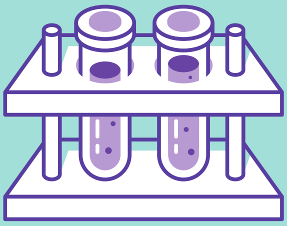
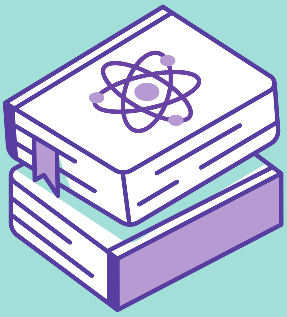


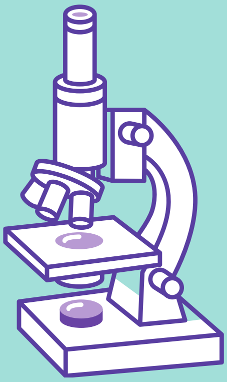
the 17th edition of the

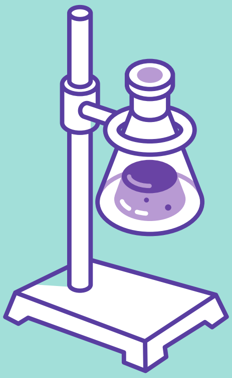
INTERNATIONAL CONFERENCE "STUDENTS FOR STUDENTS"

BOOK OF ABSTRACTS

2021







17th edition of the

INTERNATIONAL CONFERENCE
"STUDENTS FOR STUDENTS"

Book of Abstracts

21st – 24th April 2021

Partners:

Preface

On behalf of Chemistry Students' Organization, in partnership with Faculty of Chemistry and Chemical Engineering from Babeș Bolyai University Cluj-Napoca, it is our pleasure to welcome you to the XVIIth edition of the INTERNATIONAL CONFERENCE "STUDENTS FOR STUDENTS" which will take place between 21st and 24th of April 2021.

The International Conference *"Students for Students"* is a program developed by our organization that has the aim of gathering together students from all around the world offering them the chance of presenting their work, developing their communication skills and exchange ideas with other young researchers. We want to encourage and promote scientific research among young students and create a conducive environment where the world can benefit from their research. The program also offers a series of lectures and presentations held by important speakers from inside and outside the country, with the purpose of familiarizing the participants with the latest info on their fields of interest.

The conference is divided into 2 categories (Undergraduate and Master) and 3 sections for each category (Poster, Chemistry and Chemical Engineering). The participants can choose to present their work as a poster or as an oral presentation for any of the above-mentioned sections.

The work of the young researchers will be evaluated by a group of distinguished professors of our faculty. They will take into consideration the scientific relevance, originality and the knowledge level on the subject.

This year, there are 53 students, from all around the world, that registered in our conference, with 16 posters, and 37 oral presentations, in which 8 are for chemical engineering and 29 are for chemistry. We also have 4 distinguished speakers, invited to present their work in the fields of chemistry and chemical engineering, that we are very thankful for accepting our invitation. We also want to thank our professors and all the persons from Faculty of Chemistry and Chemical Engineering Cluj-Napoca, for helping the organizing committee bring this project together. We are extremely grateful for all the support and very excited to experience this year's edition together.

International Conference Students for Students Organizing Committee

The Organizing Committee

- **Diana-Maria MUNTEANU** - Coordinator and Vice-President of the Chemistry Students' Organization
- **Adrian MATEAȘ** - Coordinator and Manager of Financial department of the Chemistry Students' Organization
- **Alexandru-Răzvan VĂLEAN** - Co-Coordinator Secretary of the Chemistry Students' Organization
- **Mălina POCLID** - Co-Coordinator and Manager of Human Resources department of the Chemistry Students' Organization
- **Izabella MOLNAR** - Honorary member of the organizing committee and affiliated member of the Chemistry Students' Organization
- **Vlad-Mihai COTFAS** - Honorary member of the organizing committee and active member of the External Relations department of the Chemistry Students' Organization

- **Assoc. Prof. Dr. Gabriela-Nicoleta NEMEȘ** - Dean of Faculty of Chemistry and Chemical Engineering, Babeș-Bolyai University
- **Assoc. Prof. Dr. Eng. BARABÁS Réka** - Vice-Dean of Faculty of Chemistry and Chemical Engineering, Babeș-Bolyai University
- **Lecturer Dr. Eng. Julieta Daniela CHELARU** - Vice-Dean of Faculty of Chemistry and Chemical Engineering, Babeș-Bolyai University
- **Prof. Dr. Cristian-Sorin SILVESTRU** - Head of the Chemistry Department of Faculty of Chemistry and Chemical Engineering, Babeș-Bolyai University
- **Prof. Habil. Dr. Eng. Graziella Liana TURDEAN** - Head of the Chemical Engineering Department of Faculty of Chemistry and Chemical Engineering, Babeș-Bolyai University
- **Prof. Habil. Dr. Eng. Csaba PAIZS** – Head of the Chemistry and Chemical Engineering Hungarian Department, Babeș-Bolyai University
- **Dr. Dan PORUMB** member of the Faculty of Chemistry and Chemical Engineering, Babeș-Bolyai University

International Conference "Students for Students"
XVIIth edition
Program (GMT +3:00)

Wednesday, 21st of April 2021

10:00 - Official Opening

10:15 - Scientific Session: Chemistry + Chemical Engineering

10:15 - Synthesis and structural characterization of group 11 metal complexes of [2-(Me_2NCH_2)C_6H_4]2Se - **Maria DAVID**

10:30 - Discrete and polymeric complexes of CuII and ZnII with N-heterocyclic and carboxylato or acetylacetonato ligands - **Paul Adrian TĂRĂBUȚĂ**

10:45 - Assessment of water quality in a catchment draining a Fluorite rich region in Kenya - **Naomi MARITIM**

11:00 - Coffee Break

11:20 - **Scientific Session: Chemistry + Chemical Engineering**

11:20 - Testing different optimization algorithms for the calibration of a water quality model - **Mihaela BOROTA**

11:35 - Identification of novel potential acetylcholinesterase inhibitors through 3D-QSAR, docking and molecular dynamics simulations targeting Alzheimer's disease - **Khalil EL KHATABI**

11:50 - Organoselenium pincer ligands and their reactivity towards late transition metals - **Darius DUMITRAȘ**

12:05 - How does silver influence the physicochemical properties of silicate composites? - **Alexandra FERARU**

12:20 - Break

12:30 - **Scientific Session: Chemistry + Chemical Engineering**

12:30 - Hypercoordinated organoselenium ligands and their reactivity towards group 12 metals **- Cătălin Eduard ȘALGĂU**

12:45 - Analysis of biogas steam reforming process using mathematical modelling - **Alessandra-Diana SELEJAN**

13:00 - Bienzymatic biocatalyst for cascade transformation of limonene to limonene-1,2-diol **- Maria Cristina GHETU**

13:15 - Modeling and Optimizing the Photocatalytic Efficiency of Hydrothermally Obtained CaTiO3 via Polynomial Regression and Artificial Neural Network Models **- Bíborka BOGA**

13:30 - Lunch Break

14:30 - ***Plenary Session: Prof. Dr. Masaichi Saito - Department of Chemistry, Saitama University, Japan - "Expansion of Aromaticity from π-Aromaticity to (σ+π) Double Aromaticity"***

15:15 - Scientific Session: Chemistry + Chemical Engineering

15:15 - Novel p-terphenyl – based chiral macrocycles: synthesis, characterization and computational investigation **- Ioan STROIA**

15:30 - Luminescent lanthanides materials based on phenanthroline derivatives **- Sorin BĂNUȚOIU**

15:45 - Break

16:00 - Discussion Session with the Alumni of the Faculty of Chemistry and Chemical Engineering*

16:00 - Diana ADESPEI

16:40 - *The 10 year-journey through work/Călătoria de 10 ani prin muncă* - **Angela MOGOȘ-KIRNER,** Sales Support Engineer at ARQES SRL.

17:00 - *The teaching career - a dream came true!/Cariera didactică - un vis împlinit!* - **Prof. Dr. Marin Florin ILIEȘ,** Headmaster National College DECEBAL Deva

17:20 - Mara NAGHI

17:40 - *My way…to become an Engineer/Drumul meu …în a deveni Inginer* - **Daniela SABOU,** graduate of the Faculty of Chemistry and Chemical Engineering, Department: Informatics of Chemical Systems, class of 2004

18:00 - Program finale

Thursday, 22nd of April 2021

10:00 - ***Plenary Session: Prof. Dr. Jean-Louis Marty - IMAgES Institute of Modelling and Analysis in Geo-Environment and Health, Perpignan University, France - "Mycotoxins: Innovative approaches based on apta-sensors and apta-assays"***

10:40 - Coffee Break

11:00 - Scientific Session: Chemistry + Chemical Engineering

11:00 - Late d-metal complexes of macrocyclic ligands - **Ana HODOROGEA**

11:15 - Corrosion rate modelling for steel in acidic media using cetylpyridinium bromide as a green inhibitor - **Claudia Alice CRISAN**

11:30 - Comparative adsorption studies of benzalkonium chloride on sawdust and paper towel - **Ana-Maria DANCIU**

11:45 - Structural and Computational Characterisation for a New Hexanuclear Copper(II) Complex - **Andrei Iulian TOMA**

12:00 - Break

12:10 - Scientific Session: Chemistry + Chemical Engineering

12:10 - Synthesis and characterization of two new triorganotin(IV) halides-**Vlad PENCIU**

12:25 - Organoselenium ligands and their silver(I) complexes. Synthesis and structural characterization - **Ana-Maria LAZĂR & Maria DAVID**

12:40 - Study of Phase Separation Behavior in Flexible Polyurethane Foam-**Hicham EL HATKA**

12:55 - Spin States in Mn(III) Complexes with ligands exerting strong field regime - **Alina-Maria LUNGEANU**

13:10 - Lunch Break

14:10 - **Scientific Session: Chemistry + Chemical Engineering**

14:10 - Determination of noradrenaline using a modified electrode based on conductive polymer - **Alexandra BELCOVICI**

14:25 - 3D-QSAR, ADMET, and Docking studies for designing new indole derivatives as anticancer agents - **Reda EL-MERNISSI**

14:40 - Application of protein engineering to increase the catalytic efficiency of phenylalanine ammonia lyases - **Lilla CSEREPES**

14:55 - Synthesis and structural characterization of new heteroleptic diorganochalcogen(II) compounds - **Cosmina Maria Florina BOHAN**

15:10 - Versatility of thiourea dioxide as redox agent: case study with myoglobin - **Oleg RUDENCO**

15:25 - Break

16:00 - Discussion Session with the Employers - *opportunities, trends, directions and departments**

16:00 - *AzoMureș* - **Adrian BODAN**

16:20 - *Heidelberg* - **Adriana OPREA**

16:40 - *Saint-Gobain* - **Cristian BOTAR**

17:00 - *Knauf* - **Agnes VINCZE**

17:20 - Program finale

Friday, 23rd of April 2021

10:00 - ***Plenary Session: Prof. Dr. Antonio Laguna Castrillo - Department of Inorganic Chemistry, University of Zaragoza, Spain - "Gold: A Unique Element and a Unique Chemical Behavior"***

10:40 - Coffee Break

11:00 - Scientific Session: Chemistry + Chemical Engineering

11:00 - Investigation of coke gas absorption with CFD simulation - **László HARKÁNY**

11:15 - New folic acid esters with analogues of methylene blue–contrast agents for bioimaging of cancer cells - **Bianca-Alexandra STOEAN**

11:30 - Dual-mode determination of selenium in biofortified Allium microsamples following piazselenol formation and solid phase microextraction **- Bogdan BOȘCA**

11:45 - Interaction of hemoglobin with anti-cancer drugs: Dacarbazine and Vincristine **- Victoria CÎRJEU**

12:00 - Break

12:10 - Scientific Session: Chemistry + Chemical Engineering

12:10 - Interactions between globins and anti-cancer drugs. Cyclophosphamide and doxorubicin - **Maria-Catalina BARCARU**

12:25 - Risk analysis in biogas production: a case study of Biogas Station in Seini, Romania - **Ulmiana TENCALEC**

12:40 -- Mapping the Structural Features of Porphyrin with New Computational Experiments - **Sabrina-Maria PETRISOR**

12:55 - Synthesis and structural characterization of a new NDI-based macrocycle - **Valentina-Sorina ILIE**

13:10 - Lunch Break

14:30 - Scientific Session: Chemistry + Chemical Engineering

14:30 - Synthesis, optimization, characterization and photocatalytic activity of TiO2/Fe3O4 composite **- Simona HALMAGYI**

14:45 - Oxovanadium(V) Complexes with Schiff Base Ligands – Synthesis, Characterization and Biological Activity - **Oana Adriana PETCUTA**

15:00 - An interesting asymmetric hexadentate oxygen-containing rigid macrocyclic ligand and it's Mn(II)-complex: Preparation and Coordination Chemical Characterization **- Gergő LAKATOS**

15:15 - Cobalt(II) extended structures with divergent bipyridine-based ligands **- Cezara-Marina BOLOCAN**

15:30 - Break

16:00 - Workshop HR - *What changes and challenges does the online environment create? + Q&A session**- Alin FĂRCAȘ + Ciprian DEAK

18:00 - Program finale

Saturday, 24th of April 2021

10:00 - Plenary Session: Prof. Dr. Elaine Armelin Diggroc - Department of Chemical Engineering, Polytechnic University of Catalunya Barcelona, Spain - "Protection and maintenance of industrial equipment and facilities"

10:40 - Coffee Break

10:50 - Scientific Session: Posters

10:50 - ZrO_2-based nano-biocomposites: solid-state synthesis and morpho-structural characterization **- Claudia Andreea COJAN**

11:00 - Preparation of aza-BODIPY dyes **- Etelka KISS**

11:10 - New complexes based on a bis-thioether ligand - **Cristiana-Elena IANCU**

11:20 - Spectroscopic investigations of α-lipoic acid - **Elena-Andreea RUSU**

11:30 - Tuning of the optoelectronic properties of conjugated polymers by the addition of reduced graphene oxide or silver nanoparticles - **Iulia BABUTAN**

11:40 - Break

12:00 - **Scientific Session: Posters**

12:00 - Preparation of ZnO thin films by dip-coating from sol-gel and studying the effect of immersion speed on the formation of the thin films - **Palko GYULA**

12:10 - Voltammetric analysis of hesperidin using a disposable pencil graphite electrode - **Numan NIMET**

12:20 - Influence of Counter-Anions on the Molecular Structures of a Series of Copper(II) Complexes - **Petre-Cristian MITROI**

12:30 - Comparative efficiency of Orange G degradation by chemical and photochemical oxidation: a kinetic study - **Dragos-Sebastian BALTAG**

12:40 - Lunch Break

13:30 - **Scientific Session: Posters**

13:30 - The influence of sweeteners on the characteristics of lingonberry jams - **Sânziana-Maria VARODI**

13:40 - Green approaches for fragrances synthesis. Biotechnological production of anisyl-propionate - **Diana-Maria SCROB**

13:50 - Preliminary phytochemical investigation of Vaccinium spp. leaves - **Georgiana-Alexandra VINTILĂ**

14:00 - Luminescent Lanthanide Complexes Based on POMs Ligands - **Diana Claudia LICHI**

14:10 - Copper(II) coordination polymers self-assembled from diamines and lactic acid - **David Gabriel JIRCA**

14:20 - Break

14:30 - Discussion Session with the Alumni of the Faculty of Chemistry and Chemical Engineering*

14:30 - *Medical Writing as a Career for Chemists: Are You a Good Fit?/Scrierea medicală ca carieră pentru chimiști: sunteți o persoană potrivită?* - **Petronela M. PETRAR,** Medical Writer/Team leader, Publication writing, Life Sciences

14:**50** - *From Oxide Materials Science and Engineering to Superconducting Materials/De la Stiinta si Ingineria Materialelor Oxidice la Materialele Supraconductoare* - **Dr. Cornelia POP**, Materials Science Institute of Barcelona, Superconducting Materials and Large Scale Nanostructures Department

15:**10** - *Connecting germs with pixels for an innovative approach in diplomacy/Corelarea virusurilor cu virușii pentru o abordare inovativă în diplomație* - **Gabriela HOROSANU**, career diplomat, Ministry of Foreign Affairs of Romania; diplomat in the Political Section of the Permanent Delegation of Romania to NATO, Brussels; medical researcher at the National Institute for infectious Diseases ”Prof. Dr. Matei Balș”, Bucharest.

15:**30** - *Milestones in my career/Repere în cariera mea* - **Daniela POP**

15:50 - **Closing Ceremony**

Tabel of Contents

INVITED COMMUNICATIONS

INVITED COMMUNICATIONS

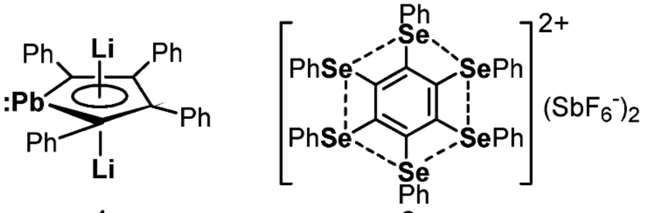
Expansion of Aromaticity from π-Aromaticity to (σ+π)-Double Aromaticity

Masaichi Saito*

Department of Chemistry, Graduate School of Science and Engineering, Saitama University, Shimo-okubo, Sakura-ku, Saitama-city, Saitama, 338-8570, Japan
email: masaichi@chem.saitama-u.ac.jp

……

Since the discovery of benzene and its unique structure was proposed by Kelulé in the 19th century, the concept of aromaticity has played an important role in many fields of chemistry. According to the Hückel rule, the aromaticity arises from electronic delocalization of (4n+2)π electrons in a ring system. We firstly became interested in the replacement of a skeletal carbon atom of an aromatic compound by a heavy group 14 atom and have succeeded in the synthesis of aromatic dilithioplumbole **1** (Fig. 1).[1] It is concluded that 2p and 6p orbitals can overlap sufficiently to create an aromatic molecule.[2] On the other hand, aromaticity arising from delocalized electrons in an orbital with different symmetry has recently attracted much attention and σ-aromatic compounds stable in the condensed phase have already been reported.[3] We next became interested in σ- and π-double aromaticity, which was precited by quantum-chemical calculations in 1979,[4] and have succeeded in the synthesis of hexaselenylbenzene dication **2** (Fig. 1), a bench-stable σ- and π-double compound.[5]



1 **2**

Fig. 1: Dilithioplumbole **1** and hexaselenylbenzene dication **2**.

[1] M. Saito, M. Sakaguchi, T. Tajima, K. Ishimura, S. Nagase, M. Hada, *Science* **2010**, *328*, 339.
[2] (a) M. Saito, *Coord. Chem. Rev*. **2012**, *256*, 627; (b) M. Saito, *Acc. Chem. Res.* **2018**, *51*, 160; (c) M. Saito, *Bull. Chem. Soc. Jpn.* **2018**, *91*, 1009.
[3] For an example of reviews, see: I. A. Popov, A. A. Starikova, D. V. Steglenko, A. I. Boldyrev, *Chem. Eur. J.* **2018**, *24*, 292.
[4] J. Chandrasekhar, E. D. Jemmis, P. v. R. Schleyer, *Tetrahedron Lett.* **1979**, *20*, 3707.
[5] S. Furukawa, M. Fujita, Y. Kanatomi, M. Minoura, M. Hatanaka, K. Morokuma, K. Ishimura, M. Saito, *Commun. Chem.* **2018**, *1*, 60.

Mycotoxins: Innovative approaches based on apta-sensors and apta-assays

Jean Louis MARTY*

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Université de Perpignan Via Domitia, Perpignan Cedex France
Phone : +33 616814591 E-mail : sensbiotech@gmail.com and jlmarty@univ-perp.fr

Mycotoxins are naturally occurring toxic, small chemical compounds (MW ~700) that are produced as secondary metabolites by certain fungi contaminating food and feed, during crop growth or processing products. These compounds "once consumed by animals and/or humans" may lead to mycotoxicosis with symptoms of intoxication, causing substantial effects on animal and human health. According to the United Nations of Food and Agriculture Organization report, 25% of the word's food is significantly contaminated with mycotoxins. The economic impact of mycotoxins includes perturbation of human and animal health, increased health care and veterinary costs, reduced livestock production, disposal of contaminated foods and feeds, and investment in research and applications to reduce severity.

The European Commission has set maximum levels for the mycotoxins to protect human and animal health.

The current tendency has driven the development of biosensors or bioassays as new analytical tools able to provide fast, reliable, and sensitive measurements with low cost; many of them aimed for on-site analysis. Biosensors may not completely replace the official analytical methods, but can be used both by regulatory authorities and by industry to add up the information for routine testing and screening of samples. Biosensors are defined as analytical devices incorporating a biological material, or bio mimic, intimately associated with or integrated within a physicochemical transducer or transducing microsystem. The main advantages of biosensors are short times of analysis, low cost of assays, portable equipment, real-time measurements, and suitability as remote devices. These new technologies have been applied in quantitative analysis of various target analytes.

Recently, a new class of namely aptamers have been emerged as promising alternative to replace the antibody in the design of biosensors. An aptamer is a sequence of single or double stranded DNA or RNA, selected from a random library according to its ability to bind a target molecule.

The presentation mainly focuses on the methods development in the sense that how mycotoxins can be detected through apta-sensors and apta-assays.

Gold: A Unique Element and a Unique Chemical Behavior

Antonio LAGUNA

Departamento de Química Inorgánica, Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), CSIC-Universidad de Zaragoza, 50009 Zaragoza, Spain

Gold has a unique position as 'the king of the elements', not only for its reddish yellow color, but mainly for its noble character; gold coins and jewelry do not tarnish, even after long exposure to extremely aggressive conditions, and the metal is resistant to enzymatic attack in biological systems. It has been a very special element, known and appreciated by everybody from the earliest civilizations.

However, gold chemistry has played a minor role in history. Initially all its known chemistry was merely regarded as an art to recover and convert gold metal into all possible forms for ornamental, monetary, anticorrosive or electrical usage. In the spectacular development of the gold chemistry, namely during the last fifty years, new observations have become available, which confirm the unique character of this element. Not only new compounds were prepared, but also novel structural phenomena came to light, mainly regarding unexpected and unprecedented gold-gold or gold with other metals bonds [1,2]. The explanation of this behavior is reached with the help of theoretical chemistry. Relativistic effects are especially important in elements with a high nuclear charge, and particularly in the case of gold.

Some frequent strategies in the synthesis of gold(I) compounds consist of: a) reactions between complexes in which gold is an acid center with basic ligands, b) reactions between complexes in which gold is a basic center with derivatives of acid character, or c) through the use of polydentate ligands that can hold together two or more metal centers. Thus, for example, derivatives with Au-Ag (**1**), Au-Te (**2**), or Au-Bi (**3**) bonds have been prepared (Figure 1).

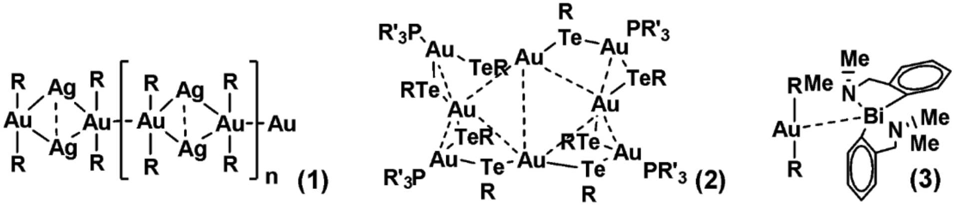

Fig. 1: Heteropolynuclear complexes with Au-Ag (**1**), Au-Te (**2**) and Au-Bi (**3**) interactions.

Gold compounds also have interesting applications arising as a consequence of their optical or biological properties. Potentially attractive in this sense are the polynuclear derivatives that, in many cases, present intense and long-lived luminescence, in solid state or in solution, with energies that appear in the visible spectrum. On the other hand, a significant number of compounds and nanoparticles are active against inflammatory diseases and also they have been thoroughly investigated in medicine, especially as antitumor agents showing several of them promising activity. Finally, some gold catalysts are excellent soft π-acids capable of activating carbon−carbon multiple bonds toward intra- or internucleophilic attack.

[1] A. Laguna (Ed.). *Modern Supramolecular Gold Chemistry. Gold-Metal Interactions and Applications*. Wiley-VCH. Weinheim (Germany). 2008.
[2] C. Silvestru and A. Laguna. *The Chemistry of gold-metal Bonds*. *The Chemistry of Organogold Compounds* (Ed. Z. Rappoport, J.F. Liebman and I. Marek). John Wiley & Sons, Ltd. Chichester (UK). **10**, 409-526 (2014).

Protection and maintenance of industrial equipment and facilities

Elaine ARMELIN[1,2]

[1] Departament d'Enginyeria Química, EEBE, Universitat Politècnica de Catalunya, C/ Eduard Maristany, 10-14, Ed. I, 2nd floor, 08019, Barcelona, Spain.

[2] Barcelona Research Center for Multiscale Science and Engineering, Universitat Politècnica de Catalunya, C/ Eduard Maristany, 10-14, Ed. I.S, 08019, Barcelona, Spain.

Corrosion is the destructive attack of a metal by chemical or electrochemical reaction with its environment. Corrosion is often thought of only in terms of equipment deterioration and its failure by cracking or loss of strength or ductility. However, the metal oxidation is also used as beneficial to protect metallic systems, as is the case of the cathodic protection. Corrosion engineers employ their knowledge to the prevention of corrosion damage by practical and economical means. By applying a correct protection and maintenance of industrial equipments it is possible to: (i) reduce the economic costs (direct or indirect) of material losses; (ii) improve safety of operating equipment and employers; and (iii) improve conservation of metal resources, which world's supply is limited, and monument conservation. This talk will teach examples of good practices for industrial equipment and facilities maintenance to enhance life services, from a point of view of corrosion scientists and engineers.

Keywords: Corrosion phenomenon, galvanic protection, equipment design, conservation.

ORAL PRESENTATIONS

Chemistry & Chemical Engineering

Synthesis and structural characterization of group 11 metal complexes of $[2\text{-}(Me_2NCH_2)C_6H_4]_2Se$

Maria DAVID[1]
Anca SILVESTRU[§]

[1§]Babeș-Bolyai University, Faculty of Chemistry and Chemical Engineering, Department of Chemistry, Supramolecular Organic and Organometallic Chemistry Centre, 11 Arany Janos, Cluj-Napoca, Romania
e-mail: maria.david1@stud.ubbcluj.ro

Organoselenium compounds attracted a continuous interest over the last decades due to their biological and technical importance. It was observed that organic groups with side arms bearing nitrogen as donor atom are capable of intramolecular N→Se interactions which improve the catalytic and biological activity.[1] Such type of compounds find applications in organic synthesis, biology, or as precursors for electronic materials.[2]

We report here on the synthesis and structural characterization of silver(I) and copper(II) complexes of the neutral organoselenium ligand $[2\text{-}(Me_2NCH_2)C_6H_4]_2Se$.

The ligand was obtained by ortho-lithiation of $2\text{-}(Me_2NCH_2)C_6H_5$, followed by the reaction with bis(diethylditiocarbamate), $Se(dtc)_2$ in a 2:1 molar ratio.[3] The metal complexes were prepared by reacting the diorganoselenide with AgOTf (OTf = triflate), $AgNO_3$, $CuCl_2{\cdot}2H_2O$ and $Cu(NO_3)_2{\cdot}3H_2O$ as shown in Figure 1.

The new silver complexes were characterized by multinuclear NMR spectroscopy (^1H, ^{13}C, ^{19}F, ^{77}Se, as appropriate), mass spectrometry and single-crystal X-ray diffraction. The new copper(II) complexes were characterized by UV-Vis spectroscopy and mass spectrometry.

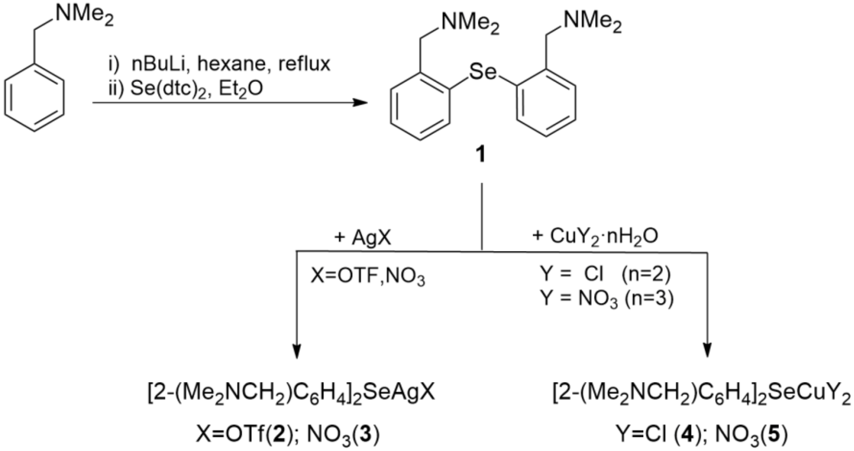

Figure 1: Synthesis of compounds **1-5**.

[1] A. J. Mukherjee, S. S. Zade, H. B. Singh, R. B. Sunoj, *Chem. Rev*., **2010**, *110*, 4357;
[2] G. Mugesh, H.B. Singh, *Acc. Chem. Res.,* **2002**, *35*, 226;
[3] A. Panda, G. Mugesh, H. B. Singh, R.J. Butcher, *Organometallics,* **1999**, *18,* 1986.

Discrete and polymeric complexes of Cu^{II} and Zn^{II} with N-heterocyclic and carboxylato or acetylacetonato ligands

Paul Adrian TĂRĂBUȚĂ[1]
Cătălin MAXIM[2], Augustin MĂDĂLAN[§], Marius ANDRUH[§]

[1, 2, §]*Inorganic Chemistry Department, Faculty of Chemistry, University of Bucharest, 23 Dumbrava Roșie, 020464, Romania*

Carboxylato complexes have a wide range of potential applications in materials science [1, 2], catalysis [3] and pharmacy [4].

Five novel carboxylato Cu^{II} complexes, **1-5**, were obtained from the reactions of three aromatic carboxylic acids with mononuclear precursors $[Cu(acac)(BB)(H_2O)]ClO_4$, where BB = 2,2'-bipyridine, 1,10-phenantroline.

2-hydroxy-5-methylbenzene-1,3-dicarboxylic acid was synthesized by oxidation of the corresponding bis(hydroxymethyl)phenol; then, it was used as a proligand in the synthesis of mononuclear complex **1**. Moreover, the blue luminescence of this hydroxydicarboxylic acid is under investigation.

1D coordination polymers **2** and **3** are built with benzene-1,3-dicarboxylato spacers and have a zig-zag topology.

Dinuclear complexes **4** and **5** were synthesized from pyridine-3-carboxylic acid. Both crystal structures reveal asymmetric coordination of the two Cu^{II} centres (Fig. 1).

Attempts to synthesize mononuclear Zn^{II} precursors for carboxylato complexes were made. Two crystalline complexes, **I** and **II**, were produced. In contrast with the aforementioned Cu^{II} precursors, these Zn^{II} complexes have the general formula $[Zn(acac)(BB)_2]ClO_4$. Two polymorphs of **II** were discovered by varying the reaction solvent: **α** and **β**. Chirality of these complexes is also discussed.

All synthesized complexes were characterized by single-crystal X-ray diffraction. Spectroscopic techniques (FTIR and UV-Vis) and powder X-ray diffraction were also employed for characterization.

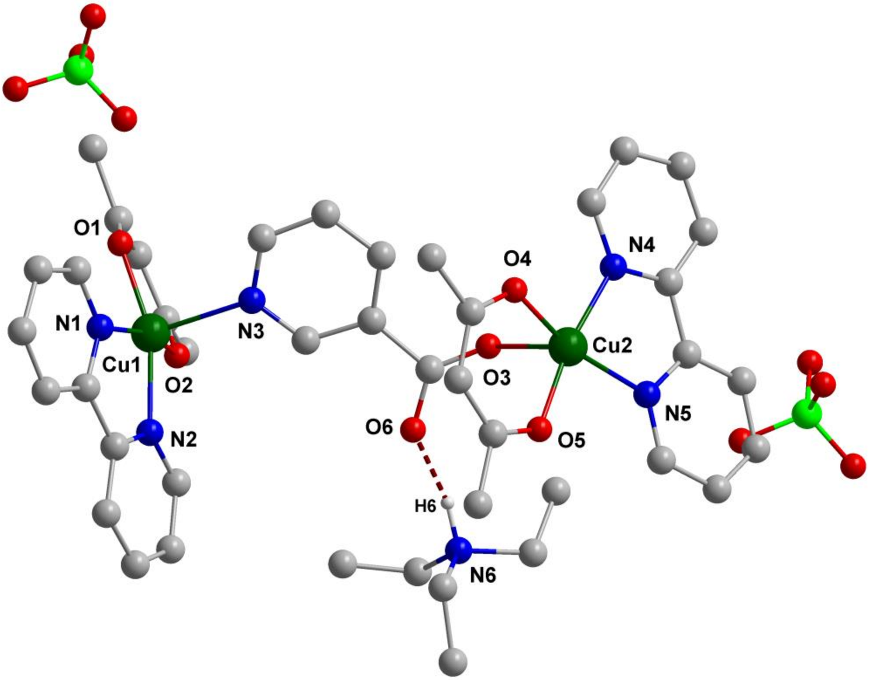

Fig. 1: Crystal structure of complex **4** showing the H bond between the uncoordinated O atom of the carboxylato group and a triethylammonium cation.

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Assessment of water quality in a catchment draining a Fluorite rich region in Kenya

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Access to water in adequate quantity and of good quality is increasingly becoming elusive especially in underprivileged rural communities. The situation is exacerbated by point and/or non-point pollution sources especially from industrial affluents [1,2,3]. Fluoride ions have been reported to contaminate surface water sources causing dental and skeletal fluorosis particularly in areas with rocks that have been subjected to hydrothermal activity such as the Rift Valley. Kenya Fluospar Company (KFC) has for over 35 years produced the acid grade fluorspar from a mining plant at Kimwarer, Kerio Valley in Kenya [4,]. Although groundwater is an important source of water for household use in this area, previous studies singled out the effects of mining activities on the parameters of surface water [2]. Moreover, all earlier studies examined the parameters of the water when the mining activities were at full scale [5]. This study investigated the influence of mining activities on selected water quality parameters of surface water and groundwater sources at a time when mining activities were largely downscaled until complete closure. Water samples were collected from eight sites during high, intermediate, and low flow periods. Fluoride ions and turbidity. The results were compared with previous findings obtained when the company was fully operational. The interaction between surface water and groundwater was explored by comparing the trends in ion concentrations of the parameters. At full operation, the ion concentrations of most of the parameters were way beyond the WHO recommendations for drinking water [6]. Fluoride levels in the downstream water samples were about five times higher while that in the effluent streams was about 20 times higher than the recommended level. Waters from nearby groundwater sources were found to have higher average Fluoride ion concentrations (> 1.15 mgL^{-1}) as compared to the surface water sources when the company's activities were minimal. Lower ion levels were observed during the high flows and the phenomenon was attributed to dilution. However, higher turbidity values were recorded due to increased sediments in runoff. The variation in levels of the parameters could directly be linked to effects of mining activities.

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Testing different optimization algorithms for the calibration of a pollutant transport model

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The present research is focused on the major problem of pollutants transport along the rivers [1, 2]. The water quality management for these problems is done with the help of models that predict the pollutants distribution in the water. A reliable and widely used approach are the models based on the analytical solutions of the fundamental advection–dispersion equation (ADE) which describes the advective–diffusive mass transport in surface waters [1, 2].

In this context the present paper presents (1) a pollutant transport model along a small river and (2) the testing of 5 different optimization algorithms for the estimation of the key parameters of the model (velocity, u and dispersion coefficient, D). The research steps are schematically presented in Fig. 1 and rely on field data from 4 tracer experiments organized along the River Murray Burn (UK) at different water flow rates.

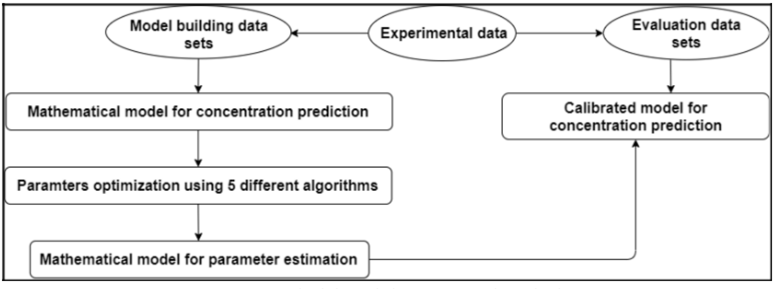

Fig. 1: Model building methodology

For each of the 4 experiments (details in [2]) a different mass of tracer has been released in the river and its concentration has been measured at a monitoring point located 120m downstream the discharge point.

The results in Fig. 2 illustrate how the initial estimation of concentration is not accurate enough (Fig 2a) and there is a need to find better estimations for u and D. Models for their estimations must rely on optimum values for each experiment and be able to estimate u and D at any water flow rate. Optimums are usually generated using an optimization algorithm. The comparative analysis of 5 algorithms (Fig 2b) has revealed that for this case the most suitable ones are based on the functions *fmincon* and *ga.* Good results are provided by *fminsearch* as well, with the remark that for other situations it may return negative values of the concentration. The models for u and D allow the calibration of the concentration model (Fig 2d). Simulated concentrations fit properly to the experimental data (Fig 2c).

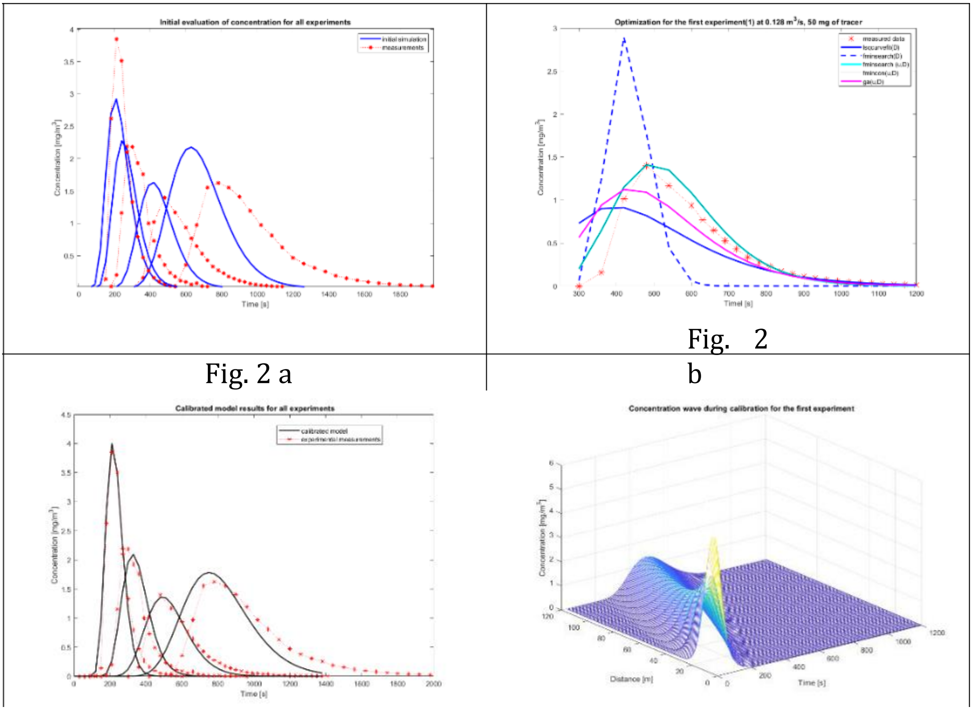

Fig. 2 a

Fig. 2 b

Fig. 2 c

Fig. 2 d

Fig. 2: Results of the model and optimization algorithms

During the configuration of optimization algorithms their particular features should be properly tuned in order to obtain good results (e.g. good values of u, D and concentration, proper fitting of peaks, leading edges and trailing edges).

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Identification of novel potential acetylcholinesterase inhibitors through 3D-QSAR, docking and molecular dynamics simulations targeting Alzheimer's disease

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Alzheimer's disease (AD) is the most common progressive neurodegenerative disorder that always related to a decline of memory and cognitive functions [1]. As yet, neither preventative cure nor a satisfying therapy is available at the present. There are several drug targets which are reported to control the severe level of Alzheimer's disease, among which acetylcholinesterase enzyme is approached as a good drug targets for this disease [2]. Hence, the present study mainly focused to discover newly N-Benzylpyrrolidine based derivatives as potential acetylcholinesterase inhibitors drug through several computational approaches. A dataset of N-Benzylpyrrolidine based derivatives previously synthetized and evaluated for acetylcholinesterase inhibitory activity was studied by using three-dimensional quantitative structure-activity relationship (3D-QSAR) study, revealing the key structural factors of acetylcholinesterase inhibitors [3].

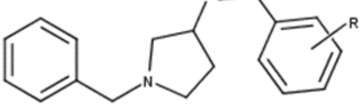

Fig. 1: The structural template of the N-benzylpyrrolidine derivatives.

Furthermore, molecular docking and molecular dynamics simulation were explored to reveal the binding mode between the selected molecules and the acetylcholinesterase receptor. The generation of 3D-QSAR pharmacophore models were followed by its validation exhibited predictive power for the experimental inhibitory concentration (IC) values. The molecular features characteristics provided by the 3D-QSAR contour plots were quite useful for designing six new compounds with high predicted potency. The designed molecules were further subjected to molecular docking and molecular dynamic simulation studies and compared to the most active compound. The identified structure features for acetylcholinesterase inhibition through docking study showed a satisfactory correlation with the 3D-QSAR study.

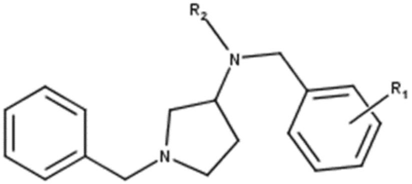

Fig. 1: The structural template of the newly designed molecules.

The comparison illustrated that designed molecule combined with acetylcholinesterase were more stable than the most active compound with the same targeted receptor. The results would provide valuable guidance for designing new reversible acetylcholinesterase inhibitors in the future.

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Organoselenium pincer ligands and their reactivity towards late transition metals

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The chemistry of organochalcogen (S, Se, Te) compounds represents a constantly evolving field due to their specific properties and the associated potential in organic synthesis, catalysis, medicine, biology and materials science.[1] Moreover, species containing, besides the *soft* chalcogen, *hard* donor atoms (nitrogen or oxygen) also, are of special interest as multidentate ligands towards transition metals. Our previous studies were dedicated to the *N,Se,N* pincer ligands of type $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]SeCl$ or $[2,6\text{-}\{E(CH_2CH_2)_2NCH_2\}_2C_6H_3]_2Se_2$ (E = MeN, O) and their coordination behavior towards group 11 metals.[2]

During last years we extended our research to a new class of ligands containing both *soft* Se and *hard* N in their skeleton (Figure 1). Such ligands can behave either as pincer *Se,N,Se*, chelating *Se,N* or bridging moieties.

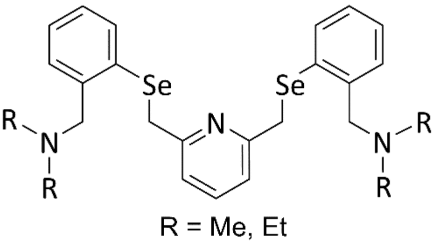

Figure 1

We report here on the synthesis and structural characterization of new *Se,N,Se* pincer ligands based on pyridine functionalized with $2\text{-}(R_2NCH_2)C_6H_4SeCH_2$ (R = Me, Et) and $2\text{-}(C_6H_5CH_2NHCH_2)C_6H_4SeCH_2$ groups.

Their coordination behaviour towards late *d* metals (Au, Ag) was studied, both in solution and in solid-state.

The *Se,N,Se* pincer ligands and the metal complexes were investigated by multinuclear NMR spectroscopy (^{1}H, ^{13}C, ^{77}Se and ^{19}F, as appropriate) and mass spectrometry. Their molecular structures were determined by single-crystal X-ray diffraction.

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How does silver influence the physicochemical properties of silicate composites?

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Bioactive glasses, metallic nanoparticles, and nanocomposite materials constitute an important group of materials with applications in the medical field. The specific objective of research and innovation in the field of advanced materials is the development of biocompatible and stable materials, with new functionalities and improved performance, to minimize the impact on the human body. A promising strategy to prevent microbial adhesion and biofilm colonization is introducing antimicrobial components in composite structures [1], [2].

In this study we will discuss the development of silicate-based composite structures with different additives, $60SiO_2{\cdot}(32\text{-}x)CaO{\cdot}8P_2O_5 {\cdot}x\mathbf{AgI}$ with x=0; 0,1; 0,2; 0,5; 1 mol%, and $60SiO_2{\cdot}(32\text{-}y)CaO{\cdot}8P_2O_5{\cdot}y\mathbf{Ag_2O}$ with y=0;0,15; 0,3; 0,6 mol%, in order to evaluate the effect of Ag transformation, either in the form of metal particles or oxidized as Ag^+, on bioactivity and antibacterial activity. Two different systems based on Ag content were synthesized successfully via the sol-gel method [3] and were characterized by XRD, FT-IR, SEM, UV-Vis, and XPS. *In vitro* evaluation was performed by immersing the samples in simulated biological fluid (SBF, pH 7.4).

The results showed that bioactive glass enhanced with Ag_2O has a more pronounced effect on the induction of the antibacterial activity, a disadvantage being the formation of AgCl after immersion in SBF, which could compromise the biocompatibility of the samples. On the other hand, the AgI system does not develop AgCl compounds but has low antibacterial activity.

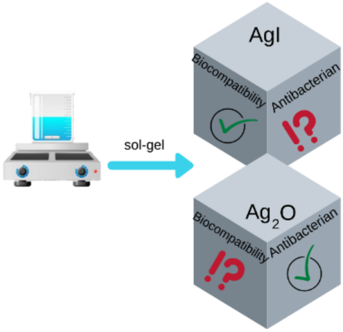

Fig 1. Comparative study between the effect of AgI and Ag_2O on *in vitro* biocompatibility and antibacterial activity.

Acknowledgment: This work was supported by a grant of Ministry of Research and Innovation, CNCS - UEFISCDI, project number PN-III-P1-1.1-TE-2019-1138, within PNCDI III. A. Feraru acknowledges the funding provided by scholarship “Bursă Specială pentru Activitate Științifică” provided by the Babeș-Bolyai University.

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Hypercoordinatedorganoselenium ligands and their reactivity towards group 12 metals

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Organochalcogen ligands have already demonstrated their importance for preparing single-source precursors for group 12 metal chalcogenidesand they still continue to raise anincreased interest forapplications in semiconducting materials for opto-electronic devices.[1]

In particular, ligands with pendant arms bearing nitrogen donor atoms are investigated for their possibility to stabilize metal complexes in monomeric form, by increasing the coordination number at the metal centrethrough additional intramolecular N→M coordination.[2]

During last years our research was focused on the synthesis and structural characterization of mercury complexes of typeRSeHgL (L = Cl, SCN) that containthe organic group R = 2-(Me_2NCH_2)C_6H_4. The single-crystal X-ray diffraction studies revealed the intramolecular N→Hg coordination in the complex [2-(Me_2NCH_2)C_6H_4Se]HgCl.[3]

As a continuation of our studies, here we report about new species of typeRSeMClwith organic groups bearing one or two pendant arms capable for intramolecular coordination [R = 2-(Me_2NCH_2)C_6H_4, M = Cd(**1**),and R = 2,6-(Me_2NCH_2)$_2C_6H_3$, M = Cd(**2**), Hg (**3**)], as well as about their solution behavior andchemical reactivity.For compound **3** an ionic structure was determined by single-crystal X-ray diffraction (Fig. 1) and it was observed that both pendant arms remained coordinated to selenium, thus resulting in a *10-Se-6*hypercoordinated cation, by contrast with the previously reported [2-(Me_2NCH_2)C_6H_4Se]HgCl, where the nitrogen atom in the pendant arm is coordinated to mercury in a selenium-bridged polymeric chain.[3]

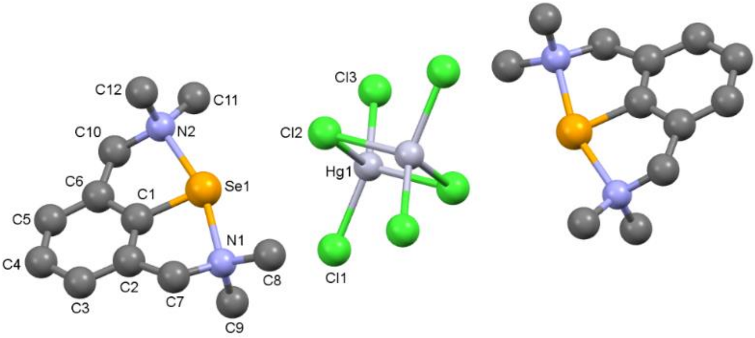

Fig. 1. $[2,6\text{-}(Me_2NCH_2)_2C_6H_3Se]^+$ cations and $[Hg_2Cl_6]^{2-}$ anion in the crystal of **3**

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Analysis of biogassteam reforming process using mathematical modelling

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Hydrogen is considered to be the power cell of the future due to its ability to produce energy with virtually no ecological impact. The production processes of this gas have been intensively studied. The two most common methods for producing hydrogen are steam-methane reforming and electrolysis (splitting water with electricity). Biogas is a renewable energy source of hydrogen for several fuel cell power plants.

This study is dedicated to developing a dynamic 1D heterogenous mathematical model for hydrogen production using biogas steam reforming processes. It employs nickel-alumina catalysts with a supposed spherical geometry, placed into the tubes of a multi-tubular reactor. The tubes are settled within a side-fired furnace. Biogas is equally fed at the tubes' base, while the reaction products are collected at their top, as presented in figure 1.

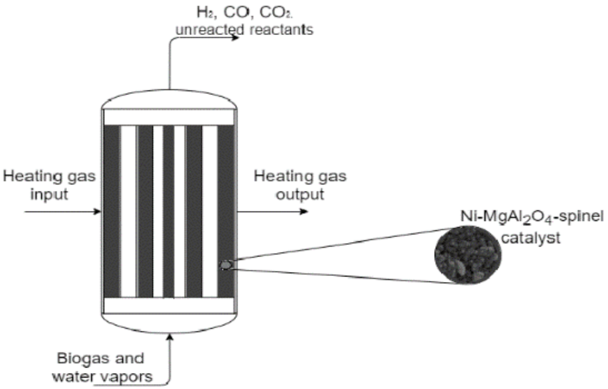

Fig. 1: Multi-tubular reactor with catalyst

Out of three possible reactions, two were chosen based on the orthogonalization rule [1]. The successive reactions are: the steam methane reforming reaction (CH_4 reacts with water vapors obtaining CO and H_2) and water gas shift reaction (CO reacts with water vapors, obtaining CO_2 and H_2).In this work the kinetic developed by Xu and Froment, based on Langmuir-Hinshelwood's approach was used [2].

The developed mathematical model includes partial differential equations to describe the time and space dependent parameters (concentration, temperature, flow).Using spatial discretization, the partial differential equations have been converted into total differential equations and then implemented in Matlab/Simulink, obtaining thus the profiles for mass, temperature and reactants' concentration. As demonstrated in figure 2, the proposed model has almost the same methane conversion as the literature data. Also, the gasses mass fractions have been validated with available industrial data found in literature, as can be seen in figure 3 [3].

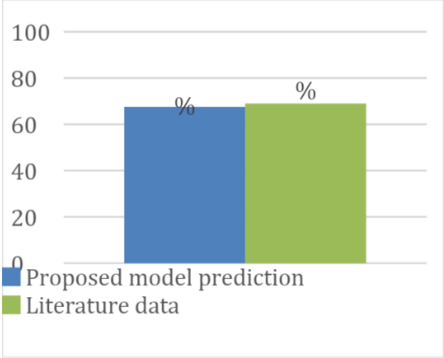

Fig. 2: Conversion of methane

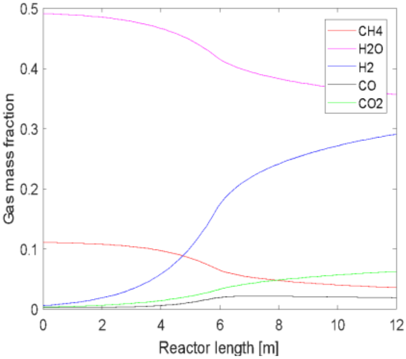

Fig. 3: Gas composition profile in multi-tubular reactor vs reactor length

The developed model would be used in evaluation of various operation conditions for optimization of technical indicators of hydrogen production process through biogas steam reforming.

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Bienzymatic biocatalyst for cascade transformation of limonene to limonene-1,2-diol

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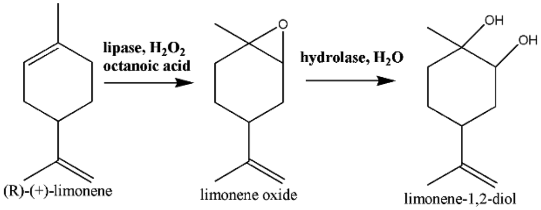
Terpenes, such as limonene, are a class of natural compounds widely occurring in plants acting as defense agents against herbivores, and to attract pollinators. Their oxygenated derivates, known as terpenoids, are used as flavor and fragrance products for centuries [1].

Previous studies showed that the bioconversion of limonene to limonene-1,2-diol is achievable using whole cell biocatalysis [2]. However, the use of whole cell biocatalysts has some disadvantages, such as: difficulty of controlling the process, low tolerance of substrate concentration, and high chances of side reactions [3]. Therefore, we propose a bienzymatic cascade pathway presented in scheme 1.



Scheme 1: Bienzymatic cascade process for conversion of limonene to limonene-1,2-diol.

The cascade process involves two steps. First step consists of (R)-(+)-limonene indirect biotransformation to limonene oxide. The lipase converts the octanoic acid present in the system into octanoic peracid using hydrogen peroxide as oxidizing agent. The obtained peracid oxidizes the (R)-(+)-limonene to its corresponding epoxide. In the second step, the hydrolase uses the water in the system to open the epoxydic cycle, resulting in limonene-1,2-diol.

We tested bienzymatic cascade system using different enzymes couple (lipase – hydrolase). Composition of the reaction mixture has been quantified offering an idea on the efficiency of the (R)-(+)-limonene biotransformation.

Therefore, the tests were performed with Novozym®435 immobilized lipase (monoenzymatic system), Novozym®435 coupled with the free hydrolase, and a biocomposite containing both enzymes immobilized. The biocomposite was prepared by adsorbing the CH55-LEH hydrolase on the surface of Novozym®435 beads.

The system containing the Novozym®435 and free CH55-LEH allowed to achieve a conversion of 45% (R)-(+)-limonene and a diol yield of 27%, while the biocomposite transformed 74% of (R)-(+)-limonene leading to 39% yield of limonene-1,2-diol and 91% enantiomeric excess for (1S, 2S, 4R)-(+)-limonene-1,2-diol.

In conclusion, the developed bienzymatic biocatalytic system exhibited the ability of efficient enantio-biotransformation of (R)-(+)-limonene into diol derivatives with many applications for the industrial field.

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Modeling and Optimizing the Photocatalytic Efficiency of Hydrothermally Obtained $CaTiO_3$ *via* Polynomial Regression and Artificial Neural Network Models

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Considerable interest has been shown towards $CaTiO_3$ due to its promising properties, such as ferroelectricity [1], dielectricity [1], gas-sensitivity [2], photocatalytic efficiency (owing to its unique energy band structure) [3], and bioactivity [4]. Since the enhancement of semiconductors' photocatalytic activity can be achieved *via* influencing the synthesis parameters through controlling the morphology [5], our curiosity led us to study the effect of synthesis parameters on the $CaTiO_3$photocatalytic activity.

The first part of this study focuses on the hydrothermal synthesis of perovskite photocatalysts based on the Box-Behnken experimental design (15+15), followed by their characterization (SEM, XRD, DRS, IR). In the second part of the study, two different modeling approaches were adopted (namely, second-order polynomial regression models and Artificial Neural Network models) to optimize the photocatalytic efficiency of $CaTiO_3$ during Rhodamine B (RhB) degradation under UV irradiation and constant stirring. Taking into account the two different Ca sources ($Ca(NO_3)_2$ and $CaCl_2$), two second-order polynomial regression models were constructed (R^2=99.67% and R^2=99.66%) using Minitab 18 software. As input variables, c_{NaOH}, temperature (T), and duration (t) of hydrothermal crystallization were used for the models. Using the SQP algorithm and 'fmincon' solver from the Optimization Toolbox of Matlab software, the values of the maximum conversion (X) and the decision variables were determined within the experimental ranges of the input variables. Depending on the Ca sources, the best obtained values were: X=82.45% - $Ca(NO_3)_2$ for T=180 °C, t=20 h, c_{NaOH}=0.67 M and X=81.72% - $CaCl_2$

for T=200 °C, t= 23.17 h, c_{NaOH}= 0.67 M. Furthermore, different classes of computational-based empirical models were developed, namely: Feedforward Backpropagation (FB), Radial Basis (RB) and Generalized Regression (GR) Artificial Neural Network models (ANNs). First, the FB ANN was trained for one hidden layer with a maximum number of 3 neurons. An outstanding determination coefficient (R^2_{test}=0.9983) was obtained when the number of neurons in the hidden layer was equal to 2. The 'purelin' and 'traincgp' functions were used as the activation and train functions. Second, promising results were obtained when two-layer networks (RB ANN and GR ANN) were implemented. Based on the previously constructed ANNs, 3-D response surfaces were generated to find the optimal synthesis conditions.

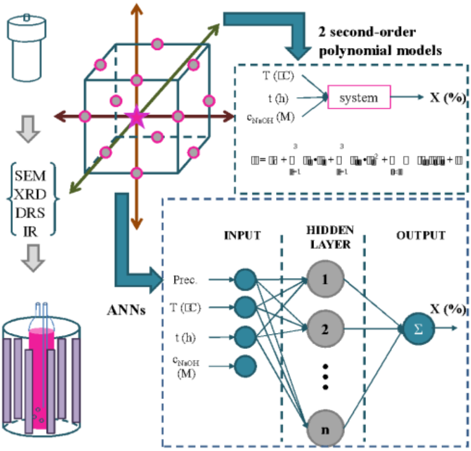

Figure 1. Graphical abstract (Abbreviations: Prec. – precursor, y – response, x_i – input variable, β_i, β_{ii}, β_{ij} – coefficients, Ɛ – error)

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Novel *p*-terphenyl – based chiral macrocycles: synthesis, characterization and computational investigation

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Chiral macrocycles are well known for their diversity, beauty and fascinating molecular structures[1]. Besides of their intriguing structures, the properties and potential applications of these molecular architectures, namely large values of specific optical rotation[2], stereospecific interaction with chiral guest, supramolecular enantiomers discrimination[3], chiral ligands in asymmetric synthesis *etc.*, have prompted researchers to develop new investigations in this field.

Structural diversity of optically active macrocycles, with helical or planar chirality, has been recently broadened, by replacing *o,o'*-briged biphenyls unit with *p*-terphenyl[5]. However, the elongation of the backbone brings in a real challenge to induce chirality by only connecting the 2, 2'' positions of the *p*-terphenyl backbone. Thus, literature reported resolved macrocycles of this type also entail the connection of the central phenyl ring to bridge.

With this overview in head, we set out to synthesis novel *p*-terphenyl – based chiral macrocycles with high racemization barriers that do not require the connection of the central ring to bridge.

On this line, our five designed macrocycles (Figure 1a) contains the dimethoxi substituted *p*-terphenyl backbone, 2, 2'' connected by etheroxime or ether-based bridges of different lengths.

The chirality of these macrocycles arises from the hindered rotation of the central phenylene ring and the racemization barrier depends on the type and length of the bridge. NMR analysis is in agreement with the free rotation of the central phenylene ring in the compound **I** and frozen structure for compounds **II**, **III**, **IV** and **V** at room temperature. Moreover, the dynamic NMR experiments made so far show that the free rotation in compound **I** still takes place at -60⁰C, while the compounds **II** and **IV** are not racemized up to 80⁰C.

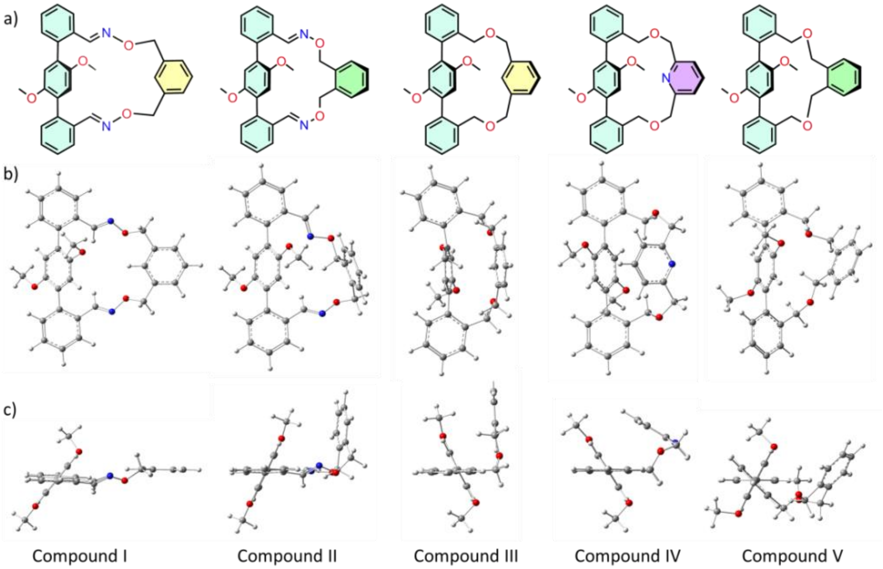

Fig. 1: Representation of the synthetized macrocycles (a) and their optimized ground state geometries - top view (b) and side view (c).

In order to gain further insight into the structural features of the synthesized macrocycles, DFT calculations were performed, employing the M06-2X hybrid functional and the Def2-TZVP basis set. The equilibrium geometries of the investigated macrocycles are illustrated in Figure 1b and 1c.

The experimental and theoretical determination of the racemization barriers, dynamic NMR and other experimental and theoretical investigations of these five macrocycles are in progress.

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Luminescent lanthanides materials based on phenanthroline derivatives

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Lately, lanthanides have been of great interest due to their luminescent properties, such as long lifetimes, large Stokes shifts, and narrow emission bands in the visible region [1]. Lanthanide based materials can be used as light emitting diodes, amplifiers for optical communications and optical storage [2].

In this work, we synthesized a new series of complexes using as ligands phenanthroline derivatives. For the first family of lanthanides based compounds we used as antenna ligand 4,7-Diphenyl-1,10-phenanthroline (Bphen) and for the other one, Pyrazino[2,3-f][1,10]phenanthroline (Pyrphen). The general structures are: $[Ln^{III}(Bphen)_2(NO_3)_3]$ (Ln^{III} = Eu, Tb, Nd, Er, Yb, Tm) and $[Ln^{III}(Pyrphen)_2(NO_3)_3]$ (Ln^{III} = Eu, Tb). The new complexes were characterized by X-ray diffraction (single-crystal and powder), IR and UV-Vis measurements. The luminescent spectra for the compounds shows specific emission for the lanthanide ions.

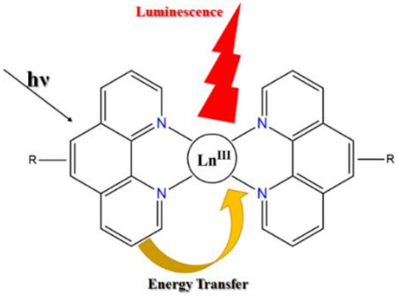

Fig. 1: Schematic representation of the obtained complexes and the antenna effect.

Acknowledgements: We are grateful to the UEFISCDI (project PN-III-P1-1.1-TE-2019-1345).

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Late *d*-metal complexes of macrocyclic ligands

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In the last years, the chemistry of macrocycle ligands containing mixed donor atoms (*eg*. O/S, N/S, N/S/O) has received an increased attention due to their unique properties, which make them valuable candidates for biological applications, ionic and molecular recognition, or as building blocks in supramolecular chemistry. Sulfur containing macrocyclic compounds such as thia-, oxathia-, and azathiacrown ethers show high affinity to transition metals with various oxidation states, thus forming stable complexes. Therefore, a lot of studies were performed during last years to develop various metal complexes bearing macrocyclic ligands, which can act as reagents or catalysts in organic synthesis.[1,2]

In the present work, we report the synthesis and structural characterization of new macrocyclic ligands containing N/S and N/S/O donor atoms. The reactivity of the new ligands was investigated towards several late *d* metals, *e.g*. Ag, Zn, Cd, Hg.

All the compounds were investigated in solution by multinuclear NMR spectroscopy (^{1}H, ^{13}C, ^{19}F, ^{31}P, as appropriate) and mass spectrometry. Several new compounds, both ligands and metal complexes, were investigated by single-crystal X-ray diffraction and their molecular structures were determined.

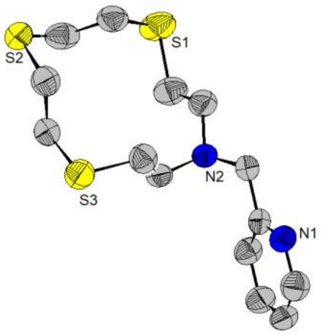

Fig. 1: Molecular structure of 10-(pyridin-2-ylmethyl)-1,4,7-trithia-10-azacyclododecane ligand.

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Corrosion rate modelling for steel in acidic media using cetylpyridinium bromide as a green inhibitor

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The present paper addresses one of the main challenges of today's industry: steel corrosion during the pickling process. Being done in aggressive solutions, this process presents a high corrosion rate. Corrosion counteraction is being done with the help of green inhibitors, not harmful to the environment. Among this class of substances, cetylpyridinium bromide has been reported as a good corrosion inhibitor for Cu-Fe (20%) alloys in H_2SO_4 solution [1] and as a synergistic inhibitor for copper in HCl solution [2].

Even though it has been studied before, there are not many reports on the modeling of the corrosion rate when this inhibitor in employed.

The aims of the present study are (1) to investigate the inhibition effect of cetylpyridinium bromide on the corrosion of steel in 1:1 solution of hydrochloric acid and water by weight loss measurements and (2) to explore the applicability of two different mathematical models to estimate the corrosion rate.

Four plates of steel were exposed to the acidic media containing different concentrations of inhibitor: 5%, 10% and 15%, and one control solution for 192.5 hours. Results regarding the measured mass loss over 192.5 hours reveal that the optimal inhibitor concentration is around 10%.

Further on, the experimental data processing was done by the means of MATLAB software to formulate mathematical models for the estimation of corrosion rate as a function of time, inhibitor concentration and contact surface.

(1) A regression model has been obtained by fitting different polynomial functions to the data sets, then using the MATLAB functions *polyfit* and *polyval*. This model proved to be successful in showing that the experimental corrosion

rate follows a polynomial curve and ensures a good agreement between the experiments and the estimation of the corrosion rate ($R^2 = 0.9981$ Blank, $R^2 = 0.9991$ 5%, $R^2 = 0.9987$ 10%, $R^2 = 0.9951$ 15%) along the 192.5 hours during which the measurements took place (see Figure 1). However, the model 1 fails in predicting the further evolution of the corrosion rate outside the time range of the experiments.

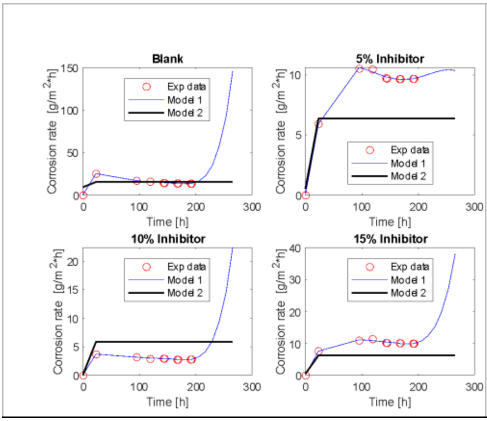

Figure 1. Compared results for the corrosion rate

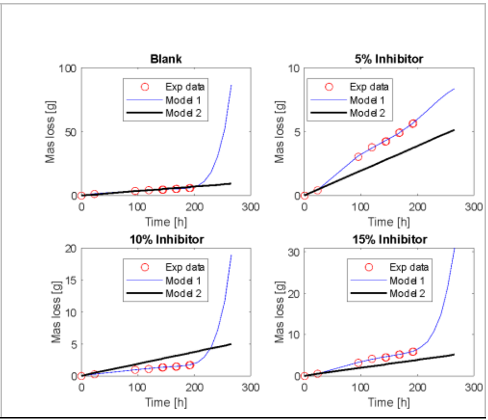

Figure 2 Compared results for the plate mass loss

(2) A second model has been formulated to ensure a better representation of the process dynamics(?). As shown in Figure 1 the model is less consistent with the experimental data compared to model 1 but it gives more realistic predictions with respect to further process evolution. When trying to predict the corrosion rate at further points in time model 2 estimates constant values corresponding to each inhibitor concentration, while model 1 estimates constantly increasing values, which are not backed up by the real phenomena.

It has been concluded that model 2 has the potential for further develoment to ensure better predictions. Therefore, more experimental data need to be collected and added to the algorithm which in turn need to be perfected.

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Comparative adsorption studies of benzalkonium chloride on sawdust and paper towel

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Benzalkonium chloride (BKC) is a cationic surfactant with biocide effect, often used in household cleaning, hygienic, cosmetic or other products of human use. It is hazardous to the environment [1], since it is usually disposed in water in form of aqueous solutions. It is highly toxic to fish and even more so to aquatic invertebrates, whereas in humans it exhibits only moderately toxic or irritating effects [2]. One of BKC most cost effective and efficient removal methods is by means of adsorption. Among readily available adsorbents are zeolites [2], activated carbon [3] or various polymer filters [4].

The present work investigates the same possibility, but when using various household materials, such as kitchen paper, tea filters, cotton yarn, sawdust [5], and viscose cloth. The yield of the adsorption of BKC from aqueous solutions was assessed by UV spectrophotometry at 262 nm. The measured absorbance was correlated with the residual biocide.

Time-resolved experiments were carried out in triplicate until equilibrium was reached. Temperature was also varied, when using sawdust and paper towels. Depending on the employed conditions, 90% of the initial benzalkonium chloride concentration is removed within 30 minutes to 8 hours. However, reaching equilibrium requires several days.

Typical examples of kinetic curves describing the values of absorbance at 262 nm *vs* contact time, for both reference and BKC containing solutions, are presented in figure 1. Aqueous mixtures containing both adsorbent and BKC (circles), and only adsorbent (triangles), were studied comparatively. It can be observed that sawdust contributes significantly to the value of absorbance, whereas the paper towel does not. However, this experimental approach proved to be successful in monitoring the evolution of such a complex process.

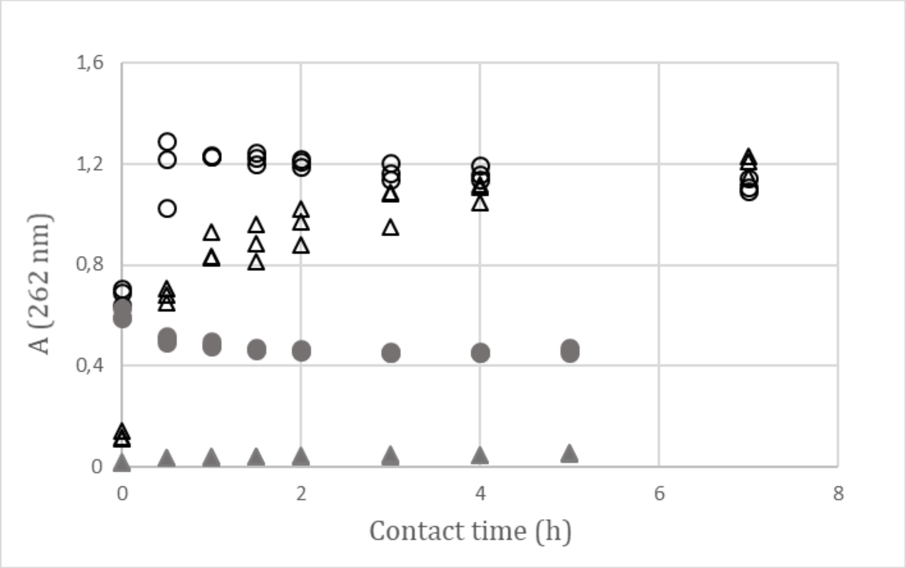

Fig. 1: Absorbance *vs* contact time for paper towel (solid fill) and sawdust (no fill), at 25°C, 10 g/L adsorbent, 0.5 g/L initial BKC concentration. Circles stand for the sample containing BKC, whereas triangles stand for the reference solutions.

The results show that the majority of the employed household adsorbents retain benzalkonium chloride from aqueous solutions. Those based on natural fibers (such as paper and sawdust) prove better adsorption yields. In addition, various adsorption kinetic and equilibrium models were considered, analyzed, and compared for the description of these complex processes.

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Structural and Computational Characterization for a new HexanuclearCopper(II) Complex

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We present the compound $[Cu_6(\mu\text{-}OH)_6(\mu\text{-dmnpz})_6(Py)_6]\cdot 6Py\cdot 2EtOH$ (**1**), with an interesting hexamer structure (Figure 1) made with 3,5-dimethyl-4-nitro-pyrazolate (dmnpz) as bridging ligand. The pyrazole was synthesized according to literature procedures [1]. The molecular unit consists in a six-membered metallacycle copper (II) pyrazolate, the Cu_6subsystem sketching a regular hexagon. There are relatively few reported compounds with the given pattern, even fewer receiving a magneto-structural characterization [2].

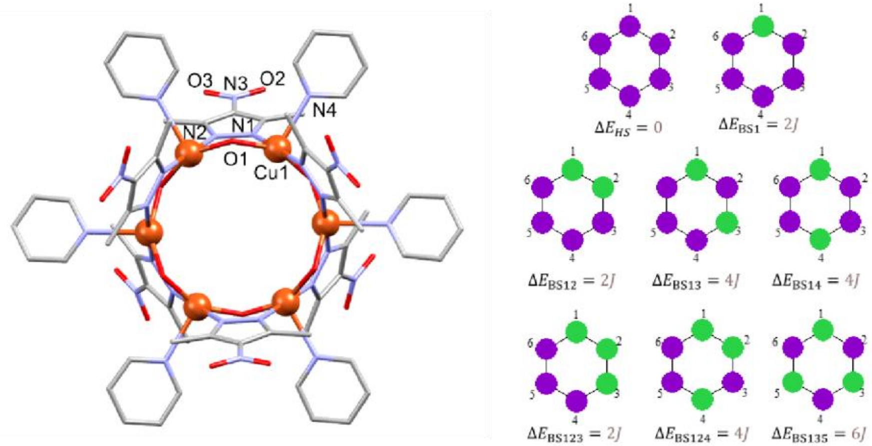

Fig. 1: Left side: Asymmetric unit of compound **1** with atom numbering scheme. Hydrogen atoms and solvent molecules are omitted for clarity. Right side: scheme of spin-polarization configurations treated in the Broken-Symmetry DFT calculations. The violet circles are standing for α-sites, while the green ones are for β spin.

The compound **1** crystalized in a triclinic system, *R*-3 space group. The monomeric units consistin distortedsquare-pyramidal coordination around the copper ions ions. The square pyramidbasis is formed by two nitrogen atoms from two dmnpz ligands arranged in transand two oxygen atoms from the OH bridging groups. The apical position of each site isoccupied by pyridine. The pyridine molecules are coordinated inthe plane of the copper ring, while the dmnpz and OH groups are forming two bowl-shaped cavities. Such voids can accommodate guest molecules, and in our case, twodisordered ethanol molecules are included. The compound **1** shows a hexagonal tubularstructure, on the packing along c axis, which can be interesting for further debate on theporosity properties.

The magnetic properties of this system is dominated by the strong antiferromagnetism along the pyrazolate bridges. The so-called Broken Symmetry (BS) approach represents the strategy usableto obtain estimations of exchange coupling parameters in the frame of Density FunctionalTheory. The Broken-Symmetry Density Functional Theory (BS-DFT) calculations are non-trivial results, being intrinsicallydifficult at high nuclearities. The right-side of the Figure 1 shows the symmetry-distinct BS configurations, obtainable by controlled spin-switch, starting from the High-Spin configuration (HS), having all the unpaired spin parallelly coupled. The coupling parameter computed by BS-DFT, namely J=-310 cm^{-1}, is in semiquantitative agreement with the value extracted from fit to experimental magnetic susceptibility data, estimated at J=-240 cm^{-1}. The BS-DFT treatments are validated by obtaining spin-density maps obeying the schemes suggested in the right-side of the Figure 1, and also by obtaining BS-type energies (relative to the HS configuration) matching well the proportionalities established formula annotated to each snippet in the presented scheme (as 2*J*, 4*J* or 6*J* quantities). The results are detailed in a recently published article [3].

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Synthesis and characterization of two new triorganotin(IV) halides

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Organotin(IV) halides and their derivatives (mainly carboxylates) have lately attracted attention for their antimicrobial[1] and antibiotic[2] activity. Our recent studies on the *in vitro* antiproliferative activity of some organotin(IV) halides and carboxylates reveal encouraging results,[3] thus supporting further investigation on similar organotin(IV) species.

In this context, we now report on the synthesis and structural features of three new organotin(IV) compounds suitable for biological studies on various carcinoma cells.

The compound $[2\text{-}\{(CH_2O)_2CH\}C_6H_4]_2SnPh_2$ (**1**) was obtained in an excellent yield and used as a starting material for the synthesis of two new triorganotin(IV) halides, $[2\text{-}\{(CH_2O)_2CH\}C_6H_4]_2SnPhI$ (**2**) and $[2\text{-}\{(CH_2O)_2CH\}C_6H_4]_2SnPhCl$ (**3**).

Compounds **2** and **3** were isolated in good yields and they were fully characterized by multinuclear (^1H, ^{13}C, ^{119}Sn) NMR spectroscopy, IR spectroscopy and mass spectrometry. Their molecular structures were established by single-crystal X-ray diffraction.

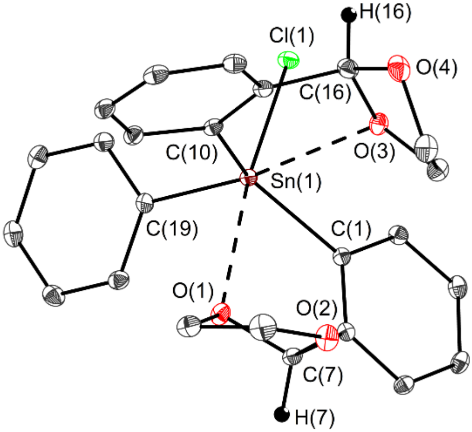

Fig. 1. Molecular structure of [2-{$(CH_2O)_2CH$}C_6H_4]$_2$SnPhCl (**3**).

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Organoselenium ligands and their silver(I) complexes. Synthesis and structural characterization.

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Organoselenium compounds have shown various uses in fields as biology, medicine, organic synthesis and materials science. They proved to be valuable ligands in coordination chemistry, thus resulting in various main group or transition metal complexes with a strong potential as antioxidants, anti-inflammatory, anticancer or antiviral agents.[1] During last years, an increased interest was observed for compounds bearing organic groups with donor atoms which can interact intramolecularly either with selenium (N→Se) or with the metal centre (N→M), thus resulting in a higher thermal and hydrolytic stability and better specific biological or catalytic properties.

Our recent research interest was focused on diorganodiselenides and diorganoselenides of type $(2\text{-}Me_2NCH_2C_6H_4)_2Se_2$, $[Me_2C(OH)CH_2]_2Se_2$ and $[R_2C(OH)CH_2](2\text{-}Me_2NCH_2C_6H_4)Se$ (R = Me, Ph).[2]

We report here on the synthesis and structural characterization of the new ligand $[(CF_3)_2C(OH)CH_2](2\text{-}Me_2NCH_2C_6H_4)Se$ (**1**) and the silver complex $[\{(CF_3)_2C(OH)CH_2](2\text{-}Me_2NCH_2C_6H_4)Se\}AgOTf]$ (**2**). Both the ligand and the silver(I) complex were characterized by multinuclear NMR spectroscopy (^{1}H, ^{13}C, ^{19}F) and mass spectrometry. The molecular structure of ligand **1** was established by single-crystal X-ray diffraction.

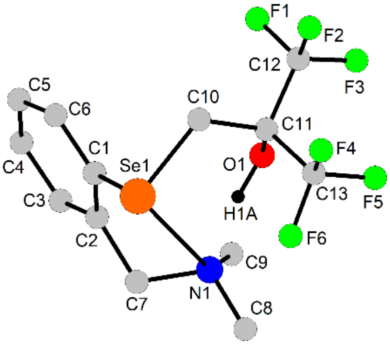

Figure 1.

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Study of Phase Separation Behavior in Flexible Polyurethane Foam

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Polyurethanes (PU) [1] are one of the most important classes of materials that have been used in foams, fibers, elastomers, coatings and adhesives [2].

Flexible polyurethane foams (FPUF) are produced by the catalytic balancing of two reactions involved. The "blowing" reaction (isocyanate-water), where an isocyanate group reacts with water to form an amine functionality and carbon dioxide (CO_2), the amine formed then reacts with another isocyanate group to form urea hard segments (Fig.1). The CO_2 generated in this exothermic reaction contributes to the expansion to form the foam cells.

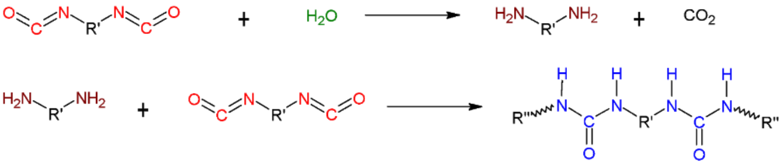

Fig. 1: Blowing reaction.

In the second reaction, known as "gelation", an isocyanate group reacts with a hydroxyl group from a polyether polyol to form a urethane bond (Fig.2).

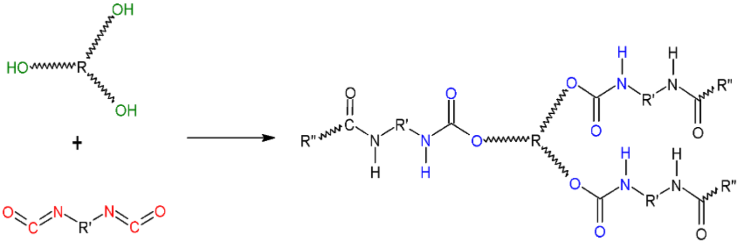

Fig. 2: Gelation reaction.

The global properties of polyurethane foams are strongly influenced by the microphase separated morphology which results from the incompatibility between the soft segments derived from aliphatic polyether alternating with the hard segments based on aromatic isocyanate commonly used [3,4].

In this study, changing the water content and adding alkaline metals (LiCl, NaCl and KCl) with different amounts to flexible polyurethane foam formulations resulted in a systematic modification of phase separation behavior, and consequently the nature of the connectivity of the urea phase. The prepared foams were found to possess different levels of urea phase connectivity, which were examined using SAXS to study microphase separation showed that the addition of alkali metals and change in water content affected the formation of urea aggregate structures and interdomain spacings in the materials, WAXS was used to examine the connectivity at the micro-level between the hard segments and FTIR used to evaluate the hydrogen bonding characteristics of flexible polyurethane foam.

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Spin states in Mn(III) complexes with ligands exerting strong field regime

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We report here the rare case of a low-spin Mn(III) complex, synthesized with a hexadentate Schiff Base ligand, capable of exerting strong ligand -field that stabilizes a state formally related with the splitting of the octahedral $^3T_{1g}$ octahedral term. Previous systems with similar ligands, reported by G. Morgan *et al.* [1] showed also interesting behavior, with spin crossover on the Mn(III) site. In our group, being interested in magnetic anisotropy and in the peculiar geometry of axially-compressed Mn(III) complexes, a spin-crossover system was serendipitously found and thoroughly characterized [2].

The compound **1,** [Mn^{III}(naphth-sal-N-1,5,8,12)]ClO$_4$, is built with a ligand obtained by the condensation of N, N'-*bis*(3-aminopropyl) ethylene-diamine and 2-hydroxy-1-naphthaldehyde. We discuss the structure and properties of this system, performing a modeling relevant for ligand field features.

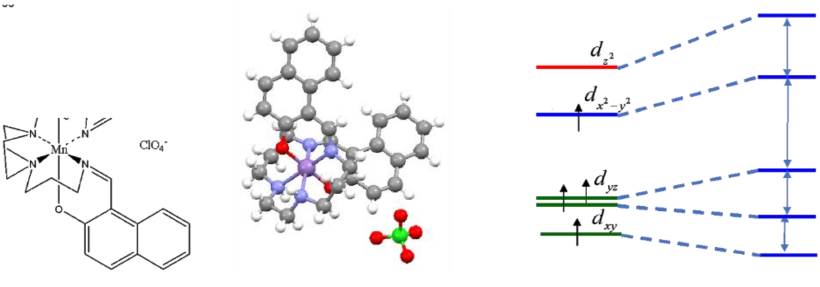

Fig. 1: Synopsis of the discussed system. Left side: scheme of compound **1.** Central panel. Molecular unit of compound **1** from X-ray crystallography. Right side: Ligand Field scheme resulted from adequate computer experiments.

The molecular unit is shown in Figure 1, as chemical scheme and as realistic X-ray picture. The complex units are quasi-tetragonal, with two oxygen donors mutually in *trans* and the four nitrogen in equatorial positions. A C_2 symmetry axis passes through the Mn site and the middle of C-C bond from the ethylenediamine moiety.

Table 1: Comparison of experimental coordination bond lengths and optimized computed values (considering B3LYP and BP86 functionals and low spin multiplicity)

Bond Length (Å)	Exp	B3LYP	BP86
Mn(1)-O(1)	1.888(1)	1.886	1.883
Mn(1)-N(1)	1.997(2)	1.990	1.945
Mn(1)-N(2)	2.062(2)	2.081	2.075

Density Functional Theory (DFT) calculations and subsequent orbital analyses confirmed that the ligand field split in this system is large (see right side of Figure 1), due to the enforced encapsulation ensured by the hexadentate ligand, determining the pairing of the electrons in a spin-triplet ground state, contrary to the customary spin-quartet nature of usual Mn(III) complexes. The modeling results are validated by the good match between experimental and computed (optimized) geometries, as observed in Table 1 for selected bond lengths.

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Determination of noradrenaline using a modified electrode based on conductive polymer

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The aim of this research was to develop a simple electrode matrix based on an electropolymerized film of PEDOT on a glassy carbon electrode (PEDOT/GCE) for the detection of noradrenaline (NA). NA is a compound belonging to the catecholamine family that functions in the brain and body as a hormone and neurotransmitter, and mobilizes the brain and body for action [1].

Electrochemical investigation of the modified sensor was done using cyclic voltammetry and differential pulse voltammetry (DPV). The modified sensor showed high sensitivity and selectivity for the determination of noradrenaline. The redox process involving NA shows an oxidation peak (Ia) at +0.280 mV and two reductions peaks at +0.16 V and -0.2 V (at 50 mV/s). In order to study the influence of the experimental conditions on the shape of voltammograms, different scan rates, and pH values of electrolyte were investigated. As expected, the redox peak current intensities increase and shifts to positive/negative potential values, when the electrolyte scan rate is increasing. Analyzing the slopes for the log I - log v dependencies we concluded that during the oxidation process there is no adsorption of the NA, the process is controlled by diffusion (the slope is 0.5).

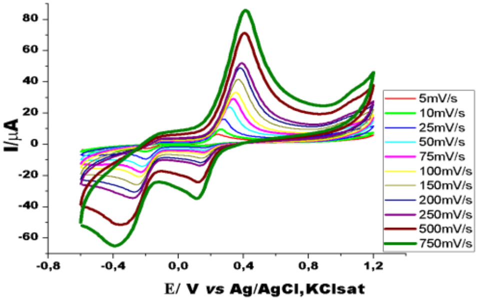

Fig. 1: The influence of the scan rate on the cyclic voltammograms of 10^{-3} M NA at GCE/PEDOT modified electrode. *Experimental conditions: electrolyte, phosphate buffer 0.1 M (pH 7); starting potential, -0.6 V vs. Ag/AgCl, KCl_{sat}, scan rate, see inset.*

During the reduction process, due to the fact that the slope value is placed between 0.5 and 1, a partial adsorption of NA could occur at the electrode surface.

Also, the short-time stability of the modified electrode was investigated, by continuous cycling the potential in a solution of 10^{-3} M NA, during 30 minutes, obtaining a good stability of the electrode response installed after the 5th cycle, with a low deactivation constant of 1.7 10^{-9} s^{-1} (estimated as the slope of I *versus* time dependency). From DPV voltammograms the calibration curve obtained at different concentrations of NA was plotted and the analytical parameters were estimated. A linear range between 5 - 40 μM and a detection limit of 4.3 μM NA was obtained, values which are in accordance with other values obtained at similar modified electrodes presented in the literature [2,3].

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3D-QSAR, ADMET, and Docking studies for designing new indole derivatives as anticancer agents

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The World Health Organization (WHO) considers cancer as the deadliest disease, according to the increase in death in the 21th century. Cancer is a pernicious disease connecting to a bundle of cellular processes, in which a group of cells become abnormal, remarked as a major public health problem worldwide [1]. Computer-Aided Drug Design (CADD) emerged as an efficient means of identifying potential lead compounds and for aiding the developments of possible drugs for a wide range of diseases such as cancer. A three-dimensional quantitative structure-activity relationship(3D-QSAR) study was performed on 34 indole derivatives as Pim kinase inhibitors [2].

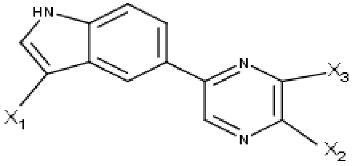

Fig. 1: The structural template of the indole derivatives

This study was built using comparative molecular field analysis (CoMFA) and comparative molecular similarity indices analysis (CoMSIA) contours. The generated models were in accordance with the model acceptance criteria. The two contours obtained specify the types of groups that can be added to increase the activity, based on these findings from the consideration of these methods we designed new compounds, and having high inhibitory activity. Docking molecular as an important method, is performed for exploring the interactions between the ligand and the protein and was also used to determine the total score [3]. The designed compounds exhibit favorable interaction and the higher total score, while the most active compound in the database showed the lower total score. Some newly proposed compounds showing good results of ADMET (adsorption–distribution–metabolism–excretion–toxicity). These compounds are important against cancer and all of them are easy to synthesize.

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Enhanced catalytic activity of mutant PAL enzymes for preparative-scale biotransformations

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In this topic, highly efficient phenylalanine ammonia lyase (PAL) enzymes were developed through protein engineering strategies. The increased catalytic power of these new developed enzymes was tested in biotransformation of several unnatural substrates in which the natural, *wild-type* enzyme showed low activity.[1] Mutant variants of PAL enzymes from *Petroselinum crispum* (*Pc*PAL), *Arabidopsis thaliensis* (*At*PAL) and *Rhodosporidium toruloides* (*Rt*PAL), were monitored and compared in both ammonia addition and elimination reactions (Figure 1).

Further investigations showed that, while strong substrate inhibition occurs in case of *Pc*PAL mutant variants [2], in case of *At*PAL enzymes, substrate and product inhibition does not occur and high conversions can be achieved even at high substrate concentration. Using whole cells, preparative scale biotransformations were performed with the aim to develop highly efficient biocatalytic synthetic procedures for the synthesis of valuable D- and L-amino acids with high optical purity.

The research results demonstrate that protein engineering based on rational design can develop highly-efficient phenylalanine ammonia lyases that provide cost-effective production of enantiomerically pure D- and L-phenylalanine analogues in accordance with the principles of green chemistry.

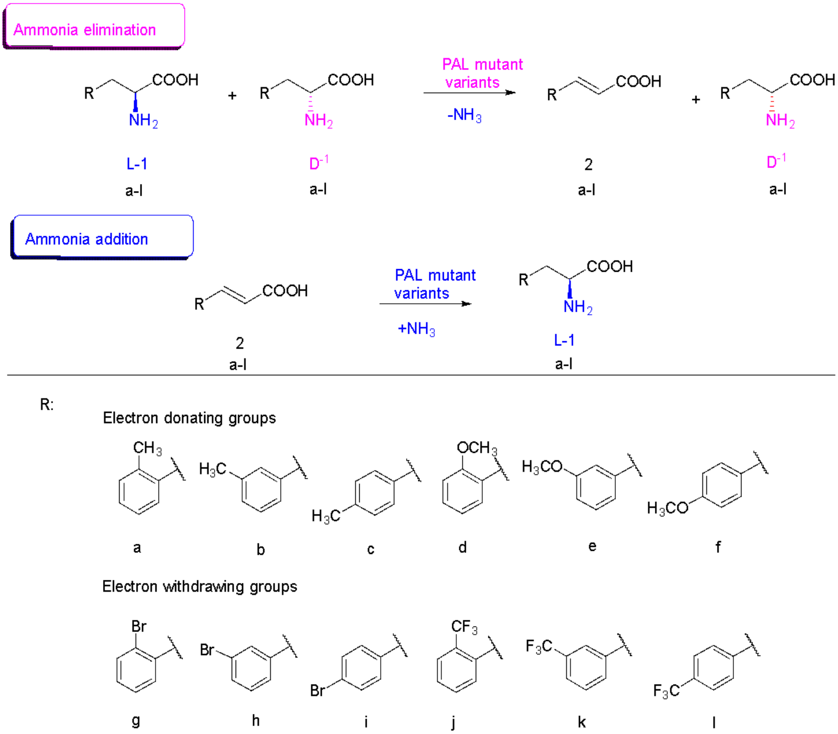

Fig. 1: The studied PAL catalyzed of ammonia elimination and addition reactions.

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Synthesis and structural characterization of new heteroleptic diorganochalcogen(II) compounds

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The synthesis of organochalcogen compounds (mainly sulfur and selenium derivatives) with organic groups having nitrogen and oxygen as donor atoms gained a continuously increasing attention in the scientific community due to their applications in different fields *e.g.* organic synthesis, biology, medicine, materials science and microelectronics due to their optical or electronic properties.[1][2]

Our interests were focused on the synthesis and structural characterization of new heteroleptic diorganochalcogen(II) compounds of REBu type (E = S, Se; R =benzaldehyde, 4-arylidene-5(4*H*)-oxazolone).

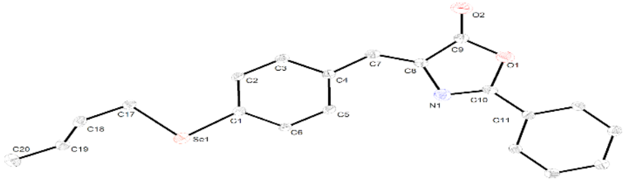

Fig. 1: Molecular structure of RSeBu

All the compounds were investigated in solution by multinuclear NMR spectroscopy (^{1}H, ^{13}C, ^{77}Se as appropriate) and mass spectrometry. The molecular structure of RSeBu (R = 4-arylidene-5(4*H*)-oxazolone) was determined by single-crystal X-ray diffraction.

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Versatility of thiourea dioxide as redox agent in globins: case study with myoglobin

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Thiourea S,S-dioxide $(NH_2)_2C(SO_2)$ (abbreviated TDO) also known as formamidine sulfinic acid (FSA) has received much interest for wide application in chemistry and chemical industry.

This is correlated with the decomposition of TDO in alkaline media (p*K*a~9.5) with generation of sulphoxylate SO_2^{2-} (SO_2H^-) or sulfoxylic acid $S(OH)_2$, - strong reducing agents employed extensively as bleaching agents in textile industry [1]. TDO was shown to efficiently induce reduction of heme proteins to Fe(II) at basic pH values, via liberation of sulfoxylate. The latter's reducing ability was shown to extend to CO_2 dissolved in solution under normal/atmospheric laboratory conditions, so that the final product of hemoprotein reaction with TDO at basic pH was a Fe(II)-CO adduct. Since CO adducts of proteins would otherwise be obtained by using a combination of reducing environment and CO gas, reduction of metalloproteins with TDO was proposed to offer a faster and much simpler route towards Fe(II)-CO adducts [2]. Importantly, TDO is water-stable and environmentally safe. Latest study shows that using TDO together with excess of L-cysteine makes reduction of colorant Orange II faster [3].

This study combined theoretical density functional theory calculations, UV-VIS technique and ^1H NMR to determine decomposition of TDO in solvents, interaction with L-cysteine and explore/expand the chemistry of TDO in relation with metalloproteins (with myoglobin (Mb) as a case study), taking into account more recent knowledge about modulation of TDO reactivity by nucleophiles, with emphasis on thiol groups.

At pH 8-12, reaction of ferric Mb with excess/solid thiourea dioxide (TDO) under initial aerobic conditions leads to oxy (pH 8) or Fe(II)-CO (pH 9) or deoxy (pH 10) Mb, but also to a sulfheme species detectable at 620 nm and to partial heme edge degradation as observed in the 650-750 nm region. Cysteine prevents the latter, generally slowing down the TDO-Mb reaction. At higher pH values (and especially at pH 13) sulfheme yields are lower.

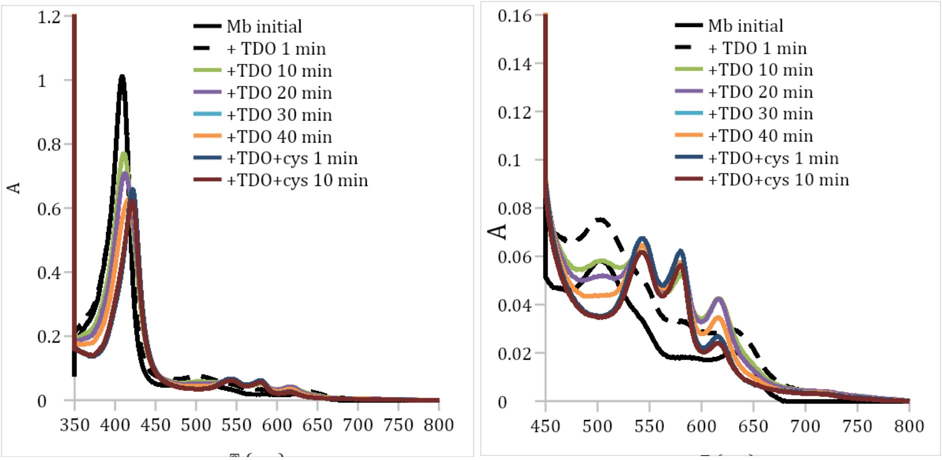

Fig. 1: UV-vis spectra of Mb treated with TDO and cysteine at pH 8. Conditions: 50 mM disodium phosphate buffer, TDO added (a few crystals) to the Mb solution in the cuvette after which the cuvette was sealed with a septum cap; 0.1 mM cysteine was added using a gas-tight microsyringe.

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Investigation of coke oven gas absorption with CFD simulation

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Nowadays, in the industry, it is extremely important to reduce the emission of environmentally harmful gases. Decreasing the amount of pollutant components has financial advantages as well because these components can be valuable in other technologies as raw materials. However, the application of the gases (for example, carbon dioxide, ammonia and hydrogen sulfide) strongly depends on their purity.

In this work an absorption process was chosen because this is one of the most commonly used processes to remove these components from gas mixtures, like coke oven gases. During absorption, the key components of the mixture penetrate to the absorbent by diffusion on the interface between the gas and liquid phases. The basis of absorption is Henry's law which describes the gas-liquid equilibrium.

For the detailed examination of absorption, COMSOL Multiphysics CFD simulator was used. The CFD simulation gives us a sharp insight into the process from a hydrodynamical aspect as well. CFD simulators are able to determine the concentration and the velocity profile of complex systems due to their large calculation accuracy. For the description of component transportation by absorption, CFD simulators use the Lewis-Whitman two-film theory. [1]

In this study, we focused on the separation of CO_2, NH_3 and H_2S from the coke oven gas with the usage of pure water as an absorbent. At first, a sensitivity analysis was performed. We examined the influence of pressure, temperature and pure water flow rate on the absorption efficiency. We used Aspen Plus for calculating the CO_2, NH_3 and H_2S content of the cleared gas mixture. The results of the sensitivity test showed that low temperature, reasonably high pressure and moderately high water flow rate should be maintained to achieve optimal operation. After this test, the mass transfer coefficients were calculated with Aspen Plus for each component, and the average mass transfer coefficient of the mixture was determined from the results. [2]

After performing the sensitivity test and calculating the average mass transfer coefficient, a CFD model was created using the COMSOL Multiphysics simulator. A simplified model was created for the system by using a rectangle in a 2D axisymmetric geometry. The process was separated into two subprocesses. The first one is the dissolution of NH_3, H_2S and CO_2 and the second one is the reaction of CO_2 and NH_3 with H_2O. Bubbly flow model was used in order to model the flow of the gas mixture. The Transport of Diluted Species model is responsible for the description of the reactions.

Overall, our simple absorber CFD model describes the simplified kinetics of the absorption in a small geometry, but our aim is to increase the size and complexity of this model to be able to model a larger system.

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New folic acid esters with analogues of methylene blue–contrast agents for bioimaging of cancer cells

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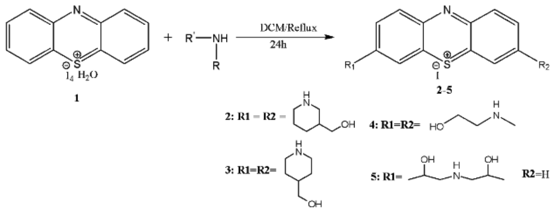
Described as "the first fully synthetic drug used in medicine", methylene blue (MB) has been used in trials to treat malaria, Alzheimer's, bipolar disorder and infectious diseases. For 70 years, it has been confirmed with each new research study that phenothiazinium dyes have virucidal properties. However, in recent years a new approach has been sought for using this class of dyes as staining agents in cell imaging. [1]

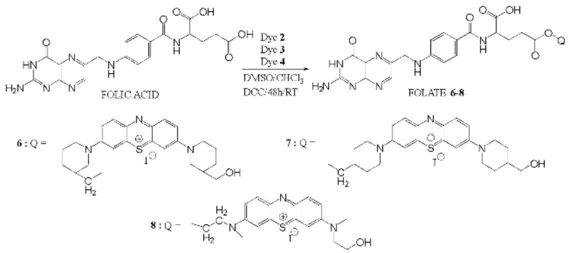
The use of MB and its analogues in bioimaging applications appears suitable not only due to characteristics such as the high values of extinction coefficients and good fluorescence quantum yields, but also due to their typical absorption/emission wavelengths situated in the NIR biological window (650-900 nm). Moreover, these properties can be properly exploited for obtaining reliable contrast agents based on the ability of these dyes to cross the cellular lipid bilayer. [1]

Binding of antitumoral drugs to folic acid, or their encapsulation in biopolymers or biocompatible materials such as pluronic became a common practice in cancer clinical trials. [2]

In this work, is described the synthesis of new MB analogues with auxochromic substituents containing pendant hydroxyl groups (Scheme 1) and their further use in the preparation of novel folic acid esters (Scheme 2). The binding of folic acid to contrast agents did not alter the absorption/emission properties of the dyes in the visible region, and no fluorescence quenching was observed. Compared to the free MB analogues, folate derivatives showed lower lipophilicity and significantly lower intercalation ability during DNA titration. These could be considered as favorable results for the ultimate purpose of the applicability of these molecules, namely, specific binding to the FRα receptor of malignant cells. [2]



Scheme 1: Synthesis of phenothiazinium dyes.



Scheme 2: Synthesis of folic acid esters with phenothiazinium dyes.

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Dual-mode determination of selenium in biofortified allium microsamples following piazselenol formation and solid phase microextraction

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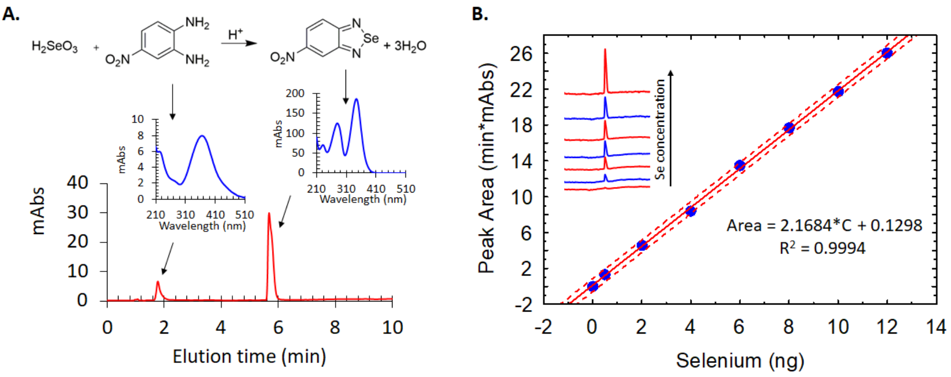
Selenium is an essential trace element in animals and humans. Compared to other micronutrients, there is a much narrower range between the normal concentration and the toxic amount of selenium in living organisms. The inorganic forms of selenium (selenate, selenite) present up to 40 times higher toxicity than the organic species (*e.g.* selenocysteine, selenomethionine).[1] Due to these considerations, a sensitive method is required for detection of selenium compounds in biological samples. A distinct method is represented by the formation of piazselenol. This kind of complexes represent the product of reaction between an aromatic *o*-diamine and Se(IV) species, in acidic conditions[2,3] as it can be observed in Figure 1. This study describes an HPLC-based optimized, sensitive and selective method for determination of selenium in biological microsamples. Molecular absorption UV-Vis analysis of piazselenol formation has also been carried out, using a nanophotometer device, as a faster but still efficient assay for selenium determination in microsamples. Before the analysis procedures, the biofortified *Allium* microsamples have been mineralized and pre-concentrated using solid-phase microextraction technique. This analytical step affords an excellent precision and accuracy as it removes the interferences form a typical biological sample, allowing thus limit of detection as low as 0.5 ng/mL Se.



A- piazselenol formation, UV-Vis spectra and chromatograms of *o*-diamine and piazselenol complex

B- calibration curve

Figure 1. A. Piazselenol formation and determination by HPLC and UV-Vis tehniques following solid phase microextraction step. **B.** Calibration curve for selenium determination using chromatographic analytical response.

Acknowledgemen: This work has been financially supported by PN-III-P1-1.1-TE-2019-1396.

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Interaction of hemoglobin with anti-cancer drugs: Dacarbazine and Vincristine

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Hemoglobin's redox reactivity was previously shown to be affected by a small number of anticancer drugs. Direct binding of these drugs to hemoglobin, with biomedically relevant affinities, was demonstrated.[1] A direct redox reaction was observed influencing the oxidative cascade and correlating with compounds' concentrations.

In the present study, the autoxidation rates of hemoglobin, the ascorbate peroxidase activity of hemoglobin, and the reaction of hemoglobin with nitrite were studied in the presence of two cytostatic drugs: dacarbazine and vincristine. Dacarbazine is a cytotoxic drug included in the category of DNA alkylating agents.[2] Vincristine is an antimitotic alkaloid that interferes directly with the tubulin system, thereby affecting tubulin stability, mitosis, cell motion and intracellular organelle transport.[3]

Reported here are data showing that dacarbazine and vincristine may bind to hemoglobin, may affect its reactivity and may serve as substrates for peroxidase activity with hemoglobin. At least some of these interactions occur at concentrations that are biomedically relevant.

The specific autooxidation reaction for metalloproteins can be highlighted in the case of oxyHb (Fe^{2+}) by the formation of toxic and non-functional heme (Fe^{3+}) and superoxide ion (which further dismutates to peroxide). These species can alter the structure of protein and heme. Both cytostatic compounds accelerate the autoxidation process of oxyhemoglobin.

Nitrite found in micromolar concentrations in the body can induce autoxidation of hemoglobin and reaction rate is affected by dacarbazine and vincristine. The results presented in Figure 1 indicate that the kinetics of the analyzed reaction is influenced by the presence of cytostatic compound in a concentration-dependent manner.

In the reaction of ferric Hb with peroxide, a high valent species is formed (ferryl Fe^{IV}) accompanied by the formation of a protein/porphyrin-based radical cation ($P^{+•}$); both of these are powerful oxidants known to affect amino acids, lipids, and nucleic acids by abstracting a hydrogen atom.[4] They also can promote heme degradation and the release of free iron.

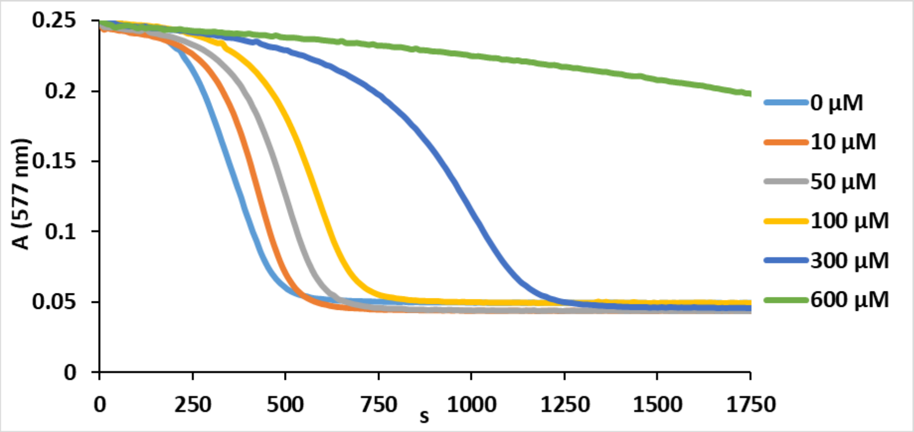

Fig. 1: Hemoglobin reaction with nitrite in presence of dacarbazine in time.

For observation of this reaction, the HAPX method (hemoglobin ascorbate peroxidase assay) was applied – a method that was firstly discussed and developed for propolis extracts[5] and then successfully used for other natural extracts. It is based on inhibition of ascorbic acid consumption by the redox-active compounds present in the sample, by monitoring the slope at 290 nm (ascorbic acid) using the peroxidase activity of haemoglobin (HAPX).[6]

This method showed that dacarbazine influences the kinetics of the reaction by having an antioxidant effect.

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Interactions between globins and anticancer drugs. Doxorubicin and cyclophosphamide.

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Hemoglobin is found in high concentrations in blood and is very susceptible to changes in redox status. Hemoglobin may be involved in toxic reactions with oxidative and nitrosative stress agents under certain circumstances, such as physiological effort or pathological conditions. Exogenous compound binding to the protein surface may change protein conformation, giving peroxide or other stress agents better access to the heme.[1]

In the present study, hemoglobin's redox reactivity: (i.e., the autooxidaton rates, the ascorbate peroxidase activity, and nitrite induced oxidation) in the presence of cyclophosphamide and doxorubicin was examined. Cyclophosphamide is a nitrogen mustard that exerts its anti-neoplastic effects through alkylation.[2] Doxorubicin is an anthracycline type antitumor antibiotic which damages DNA and may kill cancer cells.[3]

Oxyhemoglobin (Fe^{2+}) undergoes autoxidation, resulting in nonfunctional ferric heme (Fe^{3+}) and superoxide (which further dismutates to peroxide).[4] The aim of our experiment was to demonstrate the effects of cyclophosphamide and doxorubicin on hemoglobin autoxidation rates. The results presented in Figure 1. show that doxorubicin acts like a pro-oxidant. Thus, it accelerates the autooxidation rate of hemoglobin.

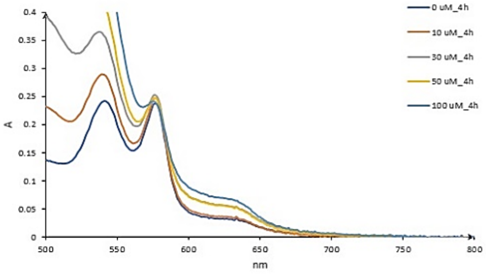

Figure 1. Hemoglobin autoxidation in presence of doxorubicin

The nitrite-induced oxidation of oxy hemoglobin is known to have a lag phase, which is marked by the accumulation of free-radical species, until met hemoglobin accumulates autocatalytically. As a result, it is widely assumed that this reaction occurs during redox multistep cycling. The transformation from oxy to met hemoglobin can be monitored at 540 nm.[5] Both of the examined cytostatic drugs affect differently this reaction.

Ferric Hb interacts with peroxide to produce ferryl, a high-valent species (Fe^{4+}), accompanied by the formation of a protein/porphyrin-based radical cation ($P^{+\bullet}$). Both of these are powerful oxidants known to affect amino acids, lipids, and nucleic acids by abstracting a hydrogen atom. They can also cause heme degradation and cause protein crosslinking, as well as the release of free iron.[4] When met-hemoglobin (Hb-Fe(III)) interacts with hydrogen peroxide in the presence of ascorbic acid (and various added antioxodants), the hemoglobin is oxidized to HbFe(IV), however the ascorbic acid easily reduces it back to Fe(III); therefore, as long as ascorbic acid (and sample antioxidants) is present in the mixture, hemoglobin primarily exists as met form.[6] Doxorubicin influences the kinetic of this reaction, having a pro-oxidant effect.

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Risk analysis in biogas production: a case study of Biogas Station in Seini, Romania

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In recent years, biogas production has become one of the most attractive renewable energy sources. This growth is supported and encouraged at EU level through policies due to its economic, climate and environmental benefits [1]. By industry convention, dry biogas is said to comprise about 65% methane, 35% carbon dioxide and a number of trace gases. Biogas composition varies considerably due to substrate composition and operational parameters [2]. Due to this format, biogas involves three major risks: explosion and fire (due to methane content), toxicity (due to the presence of hydrogen sulfide) and biological risk (due to the presence of pathogenic microorganisms). Because of them, the development of biogas industry is associated with a rapid increase in the number of industrial accidents. Therefore, an identification of the hazards associated to biogas plants is crucial to permit a safe exploitation and a sustainable development of this industrial sector [3].

This paper includes a risk analysis for the Biogas Station in Seini, Maramureș County, Romania. Qualitative (HAZOP) and quantitative methods (Fault Tree and Event Tree) were used to analyse the risks identified within the studied plant. For a more in-depth analysis, the Effect program was used to model potentially dangerous events (UVCE and VCE explosion, flash fire and jet fire, toxic dispersion) that could cause property damage or casualties.

Using the HAZOP method, three scenarios were highlighted by a high value of risk: digester explosion, fire and dispersion of toxic gas. The Fault Tree was used to represent the logical paths leading to the top event, the total rupture of the digester.

The scenarios with the highest frequencies were modeled in the Effect program to generate the areas that could be affected in case of accident. The digester explosion during maintenance, instant dispersion of gases in the atmosphere and the explosion in the cogeneration chamber were characterized by a large area of expansion, exceeding the site limits.

Following the risk analysis, it was highlighted that biogas plants have a high potential to cause industrial accident. Although the Seini Biogas Plant has certain measures to prevent and combat accidents, other useful methods have been suggested.

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Mapping structural the features of porphyrin with new computational experiments

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The class of porphyrins provides most important complexes known to act in the chemistry of life. [1,2] To manage structure-property causal relationships of such systems is of great importance, ranging from the targeted practical goals of drug design, to heuristic insights in mechanisms of life, understanding, so to say, why blood is red and grass is green.

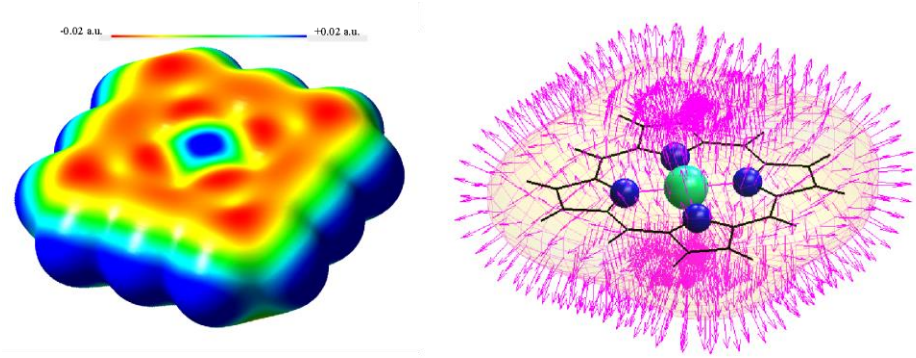

Fig. 1: Left side: Electrostatic potential surface as color map on the conventional van der Waals surface of Zn-porphyrin model complex (drawn at 0.001 e/Å^3). Right side the scheme of scanned A-O$_2$ and A-NO association profiles, moving the spin-probe molecules along the perpendiculars to the van der Waals surfaces on a selected numeric grid.

Aiming to enter this field with synthetical deals, perfected only in certain preliminary levels, we take the academic structural insight as companion of our searches.

Although the domain is thoroughly worked in various respects, we can propose new clues illuminating key features of porphyrin as ligand and in its prototypic complexes. We consider the interaction with O_2 and NO spin-carriers molecules for several series of porphyrine-based compounds (denoted by A), charting the geometrical places of equilibrium forms of the A…O_2 and A…NO non-covalent association complexes. The mapping starts from the conventional van der Waals surface as suggested in Figure 1 and briefed in its caption.

The outcome consists in a new representations of interacting potentials of the porphyrine complexes, different from customary electrostatic potential maps. The numeric experiments are continued with Time Dependent and Broken Symmetry approaches in the frame of Density Functional Theory relevant for spin chemistry and ligand field features of the selected systems. This work is done in the key of our interest for structural chemistry and prototypic case studies. [3]

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Synthesis and structural characterization of a new NDI-based macrocycle

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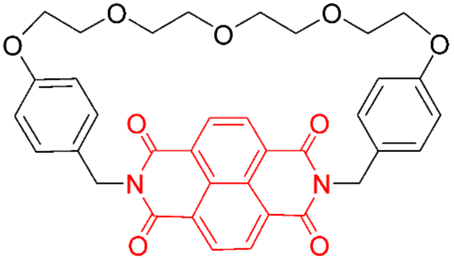
Macrocycles are defined as molecular structures consisting of a cyclic framework with more than 12 atoms.[1] They usually contain well-defined cavities that allow binding of ions and small molecules with appropriate size and shape by non-covalent interactions. Thus, macrocyclic compounds are important synthetic targets in supramolecular chemistry grace to their potential applications as efficient hosts in host-guest molecular recognition.[2] Moreover, thanks to their interesting structure and properties, macrocycles have been successfully used in distinct areas of the chemical science, ranging from medicinal chemistry[3] to material science[4].

In particular, naphtalenediimide (NDI)-based macrocycles received significant attention as molecular host systems due to their versatility to recognize molecular guest by charge transfer (CT), π-π stacking, van der Waals interactions as well as hydrogen bonding.[5]

We present herein, the design, the synthesis and the structural characterization of a new NDI-based macrocycle (I, Figure 1) that could be valued as key precursor in the synthesis of NDI-based [2]catenane. The targeted macrocycle was obtained using two synthetic approaches, namely *i*) reaction of a phenol-decorated NDI precursor with tetraethylene glycol ditosylate in presence of cesium carbonate as base and template; or *ii*) reaction of the commercially available naphthalene dianhydride (NDA) with a benzylamide functionalized tetraethylene glycol derivative; as key reactions used in the macrocyclization step.

The structures of all required intermediates and the target macrocycle were investigated by ^{1}H NMR and ^{13}C NMR as well as high resolution mass spectrometry (HRMS). The potential applications of compound **I** as host for various ions and neutral molecules are under investigation.



I

Fig. 1: Structure of the targeted NDI-based macrocycle.

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Synthesis, optimization, characterization and photocatalytic activity of TiO_2/Fe_3O_4 composite

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Pharmaceutical products are continuously introduced into municipal wastewater from hospitals, after consumer`s use, or disposals of pharmaceutical production, harming the environment and threatening human health. To date, the wastewater treatment methods are not upgraded for removing this kind of pollutants and are inefficient, as various types of drugs were identified in the surface water or even drinking water. [1] Heterogenous photocatalysis represents a promising alternative for water treatment because of low cost, the reproducibility of the method, mild reaction conditions, and use of atmospheric oxygen as oxidizing agent. Furthermore, the pollutant is mineralized to CO_2 and water. [2]

Titanium dioxide (TiO_2) has low cost, reduced toxicity, it`s stable and unsolvable in water, and the semiconductor properties provide it with great photocatalytic activity. The magnetite particles award the titanium dioxide with magnetic proprieties making the nano-scale composite easily removable after use, reusable and environmentally-friendly. Hence, a TiO_2/Fe_3O_4 composite was tailored via reverse precipitation method and its photocatalytic activity in degradation of paracetamol, a widely used analgesic, was studied. [3]

The iron oxide was previously synthesized by co-precipitation method and the reaction parameters were adjusted accordingly in order to obtain crystalline nanoparticles of magnetite. The composite was prepared with different molar ratios and different concentrations of the precursors and the structure was investigated by X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). The photocatalytical activity was measured by

UV-Vis molecular absorption spectroscopy in degradation of paracetamol in aqueous solution under UV irradiation.

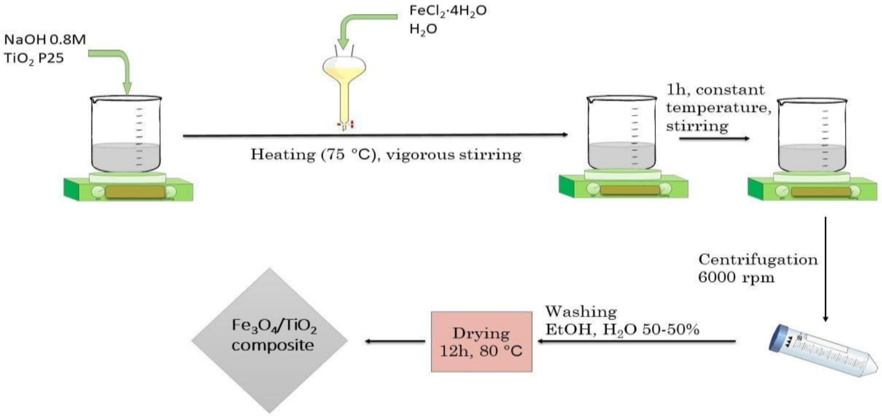

Fig. 1: Reaction scheme of TiO_2/Fe_3O_4 composite synthesis

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Oxovanadium(V) Complexes with Schiff Base Ligands – Synthesis, Characterization and Biological Activity

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A new family of oxovanadium(V) compounds was synthesized by condensation of 2-hydroxybenzaldehyde (salicylaldehyde, sal) and its 5-chloro-, 5-bromo-, and 5-iodo- derivatives with L-valine, D-valine, or D,L-valine, respectively, followed by coordination with $VOSO_4 \cdot 3H_2O$. All compounds were characterized by elemental analysis, single-crystal and powder X-ray diffraction, IR and UV-Vis spectroscopies, as well as circular dichroism measurements. The structure of complexes Br-sal-val is shown, with the octahedral coordinated vanadium moiety highlighted, in Figure 1. Similarly related vanadium compounds have shown antiviral, antibacterial, antifungal, antidiabetic, and antineoplastic activities [1] therefore, biological activity of these compounds is under evaluation; some preliminary results will be discussed.

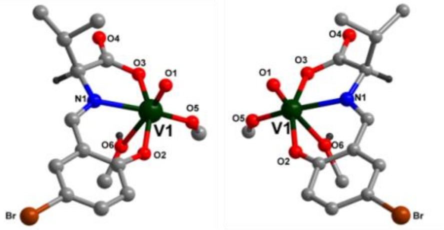

Fig. 1: Structure of *S* and *R* enantiomers of $[VO(Br\text{-}sal\text{-}val)(CH_3O)(CH_3OH)]$

Acknowledgments: This work was supported by UEFISCDI, through the grant PN-III-P1-1.1-PD-2019-0247.

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An interesting asymmetric oxygen-containing rigid macrocyclic chelator and it's Mn(II)-complex: Preparation and Coordination Chemical Characterization

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Magnetic Resonance Imaging (MRI) is one of the most versatile diagnostic tools of medical professionals in their war against diseases. The capabilities of this noninvasive imaging technique are also very impressive on its own, but paramagnetic Contrast Agents (CAs) pushed the limits of MRI even further. The market of MRI CAs today are undoubtedly dominated by Gd(III)-based CA's (i.e. chelates formed with linear and macrocyclic ligands). The use of gadolinium for this purpose has many advantages over other paramagnetic metal ions due to its exceptionally large paramagnetic moment (seven unpaired electrons) and unique relaxation properties (slow electronic relaxation), yet toxicity issues evidenced during the past two decades steamed research aimed at finding safer Gd(III) alternatives.[1,2,3]

The goal of our work was to design and synthesize a chelator which combines in its structure "building blocks" (structural elements) of two previously investigated and successful Mn(II)-binding chelators OPC2A and PCPA. We successfully prepared a hexadentate rigid macrocyclic ligand, OPCPA, possessing an etheric oxygen donor atom trans to the pyridine ring in the macrocyclic core and a picolinate pendant arm as a coordinating side chain.

The $[Mn(OPCPA)]^+$ was found to possess a high thermodynamic stability, which is not surprising in the light of the higher overall basicity of the ligand as compared to parent chelators. Using ^1H-relaxometry and ^{17}O-NMR we have proven, that there is a water molecule beside the donor atoms of the OPCPA in the Mn(II) ion's inner coordination sphere. Surprisingly in metal-ion exchange reactions with Cu^{2+} and Zn^{2+} the candidate was more prone to dissociation than the Mn(II) complexes of the parent ligands under similar experimental conditions. The differences in terms of dissociation kinetic properties of the [Mn(OPCPA)]$^+$ are likely to be rationalized by structural aspects of the complex. Interestingly, in blood serum, at physiological pH, the agent appears to be inert, as evidenced by relaxometric studies performed in Seronorm solutions. We have also discovered a strong interaction of the complex with the most abundant serum protein (Human Serum Albumin/HSA) that causes the elevation of relaxivity in blood serum as compared to those measured in "pure" aqueous solutions.

Acknowledgments: The authors are grateful to the Hungarian National Research, Development and Innovation Office (Projects NKFIH K-120224 and 134694) for their financial support.

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Cobalt(II) extended structures with divergent bipyridine-based ligands

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Porous coordination polymers (PCPs) are known for their great applications in heterogeneous catalysis, drug delivery, magnetism, gas adsorption, separation and storage etc. due to their structural properties, namely: high regularity, tunable pore sizes, and high surface area [1-3]. New PCPs of Co(II) were synthesized with exo-bidentate bipyridine-based ligands, such as: 4,4'-bipyridyl (bipy), 1,2-bis(4-pyridyl)ethane (bpa), 1,2-bis(4-pyridyl)ethylene (bpe), 1,3-bis(4-pyridyl)propane (bpp), and 4,4'-azopyridine (azopy) and fully characterized in solid state by elemental analyses, single-crystal and powder X-ray diffraction, as well as FTIR and UV-Vis spectroscopies.

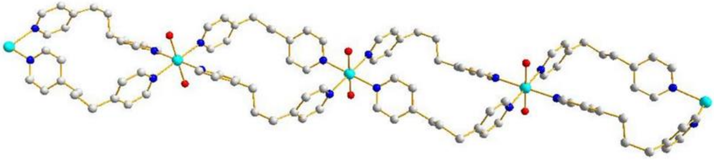

Fig. 1: Structure of $\{[Co(bpp)_2(H_2O)_2](NO_3)_2\cdot 7(H_2O)\}_n$

Networks with various topologies were obtained, depending on the starting metal salts (an example is shown in Fig. 1). Crystallography reveals a significant influence of the anions on the self-assembly of the coordination frameworks. The anion exchange properties of the obtained coordination polymers are under investigation.

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POSTERS

ZrO_2-based nano-biocomposites: solid-state synthesis and morpho-structural characterization

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Even if each biomaterial class has unique advantages for biomedical applications, there are also intrinsic drawbacks, depending on its nature and fabrication process. A solution to overcome this limitation is to combine two or more materials to design and fabricate a multiphase composite taking advantage of the single components. In the past decade, many ZrO2-based biocomposites have been developed as coating or substrate to achieve both bone reconstruction and regeneration needed in the treatment of large bone defects [1]. In our work, ZrO2-MgO-HAP biocomposites were prepared by adding different amounts of antibacterial magnesium oxide (MgO) and bioactive and biocompatible hydroxyapatite (HAP) to the inert zirconia (ZrO2). The composites were obtained by solid-state synthesis at high temperature, and structurally and morphologically analyzed by X-ray powder diffraction (XRPD) and scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS), respectively [2-4]. HAP was prepared by the coprecipitation method and used uncalcined in the synthesis of composites. Analysis of the XRPD patterns revealed the presence of both *t*- and *m*-ZrO_2 phases in different ratios. Moreover, the presence of the MgO phase was not observed, confirming the solubility of Mg in the ZrO_2. However, for the composite with the higher HAP amount in the initial raw materials mixture, small peaks belonging to the β-TCP (tricalcium phosphate) phase were identified, confirming the HAP phase transformation at 1600°C synthesis temperature. The crystallite sizes calculated from the XRPD pattern using the Scherrer equation are ranged in the nanometric domain for both *m*- and *t*-ZrO_2 phases [4]. SEM analyses revealed homogenous surface morphology. Also, pores are observed for all the studied composites. The results of EDS analysis corresponding to the same nominal cationic compositions highlight the simultaneous presence of the Zr, Mg, Ca, and P elements, and no others were systematically detected [4]. Thus, the obtained results are in agreement with XRPD analyses and prove the successful preparation of nano-sized biocomposites.

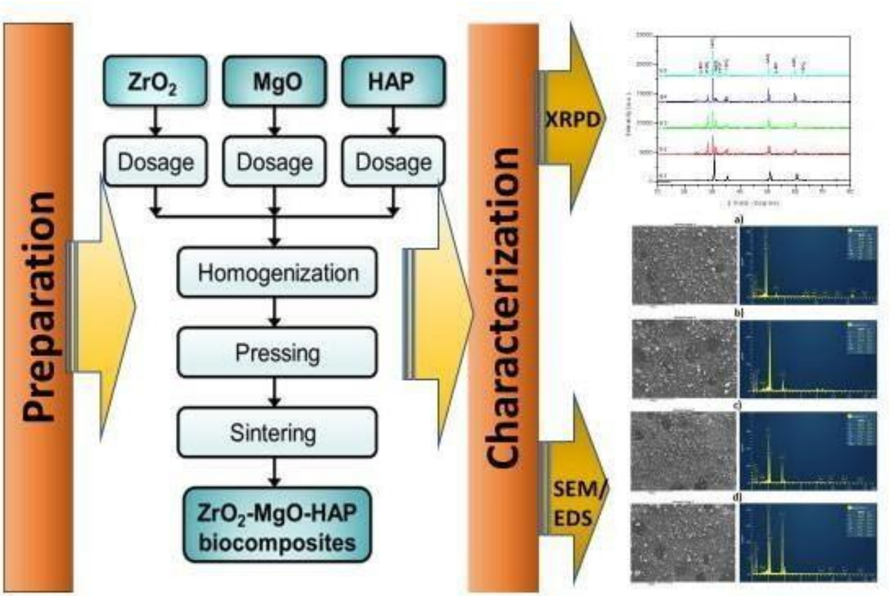

Fig. 1. Graphical abstract depicts flow chart preparation and characterization of the biocomposites.

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Preparation of aza-BODIPY dyes

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Boron-difluoride chelated aza-dipyrromethenes are fluorescent dyes with absorption and emission spectra in the near-infrared region. NIR fluorescent dyes are especially desirable for biological applications, due to low background signal and deep penetration of the near-infrared light, and are usually applied as photosentisizers for photodynamic therapy, fluorescent probes for biological imaging or laser dyes [1]. Aza-BODIPY dyes have recently gained popularity because of their high stability and great photophysical properties [2]. Their fluorescence can be easily tuned by slight modification of the core compound.

The main focus of our work was the synthesis of different aza-BODIPY dyes, as well as their structural analysis using NMR spectroscopy (^{1}H-NMR, ^{13}C-NMR, ^{19}F-NMR and ^{11}B-NMR).

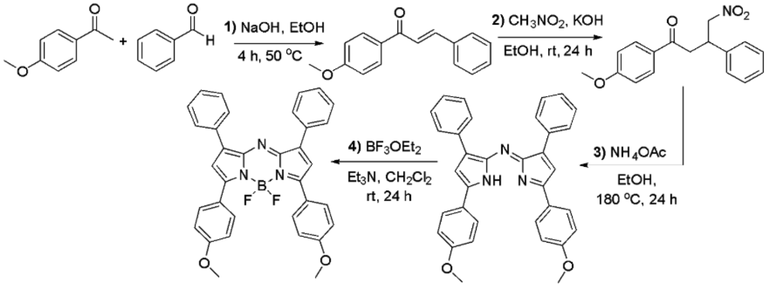

Fig. 1: Synthetic route to the aza-BODIPY **core**

The **core** compound was prepared in four synthetic steps (as presented in Fig.1.): 1) Chalcone was obtained by Claisen-Schmidt condensation; this was followed by 2) Michael addition of nitromethane and a 3) cyclization step. 4) After the complexation with BF_3-OEt_2, the product was obtained as metallic green crystals.

Functionalization of the aza-BODIPY **core**: (**2**) was prepared through a Vilsmeier–Haack reaction. After the preparation of the Vilsmeier-reagent, the starting compound was added to the mixture, which was stirred for 6 h under reflux until completion [3].

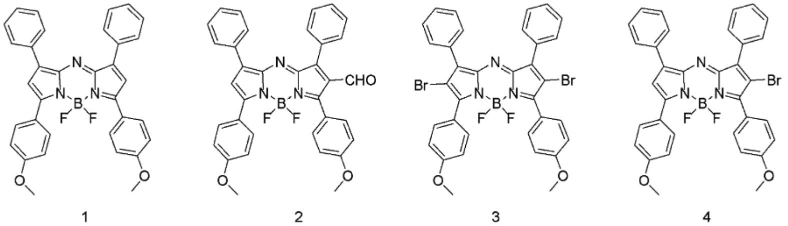

Fig. 2: Functionalization of the aza-BODIPY **core**

Preparation of (**3**) and (**4**) followed a similar procedure: to the mixture of the starting compound and solvent, N-bromosuccinimide (**3** – 2 eq., **4** – 1 eq.) was added [4]. Both products were obtained in moderate yields, and were used and analyzed without further purification.

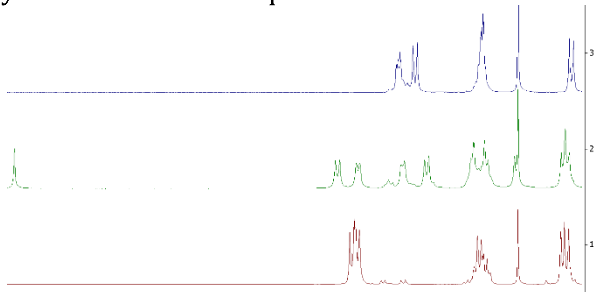

Fig. 3: ^{1}H-NMR spectra (signals of aromatic protons)

Following the syntheses, the main differences between the structure of the compounds (**1**), (**2**) and (**3**) were investigated using ^{1}H-NMR spectroscopy, the results can be seen in Fig. 3.

In conclusion, four aza-BODIPY dyes were obtained and their structure confirmed by high resolution techniques.

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New complexes based on a bis-thioether ligand

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Recently the new bis-thioether 1,3-(*para*-tolyl sulfide)-5-*tert*-butylbenzene **1** was synthesized, characterized and used for obtaining bis-sulfoxides.[1]

In the present work bis-thioether **1** was evaluated for its role as ligand to obtain transition metal complexes.

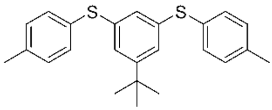

Figure 1. Bis-thioether **1**

The synthesis of new ruthenium complexes was studied starting from $(PPh_3)_3RuCl_2$, following procedures previously shown in the literature for different ligands.[2] The formation of the compounds was followed by multinuclear NMR spectroscopy.

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Spectroscopic investigations of α-lipoic acid

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ɑ-Lipoic Acid is a molecule of medical interest, being found in the human body, and especially in the blood. It has powerful antioxidant and anti-inflammatory properties [1] and other numerous roles, some of which include metabolism of glucose [2], maintaining an optimal level of E and C vitamins, prevention of the eye and skin diseases [3, 4], and was also found that it can prevent diseases of the nervous system [5].

It has a simple molecular structure, being composed of only four types of atoms, C8H14O2S2. It is found in the form of two enantiomers, (R)-(+)-ɑ-lipoic acid and (S)-(-)-ɑ-lipoic acid [6] which chemical structure can be visualized in Figure 1.

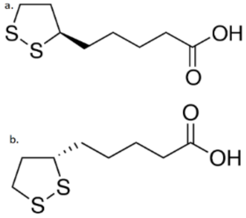

Fig. 1: Chemical structure of a. (R)-(+)-ɑ-lipoic acid and b. (S)-(-)-ɑ-lipoic acid

So far no detailed spectroscopic studies have been performed on this molecule, therefore the aim of this study was to assign the characteristic bands from the Raman and IR spectra and to analyze the SERS spectrum of ɑ-lipoic acid. Using that information we propose to study the adsorption behavior of the molecule on metallic nanoparticles.

Hence the FTIR and Raman spectra of ɑ-lipoic acid were firstly recorded. Moreover, the SERS spectrum was recorded by using silver colloidal nanoparticles excited with the 532 nm laser. The main vibrational modes were then assigned to the corresponding bands as seen in Table 1. A smaller number of characteristic vibrational bands were observed in SERS spectrum compared to those in Raman, which lead us to conclude that the molecule is adsorbed in specific sites on the metallic nanoparticles. By analyzing the SERS spectrum we remarked that most of the sulfur vibrational modes were not visible in the SERS spectrum. We, also, noticed a great amplification of the characteristic bands from 1293, 1434 and 1729 cm^{-1}. The first two are due to the C-O stretching vibration and the last one to the carbonyl group, C=O, stretching vibration. Using this information we deduced that the α-lipoic acid is most probably adsorbed on the silver nanoparticles surface via the carboxylic group of the molecule.

Table 1: Attribution of main bands in Raman, IR and SERS spectra of α-Lipoic Acid

Raman	IR	SERS	Main vibrational mode
510	520	520	CCC ring deformation; OH rocking ↓↑
932	931	941	Skeletal CCC bend+CC stretch+CH2 rocking+OH strech
1079	1078	1102	CO stretch+COH deformation
1306	1306	1293	CH2 wagging, C-O stretching, O-H bending
1405	1407	1414	C-O stretching, O-H bending
1438	1428	1435	C-O stretching, O-H bending

Acknowledgments: E.A.R. acknowledge financial support from a special grant for scientific activity awarded by STAR-UBB (Babeș-Bolyai University), 2020.

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Tuning of the optoelectronic properties of conjugated polymers by the addition of reduced graphene oxide or silver nanoparticles

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Explosives are a problem for humanity, especially in war zones. Poly [2-methoxy-5-((2’-ethylhexyl) oxy)-1,4-phenylenvinylene] (MEH-PPV) is a highly luminescent conjugated polymer, which has a fairly high permeability to nitroaromatic compounds. When exposed to trace amounts of trinitrotoluene or dinitrotoluene, MEH-PPV shows a decrease in photoluminescence quenching and thus could be used as a polymeric sensor for the detection of nitroaromatic explosives.

In this work we analyze the possibility to manipulate the absorption and photoluminescence properties of both MEH-PPV/reduced graphene oxide (rGO) thin films obtained by spin-casting MEH-PPV adding solution with rGO [1], and MEH-PPV/silver nanoparticles (AgNPs) films generated by drop-casting of the MEH-PPV solution with added AgNPs. The silver nanoparticles were obtained by the Creighton method represented in Figure 1, and rGO by introducing a dispersion of graphene oxide (GO) in DMF in a microwave synthesis reactor. While adding AgNPs leads to photoluminescence quenching, thin hybrid films made of MEH-PPV and rGO exhibit significant photoluminescence enhancement. This is most probably due to different microstructure and interactions settled between MEH-PPV and rGO as well as between MEH-PPV and AgNPs.

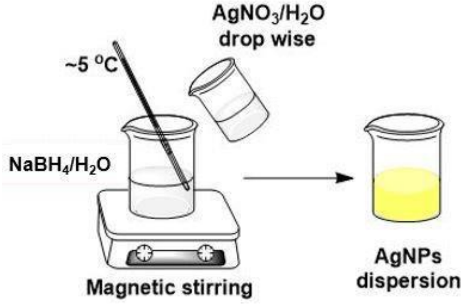

Fig. 1. Synthesis of silver nanoparticle dispersion [2]

Our results show that there is a close connection between the polymer, solvent and colloid interaction, as a result of making thin films of different thicknesses, which is reflected by photoluminescence quenching/enhancement by adding silver nanoparticles/rGO in DMF.

Acknowledgments: CNCS-UEFISCDI, project no. PN-III-P2-2.1-PED-2019-3995.

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Preparation of ZnO thin films by dip-coating from sol-gel and studying the effect of immersion speed on the formation of the thin films

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Coatings play an important role in today's industry and life, and the coating's properties are influenced by their structure. In turn, the structure of a coating is influenced by different parameters, including dipping speed, duration of the dipping, calcination temperature, etc. My works aims to study the effects of dipping speed to the structure and composition of ZnO thin layers formed through dip-coating from sol-gel on glass substrates. ZnO coating formed at 4 different dipping speeds was analyzed using SEM and EDX methods.

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Voltammetric analysis of hesperidin using a disposable pencil graphite electrode

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Introduction: Flavonoids are natural polyphenolic compounds found in fruits, vegetables, wine, roots, flowers or tea. They are well known for their anti-oxidative, anti-inflammatory, and anti-carcinogenic effects [1]. Hesperidin (HESP), a flavone glycoside, is found in the peel of citrus fruits, in dietary supplements and drugs used for the treatment of venous diseases. From chemical point of view flavonoids have a benzene-α-pyrone structure bearing, the hydroxyl groups grafted on the conjugated benzene rings being responsible for their anti-oxidant and electrochemical activity. Thus, the study of the voltammetric behavior of these compounds can help understanding their action mechanism as antioxidants [2]. There are very few literature reports on the voltametric analysis of HESP [3]. This work presents HESP electrochemical behaviour at the cost-effective and easy-to-use pencil graphite electrode (PGE) and, based on this, the development of voltammetric methods for its quantitative determination.

Materials and methods: The stock solution was daily obtained by dissolving an accurately weight amount of HESP in a small volume of 0.2 M NaOH and subsequent dilution with bidistilled water. The working solutions were prepared by serial dilutions of the stock solution with the proper supporting electrolyte. The voltammetric measurements were carried out using a three electrodes cell (working electrode-PGE (Fig. 1), auxiliary electrode-Pt, reference electrode: Ag/AgCl), connected to the Autolab PGSTAT 12 system driven by a PC equipped with the GPES 4.9 software.

Fig.1 The composite pencil graphite electrode (PGE)

Results and discussions: The influence of the electrode material on HESP voltammetric response was examined by differential pulse voltammetry (DPV) at various working electrodes: Pt, glassy carbon electrode and PGE with graphite pencil leads of different hardness. Graphite leads are composite materials containing graphite powder (~60%), clay (~30%) and a binder (resin or a high polymer) [4], the harder ones (H types) having a lower graphite content than the B types, which are softer and blacker due to higher graphite contents. In this study H type PGE was used because this electrode presented the highest sensitivity (0.743 A×L/mol×cm^2) for HESP DPV response. HESP anodic peaks were not enhanced by the PGE potentiostatic / potentiodynamic electrochemical activation in various supporting electrolytes. When the solution pH was increased the HESP oxidation peak potential values decreased by a value near to the theoretical one, of 0.059 V/pH unit, suggesting that the number of exchanged electrons and protons was equal. The highest DPV signals were obtained in Britton Robinson Buffer pH 1.81. HESP cyclic voltammograms presented in the first scan a diffusion controlled oxidation peak at about 0.78 V and, in the reversed scan, a cathodic signal at about 0.48 V due to a mixt diffusion-adsorption controlled reduction of HESP oxidation product, formed in the direct scan. The influence of HESP concentration on the currents of both, oxidation and reduction, peaks was investigated by DPV and adsorptive stripping differential pulse voltammetry (AdsDPV) in the range $2.5 \cdot 10^{-8}$ – $1.0 \cdot 10^{-6}$ mol$\cdot$L^{-1} HESP. The methods showed good linearity in the ranges $1.0 \cdot 10^{-7}$ – $1.3 \cdot 10^{-5}$ mol$\cdot$L^{-1} (R^2 0.9882; DPV-oxidation) and $7.4 \cdot 10^{-8}$ – $8.4 \cdot 10^{-7}$ mol$\cdot$L^{-1} HESP (R^2 0.9985; AdSDPV-reduction) with limits of detection of $7.4 \cdot 10^{-8}$ mol$\cdot$L^{-1} and $1.5 \cdot 10^{-8}$ mol$\cdot$L^{-1} HESP, respectively. The practical applicability of the developed DPV at PGE method was tested by assessing the HESP content in dietary supplements.

Conclusions: HESP presents a complex voltammetric behavior at PGE. Using a disposable, cost-effective and commonly available working electrode HESP can be rapidly and easily quantified using either DPV or AdSDPV.

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Influence of Counter-Anions on the Molecular Structures of a Series of Copper(II) Complexes

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Three new coordination polymers, $^{1}_{\infty}[Cu(bpp)(H_2O)_2(BF_4)_2]$ **(1)**, $^{1}_{\infty}[Cu(bpp)(NH_3)_2(ClO_4)_2]$ **(2)**, $^{1}_{\infty}\{[Cu_2(bpp)_2(CF_3SO_3)_2(\mu_2\text{-}OCH_3)_2](CH_3OH)\}$ + $^{2}_{\infty}\{[Cu_2(bpp)_2(CF_3SO_3)_2(\mu_2\text{-}OCH_3)_2](CH_3OH)\}$ **(3)** have been obtained from reaction of various Copper(II) salts with the flexible organic divergent ligand 1,2-bis(4-pyridyl)propane (bpp), by slow evaporation method. X-ray diffraction on single crystal, elemental analysis, as well as spectroscopic techniques (FT-IR and UV-Vis) were used to obtain the required data for characterization. The crystal structures of the resulting assemblies have been determined and the intermolecular interactions of the compounds in the crystalline phase have been investigated. The structural diversity of the new compounds depends on the starting Cu(II) salts, conducting to 1-D and 2-D extended structures. Compounds **1** and **2** are 1-D zigzag polymeric chains in which one molecule of bpp acts as bridging ligand. The chain-like structure of compound $[Cu(bpp)(H_2O)_2(BF_4)_2]_n$ is depicted in Figure 1. Compound **3** has an interesting and not very common structure in which coexist, as parallel layers, 2-D grid-like structures with 1-D linear coordination polymers.

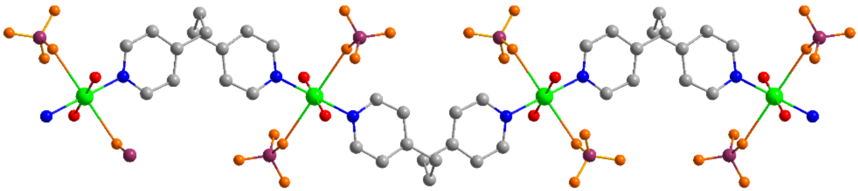

Fig.1: 1-D structure of $[Cu(bpp)(H_2O)_2(BF_4)_2]_n$, view on c-axis.
H atoms were omitted for clarity.

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Comparative efficiency of Orange G degradation by chemical and photochemical oxidation: a kinetic study

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Orange G is an acidic azo dye widely used to dye textiles, such as wool and silk, paper, leather, and more. Consequently, it is present in textile industry effluents as one of the main environmental pollutants.

Through this study we investigated the removal of Orange G from wastewater by chemical and photochemical advanced oxidation processes (AOPs), which offer a powerful treatment of wastewater. AOP's are able to produce oxidizing radicals either by chemical reactions or by UV irradiation.

For chemical oxidation of Orange G it was chosen hydrogen peroxide and sodium bicarbonate as oxidizing system; it was proven that the bicarbonate anion is an activator for hydrogen peroxide in degradation of several dyes through generation of carbonate and superoxide radicals. This method can be modified by the addition of microcomponents such as $CoSO_4$ and $NaNO_2$. Experimentally, it was observed that $NaNO_2$ had an inhibitory effect, while $CoSO_4$ in low concentrations had an activating effect, so it acts as a catalyst.

For photochemical oxidation, both hydrogen peroxide and peroxodisulphate anions were used. Hydrogen peroxide is able to form several reactive oxygen species, hydroxyl radical being the most active. Similar to hydroxyl radicals, sulfate radicals generated from peroxodisulphate anions irradiation have a high redox potential ($E_0 = 2.6$ V), which can transform azo dyes into small molecules. Compared to hydroxyl radicals, sulfate radicals have a longer half-life, but they cannot regenerate in the reaction.

For both chemical and photochemical processes, the kinetic data showed that the degradation of Orange G follows a pseudo-first order kinetics. The estimated values of kinetic rate constants were compared among methods, together with the decolorization degree.

The results showed that the best method for Orange G degradation is photochemical oxidation in which the oxidizing system is hydrogen peroxide.

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The influence of sweeteners on the characteristics of lingonberry jams

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The object of this work is to investigate the influence of some sweeteners on the properties of lingonberry jams.

Lingonberry (*Vaccinium vitis-idaea*) is one of the most important harvested wild berries from temperate climate zones. These fruits contain a large variety of different polyphenolic compounds such as anthocyanins, flavonols, and phenolic acids, also being popular for the antioxidant properties [1]. Due to high amounts of organic acids, especially citric acids, the flavor of lingonberries is very acidic and sour [2].

The phytochemical properties and sensory parameters (color, taste, texture and spreadability) of jams were influenced by their preparation: type of used sweeteners, temperature, time of preparation, etc.

Sweeteners are food additives that provides a sweet taste like that of sugar and could be natural or synthetic [3].

In this work both types of edulcorants, namely natural – white sugar, brown sugar, coconut sugar fructose, erythritol, and stevia, and artificial – cyclamate-saccharin were used for the jam preparation. Also, to avoid bioactive compounds degradation, the temperature was set at 50˚C and the time of boiling was between 55 and 90 minutes in order to obtain similar values of ˚Brix. The following properties were studied: Total polyphenolic content (TPC), Total Anthocyanin Content (TAC), Antioxidant capacity (AC), vitamin C, Titratable acidity (TA) and overall acceptability, which includes color, taste, texture and spreadability. Also, the UV-Vis spectra were recorded in order to assess the differences between jams.

The experimental results show that TPC varies between 3.67 and 10.32 mg Gallic acid/g jam, TAC between 0.164-0.263 mg Cyanidin-3-glycoside/g jam, AC between 45.3 and 93.8 µmol Trolox/g jam, vitamin C between 9.91 and

15.5 mg/g jam, TA between 4,76% and 7,92%, and the overall acceptability of the jams between 3.8 and 8.8 from 1 to 10 rating scale. These variations can also be seen in the UV-Vis spectra of jams.

The results proved that jams formulated with coconut sugar and with stevia exhibit the high value for TPC, probably also due to the polyphenols in the sweeteners. Preservation of the highest TAC and vitamin C content was found in the case of jams prepared with cyclamate and stevia. The minimum scores in overall acceptability and TA were observed in case of jam prepared with erythritol.

Concluding, the type of sweeteners significantly influences the characteristics of jams. The use of stevia in the manufacture of blueberry jam has proven to be the most appropriate choice because this natural sweetener preserves the largest amount of bioactive compounds.

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Green approaches for fragrances synthesis. Biotechnological production of anisyl-propionate.

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The efficient production of flavor esters with fruity and floral aromatic potential, enhancing taste and odor in ingredients, which are useful for food, cosmetic and pharmaceutical industries, is still a challenging task.[1] Biocatalytic procedures are a green and sustainably alternative to the classical preparation methods like the physical extraction from natural sources, or their chemical synthesis.[2] Furthermore, esters produced by biocatalysis can be labelled as “natural-produced”. The direct esterification of alcohols with various acids catalyzed by lipases using molecular sieves for water removal was successfully performed in our research group.[3] Based on our previous works the enzymatic synthesis of short-chain flavor esters was achieved successfully by developing a novel biocatalytic approach using vacuum for water removal.[4]

Here we report a biocatalytic approach for the synthesis of anisyl propionate obtained via the direct esterification of anisyl alcohol with propionic acid mediated by lipase B from *Candida antarctica* in a commercially available form (Novozym 435) using molecular sieves to efficiently remove the water formed in the system (Figure 1).

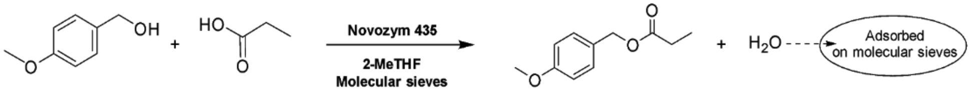

Fig. 1: Synthesis of anisyl propanoate by direct esterification of para-methoxy-benzyl alcohol with propionic acid mediated by Novozyme 435 in 2-MeTHF, in presence of molecular sieves.

Process optimization was performed by identifying the ideal solvent (2-methyltetrahydrofuran, which is a green solvent), screening the ideal reaction medium temperature (60 ˚C), and determining the optimum load of molecular sieves (100 mg/mL, ideal for removing the water formed in the system). Moreover, under optimum conditions further scaling-ups were performed by increasing the substrates concentration (up to 200 mM) with excellent conversion values obtained after 6 hours reaction time (>95 % conversion in anisyl propionate). The conversion values were determined by HPLC (Figure 2). Preparative scale biocatalytic synthesis afforded chemically pure anisyl propionate in more than 95 % yield.

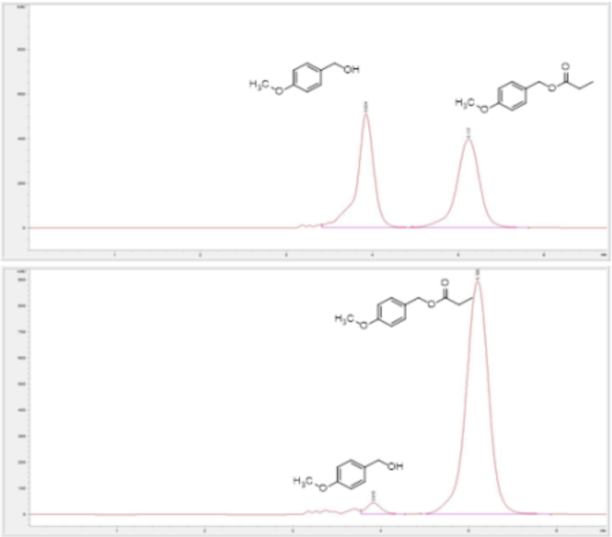

Fig. 2: HPLC separation of the mixture of authentic anisyl alcohol and anisyl propionate (A) and for the mixture of them by a sample taken from a typical enzymatic esterification reaction (B) [Phenomenex Gemini NX-C18 column (150 × 4.5 mm; 5 µm), 1 mL/min., MeOH:H_2O, 80:20, (v/v).

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Preliminary phytochemical investigation of *Vaccinium* spp. leaves

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Blueberries (*Vaccinium* spp.) have great beneficial effects, and their leaves are rich in phenolics [1]. Studies have shown that the phenolic content of *Vaccinium* spp. leaves has been linked to their antidiabetic properties [2].

The aim of this study is to investigate and compare the content in bioactive compounds of both wild and cultivated *Vaccinium* spp. leaves. As byproducts of mechanical harvesting of an important crop species, blueberry leaves are analyzed for their beneficial properties. In this preliminary research, aqueous and ethanolic extracts of the leaves were evaluated for their phytochemical content. The purpose of this study is to determine the proper species, wild or cultivated, and solvent of extraction for obtaining the maximum amount of the compounds of interest, in order to be used for pursuing further research of their antidiabetic properties.

In the present work, the total polyphenolic content (TPC), total flavonoid content (TFC), and proanthocyanidin content in the leaf extracts from a cultivated species and a wild one were analyzed. In order to see the differences between the source of origin of the leaves and the extraction solvent, the UV-Vis spectra were also registered.

The research results show that TPC varies between 80.07 and 184.01 mg Gallic acid/g of leaves, TFC between 3.9 and 9.3 mg Rutin/g of leaves and the proanthocyanidin content between 0.58 and 1.25 g CE/g leaves. The UV-Vis spectra of leaves show these differences as well.

The results indicate that the most effective extraction solvent is the 70% ethanol for all the bioactive analysed compounds. In terms of the source of origin of the leaves, the maximum amount of TPC and TFC corresponds to the wild species, whereas for the proanthocyanidin content, the highest value corresponds to the cultivated one.

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Luminescent lanthanide complexes based on POMs ligands

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A remarkable property of certain lanthanides is their luminescence, which consists in emission of radiation from an excited electronic state.[1] The fluorescence of rare-earth-metal ions has applications in many fields, such as optical switching, display, illumination, communication and imaging. However, the forbidden f−f transitions of Ln(III) ions exhibit a weak UV absorption with low luminous efficiency, so luminescence can be strongly increased by attaching an appropriate organic or inorganic ligand to the Ln^{III} ion, thus exploiting the so-called antenna effect.[2]

Polyoxometalates (POMs) are rich in surface oxygen atoms, which act as multifunctional ligands with large active sites to combine easily with lanthanides ions, resulting in the formation of lanthanide−polyoxometalate complexes. The ligand to metal excited states charge transfer (LMCT) from the O → M in Ln−POM compounds can occur under the irradiation with UV light, and the produced energy can transfer to Ln^{III} ion and thus sensitize Ln^{III} ion.[3]

The same strategy for obtaining luminescent systems was tried in the experimental part using sodium tungstate dihydrate as a tungsten precursor and lanthanide nitrates (Ln= Eu, Tb, Sm, Dy). The resulting $Na_9[Ln^{III}W_{10}O_{36}]\cdot 35H_2O$ systems are isostructural and were characterized by UV−vis, IR and powder XRD measurements.

The single-crystal structure of compound $Na_9[EuW_{10}O_{36}]\cdot 35H_2O$ displays the presence of a sandwich-type cluster $[EuW_{10}]$, Na^+ cations and 35 molecules of crystallization water. The Eu^{3+} ion in the center of the anion achieves eight-fold coordination by attachment of two W_5O_{18} ligands, constituting a distorted square antiprism. Na^+ ions that counterbalance the negative charge of the cluster $[EuW_{10}]$ form an extended network, by coordinating with the water molecules and oxygen atoms of the metallic clusters. The luminescence spectrum shows sharp emission bands, which are characteristic for lanthanides ions.

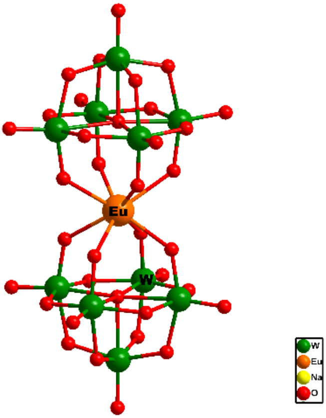

Fig 1. Molecular structure of the cluster [EuW_{10}] from the $Na_9[EuW_{10}O_{36}]\cdot 35H_2O$ compound

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Copper(II) coordination polymers self-assembled from diamines and lactic acid

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Current interest in copper complexes comes from their potential use as antimicrobial, antiviral, anti-inflammatory, or even antitumor agents, as well as their potential use in treatment of brain diseases such as Alzheimer's disease [1-2]. A family of coordination polymers were self-assembled using copper(II) salts, lactic acid (L-, D-, or L/D–lactic acid, HLac) and divergent diamine spacers, namely: 4,4'–bipyridine (bipy), 1,2-bis(4-pyridyl)ethane (bpa), and 1,2-bis(4-pyridyl)ethylene (bpe). All the synthesized compounds have been characterized using single-crystal and powder X-ray diffraction, elemental analyses, as well as different spectroscopic techniques, such as FTIR and UV-Vis in solid state. The structural characterization of the obtained compounds reveals 1-D chain-like coordination polymers with Cu(II) atoms in a distorted octahedral environment with a $Cu(Lac)_2$ coordination motifs bridged by divergent organic diamines. Structure of $[Cu(L\text{-}Lac)_2(4,4\text{-}bipy)]_n$ is depicted in Figure 1. The polymeric chains are interconnected by hydrogen bonds creating parallel supramolecular 2-D layers. Biological activity of these compounds is under evaluation; preliminary results show antibacterial and antifungal activities.

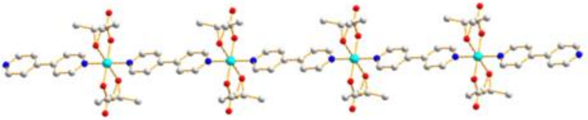

Fig. 1: Structure of $[Cu(L\text{-}Lac)_2(4,4\text{-}bipy)]_n$

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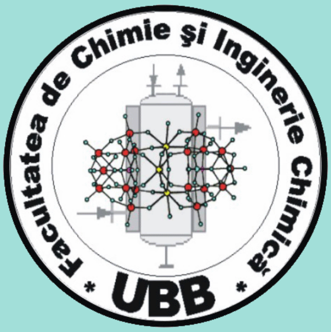
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