding orbitals*" [4]. It follows from this definition that the electronic charge transfers to and from the ligand are due to formation of such *uncompensated* bonding MOs of the entire complex. The values of the orbital charge transfers depend on the nature of the metal and the geometry of ligand coordination. They may have opposite signs ($\Delta q_i<0$ means the electron density transfer from *i*-th MO of the ligand to the metal, and $\Delta q_i>0$ in the opposite case) compensating each other and giving a small value of the total charge transfer. However, their effect on ligand activation may be additive. In the particular case of diorbital bonding the scheme of mutually compensating charge transfers [4] is qualitatively the same as the Dewar-Chatt-Duncanson one [3].

Thus, in order to clarify the nature of the metal-ligand bonding, it is necessary to calculate the electronic structure of the whole complex, as well as the values of the orbital charge transfers to and from molecular orbitals of coordinated ligand.

Bis-triphenylphosphine complexes of zero-valence Pt with acetylene and its derivatives of the type $[Pt(PPh_3)_2RCCR']$ have been the subject of several experimental studies [5-8]. In accordance with [5], these complexes are formed mainly as a result of summary model reactions:

$$[Pt(PPh_3)_4]+RCCR'\rightarrow[Pt(PPh_3)_2RCCR']+2PPh_3 \quad (1)$$

$$[Pt(PPh_3)_2]+RCCR'\rightarrow[Pt(PPh_3)_2RCCR'] \quad (2)$$

It was established also [5, 7] that in above complexes the acetylene molecule is coplanar (or nearly so) with the plane of two phosphorus atoms and the atom of Pt. It is coordinated in the scheme of the π *complex* when the C-C bond line is perpendicular to the line of bonding to the metal, being *cis*-distorted. Some explanations of this *cis*-bent geometry of the coordinated acetylene molecule were given in [9].

In the present work, the nature of the Pt(0)-C_2H_2 binding and the changes in the properties of the C_2H_2 molecule due to its coordination in the [Pt(PPh_3)$_2$HCCH] complex are analyzed on the basis of the Density Functional Theory (DFT) calculations of the electronic structure of the [Pt(PPh_3)$_4$] (**I**), [Pt(PPh_3)$_2$] (**II**), [Pt(PPh_3)$_2$HCCH] (**III**) complexes and free C_2H_2 and PPh_3 molecules.

The energy effects of the [Pt(PPh_3)$_2$HCCH] formation due to reactions (1) and (2) were also evaluated.

2. Computational details

The electronic and geometrical structures of free C_2H_2 and PPh_3 molecules and the corresponding platinum(0) complexes (**I**), (**II**) and (**III**) have been investigated by means of the DFT method, including Becke's three-parameter nonlocal-exchange functional [10] with the correlation functional of Lee, Yang and Parr (B3LYP) [11]. All the calculations were performed with the GAUSSIAN 03 program package [12]. For each compound considered, a full geometry optimization is performed using the LANL2DZ basis set with non-relativistic effective core potential for Pt and the split-valence basis set 6-31G(d) including polarization functions for all other atoms (P, C, and H) in the systems. This method is being widely used for quantum chemical studies of transition metals complexes during a few last years. It has proved its reliability in obtaining quite accurate geometrical parameters (the average B3LYP error is estimated to be ~0.01Å for bond distances and ~0.6° for valence angles) and energy characteristics (2-3 kcal/mol) of studied systems (see, for example [13] and references therein).

To calculate the values of the orbital charge transfers to and from C_2H_2 the MOs obtained by the DFT calculations are rewritten in the basis of the eigenfunctions of the free C_2H_2 and atomic orbitals (AO) of other atoms. Then the occupations of the C_2H_2 eigenfunctions in the complex are calculated as the Mulliken populations of the corresponding orbitals.

The energy gains ΔE_R of reactions (1) and (2) with R=R′=H were defined as $\Delta E_R = E(\text{product}) - E(\text{reactant})$.

3. Results and discussion

3.1 *Structure of the Complexes*

A general view of the complexes (**I**), (**II**) and (**III**) along with the used coordinate system is shown in Fig.1. Full geometry optimization for all the compounds was carried out assuming the T symmetry group for (**I**) and C_2 symmetry for (**II**) and (**III**). Calculations show that in the coordinationally unsaturated [Pt(PPh_3)$_2$] compound the P, Pt, P atoms are collinear. The optimized values of the Pt-P distances are equal to 2.29 Å for the above compound and 2.47 Å for the [Pt(PPh_3)$_4$]. These values are in a rather good agreement with the available experimental data [6, 7, 14].

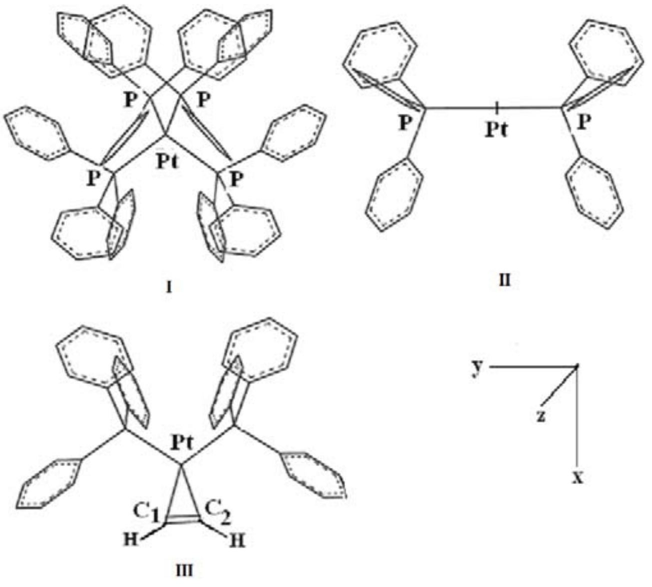

Fig. 1. Structure of the [Pt(PPh_3)$_4$] (I), [Pt(PPh_3)$_2$] (II) and [Pt(PPh_3)$_2$HCCH] (III) complexes (for the sake of simplicity the phenyl-hydrogen atoms are omitted)

In Table 1 are summarized the most relevant calculated geometry parameters for the [Pt(PPh_3)$_2$HCCH] (**III**), together with those reported for similar systems [6, 7]. Optimized geometries were found to be close to their experimental analogues. Note first of all, that the acetylene molecule is coordinated in (**III**) in the plane of P-Pt-P, being *cis*-distorted. Moreover, this compound exhibits rather high energy barrier to internal rotation of the C_2H_2 around the Pt-acetylene axis (~ 60 kcal/mol in our calculations). This value is probably overestimated as the total energies for the rotation up to 90° (the normal coordination of C_2H_2) were calculated without the corresponding geometry re-optimization. In any case, the presence of such high energy barrier of rotation is marked in a number of papers [5, 15].

Table 1

Calculated and experimental geometry parameters for the [Pt(PPh_3)$_2$RCCR′]
(distances in Å and angles in degrees)

Geometry parameters	Calculated (R=R′=H)	X-ray data
R(Pt-P)	2.36	2.28 [6,7]
$\angle$P-Pt-P	112.9	103 [6], 102 [7]
$R(\text{Pt-C}_{(\text{-C}\equiv\text{C-})})$	2.08	2.01 [6,7]
$R(\text{C-C}_{(\text{-C}\equiv\text{C-})})$	1.28	1.28 [6], 1.32 [7]
$\angle \text{C}_{(\text{-C}\equiv\text{C-})}\text{-Pt- C}_{(\text{-C}\equiv\text{C-})}$	35.9	37 [6], 39 [7]

Table 2 contains the calculated geometry parameters, the C-C bond force constants (K) and the stretching frequencies ($\nu_{C\equiv C}$) for both the free and coordinated in (**III**) acetylene molecules. The values of K were estimated in the assumption that the total energy E of the C_2H_2 molecule in the neighbourhood of the equilibrium (R^0_{CC}) can be written as $E(\Delta R_{CC}) = 1/2K(\Delta R_{CC})^2$, where $\Delta R_{CC} = R_{CC} - R^0_{CC}$. Then, using the harmonic oscillator equation, $\nu = 1/2\pi c\sqrt{K/\mu}$, where the reduced mass μ in our case is equal to the half of the mass of the C atom, and c is the velocity of light, we have evaluated the values of the $\nu_{C\equiv C}$.

Table 2

Geometrical and electronic parameters of the free and coordinated C_2H_2 molecule

Molecule	$\nu_{C\equiv C}$, cm^{-1}	K, mdyn/Å	Distances (Å), angles (deg.)		
			C-C	-C-H	$\angle$C-C-H
HCCH, coordinated	1976	13.80	1.28	1.08	148.2
HC≡CH, free*	2075	15.25	1.21	1.07	180.0

*Experimental values for free C_2H_2 are [16]: $\nu_{C\equiv C}$=2100 cm^{-1}, K=15.59 mdyn/Å

The results of Table 2 show that the geometrical structure of the acetylene molecule is changed significantly due to its coordination. The coordinated C_2H_2 molecule induces not only an elongation of the C-C distance (1.21Å in free C_2H_2 versus 1.28Å in coordinated one) but also a bending of the hydrogen atoms away from the metal (the calculated bond angle of the C-C-H group is 148.2° for the complex). The length of the C-C bond in coordinated acetylene is intermediate between this value for gas phase acetylene and ethylene (1.34 Å), while the C-C-H angle is far from that of free C_2H_2 (180°) and is near to the angle in the ethylene molecule (120°). This means that coordination of acetylene to the Pt(0) in the above complex leads to the essential change of the kind of hybridization of the valence AOs of its carbon atoms from sp (in the gas phase) to approximately sp^2. This results to the decrease in the CC bond force constant and the stretching frequency($\Delta\nu_{C\equiv C}$=100cm^{-1}) (Table 2), which means the weakening of the CC bond.

Calculated total energies of the complexes **(I), (II)** and **(III)** and free C_2H_2 and PPh_3 molecules in their optimized equilibrium geometries allow one to estimate the energy gains of the model summary reactions (1) and (2). Our calculations show that both the reactions (1) and (2) are exothermic (ΔE_R(1)=38 kcal/mol and ΔE_R(2)= 9 kcal/mol), in agreement with the data of [5].

3.2 *Orbital charge transfers and the nature of the Pt(0)-acetylene bonding*

In order to analyze the orbital charge transfers in the [Pt(PPh_3)$_2$$C_2H_2$] complex, consider first of all the changes of the molecular orbitals of C_2H_2 due to its coordination. As shown in the Section 3.1, the coordinated acetylene molecule possesses a *cis*-bent structure in the complex. In Fig.2 the highest occupied MO (HOMO) and the lowest unoccupied MO (LUMO) of the linear and the *cis*-distorted acetylene molecule are presented (letters **a** and **b** denote the irreducible representations of the C_2 point group of symmetry used throughout the calculations).

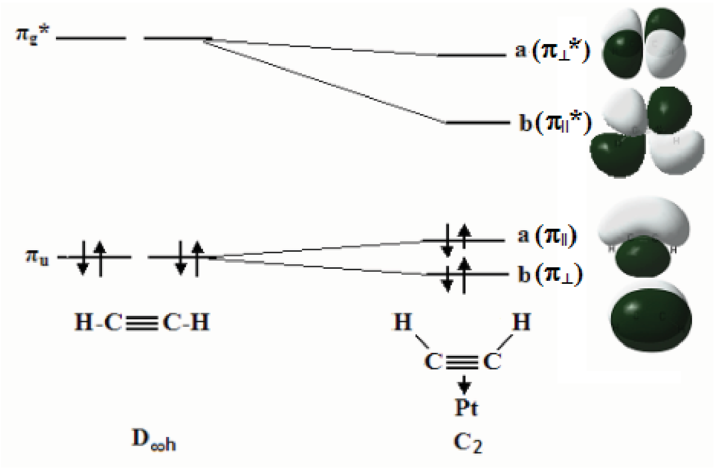

Fig.2. Splitting of the HOMO and LUMO of free C_2H_2 molecule (linear, $D_{\infty h}$) due to its coordination (cis-bent, C_2)

The *cis*-distortion causes the splitting of the double-degenerated π and π* MOs of linear C_2H_2 into the two occupied **b**($\pi_|$) and **a**($\pi_{||}$) and two unoccupied **a**($\pi_|$*) and **b**($\pi_{||}$*) MOs (Fig.2). The maximum of the electronic density of $\pi_{||}$ and $\pi_{||}$* MOs is in the plane of coordination, while that of $\pi_\perp$ and $\pi_\perp$* MOs is in the perpendicular one. This leads to increase of the energy of the HOMO ($\pi_{||}$) and to decrease of the energy of the LUMO ($\pi_{||}$*) enhancing thereby the donor-acceptor properties of acetylene. When forming the complex $[Pt(PPh_3)_2C_2H_2]$, these valence MOs of the acetylene molecule interact with appropriate orbitals of the Pt atom, giving rise to the Pt- C_2H_2 bonding.

Consider in more detail the MO energy-level scheme of the active valence zone of the whole $[Pt(PPh_3)_2C_2H_2]$ and that of its fragments, $[Pt(PPh_3)_2]$ and C_2H_2 (Fig.3). Both these fragments were considered in their pre-activated states (nonlinear P-Pt-P fragment and *cis*-distorted C_2H_2 molecule). It was done in order to understand the main electronic redistribution details accompanying the formation of MOs of the complex $[Pt(PPh_3)_2C_2H_2]$. The orbital energies and the composition of these MOs are presented in Table 3. The nomenclature of MOs in Table 3 is given in accordance with the coordinate system from Fig.1.

Table 3

One-electron states of valence zone of the $[Pt(PPh_3)_2C_2H_2]$

Orbital, №, symmetry	Energy, a.u.	Composition*
168 **b**	0.054	$0.59(5d_{xy}^{Pt})-0.44(\sigma^{*cc})-0.31(\pi_{\|}^{*cc})$
154 **b**, HOMO	-0.184	$0.72\ (5d_{xz}^{Pt})-0.31(\pi_{\perp}^{cc})$
153 **b**, HOMO-1	-0.198	$0.33(5d_{xy}^{Pt})+0.18p_{y}^{Pt}+0.21(\sigma^{*cc})+0.23(\pi_{\|}^{*cc})$
152 **a**, HOMO-2	-0.199	$0.67(5d_{x2-y2}^{Pt})-0.11(5d_{z2}^{Pt})-0.12(\sigma^{cc})-0.22(\pi_{\|}^{cc})\ -0.23(6s^{Pt})$
137 **a**	-0.293	$0.42(5d_{x2-y2}^{Pt})+0.17(5d_{z2}^{Pt})+0.20(\sigma^{cc})+0.26(\pi_{\|}^{cc})$
136 **b**	-0.295	$0.50\ (5d_{xz}^{Pt})+0.35(\pi_{\perp}^{cc})$

*For simplicity, only those contributions of the AOs of Pt and MOs of C_2H_2 are presented, whose AO coefficients are higher than 0.1 (in absolute value)

It is to be noted that some MOs of the $Pt(PPh_3)_2$ fragment on the left side of Fig. 3 are not pure *d*-AOs of the atom of Pt. For example, the MO designated as **x^2-y^2,** contains, besides the $5d_{x2-y2}$, a fairly significant contribution of 6*s*-AO and some admixture of $6p_x$-AO of the metal. The MO **xy** is the linear combination of the $5d_{xy}$ and $6p_y$ AOs of the Pt, and the 3*p*-AOs of the atoms of phosphorus.

The occupied **a**($\pi_{||}$) MO of C_2H_2 interacts with the occupied MO (**x^2-y^2**) of the $Pt(PPh_3)_2$ fragment, giving rise to the two occupied σ-type MOs of the $[Pt(PPh_3)_2C_2H_2]$ complex: the bonding MO 137**a** and the antibonding MO 152**a** (Fig.3). Because of the fact that both these MOs are occupied by electrons, they compensate each other, and hence their total contribution to the Pt-C_2H_2 bonding is very small. The results of the DFT calculations yield $\Delta q_\sigma = -0.09$ ē. This small Δq_σ value characterizes the slightly asymmetrical charge distribution in the mutual compensating bonding (137**a**) and antibonding (152**a**) σ MOs.

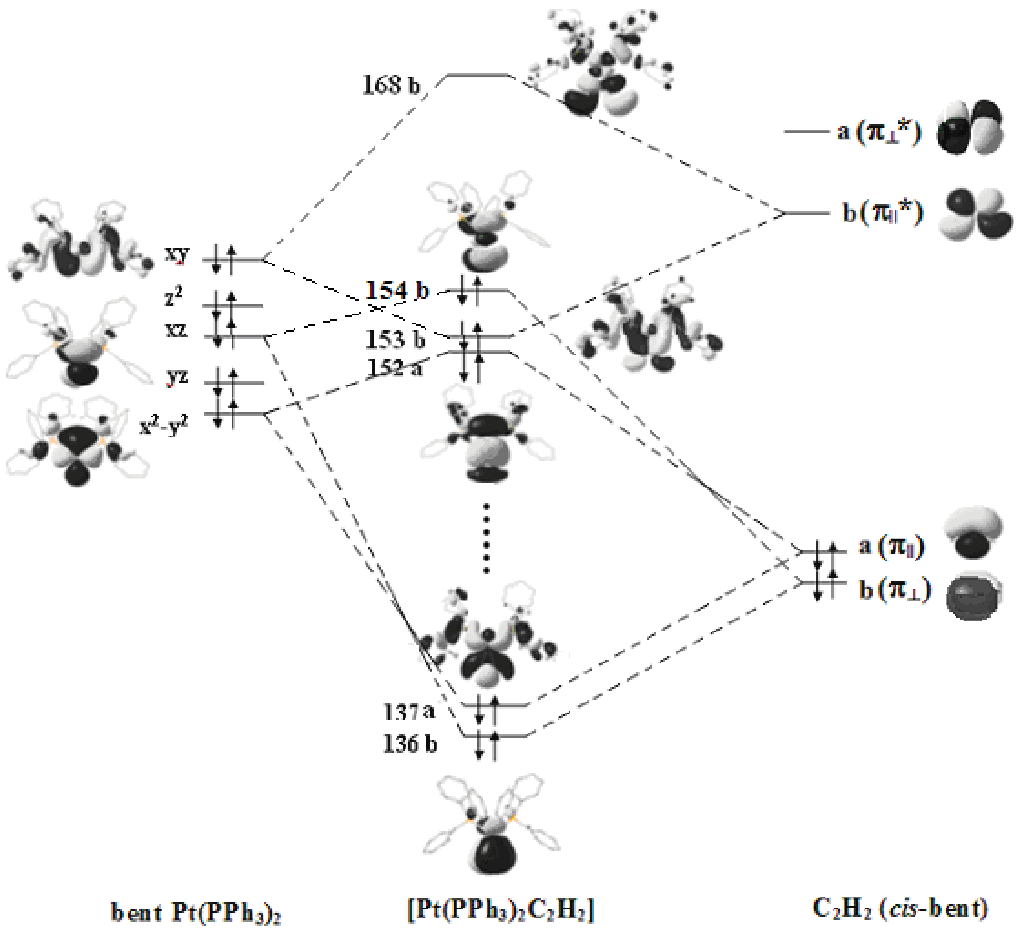

Fig. 3. MO energy-level scheme of the active valence zone of the Pt-C_2H_2 bonding.

Two other π-type MOs of the $[Pt(PPh_3)_2C_2H_2]$, the bonding MO 136**b** and the antibonding HOMO-154**b**, are formed also by the occupied MOs of the fragments: **b**($\pi_\perp$) of C_2H_2 and **xz** of $Pt(PPh_3)_2$, the latter is approximately a pure $5d_{xz}$-AO of Pt. As in the previous case, both these MOs, bonding 136**b** and antibonding 154**b**, are double occupied (Fig.3), and hence they do not contribute to the Pt-C_2H_2 bonding, due to their mutual compensation. The π -type donation is negligible, $\Delta q_\pi \cong 0$.

The main contribution to the Pt-C_2H_2 bond is provided by forming of the π-type bonding MO 153**b** from the corresponding MOs of the above fragments, namely, from the filled MO **xy** of the $[Pt(PPh_3)_2]$ and the empty antibonding $\pi_{||}$*-MO of C_2H_2. Due to forming of this (153**b**) MO the electron density from the $5d_{xy}$-AO of the Pt atom is transferred to the $\pi_{||}$*-MO of the acetylene molecule (the π-type back donation). The orbital charge transfer is quite significant, $\Delta q_{\pi^*} = 0.36$ ē. This value coincides with the decrease of the $5d_{xy}$-AO population due to formation of the complex (1.50 ē in the $[Pt(PPh_3)_2C_2H_2]$, compared with a value of 1.88 ē in the $Pt(PPh_3)_2$).

It is seen from Fig. 3 that only this one bonding MO of the complex, 153**b**, composed, as discussed above, from the filled $5d_{xy}$-AO of the Pt and the empty $\pi_{||}$*-MO of C_2H_2, is uncompensated by the antibonding orbital (the empty MO 168**b** in our calculations). Therefore the Pt(0)-acetylene bonding in the studied complex can be classified as mainly mono-orbital one [4]. Namely this MO 153**b** provides the essential charge transfer to the antibonding π*-MO of C_2H_2 causing the activation of the latter.

The net effect of the charge density redistribution due to the $[Pt(PPh_3)_2C_2H_2]$ formation is reflected in Table 4 where the values of the atomic charges and the bond indexes are presented. It is seen that the C_2H_2 molecule in the above complex carries the resulting negative charge ($Q(C_2H_2) = -0.24$ē), the fact suggesting that the π-accepting ability of C_2H_2 prevails over its σ-donor properties. The value of the C-C bond order decreases from 3.0 up to 2.3. Note also that the net atomic charge Q_{Pt} on the Pt atom is negative, while that on the P atoms is positive. This agrees with the data of the article [17], where the nature of the Pt-P bond in two model systems, $[(H_3P)_2Pt]$ и $[(F_3P)_2Pt]$, is discussed in detail.

Table 4

Atomic charges Q(ē) and bond orders (the Wiberg bond indexes) in the [Pt(PPh_3)$_2$], [Pt(PPh_3)$_2$$C_2H_2$] and free C_2H_2

Molecule	Q			Wiberg bond indexes			
	Pt	P	C_2H_2	Pt-P	Pt-C_{ac}	C-C	C-H
[Pt(PPh_3)$_2$]	-0.48	0.38	-	0.58	-	-	-
[Pt(PPh_3)$_2$HCCH]	-0.35	0.50	-0.24	0.42	0.45	2.31	0.89
HC≡CH, free	-	-	0.	-	-	2.99	0.93

Conclusion

On the base of our DFT calculations the following conclusions can be drawn. The acetylene molecule in the [Pt(PPh_3)$_2$$C_2H_2$] complex is in its activated state. It is reflected in the corresponding *cis*-distortion of the molecule, in the elongation of the C-C bond distance accompanied by the decrease in the C-C bond force constant and the stretching frequency $\nu_{C\equiv C}$. This activation is being realized mainly owing to the orbital back donation of 5*d*-electronic density from one of the occupied molecular orbitals of the precursor complex [Pt(PPh_3)$_2$] to the unoccupied antibonding π* MO of the C_2H_2 molecule.

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THE INTERNATIONAL CONFERENCE DEDICATED TO THE 50TH ANNIVERSARY FROM THE FOUNDATION OF THE INSTITUTE OF CHEMISTRY OF THE ACADEMY OF SCIENCES OF MOLDOVA

On behalf of the organizing committee We would like to welcome you, the participants of the International Conference dedicated to the 50thanniversary of the foundation of the Institute of Chemistry of the Academy of Sciences of Moldova. This conference is organized with the active assistance of the Supreme Council for Science and Technological Development of Academy of Sciences of Moldova, the Department of Natural and Life Sciences of the Academy of Sciences of Moldova and the Institute of Chemistry of the Academy of Sciences of Moldova. We wish you a pleasant and useful stay in the capital of our country, Chişinău.

Though not very numerous, the researchers of the Institute of Chemistry perform investigations in many branches of contemporary chemistry: inorganic and bioinorganic, analytical and ecological, organic and bioorganic, physical and quantum chemistry. Certain directions have been, and are being developed and certain well-known scientific schools have been founded. Fundamental research of great importance is carried out, as well as applied investigations, which are of importance for the economy of our country. There are many such issues, but two of them are, perhaps, the most important, and I would like to mention them here. Moldova has no mineral resources, it is an agricultural country. A lot of by-products and different waste are accumulated annually during crop harvesting and processing of agricultural raw materials. These so-called *second raw materials* should be chemically investigated, due to the fact that useful chemical products may be isolated which could be starting substances for the synthesis of compounds with potential utilization in food industry, in perfumery and cosmetics, in medicine, in tobacco industry and agriculture.

Another important issue to be solved is the problem of limited water resources, which persists in Moldova due to the fact that many aquatic resources are not suitable for drinking because of the high content of undesirable chemical compounds (fluorine containing compounds, iron salts, hydrogen sulfide, etc.). Methods should be developed for purification of such waters, as well as of waste waters.

We would like to evidence that a significant progress was achieved during the last two years in our science. The Institute obtained essential financial support for acquisition of expensive spectral equipment (NMR, IR, UV-Vis spectrometers), elemental analyzer, digital polarimeter etc., for materials and access to information. In 2006, the Institute began publishing the Chemistry Journal of Moldova.

We are very interested in multilateral collaborations with our foreign colleagues, we are eager to do joint research, and we hope for more opportunities for our young specialists for joint participation in different international programs and fellowships. Let's hope that this conference will also contribute to the establishment of new relationships and agreements of scientific collaborations.

We would like to wish good luck and successful results to all participants of the conference.

The Organizing Committee